## SHORT TITLE

## Solvent Extraction of Trialkylammonium Salts

Miçhel Gérin

Department of Chemistry

McGill University

A STUDY OF THE SOLVENT EXTRACTION PROPERTIES

OF TRIALKYLAMMONIUM SALTS AND THEIR USE AS ION EXCHANGERS

IN LIQUID MEMBRANE ANION-SELECTIVE ELECTRODES

by

Michel Gérin

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Michel Gérin

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Department of Chemistry, McGill University,

Montréal, Québec.

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ABSTRACT

A STUDY OF THE SOLVENT EXTRACTION PROPERTIES OF TRIALKYLAMMONIUM SALTS AND THEIR USE AS ION EXCHANGERS IN LIQUID MEMBRANE ANION SELECTIVE ELECTRODES

by

### Michel Gérin

Ph.D. Thesis Department of Chemistry McGill University

Properties of tertiary alkylammonium chloride, bromide, iodide and perchlorate salts of various chain lengths dissolved in nitrobenzene were studied. The dissociation constants of the salts in the organic phase were measured and appeared to depend essentially on the nature of the anion. Partition constants of the salts between the organic phase and water were obtained and the influence of alkyl chain length and anion nature were discussed.

Two phase hydrolysis constants were measured by potentiometry. The basicity of the amines appeared to be independent of alkyl chain length. Organic solutions of the

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salts behave as liquid ion exchangers, and their anion exchange constants were deduced.

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/ These solutions were used as membrane material for anion selective electrodes. Response curves were obtained and interference studies undertaken. The interference coefficients and response limits of the electrodes were related to the ion exchange constants and partition constants determined previously.

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#### Résumé

ETUDE DES PROPRIETES D'EXTRACTION PAR SOLVANT DES SELS DE TRIALKYLAMINES ET DE LEUR USAGE EN TANT QU'ECHANGEURS IONIQUES

DANS DES ELECTRODES SELECTIVES ANIONIQUES A MEMBRANE LIQUIDE

par

### Michel Gerin

Thèse de doctorat Department of Chemistry McGill University

On a étudié les propriétés de chlorures, bromures, iodures et perchlorates de trialkylamines de diverses longueurs de chaîne carbonée dissouts dans le nitrobenzène. On a mesuré les constantes de dissociation des sels dans la phase organique et constaté leur dépendance de la nature de l'anion. On a obtenu les constantes de partition des sels entre la phase organique et l'eau et discuté de l'influence de la longueur de la chaîne alkyl et de la nature de l'anion.

On a mesuré par potentiométrie les constantes d'hydrolyse biphase. La basicité des amines semble indépendante de la longueur de chaîne. Les solutions organiques de ces sels ont les propriétés d'échangeurs ioniques liquides. On a calculé leurs constantes d'échange anionique.

On a utilisé ces solutions en tant que milieux pour membrane d'électrodes sélectives anioniques. On a étudié les courbes de réponse et les effets d'interférence. On a relié les coefficients d'interférence et les limites de réponse des électrodes d'une part aux constantes d'échange partition déterminées auparavant d'autre part.

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## LIST OF SYMBOLS

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tripropylamine
tributylamine
tripentylamine
trihexylamine
trioctylamine
tridodecylamine (trilaurylamine)
nitrobenzene
denotes activity
denotes concentrations
universal gas constant (resistance in chapter III)
absolute temperature
standard free energy change
number of milliequivalents
Stokes radius .
van der Waals radius
degree of dissociation
activity coefficient
dielectric constant
viscosity
cell constant
equivalent or molar conductance
standard deviation

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## INTRODUCTION

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Amines and ammonium salts have become increasingly important agents for chemical separations in the metallurgical and nuclear industries and in the analytical chemistry laboratory. Long chain amines dissolved in various solvents are currently used to purify and recover uranium from acid liquors. Similarly other actinides, lanthanides and transition metals can be selectively separated and extracted from aqueous solutions. Various acids or anions have been removed from industrial effluents by contacting with organic amine or ammonium salt solutions. (1-4) Amines and their salts are correspondingly powerful reagents in analytical solvent extraction and liquid ion exchange processes. The analytical applications in inorganic analysis involve essentially aqueous metal separations and extractions down to the trace level. (5,6)

Among the amine extractants long chain tertiary aliphatic amines and their salts play a leading role. <sup>(1,5,7)</sup> The two basic reactions involved in using those can be summarized by the following equilibria:

extraction:  $\overline{R_3N}$  + HX  $\neq \overline{R_3NHX}$ 

ion exchange:  $\overline{R_3NHX} + Y \neq \overline{R_3NHY} + X$ 

In the first process an aqueous acid migrates into the organic phase to neutralize an amine molecule. In the second process

an aqueous anion undergoes an exchange with the anion present in the organic phase as the ammonium salt. The organic phase, or liquid ion exchanger, behaves in a way which is reminiscent of the more classical resin ion exchange. Metal separations and extractions can occur by ion exchange of their metal anionic complexes of the kind  $\operatorname{FeCl}_4^{-}$ ,  $\operatorname{Pu}(\operatorname{NO}_3)_6^{2-}$ ,  $\operatorname{UO}_2(\operatorname{SO}_4)_3^{4-}$ .<sup>(8)</sup>

Liquid ion exchangers in general and long chain alkylammonium salts in particular have also found recent wide use in the field of ion selective electrodes, mostly of the liquid membrane type.<sup>(9)</sup>

In order to describe precisely the purpose and the aims of the present study as well as give an outline of the work undertaken on the chosen system, it is necessary to introduce the mechanisms involved in amine extraction, liquid ion exchange and liquid ion selective electrodes.

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## 1. Alkylamine extraction

The extract of aqueous acids by amines dissolved in water-insoluble organic solvents is a complex process depending on several variables. The class and chain length of amine, its concentration, the type of diluent, the strength of the aqueous acid will influence both the mechanism of extraction and the nature of the extracted species.

a) Basicity of alkylamines (10-k3)

The lone-pair of electrons responsible for amine basicity is situated in an s-p hybrid orbital directed away from the pyramid formed by the three bonds on the nitrogen atom. The inductive effect of the alkyl chains governs the increased basicity of each class of amine with increased chain length. If inductive effects alone were important, the. basicity should also increase with increasing substitution on the nitrogen atom, i.e. from primary to tertiary amines. However the variation of basicity with amine class is dependent on the diluent. In aqueous solutions the order of basicity is usually secondary > primary > tertiary. The relative weakness of tertiary amines is based on steric effects. Solvation of the tertiary ammonium cation by hydrogen bonding to water molecules is decreased as compared to secondary and primary ammonium cations. 'In organic diluents the various effects of solvation, inductive effect and steric hindrance

to the approach of the anion have been invoked to explain the different trends of basicity with amine class depending on the diluent.

b) Extractability of aqueous acids (14)

 $\left( \right)$ 

For a certain amine-organic solvent system, the factors effecting the order of extraction of various aqueous acids are of interest. The extraction can be viewed as a competition between the amine and the anion of the aqueous acid for coordination with the proton. The more basic the anion, i.e. an extremely weak acid, the less extractable the acid is by the organic amine. In the case of a monovalent weak acid the reaction can be described by:

 $\overline{R_3N}$  + HA  $\neq \overline{R_3N \cdot HA}$ 

In the organic complex, the amine is bound to the acid through a hydrogen bond. However in the case of a strong acid, the acid hydrogen is chemically bound to the amine to form an ammonium ion and the anion is held by electrostatic forces. The reaction is better described as:

 $\overline{R_3N} + H^+ + A^- \neq \overline{R_3NH^+A^-}$ 

For completely dissociated strong acids the order of extraction

is governed by the extent of hydration of their anions. The larger less hydrated anions (e.g.,  $ClO_4^-$ ) are more readily extracted than the smaller more hydrated ones (e.g.,  $Cl^-$ ).

c) Influence of the diluent on the extraction (14,15)

The chemical and dielectric properties of the diluent in which the amine is dissolved will influence the extraction of aqueous acids. The extraction may be viewed as the transfer of a pair of dissociated ions (strong acid) from a medium of high dielectric constant to one of lower dielectric constant in which ions exist mainly as ion-pairs. The free energy corresponding to this transfer is less positive if the dielectric constant of the organic medium is higher. The chemical properties of the diluent play also a major role. If the diluent is a good solvating agent for either cation or anion in the ammonium salt the extraction will be improved. Basic diluents can interact with the positively charged H atoms of the ammonium cation thus improving the extraction.

Depending on the properties of the diluent used for the extraction by alkylamines, the extracted alkylammonium salt might exist in the organic phase as different species. This aspect will be reviewed in the following part dealing with liquid ion exchangers and the mechanism of liquid ion exchange. 2. Alkylammonium salt liquid ion exchangers

Liquid ion exchange is one case of solvent extraction and liquid ion exchangers are high molecular weight ionogenic substances dissolved in an organic solvent and insoluble in aqueous solutions. The extraction involves ions transferred from one phase to the other. The ionogenic substance comprises one ion which can be exchanged with an aqueous ion, e.g.,  $\overline{B^+X^-} + \overline{Y^-} \neq \overline{B^+Y^-} + \overline{X^-}$  in the case of anion exchange. The counter ion B is of sufficiently high molecular weight so that BX and BY are practically insoluble in water.

The selectivity of the ion exchange depends on several factors: size and hydration of exchanged ions, <sup>(16)</sup> dielectric constant and solvating power of the organic diluent <sup>(15)</sup>, size and specific interactions of ion and counter ion in the organic phase. <sup>(17)</sup> Studies of liquid ion exchange using alkylammonium salts have been focused essentially on metal anion separation. <sup>(18)</sup> The importance of aggregation  $_{\circ}$ of the salts in the organic phase has been stressed. In an organic solvent an alkylammonium salt  $B^{+}X^{-}$  can exist in various forms: dissociated ions, ion-pairs, triple ions, dimers and higher polymers. The existence of an internal hydrogen bond in many substituted alkylammonium salts has been stressed. Many salts have been found to exist in the organic phase as hydrated species.

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3. Liquid ion exchange membrane selective electrodes

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Ion selective electrodes have been developed in which the active element is a liquid ion exchanger membrane. (9,17)Electrodes specific for Ca<sup>2+</sup>, NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup> or Cl<sup>-</sup> use different combinations of organic solvent and ion exchanger. Usually the water-immiscible ion exchanger liquid is absorbed on an inert porous membrane. This membrane separates an outer -aqueous phase from an internal aqueous solution of constant composition in which an internal electrode dips. In a design similar to the one used for glass pH electrodes the ion selective electrode is associated with an external reference electrode. The potential difference developed between the internal reference and the external reference electrodes is of the form:

$$E = E_{Ct} + \frac{RT}{zF} \ln \frac{a'x}{a''x}$$

 $E_{ct}$  is a constant term, a'<sub>X</sub> and a"<sub>X</sub> are the activities of the ion for which the membrane is selective in the solutions on each side of the membrane. Since the activity of the ion in the internal reference solution is maintained constant, the potential becomes a linear function of the log of the ion activity in the external solution with a slope of  $\pm$  59.16 mV per decade of activity at 25° for an ionic charge of  $z = \pm 1$ .

The membrane and the two solutions which it contacts can be represented as:

>

. w + x - | s' - x | M + x -

SX is an anionic exchanger dissolved in an organic solvent. Both are insoluble in water. On each side of the membrane the exchanger participates in exchanges with  $X^-$  ions in the aqueous solutions. The anion  $X^-$  is able to penetrate the organic phase but cation  $M^+$  is excluded. A potential builds up through the permselective membrane opposing the diffusion of  $X^-$  from the aqueous solution of high activity to the one of low activity. This potential is Nernstian.

If an interfering anion Y is present in an aqueous solution, it will contribute to the potential if it is accepted significantly in the organic phase. The selectivity of the electrode for X vs. Y depends on the ion exchange equilibrium constant for SX + Y  $\stackrel{?}{\rightarrow}$  SY + X.

Theoretical equations <sup>(17)</sup> have been developed to account for the potential of liquid ion exchange membrane electrodes. These are relatively complex and involve several factors: dissociation constant of the ion exchanger in the solvent, ion exchange constants with interfering ions, mobilities of the different species in the solvent. Detailed knowledge is lacking on certain properties of liquid ion exchangers and few studies, thus far, have attempted to relate the chemistry of these systems with the potential response of electrodes.

## 4. System studied - Plan of research

This study deals with the solvent extraction of trialkylamines and their salts. The high molecular weight trialkylamines have been extensively studied in several organic solvents. <sup>(18)</sup> Investigators have measured equilibrium constants of the two-phase formation of simple and complex salts, and studied their aggregation. In the present study the anions selected were Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> and Clo<sup>-</sup><sub>4</sub> which are anions of differing size and basicity.

Nitrobenzene, the organic solvent chosen, is a water insoluble high dielectric constant liquid. Aggregation of the salts should be minimized compared to low dielectric constant solvents.<sup>(19)</sup> Various amines from tripropyl to tridodecyl were selected in order to study the influence of the alkyl chain length on various solvent extraction equilibria.

A preliminary literature survey indicated that tridodecylammonium chloride, bromide, iodide and perchlorate in nitrobenzene exist essentially in the form of ion-pairs or dissociated ions. <sup>(20,21)</sup> Thus a systematic study of the dissociation constant of the salts by conductometry was undertaken first. The partition of the salts between nitrobenzene and water was expected to vary drastically with chain length. It was thus measured by distribution experiments. Then the two-phase formation of salts from amines was measured by a potentiometric method. Liquid ion exchange constants were

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deduced. Finally the organic salt solutions were tested as liquid ion exchangers in an electrochemical cell in order to check their applicability in liquid ion exchange electrodes.

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# 5. Acid <sup>o</sup>and water extraction. Hydrates in the organic phase.

The partition coefficients of inorganic acids between water and organic solvents corresponding to the equilibrium  $H^+ + X^- \ddagger HX$  are usually very small.<sup>(22)</sup> Müller et al.<sup>(23)</sup> reported a value of  $3 \times 10^{-7}$  for the partition of HCl between water and nitrobenzene. Högfeldt et al.<sup>(24)</sup> studied the distribution of HClO<sub>4</sub> between water and nitrobenzene and it can be concluded that HClO<sub>4</sub> (dissociated or ion-paired) should be in negligible concentrations in the systems studied.<sup>(20)</sup> On this basis significant extraction of aqueous acids into nitrobenzene was disregarded in this study.

Water is slightly soluble in nitrobenzene (.24% w/w at 20°).<sup>(25)</sup> At 25° the molarity of  $H_2O$  is .15. Tertiary alkylammonium salts in organic solvents have been found to be hydrated.<sup>(4,15)</sup> The extent of hydration depends on the anion 'species and the solvent. In aromatic solvents trialkylammonium chlorides probably exist as monohydrates.<sup>(8)</sup> Tridodecylammonium chloride has been found to be entirely monohydrated in nitrobenzene.<sup>(23)</sup> In general the extent of hydration decreases in the sequence  $Cl^- > Br^- > l^- > Clo_4^-$ , which corresponds to the decreasing order of basicity of the anions. (21, 26, 27) Water of hydration is generally believed to be associated with the anion. On this basis, it can be assumed that tertiary alkylammonium salts reported here are at least partially hydrated in nitrobenzene. In the present study no attempt was made to identify hydrates for each ammonium salt.

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## 6. <u>Concentration scales.</u> Reference and standard states.

The molar scale has been adopted to express the concentration of solutes in both the aqueous and the organic phases. The convention of dimensionless activity coefficients for these solutes has been adopted, thus activity has the dimension of a concentration. Some of the thermodynamic equilibrium constants have dimensions too.

The standard state for solutes in each solvent is chosen as the hypothetical molar solution in that solvent for which the activity coefficient of the solute was unity. The reference state was chosen to be an infinitely dilute solution of the solute for which the activity coefficient was unity.

The Debye-Hückel theory is used to estimate activity coefficients of ionic solutes in both phases. The activity coefficients yielded belong to the rational scale. However when applied to dilute enough electrolyte solutions (<  $10^{-1}$  M in water and <  $10^{-2}$  M in nitrobenzene) the activity coefficients

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13 C on the rational and molar scale are taken as equal (< 1% æ., difference). 2  $\overline{}$ (+ ') `\$*\`* 

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STUDY OF THE PREPARATION OF TRIALKYLAMMONIUM SALTS AND PURIFICATION OF TRIALKYLAMINES AND NITROBENZENE

CHAPTER II

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In this chapter the preparation of trialkylammonium salts and the assessment of their purity are described. The purification of trialkylamines and nitrobenzene and their purity are also considered.

#### A) PREPARATION AND PURITY OF TRIALKYLAMMONIUM SALTS

The chloride, bromide, iodide and perchlorate salts of tripropylamine, tributylamine, tripentylamine, trihexylamine, trioctylamine and tridodecylamine are not all commercially available. "With the exception of the chloride, bromide and iodide of tripropylamine and tributylamine, the chloride and bromide of trioctylamine and tridodecylamine and the iodide and perchlorate of tridodecylamine, these compounds have not been reported in the chemical literature or have been reported without any melting point determination or chemical analysis.

The salts were prepared by reacting a solution of the purified amine in water or an organic solvent with a quantity of concentrated acid in excess of approximately 10% over the stoichiometric amount. After recrystallizing the salt several times from organic solvents the compound was then dried under vacuum and stored in a vacuum dessicator. The purity of the salt was checked by potentiometric titration and elemental analyses.

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#### 1. Materials

Tripropylamine (98% Aldrich), tributylamine (Eastman), tripentylamine (Eastman), trihexylamine (Eastman), and trioctylamine (97% Aldrich) were distilled under reduced pressure by Tridodecylamine (Eastman) was use of a spinning band column. used without purification. The acids used were concentrated aqueous solutions: HCl 37.9% (Baker, reagent grade), HBr 47.9% (Baker, reagent grade), HI 64% (BDH, AnalaR), HClo, 70% (Anachemia, reagent grade). The solvents used for recrystal. lizations were acetone (Fisher, reagent grade), ethyl acetate (Fisher, reagent grade), diethyl ether (Mallinckrodt, USP) and petroleum ether (37°-51°C, Fisher certified). For the titrations potassium hydroxide (Anachemia, reagent grade) and potassium biphthalate (Baker, primary standard) were used. The melting points were taken on a Gallenkamp Melting Point The microanalyses were performed by Microanalysis Apparatus. Laboratories Ltd., Toronto, Ontario, and Daesslé Organic Microanalyses, Montréal, Québec. Halide analyses were performed by the Volhard method.

2. Trialkylammonium salts preparations

Tripropylammonium chloride

A 20 g quantity of conc HCl was added to 28 g of tripropylamine dissolved in 100 ml of water. After most of the water was boiled off by heating on a hot plate, the salt

precipitated on cooling. The solid was redissolved in 250 ml hot acetone and recrystallized in an ice bath. After two further recrystallizations from acetone, the product was dried in an oven at 110°.

#### Tripropylammonium bromide

A 36 g amount of conc HBr was added to 30 g of tripropylamine dissolved in 400 ml acetone. The salt separated upon cooling the solution in a dry ice - acetone bath. The filtered product was redissolved in hot ethyl acetate and crystals precipitated when the solution was cooled. The compound was recrystallized twice from ethyl acetate and dried in an oven at 110°.

Tripropylammonium iodide The procedure used was the same as described for tripropylammonium bromide using 28 g tripropylamine and 42 g conc HI.

Tripropylammonium perchlorate

A 16 g amount of conc HClO<sub>4</sub> was added to 15 g of tripropylamine dissolved in 200 ml acetone. The acetone was evaporated under vacuum and the crystalline residue was redissolved in a minimum volume of acetone. Ethyl acetate was " added gradually until the compound precipitated. Precipitation was completed by cooling the mixture in an ice bath. The salt was filtered and washed with ether. Recrystallization was carried out twice by the same procedure, dissolving first in the minimum amount of acetone, then adding ethyl acetate.

Tributylammonium chloride

A 12 g quantity of conc HCl was added to 20 g tributylamine dissolved in 100 ml of water. The volume was reduced by evaporation of water in a warm rotavapor still under vacuum. The product was dissolved in a small volume of ethyl acetate and crystallized in an ice-acetone bath; it was then washed with cold ether. The compound was recrystallized twice from ethyl acetate in the same manner.

#### Tributylammonium bromide

An 18 g quantity of conc HBr was added to 18 g tributylamine dissolved in 125 ml ethyl acetate. After the salt precipitated in a dry ice - acetone bath, it was filtered on a precooled Büchner fritted glass filter and washed with cold ether. It was recrystallized twice from 100 ml ethyl acetate cooled in an acetone-ice bath and washed with ether.

#### Tributylammonium iodide

The procedure used was the same as described for tributylammonium bromide with 18 g tributylamine and 22 g conc HI-and an ice bath for recrystallizations.

Tributylammonium perchlorate

The procedure used was the same as described for

tributylammonium bromide with 18 g tributylamine, 16 g conc  $HClO_4$ , 75 ml ethyl acetate and a dry ice - acetone bath for recrystallizations.

#### Tripentylammonium chloride

A 7 g quantity of conc HCl was added to 15 g tripentylamine dissolved in 150 ml of ethyl acetate. The precipitate formed in an acetone - dry ice bath was filtered and washed with cold solvent and cold ether. The salt was recrystallized twice from ethyl acetate in an acetone-ice bath, washed on the filter with cold solvent and dried under suction.

Tripentylammonium bromide -

The procedure just described for the chloride salt was used with 15 g tripentylamine and 12 g conc HBr.

Tripentylammonium iodide

The procedure was the same as described for the chloride with 15 g tripentylamine and 14 g conc HI and dry ice - acetone baths for recrystallizations.

Tripentylammonium perthlorate Not obtained.

Trihexylammonium chloride

A 5.6 g quantity of conc HCl was added to 15 g tri-

precipitated in a dry ice - acetone bath and then filtered on a precooled fritted glass Büchner, washed with cold ether and dried under suction. The salt was recrystallized twice under the same conditions.

Trihexylammonium bromide

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The procedure was the same as described for the chloride with 15 g trihexylamine and 10 g conc HBr.

Trihexylammonium iodide

The procedure was the same as described for the chloride with 15 g tribexylamine and 12 g conc HI.

Trihexylammonium perchlorate

Trioctylammonium chloride

A 5.4 g amount of conc HCl was added to 18 g trioctylamine dissolved in 200 ml ethyl acetate. The precipitate formed in a dry ice - acetone bath was filtered, washed with cold solvent and cold ether. The salt was recrystallized ' twice from ethyl acetate in an acetone-ice bath and washed with cold solvent and ether.

Trioctylammonium bromide

A 5.3 g quantity of conc #Br was added to 10 g trioctylamine dissolved in 200 ml diethyl ether and the solution shaken. Crystals which separated after placing the solution in a dry ice - acetone bath were dried on the filter under vacuum. The salt was recrystallized twice under the same conditions.

#### Trioctylammonium iodide

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A 6.1 g amount of conc HI was added to 10 g trioctylamine dissolved in 200 ml diethyl ether. The precipitated product was collected from the solution cooled at dry ice acetone bath temperature. The precipitate was recrystallized three times from ether at the same temperature.

#### Trioctylammonium perchlorate

A 4.5 g quantity of conc HClO<sub>4</sub> was added to 10 g trioctylamine dissolved in 250 ml diethyl ether. The salt precipitated at acetone - dry ice temperature and was re-crystallized twice under these conditions.

Tridodecylammonium chloride

A 4 g amount of conc HCl was added to 20 g tridodecylamine dissolved in 200 ml diethyl ether. A precipitate formed when the solution was cooled in an ice bath. The salt was recrystallized four times from petroleum ether in an ice bath.

Tridodecylammonium bromide

A 7 g quantity of conc HBr was added to 20 g tri-

dodecylamine dissolved in 100 ml petroleum ether. The precipitate formed at ice bath temperature was collected and recrystallized three times under the same conditions.

#### Tridodecylammonium iodide

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An 8.3 g amount of conc HI was added to 20 g tridodecylamine dissolved in 200 ml acetone. The salt separates in an acetone-ice bath and is recrystallized four times from petroleum ether in an ice bath.

#### Tridodecylammonium perchlorate

A 6 g quantity of conc HClO<sub>4</sub> was added to 20 g tridodecylamine dissolved in 200 ml acetone. A precipitate separated at the temperature of a dry ice - acetone bath. The salt was recrystallized three times from acetone in an iceacetone bath, then twice from petroleum ether in an ice bath.

#### 3. Potentiometric titrations

Substituted ammonium salts<sup>(1)</sup> and specifically tertiary alkylammonium salts<sup>(2)</sup> can be titrated in alcoholic solutions. In the present study, the end-point was signalled potentiometrically by means of a glass-saturated callomel electrode pair conditioned in water. In this procedure approximately one millimole of compound was accurately weighed and transferred in a beaker. A standardized (ca.  $4 \times 10^{-2}$  N) solution of potassium hydroxide in ethanol was delivered by a 25 ml burette to the salt blanketted by a nitrogen atmosphere. Titrant and salt were mixed by a small Teflon-encased magnetic bar. The titration reaction is:

 $R_3NHX + KOH \rightarrow R_3N + KX + H_2Q$ 

A steep potential change of ca. 100 mV was recorded within ± .5% of the end-point which was calculated by the second derivative method. The molecular weight as obtained by titration is compared to the theoretical molecular weight in Table I. The alcoholic solution of potassium hydroxide was prepared by weighing out ca. 5.2 g of KOH pellets. After first rinsing in water to remove any superficial carbonate and then rinsing in ethanol a few times, the pellets were dissolved in 2 l of absolute ethanol under, a nitrogen atmosphere. The solution was stored in a polyethylene bottle and dispensed through a system protected from atmospheric carbon dioxide. The solution was standardized by potentiometric titration of ca. 0.2 g of potassium hydrogen phthalate dissolved in 25 ml H<sub>2</sub>O. Standard deviations on titration results were of ca. 0.2-0.3%.

#### 4. Purity of compounds

In all cases the molecular weight obtained by titration was found to be within less than .5% of the theoretical

one, usually on the high/side. An elemental analysis (C, H, halogen) was performed on those compounds for which no melting <sup>o</sup> point was reported in the chemical literature. For these new compounds the C, H composition agreed with the theoretical composition within experimental errors. In three cases the &C disagreed by one point or more. The halide analyses were conform to theoretical percentages. In the course of this study solutions of TPRAHClO<sub>4</sub> and TOAHClO<sub>4</sub> were preferably prepared in situ by neutralisation of the amine by the corresponding acid. Solutions of TPTAHClO<sub>4</sub> and THAHClO<sub>4</sub> were prepared in situ since<sup>6</sup> these salts could not be isolated.

#### TABLE 1

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# Trialkylamine chloride, bromide, iodide and perchlorate salts properties

-		<b>k</b> .		C, H analyses		Halide analyses	ς.	
Compound	mp	Literature mp and references	mol wt calcd obsd	€C calcd obsd	ξH calcd obşd	₹X calcd obsd	Remarks	
Tripropylammonium			1 4	-			-	
- chloride	140-141	137 <sup>(3)</sup>	179.73 180.1	-		<b>F</b>	hygroscopic	
- bromide	185-186	180 <sup>(4)</sup>	224.19 224.9		-		hygroscopic	
- iodide	233-5	166 <sup>(5)</sup>	271.18 272.0			46.8 47.1	-	
- perchlorate	265-7		243.73 244.9	44.3 42.3	9.10 9.2		, ,	
Tributylammonium			_	~		t	•	
- chloride	72-73	(d) 182 <sup>(6)</sup>	221.82 221.8		o 2 '	16.0 16.0	very hygroscopic	

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<u>Table 1</u> - cont'd.

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Compound	, , mp	mp and references	calcd obsd	Calcd obsd	%H calcd ∕bsd	€X calcd obsd	Remarks	
- bromide	74	74-75 (7) 75-76 (8)	266.28 267.1		· · · · · · · · · · · · · · · · · · ·		hygroscopic	
- iodide	101-102	102,103 <sup>(4)</sup> 101.0-101.5 <sup>(7)</sup>	313.27 314.2		t	- <u>-</u> ,	yellowish	
- perchlorate	85		285.82 286.8	50.4 50.1	9.9 9.8		٩	
Tripentylammonium	، 1			3	_			
- chloride	33	<b>:</b>	263.90 264.6	68.3 67.5	13.0 - 13.4	13.4 13.5	hygroscopic	
- bromide	65-67		308.36 309.3	58.4 58.1	11.1 10.8	25.9 X 25.9	~	
- iodide	50-51	-	355.35 355.0	50.7 50.9	9.6 9.8	35.7 35.8		
- perchlorate		2	327.90				not obtained	

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	mp	Literature mp and references	mol wt calcd obsd	C, H analyses		analyses	
Compound				%C calcd ⊘bsd	%H calcd obsd	&X calcd obsd	Remarks
ihexylammonium						- V	· .
- chloride	50	ت <b>م</b> و	305.98 30 <b>6</b> .0	70.7 70.7	13.2 13.0	11.6 11.7	١
- bromide	56		350.44 351.1	61.7 63.3	11.5 11.6	22.8 22.7	
- iodide	40	· ·	397.43 398.8	54.4 54.4	10.1 9.8	31.9 31.9	t.
- perchlorate		-	369.98		_		not obtained
rioctylammonium						-	и 1
- chloride	72	72-74 <sup>(4)</sup> 71-72 <sup>(9)</sup>	390.14 390.1				1 <sup>3</sup> 3 ~
- bromide	72-73	72-73 (10)	434.6 435.0		٥		e
- iodide	60	4	481.59 482.4	59.9 58.2	10.9 11.0	26.4 26.3	yellowish

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Table 1 - cont'd.

Halide C, H analyses analyses Literature mol wt\_ %H calcd %X calcd %C calcd obsd mp and calcd Compound references obsd obsd obsd mp Remarks 454.14 11.5 - perchlorate 49 63.5 454.8 64.4 11.6 Tridodecylammonium 78-79<sup>(4)</sup> 84-85<sup>(2)</sup> 82-83<sup>(9)</sup> 558.46 - chloride 84-85 560.2 86-87<sup>(2)</sup> 602.92 - bromide 86 604.1 52<sup>(10)</sup> 649.91 66.5 11.8 yellowish - iodide 67-68 67.0 652.6 11.7 58-59 (2) 622.46 pinkish perchlorate 59 624.1

Melting points are reported without stem correction

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#### B) PURIFICATION OF TRIALKYLAMINES

Trialkylamines used in this study were all commercially available. They were distilled and their purity assessed.

#### 1. Chemicals and purification

The following amines were distilled on a spinning band column under reduced pressure: tripropylamine (Aldrich 98%): 54° and 20 mm; tributylamine (Eastman): 88° and 10 mm; tripentylamine (Eastman): 72° and 1 mm; trihexylamine (Eastman): 128° and 3 mm and trioctylamine (Aldrich): 110° and < 1 mm. Tridodecylamine (Eastman) was non distillable under normal conditions. It was used directly after decantation away from a white solid deposit.<sup>(11)</sup> The melting point was measured as 15.8-16.0° (reported as 15.7° in (12)).

Although tertiary alkylamines are considered relatively stable, <sup>(13,14)</sup> most showed a tendency to gradually become yellow and were stored in dark bottles in a nitrogen filled box. They were periodically redistilled.

2. Purity of amines

The purity of amines was assessed by non aqueous titration in glacial acetic acid with an anhydrous acetic acid solution of perchloric acid. (15,16,17,18)

A 0.1 N perchloric acid solution was prepared by

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mixing 8.5 ml  $HClo_4$  70-72% (Anachemia, reagent) with 300 ml glacial acetic acid (Fisher, reagent), and adding 20 ml of acetic anhydride (Fisher, certified) followed by dilution to one liter with glacial acetic acid. Standards were prepared by dissolving ca. 0.5 g potassium hydrogen phthalate in 50 ml hot glacial acetic acid. Two to four meq of amine were dissolved in 50 ml glacial acetic acid and titrated with the standardized  $HClo_4$  solution. End-points were detected potentiometrically with a calomel-glass electrode pair conditioned in glacial acetic acid. A potential break of ca. 150 mV was observed within  $\pm$  .5% of the end-point. The equivalent weights from titration were found as: TPRA (calcd: 143.27, obsd: 143.6), TBA (calcd: 185.36, obsd: 185.4), TPTA (calcd: 227.44, obsd: 227.7), THA (calcd: 269.52, obsd: 271.1), TOA (calcd: 353.68, obsd: 356.9), TLA (calcd: 522.00, obsd: 524.6).

#### C) NITROBENZENE

The nitrobenzene used throughout this study was Fisher certified. It was purified for conductometric and solvent extraction studies.

#### 1. Impurities and purification

Commercial nitrobenzene is obtained as a deeply yellow coloured liquid. Purified nitrobenzene has been reported to have a pale yellow colour and is to be kept in dark bottles because of its photosensitivity. Nitrobenzene may contain water soluble acidic impurities remaining from its synthesis.<sup>(19)</sup> A yellow impurity attributed to the presence of nitrophenols<sup>(20)</sup> can be removed in part by washing the solvent with alkali<sup>(21)</sup> or passing it through a column of alumina.<sup>(20,22)</sup> Müller and Diamond<sup>(15)</sup> observed that the pH values of aqueous phases of low acidity increased when saturated with nitrobenzene.

In this study the presence of acidic and basic impurities and the efficiency of the various means of puri<sup>(2)</sup> fication were checked by titration. Volumes of 50 ml aqueous HCl (1.000 x 10<sup>-3</sup> N HCl and 9.90 x 10<sup>-2</sup> N KCl) were titrated with a KOH aqueous solution (1.000 x 10<sup>-2</sup> N KOH and 9.00 x  $10^{-2}$  N KCl) in the presence of various samples of nitrobenzene. These conditions which can produce a wide range of acidity and basicity reproduce the experimental conditions of a

solvent extraction experiment by two-phase emf titration. The denser nitrobenzene phase was stirred with a magnetic bar and mixed with the aqueous phase. Potential readings were taken on the aqueous phase by a glass-calomel electrode pair in a constant temperature system.

The titration curve obtained with nitrobenzene absent appears as curve 1 in figures 1, 2 and 3. The potential varies from approximately +220 mV for a  $10^{-3}$  M HCl solution to ca. -220 mV for a  $10^{-3}$  M KOH solution. The presence of acidic or basic impurities extractable into acidic or basic aqueous solutions is expected to influence the shape of the standard titration curve and shift the equivalence point.

Curves 2 and 3 in figure 1 were obtained in the presence of 10 ml and 20 ml respectively of non-purified nitrobenzene in equilibrium with the aqueous phase. In curve 4 of figure 2 the nitrobenzene present had been washed twice with 0.1 N NaOH solution which extracted a red-orange compound, then rinsed three times with distilled water. In curve 5 the nitrobenzene had been passed through a column of alumina (Fisher certified, neutral, for chromatography) which adsorbed a red-yellow compound. In curve 6 of figure 3 the nitrobenzene had been washed twice with 0.1 N  $H_2SO_4$  and rinsed three times with water.

If vacuum distilled nitrobenzene was titrated, the

## FIGURES 1, 2 and 3

Aqueous acid-base potentiometric titration curves obtained in the presence of various samples of nitrobenzene. Sample: 50 ml aqueous HCl  $(1.000 \times 10^{-3} \text{ N HCl and})$ 

 $9.90 \times 10^{-2} N KCl)$ .

Titrant: aqueous KOH (1.000 x  $10^{-2}$  N KOH and

 $9.00 \times 10^{-2} N KC1$ ).

Curves:

(2) with 10 ml reagent grade nitrobenzene;

(1) blank: no nitrobenzene present;

(3) with 20 ml reagent grade nitrobenzene;

(4) with 20 ml-nitrobenzene after NaOH extraction;

(5) with 20 ml nitrobenzene after purification on alumina;

(6) with 20 ml nitrobenzene after sulfuric acid extraction.



FIGURE 1





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FIGURE 3

titration curve would appear in figure 1 between curves 1 and 2 in the high potential region and between 2 and 3 for the lower region. Titrations performed on  $HClO_4$  solutions. with aqueous NaOH in a  $NaClO_4$  medium gave similar results as reported in figures 1, 2 and 3 for a KCl medium.

The presence of acidic and basic water extractable impurities in nitrobenzene was thus demonstrated. An acidic impurity appears to displace the end-point (see figure 3). The aqueous phase becomes more intensely yellow as the solution becomes basic. Acid impurity can be removed by washing with aqueous alkali or by adsorption on alumina; it is only partly removed by vacuum distillation. The basic impurity (see figure 2) can be removed by washing with aqueous acid or in large part by vacuum distillation. This impurity seems to account for the effects observed by Müller and Diamond.

The following purification method was adopted: <sup>(23)</sup> nitrobenzene was first distilled under reduced pressure on a spinning band column. It was then washed three times with 0.1 N NaOH, rinsed once with distilled water, washed three times with 0.1 N H<sub>2</sub>SO<sub>4</sub>, then rinsed three or four times with distilled water. The pH of the last washing was checked for neutrality. The solvent obtained was of a pale straw colour. Nitrobenzene thus obtained did not interfere in the standard titrations described above. Potential readings were the same as in curve 1 within  $\pm$  .3 mV.

#### 2. Physical constants

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The specific conductance of the water saturated nitrobenzene was measured with a Beckman RC18-A conductivity bridge and a cell of known constant (see chapter III) and was found to be 2.9 (± .2) x  $10^{-8} \Omega^{-1}$  cm<sup>-1</sup> at 25°.

The density of purified and water saturated nitrobenzene was determined at 25°C using a pycnometer and found to be 1.1971 (1.1986 for anhydrous nitrobenzene in (24)).

The viscosity was determined at 25° using three calibrated u-tube capillary type viscosimeters (Cannon - Fenske) and found to be  $\eta = 1.82 \pm .01$  cp using the density value previously determined ( $\eta = 1.811$  cp for anhydrous nitrobenzene in (24)).

The dielectric constant at 25°C of the water saturated nitrobenzene was determined on a Dipolmeter type DM 01 WTW using distilled, deionized water and anhydrous nitrobenzene (distilled and stored over 4 Å molecular sieves) as reference points. The dielectric constant was found to be 34.87 ¢ompared to 34.82 for anhydrous nitrobenzene. (24)

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#### CHAPTER III

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CONDUCTOMETRY AND THE DISSOCIATION OF TERTIARY ALKYLAMMONIUM SALTS IN NITROBENZENE Conductivity measurements of water-saturated nitrobenzene solutions of tertiary alkyPammonium salts were undertaken to determine the nature of the solute and the equilibria prevalent among the different solute species. In nitrobenzene ionophores usually experience a partial dissociation<sup>(1)</sup> depending on the sizes of anion and cation.

Conductometry of solutions of quaternary ammonium salts in nitrobenzene has led to the estimation of their dissociation constants. For these salts dissociation was found to be important and to increase with increasing size of anion and cation in agreement with an electrostatic model for their association.<sup>(1)</sup> Tertiary ammonium salts generally experience a much smaller dissociation than quaternary ammonium salts in dipolar aprotic solvents due to the formation of an internal hydrogen bond between cation and anion in the ionpair.

Only fragmentary data exist on the dissociation of tertiary alkylammonium salts in nitrobenzene. (2,3,4,5) In<sup>6</sup> this study the chain length of the alkylammonium cation was increased and anions of differing hydrogen bonding affinities were introduced to reveal the influence of the structure of tertiary amine salts on their solution properties.

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#### A) CONDUCTOMETRY AND THE MEASUREMENT OF DISSOCIATION CONSTANTS

The electrical resistance of a solution depends on the number, mobility and charge of the different ions present.

1. Basic relations and units

The molar conductance,  $\Lambda$ , of a solution of molarity c is related to its specific conductance  $\kappa$  by:

$$\Lambda = 1000 \text{ k/c}$$

The specific conductance  $\kappa$  is in turn related to the resistance R of the solution measured in a cell of constant k by  $\kappa = k/R$ . The two equations are combined to give:

$$\Lambda = \frac{1000 \text{ k}}{\text{R c}}$$

where k is in  $cm^{-1}$ ,

R, in  $\Omega$ ,

c, in mol  $l^{-1}$ ,

$$\kappa$$
, in  $\Omega^{-1}$  cm<sup>-1</sup>,

$$\Lambda$$
, in  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

The limit towards which  $\Lambda$  tends at infinite dilution is called the molar conductance at infinite dilution or the limiting molar conductance  $\Lambda_{o}$ .

In general for solutes dissociating completely or

partially into ions the molar conductivity is observed to increase with increasing dilution.

## 2. Incompletely dissociated solutes (1)

If the solute AB dissociates in solution into ions  $A^+$  and  $B^-$  according to the equilibrium:  $AB \not\equiv A^+ \not\equiv B^-$ , the dissociation is described by  $K_{d}$ , the dissociation constant:  $K_{d} = (A^+)(B^-)/(AB)$ . Assuming that the change in molar conductance with dilution is due to the change in the degree of dissociation  $\dot{x}$  ( $\dot{x}$  is one at infinite dilution), one can write:

and

hese equations are combined to give:

 $\frac{1}{\Lambda} = \frac{1}{\Lambda_{\circ}} + \frac{c \Lambda}{K_{d} \Lambda_{\circ}^{2}}$ 

 $K_{d} = cx^{2}/(1-x)$ 

When  $\Lambda_o$  can be obtained by extrapolation or through Kohlrausch's law,  $K_{d}$  can be calculated at any concentration or estimated graphically from measurements on a series of solutions.

This treatment suggests that solutes behave ideally and that ionic mobilities are independent of the concentration. However data on completely dissociated electrolytes show a dependence of ionic mobilities on concentration.

3. Onsager's interionic attraction treatment of conductivity<sup>(1,6)</sup>

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The Debye-Hückel theory, introducing the concept of the ion atmosphere, was modified by Onsager and applied to conductivity measurements on very dilute solutions of completely dissociated electrolytes, leading to the equation:

 $\Lambda = \Lambda_{o} - (\alpha \Lambda_{o} + \beta) \sqrt{c}$ 

where  $\alpha$  and  $\beta$  depend only on the dielectric constant of the solvent, its viscosity and the absolute temperature. This treatment accounts for the increase in molar conductance with increasing dilution through two effects arising from the ion atmosphere, the "electrophoretic effect" and the "time of relaxation effect", reflected in the two constants  $\alpha$  and  $\beta$ . Since the equation described a limiting law, it was further modified to take into account solute size. The new treatment led to the Fuoss-Onsager equation:

 $\Lambda (1 + F c) = \Lambda_{0} - (\alpha \Lambda_{0} + \beta) \sqrt{c} + E c \log c + J$ 

, where F and J depend on the size of the ions.

## 4. Weakly dissociated solutes (7)

The treatment of interionic effects on conductivity of strong electrolytes through Onsager's equations and on activity through Debye-Hückel laws have permitted calculation of more accurate dissociation constants of incompletely dissociated solutes. In the case of a solute with a dissociation constant less than approximately 0.01, (7,8,9) the E, J and F terms are often dropped and the conductance data treated by the methods of Fuoss and Kraus or Shedlovsky. (10,11) Onsager's limiting law equation is modified to take into account association

 $\Lambda = \mathbf{x} \Lambda_{o} - \frac{\Lambda}{\Lambda_{o}} (\alpha \lambda_{o} + \beta) \sqrt{\mathbf{c}\mathbf{x}}$ 

Starting from molar conductance data at several concentrations and an approximate value of  $\Lambda_{\circ}$  found by extrapolation of  $\Lambda$  vs.  $\sqrt{c}$ , these methods lead to rapid graphical solutions yielding values for the thermodynamic dissociation constant Kd and improved values of  $\Lambda_{\circ}$ .

#### B) EXPERIMENTAL

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Conductivity measurements were performed on watersaturated nitrobenzene solutions of tripropylammonium, tributylammonium, tripentylammonium, trihexylammonium, trioctylammonium and tridodecylammonium chlorides, bromides, iodides and perchlorates.

### 1. Chemicals

The preparation of trialkylammonium salts and the purification of amines and nitrobenzene have been described in chapter II.

# 2. Preparation and standardization of trialkyl-

Salts obtained as pure solids were dissolved in water-saturated nitrobenzene and diluted to approximate decimolar solutions. Nitrobenzene solutions of the other salts which were not isolated as pure crystalline compounds (see chapter II) were prepared by neutralisation of the appropriate amine solution in nitrobenzene with an aqueous solution of the corresponding acid. An approximate decimolar solution of amine in nitrobenzene was prepared and shaken with an equal volume of 0.2 M aqueous solution of acid. The separated organic phase was therefore decimolar in ammonium salt. To insure the organic phase was water-saturated at the temperature of the conductometric measurements the salt solutions prepared either way were further equilibrated at 25° in a constant temperature bath (Wilkens-Anderson) with a solution of the corresponding 0.1 N aqueous acid. A 1 M acid solution was used for the more soluble TBAHC1, TPRAHBr, TPRAHI. The TPRAHC1 solution was not further equilibrated with water. The acid was introduced to prevent hydrolysis of the trialkylammonium ions.

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The trialkylammonium salt solutions were standardized by potentiometric titration with standard potassium hydroxide in ethanol (see chapter II, section A), part 3). The end-point was detected with a calomel-glass electrode pair previously conditioned by soaking in water.

The standardized decimolar solution was used as stock solution for the preparation by dilution of a series of eight solutions ranging from  $10^{-2}$  to  $10^{-4}$  M. These dilutions were performed at 25° using volumetric flasks immersed in the constant temperature bath. Nitrobenzene used for the dilutions was water-saturated at this temperature. The volumetric glassware used during this study was calibrated and conformed to class A requirements. The stated volumes were used. No significant difference was observed when pipettes delivered nitrobenzene rather than water.

3. Conductance measurements

#### a) Conductivity cell

The conductivity cell was a cylindrical flask with two planar square parallel platinum electrodes situated inside near the bottom of the flask. The electrodes, covered with platinum black, were in electrical contact with pools of mercury contained in sealed glass tubes. Platinum wires immersed in the mercury pools were connected to the conductivity bridge. The capacity of the ground glass stoppered flask was 40 ml. Temperature control was achieved by immersing the cell in water contained in a double-walled beaker maintained at 25.00 ± .02° by a circulating bath (Hetotherm, type 623) calibrated with a 2801 A H.P. Quartz thermometer. The Teflon-encased magnetic bar used to stir the water in the beaker actuated a 1 cm stirring bar in the conductivity cell. Solution volumes of 25 ml were transferred to the cell. The resistance of the solution was shown to increase with decreasing volume of solution for volumes below 20 ml. This was probably caused by a gradual cut-off of current lines as the level of the solution approached the electrodes.

#### b) Conductivity bridge

The conductance of the solutions was measured using a Beckman RC-16 B2 bridge. The accuracy of the resistance scale of the bridge was verified at the two available fre-

quencies (50 Hz and l kHz) by means of a calibrated resistance decade box. In the range 200000 to 500  $\Omega$  the bridge showed no deviation higher than .3%. This corresponds also to the sensitivity claimed by the manufacturer.

c) Frequency dependence and resistance range

In conductivity measurements a dependence of the resistance of solutions with applied frequency is generally observed.<sup>(6)</sup> This is attributed to various electrostatic and electromagnetic couplings and introduces uncertainties in the measurement.

In this study solutions with resistances between 1000 and 100000  $\Omega$  gave readings at 50 and 1000 Hz which did not differ by more than .5% and were .5% only at these limits. Consequently only solutions falling within this resistance range were used. The frequency dependence increases rapidly outside of these limits with a change of 2% for a solution of 200  $\Omega$  resistance and 1% for a solution of 150000  $\Omega$ .

d) Measurement of the cell constant

The resistance of an aqueous solution of KCl of known molarity ( $c = 1.000 \times 10^{-3}$  M) was measured at 50 Hz . and 1 kHz and the cell constant k calculated by:

 $k = \frac{\Lambda c}{1000} \times \frac{1}{\frac{1}{R} - \frac{1}{Rw}}$
with R = measured resistance of the KCl solution,

Rw = resistance of the deionized water,

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 $\Lambda$  = molar conductance of the solution (146.95 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> at 25° (12)).

The 1.000 x  $10^{-3}$ M KCl solution was obtained by dilution of a 1.000 x  $10^{-2}$  M KCl solution prepared by dissolving 7.4557 g of KCl (Baker, analyzed reagent, 99.9% purity, dried three hours at 110°C) in a one  $\ell$  volumetric flask and diluting to the mark. The values of resistance at 50 Hz and 1 kHz (1625  $\Omega$  and 1620  $\Omega$ ) were averaged. The resistance of water (distilled and deionized on a mixed bed ion-exchange resin) was measured as 5 (± 1) x  $10^5 \Omega$ . The value of k was calculated to be .239 ± .001 cm<sup>-1</sup>.

#### 4. General procedure

Before a measurement the cell was rinsed with acetone and dried by circulation of air. The solution to be measured was used first to rinse the cell. During storage the cell was kept filled with distilled water.

The solution to be measured was pipetted from its flask maintained at 25° and transferred into the conductivity cell. The resistance was measured at 50 Hz and 1 kHz after five minutes stirring. For all cases two series of measurements were undertaken on each system with dilutions starting from the same decimolar solutions. A characteristic set of

concentrations was:  $10^{-2}$  M, 6.0 x  $10^{-3}$  M, 4.0 x  $10^{-3}$  M, 2.0 x  $10^{-3}$  M,  $10^{-3}$  M, 4.0 x  $10^{-4}$  M, 2.0 x  $10^{-4}$  M, 1.0 x  $10^{-4}$  M. The lower limit corresponds to instrumental limitations since the resistance becomes excessively large.

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#### C) METHOD OF CALCULATION

#### 1. General

An estimate of the limiting molar conductance and the dissociation constant,  $K_d$ , of each salt was obtainable from measured solution resistances. The molar conductance,  $\Lambda$ , is calculated according to  $\Lambda = \frac{(k/R-K_s)}{c} 10^3$  where R is the solution resistance and  $K_s$  is the specific conductance of the solvent. A phoreogram is prepared by plotting  $\Lambda$  vs.  $\sqrt{c}$  where c is the solute concentration.

The data were treated according to the method of Shedlovsky<sup>(6,11)</sup> applicable to poorly dissociated solutes. By extrapolation of the linear part of the phoreogram on the low concentration side, an initial value of  $\Lambda_{\circ}$  is obtained. The Shedlovsky parameter S(z) and  $y_{\pm}$  (see Appendix I) have been related to  $\Lambda_{\circ}$ ,  $K_{d}$ ,  $\Lambda$  and c according to

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_o} + \frac{\Lambda c y_{\pm}^2 S(z)}{K_a \Lambda_o^2}$$
(1)

A plot of  $1/\Lambda S(z)$  vs.  $\Lambda c y_{\pm}^2 S(z)$  yields a value for  $\Lambda_{\circ}$  and  $K_{d}$  from the intercept I and slope S. A least-squares method was used to fit the data to a straight line. The new value  $\Lambda_{\circ}^{*}$  for the limiting molar conductance was used to iterate the calculation yielding final values of  $\Lambda_{\circ}$  and  $K_{d}$ . In the least-squares method an equal weight was given to all points and standard deviations were calculated for  $\Lambda_{\circ}(\sigma_{\Lambda})$  and  $K_{d}({}^{\sigma}K_{d})$ .

## 2. Concentration limits

The range of concentrations over which the method is applicable is limited, aside from instrumental limitations, by the same conditions as applicable to the Debye-Hückel treatment. <sup>(8)</sup> Within an order of magnitude the upper limit of concentration is given by  $2 \times 10^{-4} \varepsilon$  ( $7 \times 10^{-3}$  M for nitrobenzene). The possibility of formation of triple ions sets another limitation which has been estimated to correspond to a concentration limit of  $3.2 \times 10^{-7} \varepsilon^{3(7)}$  (i.e. 4 x  $10^{-2}$  M in nitrobenzene).

In practice the upper concentration is found experimentally from the Shedlovsky plot by rejecting the points in the high concentration range which deviate from the straightline relationship. In nitrobenzene the limit was usually set at 3-5 x  $10^{-3}$  M. <sup>(5,13)</sup>

#### D) RESULTS

Individual data and calculated values for each system are tabulated in Appendices II and III.

## 1. The perchlorate and iodide systems

For these systems two series of measurements at eight different concentrations ranging from  $10^{-2}$  to  $10^{-4}$  M were obtained. Phoreograms appear in figures 4 and 5. Extrapolations in the low concentration range of the perchlorate and iodide phoreograms were possible and yielded preliminary values of  $\Lambda_o$ . These values were used for first calculations of Shedlovsky plots. Visual inspection of the Shedlovsky plots indicated the critical concentration above which calculated data points deviate from a straight line. In general points at  $10^{-2}$  M and some at  $6 \times 10^{-3}$  M deviated in a systematic fashion and the data were recalculated using  $4 \times 10^{-3}$  M as the limiting concentration. Data are presented in figures 8 and 9. New values of  $\Lambda_o$  thus obtained were used to determine final  $\Lambda_o$  and  $K_d$  values reported in Table 2.

#### 2. The bromide and chloride systems

For these systems measurements at low concentrations were limited by solution high resistance (lower limit was at  $6 \times 10^{-4}$  M for chlorides and  $3 \times 10^{-4}$  M for bromides). For this reason extrapolations to infinite dilution could not be

# EIGURES 4, 5, 6 and 7

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Phoreograms of trialkylammonium perchlorates, iodides, bromides - and chlorides.



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# FIGURES 8, 9, 10 and 11

Shedlovsky plots of trialkylammonium perchlorates, iodides, bromides and chlorides.

 $X = 1/\Lambda S(z)$ 

 $Y = \Lambda c y_{\pm}^2 S(z)$ 

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used to obtain initial  $\Lambda_0$  values. Phoreograms are presented in figures 6 and 7. The following procedure was adopted. Literature values<sup>(5)</sup> for the ionic limiting conductance of  $Clo_4^-$ , 20.9, and  $I^-$ , 20.4, in  $\phi NO_2$  and the experimentally determined limiting conductances of the trialkylammonium perchlorates and iodides were combined to estimate average values for the limiting conductance of the tertiary ammonium cations (see Table 4). These values and literature values<sup>(5)</sup> of the limiting conductance of  $Cl^-$ , 22.2, and  $Br^-$ , 21.6, yielded estimates of  $\Lambda_0$  for the different chloride and bromide trialkylammonium salts with a confidence limit estimated at  $\pm$  10%. These  $\Lambda_0$  values were used to calculate the points of the Shedlovsky plots (figures 10 and 11).

In the bromide plots points at  $10^{-2}$  M and 6 x  $10^{-3}$  M were rejected. In all cases but one, recalculated  $\Lambda_{\circ}$  values fell within 10% of the initial ones and were associated with standard deviations of the order of 5-10%. This fact and the sensitivity of the calculated  $\Lambda_{\circ}$  to experimental errors in the case of solutes with very low dissociation constants <sup>(9, 14,15)</sup> render the direct use of the Shedlovsky method uncertain. In this case  $\Lambda_{\circ}$  values were assumed to be as initially estimated from the perchlorate and iodide experiments and  $K_{\rm d}$  values were calculated for each point using eq. (1) and averaged for each system. These values are recorded in Table 2. The standard deviations of  $K_{\rm d}$  values thus obtained

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are roughly 3%, however the confidence limit is close to 20% since it is approximately 10% for  $\Lambda_{\circ}$  (see also Appendix III).

In the chloride system points at  $4 \times 10^{-3}$  M,  $6 \times 10^{-3}$  and  $10^{-2}$  M were rejected. Calculated values of  $\Lambda_{\circ}$  from the Shedlovsky plot were not used for the calculation of  $K_{d}$  for the same reason as advanced for the bromides. The estimated  $\Lambda_{\circ}$  values yield values of  $K_{d}$  for each salt with relative standard deviations and limits of confidence similar to the bromide values. These values appear in Table 2.

## 3. Reproducibility and the limits of the method of Shedlovsky

Reproducibility of conductance data in this study between two independent sets of measurements was found to be of the order of 1% on an average. It was usually poorer on the low concentration side than on the high concentration side. Both adsorption effects and uncertainties associated with successive dilutions can affect the reproducibility. In the case of some chloride and bromide salts adsorption on the walls of containers can explain variations of conductivity with time. The reproducibility of the resistance measurement itself is of the order of .3%.

A limitation to the method comes from the fact that the terms F, E and J in the Fuoss-Onsager general equation have to be abandoned in the Shedlovsky equation. However a

Limiting molar conductances and dissociation						
, k	constants of	trialkylam	menium salt	ts in nitro	benzene	
•	, R <sub>3</sub> NHClO <sub>4</sub>		R	3 <sup>NHI</sup>	R <sub>3</sub> NHBr	R <sub>3</sub> NHC1
Amine	Λ.*	-log K <sub>d</sub> **	٨	-log K <sub>d</sub>	-log K <sub>d</sub> t.	-log K <sub>d</sub> †
Tripropyl TPRA	36.5±.1	_ 2.38±.01	34.8±.4	3.40±.01	4.5	5.0
Tributyl TBA	35.1±.2	2.41±.01	33.4±.5	3.41±.01	4.5	5.0
Tripentyl TPTA	33.9±.1	2.45±.01	31.9±.4	3.41±.01	4.5	5.0
Trihexyl THA *	33.3±.1	2.46±.01	31.0±.3	3.43±.01	4.5	5.0
Trioctyl TOA	32.2±.2	2.46±.01	30.6±.3	3.48±.01	4.5	5.0
Tridodecy] TLA	30.9±.2 *	2.47±.01	, 29.5±.2	3.50±.01	, 4.5	5.0
* A. in S ** K <sub>d</sub> in T	$2^{-1} cm^2 mol^{-1}$ nol. $2^{-1}$	۰ ۲	<sup>†</sup> Confid unit	ence-limit	estimated as	±.l log

TABLE 2

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complete analysis using the Fuoss-Onsager equation necessitates a reproducibility of the order of 0.1%.<sup>(7)</sup> The error introduced by the use of a simpler equation should be reflected in the  $K_d$  value. It has been estimated to be of the order of 10% in nitrobenzene for a salt with a  $pK_d$  of 1.7.<sup>(16)</sup>. The error should be smaller for the more strongly associated salts in this study  $(pK_d > 2)$ .<sup>(7)</sup>

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#### E) DISCUSSION

#### 1. Ion pairing and internal hydrogen bonding

In dipolar aprotic solvents salts of tertiary amines experience a degree of internal hydrogen bonding.  $^{(17)}$  Spectroscopic studies of selid and dissolved salts  $^{(18,19,20)}$  by nmr and ir techniques have shown that the hydrogen atom bound to the central nitrogen atom interacts strongly with a small or basic anion. This has the effect of increasing the association of the ion-pair in dipolar aprotic solvents over the purely electrostatic association. Dissociation constants from conductometry in various solvents are found to be orders of magnitude lower than for the corresponding quaternary 'ammonium ions.  $^{(5,13,17,21,22)}$  This comparison appears in Table 3.

#### TABLE 3

## Comparison of butylammonium Kalvalues

1	1 .	А
1	Tributylammonium	Tetrabutylammonium
Anion	•	
Bromide	$3.1 \times 10^{-5*}$	$1.79 \times 10^{-2} (5)^{-2}$
Iodide	$3.9 \times 10^{-4*}$ 9.5 x 10 <sup>-5</sup> (5)	$3.7 \times 10^{-2}$ (23)
Picrate	$1.9 \times 10^{-4}$ (21)	$3.3 \times 10^{-1}$ (13) 1.4 x 10 <sup>-1</sup> (23)

\* This work

The methods of Denison and Ramsey <sup>(24)</sup> or Bjerrum and Fuoss <sup>(25)</sup> based on purely electrostatic effects permit the calculation of the dissociation constant of an ion-pair from an estimate of their distance of closest approach a. Reciprocally this distance can be estimated from the known dissociation constant. The failure of a purely electrostatic model of the ion-pair formation in the case of the present study is illustrated by the very low values for the average distance of closest approach calculated from experimental results for each series. Values of a in Å calculated according to (25) appear in the following list: R<sub>3</sub>NHClO<sub>4</sub>, 1.40; R<sub>3</sub>NHT, . 1.06; R<sub>3</sub>NHBr, 0.87; R<sub>3</sub>NHCl, 0.80. A similar calculation done on tributylammonium picrate in anhydrous nitrobenzene <sup>(21)</sup> gave a value of 1.02 Å.

## <sup>5</sup>2. <u>Dissociation and anion basicity</u>

The dissociation constants of trialkylammonium salts found in this study are seen to be strongly dependent on the anion species. Although no significant dissociation of trilaurylammonium chloride was observed by Diamond, <sup>(3,4)</sup> he reported the bromide, iodide and perchlorate salts were increasingly dissociated. Dissociation constants were not reported. The average  $K_d$  from each series in this study are found to be ca. 3.6 x 10<sup>-3</sup> for  $R_3NHClo_4$ , 3.7 x 10<sup>-4</sup> for  $R_3NHI$ , 3.1 x 10<sup>-5</sup> for  $R_3NHBr$  and 1.0 x 10<sup>-5</sup> for  $R_3NHCl$ . For tetra-

butylammonium salts in nitrobenzene (Table 3 and (26)) the decrease in K<sub>d</sub> going from I to Br and Cl. is seen to be of a much smaller amplitude. Again this difference may be explained by the influence of hydrogen bonding on the ion pairing of partially substituted ammonium salts.

Hydrogen bonding of the type  $NH^+...X^-$  should be stronger, the smaller and more basic the anion. <sup>(27)</sup> Kertes et al. <sup>(18)</sup> by ir spectroscopic measurements of Long chain partially substituted ammonium salts related hydrogen bonding strength to ionic radius and proton affinity of the anions, the strength decreasing in the order  $CI^- > Br^- > I^- > Clo_4^-$ . Keder and Burger <sup>(19)</sup> studied  $CCl_4$  solutions of trioctylammonium salts by nmr and observed a similar order. Chenon and Sandorfy <sup>(28)</sup> report similar observations on shorter chain trialkyl-

ammonium halides.

## 3. Dissociation and alkyl chain length

Examination of data in Table 2 on experimental dissociation constants reveals that dissociation of tertiary ammonium salts does not increase with increasing chain length. Indeed a slight increase in association is observed going from tripropyl to tridodecyl ammonium salts. The trends in the chloride and bromide systems are not considered significant since these data have been associated with a large confidence limit. The relative 20% decrease in dissociation constant observed proceeding from tripropyl to tridodecylammonium iodides or perchlorates has to be contrasted to the situation for quaternary ammonium salts. For short to median chain length quaternary ammonium salts in most solvents an increase in chain length is reflected in an increase in the dissociation constant. (1,29) This is in agreement with the electrostatic theory of ion-pairing where the contact distance of the ions is increased with increased chain length.

For the tertiary ammonium cation an increase in alkyl chain length should not provide additional steric hindrance to the approach of the anion, since the positively charged attracting site is situated close to the apex of a pyramid. Thus the purely electrostatic part of the association of tertiary ammonium salts should not be directly influenced by alkyl chain length.

It has been reported that at least up to a certain chain length hydrogen bonding increases with chain length <sup>(18,30)</sup> in tertiary ammonium salts. However this effect seems to taper off after a chain length of three or four is reached and could not explain the observed dissociation trends. Solvation of the cation could also play a role. The alkylammonium cation in the dissociated salt should experience a stronger stabilization by ion-dipole interaction with nitrobenzene molecules

the smaller its size, thus favoring dissociation. This could partly explain the observed trends. However conductance data of a higher reproducibility would be necessary in order to apply a complete Fuoss-Onsager equation and analyze small differences among K<sub>d</sub> values in a non equivocal way.

# 4. The limiting molar conductance of trialkylammonium salts

Values of the limiting molar conductance of trialkylammonium salts in nitrobenzene as in other solvents are as sparse as data on their dissociation constants.  $^{(5,13,31)}$ The value for TBAHI (33.33) can be compared to 33.4 ± .5 obtained in this work. An estimate of the single ion conductance of the trialkylammonium cations (Table 4) can be obtained using published values for the anions.  $^{(5)}$  As expected these values appear to decrease when the chain length is increased.

Stokes radii,  $r_s$ , can be calculated using the classical Stokes expression. <sup>(32)</sup> As a basis of comparison van der Waals radii,  $r_w$ , obtained from calculated van der Waals volumes <sup>(33)</sup> are shown.

#### TABLE 4

. Limiting	ionic conduc	ctance	(in $\Omega^{-1}$	cm <sup>2</sup> mol <sup>-1</sup> ),	Stokes
and van dër	Waals radii	(in Å)	for tri	alkylammoni	um cations
Ammonium ion	*	٨. /		r <sub>s</sub> .	r <sub>w.</sub>
tripropyl		5.0 ± .	.8	3.0	3.5
tributyl	. 13	8.6 ±.	.8	3.3	3.8
tripentyl	7 } 12	2.3 ± 1	.1 、	3.7	, 4.1
trihexyl	5 11	L.5 ± 1	(Ĵ3	3.9	4.3
trioctyl	10	).8 ± /	.7	4.2	,4 . 7
tridodecyl	9	.5 ±	.6	<b>4.</b> 7 <sup>°</sup>	5.3

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In Table 5 Stokes radii of tetraalkylammonium cations calculated from published  $\Lambda_o$  values in nitrobenzene are compared to their calculated van der Waals radii.

#### TABLE 5

Limiting	j ionic conductance	, Stokes ar	nd , .
van der Waals	radii for tetraalk	ylammonium	cations
, 0	, ,		
Ammonium ion	Λ.	rs	rr W 1
tetraethyl	16.4 <sup>(5)</sup>	2.8	3.4
tetrapropyl 🦯	13.5 <sup>(13)</sup>	3.3	3.8
tetrabutyl	11.9 (5)		4.1
tetrapentyl	10.8 <sup>(13)</sup>	4.2	4.4

A comparison of data in Tables 4 and 5 suggests similar hydrodynamic behaviour for trialkyl- and tetraalkylammonium cations in nitrobenzene. The low Stokes radius values, also observed for tetraalkylammonium cations in other solvents, (34)

(34) are consistent with the fact that these cations are not considered to be solvated strongly in dipolar aprotic solvents.

(17) The adequacy of the Stokes equation can also be questioned since the solvent cannot be regarded as a continuum. (32,33) Geometrical factors related to the shape of molecules, have also been pointed out. (33)

## 5. Triple ions and higher aggregates

Tertiary ammonium salts dissolved in organic solvents "can exist as species more complex than ions and ion-pairs.<sup>(35)</sup> Limited information on high Molécular weight halides and perchlorates (3,4,36) indicates that aggregation beyond the ionpair seems not to occur in nitrobenzene up to concentrations of approximately 0.1 M. In conductivity studies minima in phoreograms and deviations from a straight-line relationship in the Shedlovsky plots have been attributed to triple ion formation.<sup>(7)</sup>

For all salts in this study measurements in the  $10^{-1}$  M region showed that no minimum in molar conductance was observable up to decimolar concentrations. However on the Shedlovsky plots for the bromide and chloride salts data points on the high concentration side deviated below the Shedlovsky straight line (see figures 10 and 11). Thus the possibility exists of limited triple ion formation for these systems in the concentration range studied. Other approaches than conductometry are necessary to estimate quantitatively the extent of formation of triple ions and higher aggregates.

## 6. Influence of hydration on dissociation

In this study the dissociation constant of TBAHI appears different (4 x  $10^{-4}$ ) from that found by Witschonke and Kraus<sup>(5)</sup> in anhydrous nitrobenzene ( $10^{-4}$ ). This may be

attributed to the effect of water.

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Interaction of the anion of the dissociated ionpair with water molecules by ion dipole and hydrogen bonding should be stronger than the interaction of water with the neutral non-dissociated ion-pair. Dissociation should thus be more important in water-saturated nitrobenzene than in anhydrous solutions.

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## A) INTRODUCTION

High molecular weight (8 C or more per chain) tertiary ammonium salts are known to be practically water insoluble.<sup>(1)</sup> On the other hand some of the low to middle molecular weight salts should have a degree of solubility in water comparable to that of the corresponding soluble quaternary\_ammonium salts. Similarly in a solvent extraction experiment where a tertiary ammonium salt dissolved in an organic phase is contacted with an aqueous phase, the low molecular weight salt is expected to partition between the two phases to a greater extent than a high molecular weight one. To understand the basis for the application of tertiary ammonium salts in solvent extraction it is necessary to be able to estimate their partition constants. In the case of the more water soluble salts a knowledge of the partition constant is necessary to obtain other solvent extraction constants.

Trialkylammonium salts in nitrobenzene exist mostly as ion-pairs. The extent of dissociation is a function of the hydrogen bonding strength between the ammonium cation and the anion. In the preceding chapter dissociation was shown to be lowest with Cl<sup>-</sup> and highest with  $\text{Clo}_{4}^{-}$  in the order  $\text{Cl}^{-} < \text{Br}^{-} < \text{I}^{-} < \text{Clo}_{4}^{-}$ . Dissociation has been seen to be essentially independent of alkyl chain length. In water the

tertiary ammonium salt cation and anion can form hydrogen bonds with water molecules and the salt is believed to be completely dissociated. (2,3) The partition of a tertiary ammonium salt between nitrobenzene and water is thus best represented by the equilibrium:

$$\overline{R_3}NHX \neq R_3NH^+ + X^-$$

to which the constant  $K_{p}$  corresponds

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 $\kappa_{p} = \frac{(R_{3}NH^{+})(X^{-})}{(\overline{R_{3}NHX})}$ 

K<sub>p</sub> can be determined by equilibrating an aqueous and an immiscible organic ammonium salt solution and measuring the equilibrium concentrations. Corrections are calculated by taking into account dissociation in the organic phase and activity coefficients in both phases (see section C).

#### B) EXPERIMENTAL

## 1. Chemicals and solutions

The preparation of solid crystalline TPRAHC1, TBAHC1, TPTAHC1, THAHC1, TOAHC1, TPRAHBr, TBAHBr, TPTAHBr, THAHBr, TPRAHI, TBAHI, TPTAHI, THAHI, TPRAHC10<sub>4</sub> and TBAHC10<sub>4</sub> has been described in chapter II. The purity of these salts has been assessed by acid-base titration and elemental analyses.

Aqueous solutions of the salts TPRAHC1, TBAHC1, TPTAHC1, TPRAHBr, TBAHBr, TPRAHI and TPRAHC104 were prepared by dissolving the solid salt in nibrobenzene-saturated deionized water. Their molarity was calculated using the experimental molecular weights of the solid salts as found by acid-base titration (see Table 1). The organic salt solutions were prepared by dissolution or solvent extraction in a procedure similar to that described in chapter III. They were standardized by potentiometric titration with ethanolic KOH.

#### 2. Experimental procedure

In a typical determination, known volumes of organic solution (or plain water-saturated nitrobenzene) and aqueous solution (or nitrobenzene-saturated water) were pipetted into a jacketed beaker in which a large Teflon-encased magnetic bar was placed. The beaker was maintained at 25° by circulation of water from a constant temperature bath.

The beaker was covered with a plastic lid, blanketed with  $N_2$ , and the two phases were equilibrated by slowly rotating the magnetic bar immersed in the organic phase. After ca. 1/2 h the pH of the aqueous phase was measured by introducing a glass-calomel electrode pair. An aliquot of the organic phase was pipetted out of the beaker and titrated with alcoholic KOH in a CO<sub>2</sub> free atmosphere (see chapter II).

For the pH measurement a shielded Beckman glass electrode (39000) associated with a calomel electrode (Fisher 13-639-51) was adjusted using pH buffers and an Accumet 320 Fisher pH meter.

In each case the two phases were allowed to equilibrate for 30 min even though equilibration was believed to be achieved in 5-10 min as suggested by constant pH readings. In order to check that equilibrium was reached some solutions were left to equilibrate for 2 hours; no difference was noticed in their final concentrations. Only in the cases of THAHI, THAHClO<sub>4</sub> and TOAHCl solutions was equilibration found to require more than 30 min. The phases in these cases were contacted for one hour and compared with duplicates run for two hours.

In a typical determination, a nitrobenzene solution of the ammonium salt was contacted with water. Three initial organic phase concentrations were used (ca.  $10^{-1}$  M, 3.3 x  $10^{-2}$ M,  $10^{-2}$  M). The ratio of organic phase volume to aqueous phase volume was made small enough so that a change in organic phase
concentration of at least 10% occurred. The concentration changes in the organic phase did not exceed  $2 \times 10^{-2^2}$  M. On the basis of a 300 cm<sup>3</sup> molar volume for the salt, volume changes of not more than .6% occurred.

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For the salts that would undergo excessive transfer into the aqueous phase because of high partition constants, the organic phase was equilibrated with an aqueous solution having a concentration near the equilibrium condition. In those few cases where the partition constant was very high the salt was initially present only in the aqueous solution. Duplicates were run for all determinations to produce usually six measurements for each salt.

# C) METHOD OF CALCULATION

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The organic and/or aqueous salt concentrations before and after equilibration of the phases and the pH of the aqueous phase may be used to calculate an apparent partition constant. If  $c_{org}^{o}$  and  $c_{aq}^{o}$  are the initial salt concentrations in the organic and aqueous phase volumes  $V_{org}$  and  $V_{aq}$  respectively the mass balance equation for the species X is:

 $[\overline{R_{3}NHX}]_{T}V_{org}+[X]V_{aq} = c_{org}^{O}V_{org}+c_{aq}^{O}V_{aq}$ 

Acid-base titration of an aliquot of the organic phase gives the total  $[\overline{R_3NH^+}] + [\overline{R_3NHX}]$  which is also  $[\overline{X}^-] + [\overline{R_3NHX}]$  or  $[\overline{R_3NHX}]_T$  or  $c_{org}$ . Thus  $[X^-]$  can be calculated.  $[R_3NH^+]$  can be determined from the charge balance equation for the aqueous phase:

 $[R_3NH^+] + [H^+] = [X^-] + [OH^-]$  (2)

The hydrogen ion concentration is obtained from the pH after an activity coefficient correction<sup>(4)</sup> using the extended form of the Debye-Hückel limiting law (see Appendix IV). The apparent partition constant  $Q_1$  is thus obtained as

$$Q_{1} = \frac{[R_{3}NH^{+}][X^{-}]}{[\overline{R_{3}}NHX]_{T}}$$

To obtain the non-thermodynamic constant  $Q_3$  defined as follows:

$$P_3 = \frac{[R_3NH^+] [X^-]}{[R_3NHX]}$$

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it is necessary to subtract from the total organic phase salt concentration the part which is ionized.

The thermodynamic dissociation constant of the salt in the organic phase  $K_d$  has been obtained from conductivity measurements at low concentrations (see chapter III). Assuming that no appreciable amount of more highly associated species than the ion-pair are present at concentrations up to  $10^{-1}$  M one can write:

$$x_{d} = \frac{[\overline{R_{3}NH^{+}}]^{2}}{c_{org} - [\overline{R_{3}NH^{+}}]} \times \overline{y}_{\pm}^{2}$$

where  $\overline{y}_{\pm}$  is the mean activity coefficient of dissociated  $R_3^{NHX}$  in the organic phase.

By knowing  $K_d$ ,  $c_{org}$  and estimating a in the Debye-Hückel activity coefficient factor (see Appendix IV), one can calculate  $[\overline{R_3}NHX]$  and  $Q_3$ .  $Q_2$  is obtained in the same manner as  $Q_3$  but neglecting activity coefficient correction in the organic phase, i.e. letting

 $K_{d} = \frac{\left[\overline{R_{3}NH^{+}}\right]^{2}}{\left[\overline{R_{3}NHX}\right]}$ 

The thermodynamic partition constant  $K_p$  can be obtained from  $Q_3$  by estimating the mean activity coefficient.  $y_{\pm}$  of the aqueous salt using a Debye-Hückel equation (see Appendix IV). Thus if a can be estimated (see Appendix IV) and an activity coefficient of one assumed for the ion-pair in the organic phase (see chapter V) one obtains:

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$$\kappa_{p} = \frac{[R_{3}NH^{+}][x]}{[\overline{R_{3}}NH\overline{x}]} = Q_{3}Y_{\pm}^{2}$$

Details on calculations performed to obtain  $Q_1$ ,  $Q_2$ ,  $Q_3$  and  $K_p$  can be found in Appendix V

#### D) RESULTS

Individual data for each system can be found in Appendix VI. In Table 6 the values of the coefficients  $Q_1$ ,  $Q_2$  and  $Q_3$  and of the constant  $K_p$  are listed. For the five salts noted with one asterisk the values were obtained from only one organic or aqueous solution concentration for practical reasons (too low or too high extraction constant). For the other constants determined at three different organic solution concentrations, it is generally observed that the relative standard deviation decreases in the order  $Q_1 > Q_2 > Q_3 > K_p$ .

The difference between  $Q_1$  and  $Q_2$  due to dissociation in the organic phase is best observed in the  $Clo_4^-$  and I<sup>-</sup> columns. The difference between  $Q_2^+$  and  $Q_3^-$  due to activity coefficients of the dissociated salt in the organic phase is best observed in the  $Clo_4^-$  column. The effect of activity coefficients in the aqueous phase explains the difference between  $Q_3^-$  and  $K_p^-$  and is best observed on those salts that have higher partition coefficients (log  $K_p^- > -3$ ).

It is of interest to test the influence on  $K_p$  of different factors. An error in  $K_d$  of 10% can be calculated to influence the final  $K_p$  by only 3% for  $Clo_4$  salts, 1% for I salts, .2% and .1% for Br and Cl salts. If an activity coefficient correction for the dissociated salt in the organic phase was not applied results would differ by 13% for  $Clo_4^7$ ,

3% for I, .4% and .2% for Br and Cl salts.

The partition constant determinations for TOAHC1, THAHI and THAHC10<sub>4</sub> represent limiting cases. The partition equilibrium constant is below  $10^{-5}$  and a high aqueous to organic phase volume ratio (=40) was necessary to permit a significant (10%) transfer into the aqueous phase. This creates a limit due to the volume capacity of the equilibration cell. The aqueous phases in equilibrium for these salts are of low ionic concentration (<  $10^{-3}$  M) and are thus more sensitive to possible low level impurities and their pH values less certain. However when applying eq. (2) for these systems the [H<sup>+</sup>] term appears important (25 to 80% of the [X<sup>-</sup>] term).

The reason for the increasing importance of the  $[H^T]$  term in eq. (2) when one considers salts with low partition constants lies in the increasing importance of the hydrolysis equilibrium of the salt:

 $\overline{R_3NHX} \neq \overline{R_3N} + H^+ + X^-$ 

compared to the partition equilibrium.

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> In Table 6 the values for the partition constants of TOAHC1 and THAHC104 being obtained at only one concentration level and corresponding to limiting cases are thought to be only approximate and reported only as an indication of their order of magnitude.

In the case of the salts with high partition equilibrium constants (> 1) it is necessary to use aqueous solutions of high salt concentration in order to obtain a measurable equilibrium concentration in the organic phase. The  $K_p$  value obtained for TPRAHC1 from 0.5 M aqueous solutions is approximate since the calculated activity coefficients in such solutions are approximate. The  $K_p$  values for TBAHC1 and TPRAHBr have been calculated on the basis of the 0.1 M aqueous solutions, disregarding the 0.5 M ones.

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	Partition con	stant and coer.	ricients or var	1049
tr	ialkylammonium	salts between	nitrobenzene an	d water:
	log K_	and log Q3, lo	$g Q_2, \log Q_1$	
	· · · ·			1.
۲	Cl	Br	` I	Cl04
` -	**1.60 ±.01	*0.586±.002	-0.672±.026	-1.595±.014
TPRAH	1.93 ±.01 1.93 ±.01 / 1.90 ±.01	0.794±.003 0.790±.003 0.731±.002	-0.46 ±.06 -0.48 ±.06 -0.53 ±.08	-1.470±.03 -1.532±.04 -1.781±.16
	*0.055±.011	-0.924±.02	-2.269±.01	-3.088±.02
ТВАН	0.250±.017 0.250±.017 0.228±.018	-0.744±.04 -0.746±.04 -0.763±.04	-2.177±.02 -2.190±.02 -2.253±.06	-3.031±.009 -3.093±.01 -3.274±.14
	-1.666±.01	-2.676±.023	-3.928±.026	-4.793±.01
TPTAH	-1.536±.01 -1.538±.01 -1.547±.01	-2.599±.01 -2.601±.01 -2.619±.01	-3.89 ±.03 -3.90 ±.04 -3.96 ±.06	-4.769±.01 -4.825±.01 -4.99 ±.08
i	-3.362±.02	-4.458±.012	-5.688±.01	*-6.133±.01
тнан	-3.30 ±.01 -3.30 ±.01 -3.31 ±.01	-4.426±.02 -4.428±.02 -4.445±.03	-5.670±.01 -5.679±.01 -5.714±.01	-6.119±.01 -6.162±.01 -6.249±.01
`	*-6.15 ±.13	· ·		
TOAH	-6.12 ±.13 -6.12 ±.13 -6.12 ±.13		, I	
¥	elita,			

TABLE 6

based on one concentration level.

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based on a 0.5 M aqueous solution.

 $\begin{array}{c} \log \ \mathbf{K} \\ p \\ \log \ \mathbf{Q}_3 \\ \log \ \mathbf{Q}_2 \\ \log \ \mathbf{Q}_1 \end{array}$ 

 $K_p$  and other coefficients in mole  $l^{-1}$ 

### E) DISCUSSION

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Only few studies have dealt with the measurement of partition equilibrium constants of alkylammonium salts. (5,6,7,8) Smulek and Siekerski <sup>(5)</sup> reported approximate distribution coefficients for some tertiary amines between several immiscible solvents (including  $\phi NO_2^4$ ) and 8 M HCl. From these data obtained under different conditions than this work, the ratio of partition constants for TBAHCl and THAHCl in  $\phi NO_2$  should be approximately three orders of magnitude, compared to 2700 in this work.

Freiser et al.<sup>(6)</sup> studied the partition of various tetrahexylammonium salts between water and various aliphatic alcohols. Using organic anions they report an increasing extractability into the organic phase as the number of carbon atoms increases in the anion. A systematic study by Schill et al.<sup>(7)</sup> dealt with the partition of various tetraalkylammonium salts of inorganic anions between water and methylene chloride and the various equilibria in the organic phase. The same trends are observed as in the present study, i.e. a regular increase in the extraction constant into the organic phase in the order Cl<sup>-</sup> salt < Br<sup>-</sup> salt < I<sup>-</sup> salt < Clo<sup>-</sup><sub>4</sub> salt. Similarly the extraction constant for the same anion increases drastically with increasing chain length of the alkyl chain of the ammonium ion from tetrapropyl to tetrahexyl.

In order to provide a more fundamental basis for the trends observed in the present study it is useful to compute the free energy of transfer of the dissociated ions and test an electrostatic model of the Born-charging type.

1. Transfer equilibrium constant of dissociated

The equilibrium constant for the transfer of the dissociated ions  $(K_t)$  is defined as:

$$V_{t}^{K} = \frac{(R_{3}NH^{+})(\bar{x})}{(R_{3}NH^{+})(\bar{x})}$$

For the reaction:

$$\overline{R_3NH^+} + \overline{X}^- \stackrel{2}{\leftarrow} R_3NH^+ + X^-$$

 $K_t$  is related to  $K_p$  and  $K_d$  through

ions

$$K_{t} = K_{d}$$

The relationship between the three equilibria can be represented as the following cycle:

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where  $\Delta G^{O}$  is the standard free energy for each reaction.

The calculated values for  $K_t$  and  $\Delta G_t^o$  from the experimental  $K_p$  and  $K_d$  are summarized in Table 7. The transfer equilibrium constant of the dissociated ion-pair between nitrobenzene and water is seen to be highest for the chloride salts in the order  $Cl^- > Br^- > I^- > Clo_4^-$  and highest for the lowest molecular weight alkylammonium salt in the order tripropyl\_> tributyl > tripentyl > trihexyl. This order is to be expected on the basis of a simple electrostatic model of the transfer of ions between two phases.

# 2. Electrostatic model

The Born charging model applied to the transfer of two separated ions of radii  $r_+$  and  $r_-$  from a medium of dielectric constant  $\varepsilon_2$  to a medium of dielectric constant  $\varepsilon_1$  gives an expression for the standard free energy of transfer<sup>(9)</sup> on

a molar, scale<sup>(10)</sup>:

or

 $\Delta G_{t}^{o} = \frac{N_{e}^{2}}{2} \left(\frac{1}{r_{+}} + \frac{1}{r_{-}}\right) \left(\frac{1}{\varepsilon_{1}} - \frac{1}{\varepsilon_{2}}\right)$ 

For the transfer from nitrobenzene to water

 $\Delta G_{t}^{O} = -2.64 \left(\frac{1}{r_{+}} + \frac{1}{r_{-}}\right) \text{ kcal } \text{ with } r \text{ in } \mathring{A}$ (3)

$$\log K_{t} = 1.94 \left(\frac{1}{r_{+}} + \frac{1}{r_{-}}\right)$$
(4)

Values for  $\Delta G_t^o$  (or log  $K_t$ ) can be calculated from eqs. (3) or (4) from known values of ionic radii. van der Waal's radii have been used for the cations (see Table 4) and crystallographic radii for the anions. <sup>(11)</sup> The theoretical  $\Delta G_t^o$  values thus obtained are listed in the last column of Table 7.

The typends, predicted by eq. (4) correspond to the experimentally observed  $K_t$  values. The transfer equilibrium constant  $K_t$  increases with decreasing size of the anion and decreasing size of the cation. However these values differ very significantly from the experimental values by magnitude and sometimes sign. This confirms the well-established fact that the simple electrostatic model is insufficient in many instances to properly describe details of the process of

TABLE '7

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<u>Equilibrium c</u>	constant	s for	the t	ransfer	of
the dissociate	d ions	and re	elated	quanti	ies

		۵G <sup>o</sup> (kca	<b>1)</b> , .1
, ,	log K <sub>t</sub>	experimental	Born <sup>*</sup>
TPRAHC1	6.64±.1	-9.00±.14	-2.21
TBAHC1	5.06±.1	-6.90±.14	-2.15
TPTAHCL	`3.33±.1	-4.54±.14	-2.11
THAHC1	1.64±.1	;-2.24±.14	-2.07
TPRAHBr	5.09±.1	6.94±.14	-2.10
TBAHBr	3.58±.1	-4.88±.14	-2.04
TPTAHBr	1.82±.1	-2.48±.14	-2.00
THAHBr	0.04±.1	-0.05±.14	-1.96
TPRAHI	2.73±.04	-3.72±.06	-1.96
TBAHI	1.14±.02	-1.55±.03	-1.90
TPTAHI	-0.52±.04	0.71±.06	-1.86
THAHI	-2.26±.02.	3.07±.03	-1.82
TPRAHC104	0.78±°.02.	-1.06±.03°	-1.83
TBAHCIO	0.68±.03	0.92±.04	-1.77
TPTAHC104	+2.34±.02		-1.73

values of anionic radii used  $\binom{(11)}{2}$ : Cl<sup>-</sup>, 1.81; Br<sup>-</sup>, 1.96; I<sup>-</sup>, 2.19; Clo<sub>4</sub><sup>-</sup>, 2.45 `101

ionic solute transfer. It predicts that the transfer of ions will always favor the phase of higher dielectric constant  $(\Delta G_t^O < 0$  from most organic solvents to water). Other studies and this work give many examples of the contrary.

# 3. Anionic and cationic contributions to $\Delta G_{\perp}^{O}$

The experimentally determined free energy of transfer of a pair of ions can be decomposed into its cationic and anionic parts.

 $\Delta G^{o}_{t^{R_{3}NH^{+}}, x^{-}} = \Delta G^{o}_{t^{R_{3}NH^{+}}} + \Delta G^{o}_{t^{x^{-}}}$ 

By using the values in Table 7 it is thus possible to calculate differences in free energy of transfer of single ions by subtracting the values of two salts having another ion in common. These differences are averaged for each pair of ion and tabulated in Table 8 with the corresponding standard deviations. These values are at least an order of magnitude bigger than the predicted values from a Born charging model. In the case of the halides they are however comparable to values obtained in transfers between water and other dipolar aprotic solvents of polarity similar to that of nitrobenzene (e.g. in acetonitrile  $\Delta G_{tC1}^{O} - \Delta G_{tBr}^{O} = -3.4$  kcal,  $\Delta G_{tBr}^{O} - \Delta G_{tI}^{O} = -3.3$ kcal; in nitromethane  $\Delta G_{tC1}^{O} - \Delta G_{tI}^{O} = -4.5$  kcal). (12) The simple Born charging model considers each solvent

as a continuum and does not take into account specific inter-

actions between the ions and the solvent molecules. (13)

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Diff	erences of free energies	of transfer of sin	gle ions
*` *~	$\Delta G_{t_1}^{o} - \Delta G_{t_2}^{o}$	(kcal)	
	C1 - Br	-2.08 ± .07	c
	Br - I	-3.22 ± .09	
ı	$I^{-} - C10_{4}^{-}$	-2.53 ±`.09	
	TPRAH <sup>+</sup> - TBAH <sup>+</sup>	-2.08 ± .08	
	TBAH <sup>+</sup> - TPTAH <sup>+</sup>	$-2.32 \pm .07$	
	TPTAH <sup>+</sup> - THAH <sup>+</sup>	-2.36 ± .07	

The larger the ion introduced in the aqueous phase the more hydrogen bonds linking water molecules will be broken in order to fit the ion into the ice-like structure of water.

(14) The anions considered in this study are solvated in water mostly through hydrogen bonding with water molecules and ion-dipole interactions. However the smaller more basic Cl<sup>-</sup> is more stabilized by hydration than the larger  $Clo_4^-$ . Hydration energy decreases in the order  $Cl^- > Br^- > I^- > Clo_4^$ which is also the order of hydrogen bonding affinity of the anions and the reverse order of their size. Thus the transfer into water of the anions can be explained through the combined » effects of water structure breaking and ion solvent interactions.<sup>(14,15)</sup>

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In the dipolar aprotic solvent nitrobenzene anions are solvated through ion-dipole interactions and interactions due to the mutual polarizability of the ion and the solvent molecule.  $^{(16)}$  The solvation energy in anhydrous nitrobenzene should decrease in the order  $Clo_4^- > I^- > Br^- > Cl^-$ . However tertiary alkylammonium salts are known to be partially hydrated in nitrobenzene and the anion usually considered as carrying water of hydradion (see chapter III, section E, part 6). Thus solvation of the anions in the organic phase is a complex process made up of several contributions.

Considering the different factors affecting the transfer of anions the dielectric effect involved in the Born equation is seen to be insufficient to describe the process. Furthermore assuming the predominance of effects in the aqueous phase it is reasonable to assume that the free energy of transfer should vary from one anion to another to a greater extent than predicted by the Born equation.

It is interesting to note here that plots of  $\Delta G_t^O$ vs. the reciprocal of the ionic radius for the anions appear linear (see figure 12). This dependence on the ionic size has been observed in many systems. <sup>(17,18,19)</sup> The Born charging approach is not supported however since the slopes of the plots, differ widely from the theoretical Born slope; furthermore the

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# FIGURE 12

Standard free energy of transfer of trialkylammonium salts from nitrobenzene to water versus the inverse of anionic radii.



linearity is only approximate and depends on the value chosen for the radius of  $Clo_{\overline{A}}$  which is controversial.

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Alfenaar and De Ligny<sup>(11)</sup> suggested that for very large ions  $\Delta G_t^O$  could be decomposed into the sum of two terms, one being the Born charging term, the other one being the free energy of transfer of a neutral molecule of the same size as the ion:

 $\Delta G_{t}^{O} = \Delta G_{neutral}^{O} + \Delta G_{BOrn}^{O}$ 

It was reasoned that a very large ion, having a weak electrical field, would interact with solvents in a fashion similar to a neutral species of the same size.

In the case of the anions considered here their free energy of transfer could not be decomposed in such a way because of their small size and specific solvation effects. In the case of the larger trialkylammonium ions a similar decomposition is probably unrealistic too because of the existence of a high charge density centre near the N-H bond. However the importance of a non electrostatic term could be indicated by what seems to be the existence of a methylene effect. Values of  $\Delta G_t^0$  appear to increase regularly in each series of salts as the alkyl chain length increases by the addition of methylene groups (see figure 13). An increase in chain length must have the effect of disturbing the hydrogen bonded structure

# FIGURE 13

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Standard free energy of transfer of trialkylammonium salts from nitrobenzene to water versus the number of carbon atoms in the cation.



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of water. Additive methylene effects have been observed in many systems. These are reflected either in values of the enthalpy of transfer of ions or neutral molecules between organic solvents and water <sup>(20)</sup> or their distribution ratios. <sup>(13)</sup>

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Dyrssen et al. (8,21) pointed out an empirical rule governing the partition ratio of free amines and of ammonium salts  $(K_p)$  between organic solvents and water: the logarithm of the equilibrium constant is a linear function of the number of methylene groups, n, the slope being 0.6. In this work a similar result can be found. From log K<sub>p</sub> values tabulated in Table 6 it is deduced that log K<sub>p</sub> decreases as an average by 0.51 per methylene group between tripropyl and tributylammonium salts, 0.57 between tributyl and tripentylammonium salts and 0.58 between tripentyl and trihexylammonium salts.

Additive methylene effects may be attributed to hydrophobic effects in the aqueous phase. The free energy of solvation of a -CH<sub>2</sub> group in water is positive and made up of two contributions.<sup>(22,23)</sup> The coulombic or "normal" hydration involves the breaking down of hydrogen bonds linking water molecules to create a cavity for the group (positive enthalpy change). The structural contribution concerns the rearrangement of water molecules as an "iceberg" around the hydrocarbon group. Similar effects are observed around non polar gases in solution. The structural contribution contains a negative enthalpy term. Considering entropy, the overall entropy of

solvation should be negative due to the rearrangement of the water structure into the more ordered ice-like structure. The relative importance of the different terms forming the free energy of solvation is controversial, but the total effect of all contributions should be a strong positive free energy of hydration for  $-CH_2$  groups coming mostly from the ' positive enthalpy of the coulombic part of the hydration. <sup>(18)</sup>

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CHAPTER V

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TWO PHASE EMF TITRATIONS AND ION EXCHANGE CONSTANTS

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In the preceding chapter partition constants have been obtained for some low to medium molecular weight tertiary alkylammonium salts. By combination, ion exchange constants can be estimated. In the present chapter the experimental determination of two-phase hydrolysis equilibria is described for medium to high molecular weight trialkylammonium salts. The ion-exchange constants obtained by combination of these constants are discussed together with ion exchange constants determined from results in the previous chapter.

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A) INTRODUCTION

The evaluation of the two-phase equilibrium constant K corresponding to the equilibrium:

 $\overline{R_3NHX} \stackrel{2}{\leftarrow} \overline{R_3N} + H^+ + X^-$ 

yields information on several aspects of organic solutions of higher molecular weight tertiary ammonium salts. K represents the inverse of the formation constant of the salt from the organic dissolved amine and aqueous acid. It is thus a measure of the hydrolysis of these solutions in contact with aqueous solutions. Combination of these equilibrium constants yields ion exchange constants of the dissolved salts considered as liquid anion exchangers. Furthermore, during the course of the establishment of K, information on the state of dissociation or aggregation of the salt can be collected.

Several methods have been employed to evaluate K. <sup>(1)</sup> These consist in equilibrating an organic phase containing  $R_3NHX$  or  $R_3NHX-R_3N$  mixtures with an aqueous phase, pure water or constant ionic medium.

In the technique known as back extraction, ammonium salt organic solution is contacted with water, the pH of the aqueous phase is measured and/or the concentration of ammonium salt is determined by titration. (2,3,4,5,6,7) Values of concentration and activity for H<sup>+</sup> and X<sup>-</sup> and free amine and ammonium salt concentrations are thus obtained. A semithermodynamic constant  $K_{ST}$  is determined as:

$$K_{ST} = \frac{[\overline{R_3N}] (H^+) (X^-)}{[\overline{R_3NHX}]}$$

If the salt is dissociated or aggregated the constant will vary with concentration of the organic phase and corresponds to an apparent constant  $K_{ST}^{*}$  with:

$$\kappa_{ST} = \frac{[\overline{R_3N}] (H^+) (X^-)}{[\overline{R_3NHX}]_T}$$

where  $[\overline{R_{3}NHX}]_{T} = [\overline{R_{3}NHX}] + [\overline{R_{3}NH^{+}}] + 2[\overline{(R_{3}NHX})_{2}] + \dots$ In another technique <sup>(8,9)</sup> an organic amine solution is contacted with enough aqueous acid to transform one-half to ammonium salt and the pH is measured. The constant  $K_{ST}^{'}$  is then equated to  $[H^{+}]^{2}$ . The same result can be achieved by titrating the organic ammonium salt with aqueous base and taking the pH at half neutralisation. <sup>(10)</sup> Intermediate techniques have also been used. <sup>(11,12)</sup>

The above mentioned techniques have several disadvantages. Each experiment yields only one value of the equilibrium quotient; some techniques rely on a pH measurement of a non-buffered medium or they involve analyses by titration of aliquots of the organic or aqueous phase or both. The back extraction suffers from extrême sensitivity to acidobasic impurities in the aqueous phase.

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For this study the more rigorous two-phase emf titra-

## B) TWO-PHASE EMF TITRATIONS - THE TECHNIQUE

In the technique of two-phase emf titration (13,14) the ratio  $[\overline{R_3NHX}]_T/[\overline{R_3N}]$  is constantly varied in the organic phase by addition of acid or base to the aqueous phase in contact with it. The ratio is then obtained from the initial organic phase amine or ammonium salt concentration and the number of equivalents introduced as  $H^+$  or  $OH^-$  in the aqueous phase. Correction has to be made for the  $H^+$  or  $OH^-$  concentration at equilibrium in the aqueous phase.

In the aqueous phase a constant ionic strength medium method is employed with the purpose of keeping the activity coefficients of reacting ions constant (see section D). The solute used to maintain constant the ionic strength is a salt of the anion,  $X^-$ , in the equilibrium considered: e.g., MX, 0.1 M. This way the concentration  $[X^-]$  of one species in the equilibrium is maintained constant and known. The other species  $H^+$  is determined by a glass electrode reference electrode system appropriately designed to be compatible with the aqueous phase (see section E, part 3) and allowing the direct determination of  $H^+$  ion concentration in the medium. Defining Q' as:

$$Q' = \frac{[\overline{R_{3N}}] [H^+]' [X^-]}{[\overline{R_{3NHX}}]_{T}}$$

this concentration quotient can thus be calculated.

The constant Q defined as:

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$$= \frac{[\overline{R_3N}][H^+][X^-]}{[\overline{R_3NHX}]}$$

can be estimated from Q' if the state of dissociation or aggregation in the organic phase is known. The semi-thermodynamic constant  $K_{ST}$  may be determined from estimates of  $y_{H^+}$ ,  $y_{X^-}$  or  $y_{\pm HX}$  given by the Debye-Hückel equation or tables (see section G, part 5).

Knowledge of activity coefficients in the organic phase is necessary to determine the thermodynamic equilibrium constant K. No information is available on the activity coefficients of the ion-paired salt  $R_3NHX$  or of the free amine  $R_3N$  in nitrobenzene. However, departures from ideality are usually small for uncharged solutes at the level of concentration encountered in this study. <sup>(15)</sup> The activity coefficients of  $R_3NHX$  and  $R_3N$  in the organic solvent were taken as unity. (3,11,16,17,18) Furthermore on the basis of results obtained in other solvents <sup>(7,17)</sup> trialkylamines were considered as non associated in nitrobenzene. <sup>(1,18)</sup>

# C) SLOPE ANALYSIS ON LOG-LOG PLOTS

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The state of aggregation or dissociation of alkylammonium salts in organic solvents has been studied by several different approaches: cryoscopy, ebulliometry, vapour pressure osmometry, conductometry, light scattering, viscosimetry and spectroscopy. (1,19,20) Two-phase emf titration provides an additional means to study the state of the solute in the organic phase in contact with an aqueous phase.

The so-called Z analysis of data from two-phase emf titrations has been developed and used extensively by the Swedish school for studies of aggregation. In this method the change in shape of the curve obtained by plotting the quantity  $Z = [\overline{R_3NHX}]_T / [\overline{R_3N}]$  vs. log  $[H^+][X^-]$  for different initial organic amine concentration is indicative of aggregation. <sup>(14)</sup>

A related way of analyzing two-phase emf titration data is through a slope analysis of a log-log plot. <sup>(21)</sup> The quantity log  $[\overline{R_3NHX}]_T$  is plotted vs. log  $[\overline{R_3N}][H^+][X^-]$ . This method has the advantage over the Z analysis of offering the possibility of direct graphical interpretation by slope analysis.

Consider a solute  $R_3NHX$  existing in the different forms  $R_3NH^+X^-$ , dissociated, at low concentrations,  $R_3NHX$ , ionpair, at intermediate concentrations and  $(R_3NHX)_2$ , dimer, at higher concentrations.

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In the region where the salt exists essentially as an ion-pair a log-log plot as defined above will be a straight line of slope one indicative of the relation:

$$\log \left[\overline{R_3^{NHX}}\right]_{T} = \log \left[\overline{R_3^{N}}\right] \left[H^+\right] \left[X^-\right] - \log Q$$

In the region of low concentration where the salt is completely dissociated the hydrolysis equilibrium is represented by:

$$\overline{R_3NH^+} + \overline{X}^- \stackrel{2}{\leftarrow} \overline{R_3N} + H^+ + X^-$$

with a constant  $Q_{1/2}$ , whereby:

 $\log \left[\overline{R_3^{NHX}}\right]_{T} = \log \left[\overline{R_3^{NH^+}}\right] = \frac{1}{2}\log \left[\overline{R_3^{N}}\right] \left[H^+\right] \left[X^-\right] - \frac{1}{2}\log Q_{1/2}$ 

The plot will be a straight line of slope 1/2. Similarly in the region where the salt exists as a dimer only the slope of the plot will be 2. Higher aggregates would give slopes of correspondingly higher value.

The general shape of the log-log plot over a wide range of concentration is depicted in figure 14. The actual plots should have a similar shape with variations depending on the location and extent of the various concentration stability zones of the different solute species.

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FIGURE 14

Hypothetical log-log plot for the two-phase trialkylammonium salt hydrolysis over a wide range of concentrations.

## D) THE CONSTANT IONIC STRENGTH MEDIUM

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The ionic medium used in the aqueous phase serves several purposes. A constant and known concentration of x, one of the participants in the equilibrium studied, is main-It also allows an accurate determination of the tained. concentration of the hydrogen ion by maintaining constant its activity coefficient. (22) The H<sup>+</sup> concentration rather than the activity is needed in mass and charge balance equations leading to the estimate of Q'. Furthermore a direct reading of H<sup>+</sup> activity from a glass electrode system in a constant ionic medium is doubtful since junction potentials differ from a regular buffer to a given constant ionic strength medium. (23,24) In the procedure used here the glass electrode system is calibrated in the given medium to allow H<sup>+</sup> concentration and emf to be directly related. Errors due to variations of liquid junction potential with ionic strength are accordingly eliminated together with errors due to the possible non ideality of the glass electrode or the measuring instrument. The presence of the constant ionic medium MX also serves to repress the partition of the salt into the aqueous phase through the constant  $K_n$  (see chapter IV) in the case of the low to medium molecular weight salts.

The molarity of the ionic media was chosen as 0.1 since the Debye-Hückel law is considered to be valid at that
concentration. Thus activity coefficients for ionic species in the aqueous phase could be estimated. More concentrated solutions could also increase the alkaline ion error in potential measurements with the glass electrode.

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Potassium salts were chosen (except for the perchlorate) because they minimize alkaline ion interference on the glass electrode. The potassium perchlorate salt was rejected on the basis of ion-pair formation in aqueous solution. (25) Finite alkaline ion in access the solution is a solution.

(25) Furthermore a decimolar solution being close to saturation (at 0.15 M), problems of liquid junction clogging by precipitation could be expected if the 1 M KCl solution was used as a salt bridge. A decimolar solution of the sodium salt was used in the case of perchlorate extraction systems.

The glass electrode - calomel electrode system was calibrated for each constant ionic medium. The relationship between potential and hydrogen ion concentration was established and the measurement of the ionization product of water in each medium was effected. These experiments and their results are described in Appendix VII.

#### E) EXPERIMENTAL PROCEDURES

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1. Chemicals

The salts KC1 (Baker analyzed reagent), KBr (crystals, Fisher certified), KI (crystals, Fisher certified) and  $NaClO_4 \cdot H_2O$  (Fisher purified) were used without purification. The salts KC1, KBr and KI were dried for two hours at 120°.

The concentrated acids were HCl 37.9% (Baker, reagent grade), HBr 47.9% (Baker, reagent grade), HI 64% (BDH, AnalaR) and HClO<sub>4</sub> 70% (Anachemia, reagent grade). The preparation of trialkylammonium salts and the purification of trialkylamines and nitrobenzene have been described (see chapter II).

# 2. Preparation of solutions

#### a) Aqueous solutions

Stock molar aqueous solutions of KCl, KBr, KI, NaClO<sub>4</sub>, HCl; HBr, HI and HClO<sub>4</sub> were prepared. Since the salt NaClO<sub>4</sub>·H<sub>2</sub>O is hygroscopic, the molarity of the stock solution was determined by titration of the acid equivalent displaced on a cation exchange resin<sup>(26)</sup> (Dowex 50W-X8, H form). A standardized decimolar NaOH solution was used to determine the normalities of the aqueous acids. The NaOH solution was prepared from a carbonate free 50% solution. A stock KOH solution (ca. 1.5 M) was prepared by dissolving 60 g of KOH (Anachemia, reagent) in 500 ml water. The carbonate was removed by addition of small quantities of concentrated BaCl<sub>2</sub> solutions until no more precipitate formed. The solution was then filtered through glass fibres. Alkali solutions were kept in plastic bottles and protected from atmospheric carbon dioxide during delivery. They were standardized using primary standard potassium hydrogen phthalate.

All other solutions were prepared by dilution of the stock solutions and when necessary their normalities were checked by standard methods. Water used to prepare solutions was distilled deionized water which was boiled shortly before use to remove  $CO_2$ . It was saturated with nitrobenzene at room temperature.

Denoting the constant ionic medium salt, the acid and alkali used in titrants as MX, HX and MOH respectively, the following solutions were prepared: MX 0.1 M, HX 0.1 M and MX 0.1 M, HX 0.01 M and MX 0.1 M, HX 0.001 M and MX 0.1 M, MOH 0.1 M, MOH 0.01 M and MX 0.09 M.

b) Organic solutions

Organic trialkylammonium salt solutions of sixteen different salts were prepared. These were the chlorides, bromides, iodides and perchlorates of tridodecylammonium to tributylammonium with the exceptions of TBAHC1, TBAHBr, TBAHI and TPTAHC1. The procedure followed for the preparation was by dissolution of the salt or by solvent extraction from the

organic amine solution. This was identical to the procedure described in chapter III. The decimolar solutions were standardized by potentiometric titration with ethanolic KOH. Centimolar and millimolar solutions were prepared by dilution.

Organic decimolar trialkylamine solutions were prepared by direct dissolution of the purified amines. Pipettes were not used to deliver volumes of these solutions since these were found to deliver unevenly. Known quantities were thus transferred gravimetrically. The decimolar solutions were standardized by titration with HClO<sub>4</sub> in acetic acid. The procedure used was the same as the one described for amines (see chapter II, section B). The end-point was detected potentiometrically and the potential break represented ca. 120 mV within .5% of the end-point. Centimolar and millimolar solutions were prepared.

# 3. Electrodes and potential measurement

The electrodes used were a Beckman double shielded 39000 glass electrode and a Fisher calomel electrode #13-639-51. The originally saturated calomel electrode was modified to a 1 M KCl calomel electrode. The main reason for this change is the considerably lower temperature dependence of the potential of this electrode compared to the saturated calomel electrode (.2 mV/ vs. .8 mV/°). In the saturated calomel electrode crystallization of KCl in the tip can also occur frequently.

The calomel electrode was separated from the solution in which a potential measurement was to be done by a salt bridge of 1 M KCl provided by a Remote Reference Junction (Fisher #13-639-55). The calomel electrode was thus protected from the temperature change that would occur from room temperature (23 ± 1°) to 25°, the temperature of the solutions. The reference electrode was placed ca. one foot above the solution, dipping three cm in a 125 ml separatory funnel connected by the stem to the remote reference through Tygon tubing. The ? funnel, tubing and remote reference were filled with 1 M KCl solution (see figure\_15). The hydrostatic head was believed to give improved stability to the flow of electrolyte in the porous ceramic plug serving as liquid junction between the salt bridge and the solution. Stable potentials could be read with a reproducibility of ± .2 mV shortly after inserting the solutions.

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The potential of the electrode pair was measured using a Fisher Accumet pH meter Model 320 with expanded scale. The expanded mV scale only was used and calibrated using a precision potentiometer (Leeds and Northrup Volt Potentiometer #8687). Overlap of the different scales was adjusted. The meter was found not to be perfectly linear in the low mV range.

Experimental setup

The two-phase emf titrations were carried out in a

100 ml jacketed beaker maintained at constant temperature by circulation of thermostated water (see chapter III). A 50 ml volume of aqueous constant ionic strength solution was pipetted into the beaker which was later covered with a lid to maintain a nitrogen blanket. The solution was agitated for 30 min in order to degas. The organic phase was then introduced (usually 10 ml) by means of a pipette: Decimolar amine solutions were transferred directly from their flasks and the volume calculated by weight difference (see part 2 above). The belectrodes were introduced through holes in the lid and dipped in the aqueous phase to a depth of ca. two cm. The titrant was added from a burette, the tip of which was inserted in another hole in the lid (see figure 15).

For each salt six titrations were performed covering approximately three decades of total organic salt concentrations from  $10^{-1}$  to  $10^{-4}$  M. Three titrations were performed by titrating the amine in nitrobenzene with aqueous acidic titrant. Three titrations involved titrating the ammonium salt in nitrobenzene with base. The three titrations covered an organic amine or salt concentration which was successively decimolar, centimolar and millimolar. For each titration five points were usually recorded, i.e. at 10%, 20%, 40%, 60% and 80% of -equivalence.

After addition of titrant the two phases were mixed by means of a four cm magnetic bar immersed in the lower organic

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FIGURE 15

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# Two-phase emf titration experimental set-up.

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phase. Equilibrium was attained when the potential reached a stable value (change of less than .2 mV in 10 min). The speed of rotation of the stirrer had no significant influence on the equilibrium potential reading. It had however an influence on the equilibration time. A high enough rotation speed was adopted so that equilibrium could be reached in less than one hour for each point. The two phases never formed a stable emulsion and separated quickly into two transparent phases when stirring was stopped.

In order to estimate the  $E_A^O$  value applicable in the potential - hydrogen ion concentration relation (see Appendices VII and X) the potential of a reference acidic solution was measured before and after each titration.

# F) METHOD OF CALCULATION

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For each point in a two-phase emf titration the quantities  $[R_3NHX]_T$ ,  $[R_3N]$ ,  $[H^+]$  and  $[X^-]$  can be determined from the potential reading and the knowledge of initial concentrations: the total concentration of amine,  $c_B^O$  (or ammonium salt,  $c_A^O$ ) in the organic phase of volume  $V_{org}$  and the salt concentration c of MX in the aqueous phase of volume  $V_{aq}^O$ . A known volume  $V_{add}$  of titrant of known composition is added and the concentration of  $H^+$  ions in the aqueous phase is determined by a potential measurement.  $n_{H^+}$  (or  $n_{OH^-}$ ) is the number of meg of acid (or base) introduced by the titrant.

#### 1. <u>General</u>

For the case of a two-phase titration of an amine organic solution with an acid HX mass balance and charge balance equations may be written:

 $c_{\rm B}^{\rm O} = [\overline{R_3^{\rm N}}] + [\overline{R_3^{\rm NHX}}]_{\rm T}$ (5)

 $[\overline{R_3}NHX]_T$  is the total concentration of all forms of ammonium salt (ion-paired, dissociated or aggregated).

$$v_{aq}^{o} c + v_{add}(c + \frac{n_{H^+}}{v_{add}}) = v_{aq}[x] + v_{org}[\overline{R_3^{NHX}}]_{T}$$

where  $V_{aq} = V_{aq}^{o} + V_{add}$ 

and:

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$$[H^+] + [K^+] = [X^-] + [OH^-]$$
 with  $[K^+] = c$ .

The following expressions can be deduced:

$$[\overline{R_{3N}}] = c_{B}^{O} - \frac{v_{H}^{+}}{V_{org}} + \frac{v_{aq}}{v_{org}} \{ [H^{+}] - [OH^{-}] \}$$
(6)

$$[\overline{R_{3}NHX}]_{T} = \frac{n_{H^{+}}}{V_{org}} - \frac{V_{aq}}{V_{org}} \{ [H^{+}] - [OH^{-}] \}$$
(7)

$$[X^{-}] = c + [H^{+}] - [OH^{-}]$$
(8)

In the reverse case of a titration of the organic ammonium salt by aqueous alkali, eqs. (6) and (7) are changed to:

$$[\overline{R_{3N}}] = \frac{n_{OH}^{-2}}{v_{org}} + \frac{v_{aq}}{v_{org}} \{ [H^{+}] - [OH^{-}] \}$$
(9)

$$[\overline{R_{3}}NHX]_{T} = c_{A}^{O} - \frac{n_{OH}}{V_{Org}} - \frac{V_{aq}}{V_{org}} \{ [H^{+}] - [OH^{-}] \}$$
(10)

[OH<sup>-</sup>] is deduced from [H<sup>+</sup>] through values for  $K_w$  which were measured (see Appendix VII).

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### 2. Applicability

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In the cases considered above the ammonium salt is considered as being absent from the aqueous phase. However for some medium and low molecular weight species a non negligible fraction of the ammonium salt might migrate to the aqueous phase. Thermodynamic  $K_p$  values representative of the equilibrium  $\overline{R_3NHX} \stackrel{2}{\leftarrow} R_3NH^+ + X$  have been determined in the preceding chapter.

As an approximation the partition ratio  $[R_3NH^+]/[\overline{R_3NHX}]_T$  of salt between nitrobenzene and the aqueous phase can be equated to  $K_p/y_{\pm}^2$  c (see following part 3) and the percentage loss of organic salt to the aqueous phase to 100 K<sub>p</sub>  $V_{aq}/y_{\pm}^2 V_{org}$  c, i.e. ca. 8000 K<sub>p</sub>. If an error of 1% (corresponding to the potentiometric error of .2 to .3 mV) is incurred, the maximum value of  $K_p$ , admissible before appreciable loss of organic salt to the aqueous phase occurs, is seen to be:  $K_p = \frac{1}{8000} = 1.25 \times 10^{-4}$ .

From Table 6 in chapter IV the following thirteen salts can be considered to be negligibly extracted into the aqueous phase: TLAHC1, TOAHC1, TLAHBr, TOAHBr, THAHBr, TLAHI, TOAHI, THAHI, TPTAHI, TLAHC10<sub>4</sub>, TOAHC10<sub>4</sub>, THAHC10<sub>4</sub> and TPTA-HC10<sub>4</sub>. For the other salts of low molecular weight in each series, eqs. (7), (8) and (10) do not apply and a different approach is necessary.

## 3. Lower molecular weight salts

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For these salts eq. (5), the total amine mass balance equation, has to be modified to:

$$\mathcal{L}_{B}^{O} \mathbf{v}_{Org} = [\overline{\mathbf{R}_{3}\mathbf{N}}]^{V} \mathbf{v}_{Org} + [\overline{\mathbf{R}_{3}\mathbf{N}\mathbf{H}\mathbf{X}}]_{T} \mathbf{v}_{Org} + [\overline{\mathbf{R}_{3}\mathbf{N}\mathbf{H}^{+}}] \dot{\mathbf{v}}_{aq}$$
 (11)

Introducing the partition constant  $K_p$  one can write:

where  $y_{\pm}$  is the mean activity coefficient of  $R_3NHX$  in the aqueous phase. If the following assumptions are made:

 $K_{p} = \frac{[R_{3}NH^{+}][x^{-}]}{[\overline{R_{3}NHx}]} Y_{\pm}^{2}$ 

 $[\overline{R_3NHX}]_{T} = [R_3NHX]$  and  $[X^-] = c$ 

the following expression is valid:

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$$[R_{3}NH^{+}] = \frac{K_{p}}{y_{+}^{2}c}[\overline{R_{3}}NH\overline{X}]_{T}$$

Eq. (11) can be rewritten and expressions developed for  $[R_3NHX]_T$ and [X] replacing eqs. (7), (8) and (10). These expressions can be found in Appendix VIII. Their range of validity is limited<sup>4</sup> however to the less dissociated and the less water partitioned salts: THAHC1, TPTAHBr and TBAHClO<sub>4</sub> (see Appendix IX).

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# 4. Partition of the amine

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In deriving the preceding equations the assumption was made that the free amine dissolved in the organic phase did not migrate significantly to the aqueous phase. This was verified to be the case for tripropylamine. The constant relative to the equilibrium  $\overline{R_{3}N} \stackrel{*}{\neq} R_{3}N$  was measured to be ca.  $10^{-3}$ . Constants for higher molecular weight amines were considered to be even smaller and the concentration of free amine in the aqueous phase to be in all cases negligible.

A 10 ml volume of a I M TPRA solution in nitrobenzene was contacted with 50 ml of nitrobenzene-saturated deionized water. The pH was measured as 10.88. Knowing the pK<sub>a</sub> value for  $R_3NH^{+(27)}$  (10.7) and calculating for  $[R_3N]$  as  $[R_3N] = K_a K_w/[H^+]^2$ , the value of the equilibrium constant was estimated as 1 x 10<sup>-3</sup>. (See also reference (21) in chapter IV.)

#### G) RESULTS

#### 1. Values from log-log plots

The log-log plots for various trialkylammonium salts appear in figures 16 to 31. The experimental data from twophase emf titrations appear in Appendix X.

In the low concentration decade  $10^{-3}$  to  $10^{-4}$  M in total ammonium salt drift and oscillations were frequently observed. Drifty values were not recorded and oscillating values were averaged. In the case of the iodide salt solutions systematic drifts towards lower E values were observed in the three concentration decades for solutions with E values above certain thresholds (see data in Appendix X). This seems to indicate the onset of a decomposition reaction and renders uncertain the values recorded even for the more stable points. It was found that in this system all values would eventually drift in the low concentration ranges ( $10^{-2}$  to  $10^{-4}$  M total ammonium salt). No attempt was made to clarify the reaction responsible for these drifts. One possibility is oxidation of iodide by traces of dissolved oxygen through the reaction<sup>(28)</sup>:

 $4I^{-} + O_2^{+} + 4H^{+} \stackrel{?}{=} 2I_2^{+} + 2H_2^{-}O$ 

The rate of this oxidation increases rapidly with increasing acidity (i.e. increasing E values here). The reaction would

# FIGURES 16 to 31

Log-log plots of various trialkylammonium salts from nitrobenzene-water two-phase emf titrations.
O, organic amine titrated with aqueous acid;
•, organic ammonium salt titrated with aqueous base; straight lines are of unit slope and were calculated on the basis of the equilibrium:

 $\overline{R_3NHX} \neq \overline{R_3N} + H^+ + X^-$ 

































be catalyzed by strong light,

In the experiments performed, iodide containing solutions, prepared from boiled distilled water, were stored under a nitrogen atmosphere. Oxygen could remain as traces and be further introduced through transfers and delivery of the titrant.

# 2. Log-log plots - qualitative examination

# a) Chloride system

All plots were linear with a slope of one. On this basis the solute should exist under the form of an ion-pair over the concentration range studied. No significant dissociation was evident. Values of Q seemed to vary little from the trihexyl to the tridodecylammonium salt.

### b) Bromide system

All plots appeared linear with a slope of one in the  $10^{-1}$  M concentration decade. Deviations begin to appear in the  $10^{-2}$  M decade and increase in the  $10^{-3}$  M decade. The solute may be considered as ion-paired at higher concentrations and to/undergo a degree of dissociation in the lower concentration ranges. 'Values of Q accessible from the first decade seem to be constant from the tripentyl to the Tridodecylammonium salt.

Behaviour similar to that of the bromide system was observed. However deviations from a slope one in the lower concentration decades was more important than in the bromide plots, indicating a higher dissociation. Values of Q accessible from the first decade seemed not to vary from tripentyl to tridodecyl salts.

# d) Perchlorate system

All plots showed similar behaviour. The slope decreased regularly from high to low concentrations corresponding to a value close to one to a value close to one half. Thus ion-pairs seemed to be predominant at high concentration and dissociated ions at low concentrations. The relative positions of the plots at high concentration seemed to indicate that Q values are similar for tributyl to tridodecylammonium perchlorates.

# é) Higher organic salt concentration region

Examination of the region of higher organic salt concentration on all log-log plots showed that in no system did the experimental curve have a slope significantly higher than one. This is interpreted as showing that no extensive formation of species of higher molecular weight than the ion-pair occurs in the range of concentration studied (see section H).

# 3. Estimation of Q and K<sub>d</sub> - Graphical method

From an examination of the log-log plots it was shown that the alkylammonium salt existed mainly in the forms of ionpair and dissociated ions. No systematic or significant sign of aggregation could be found.

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If the systems can be entirely represented by the two equilibria with constants K and K<sub>d</sub> then the following graphical procedure can be used. A family of curves is calculated and reproduced in figure 32 which represents the theoretical loglog plots of a number of systems for a given Q value with varying K<sub>d</sub> values. The straight line of slope one represents the system without dissociation; systems with increasing K<sub>d</sub> values (from  $10^{-5}$  to 7 x  $10^{-3}$ ) deviate from the straight line in an increasing manner. The deviation is minute for a K<sub>d</sub> of  $10^{-5}$  and noticeable only at the lowest concentrations; it is important for a higher K<sub>d</sub> and noticeable at all concentrations. A change in Q value does not change this pattern but just shifts the set of curves horizontally on the log-log plot.

To calculate the set of curves an iteration method similar to the one described in Appendix V, with an average a value of 6, permits for given  $K_d$  and  $[\overline{R_3NHX}]_T$  values to calculate  $[\overline{R_3NHX}]$ . Then once the reference straight line of slope one on the log-log plot is selected data points of ordinate  $[\overline{R_3NHX}]_T$  can be placed above points on the straight line of ordinate  $[\overline{R_3NHX}]$ . FIGURE 32

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Hypothetical log-log plots for two-phase emf titrations using various  $K_d$  values and a constant Q, two-phase hydrolysis constant.


The experimental log-log plots can then be compared by superimposition to the standard curves. The best fit is selected. The  $K_d$  value is thus estimated and the Q value evaluated from the position of the corresponding straight line of slope one.

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In the case of the chloride plots  $K_d$  could be estimated to be smaller than  $10^{-5}$ . All experimental curves could fit in between the curve for a  $K_d$  of  $10^{-5}$  and the curve for a non-dissociated species. Furthermore it can be calculated that points on a theoretical curve of  $K_d$  of  $10^{-5}$  deviate as an average by less than 10% (in Q' values) from the corresponding straight line. This is of the same magnitude as the reproducibility of several points in an experimental chloride plot. No attempt was made to estimate  $K_d$  values graphically or by computation in that series.

Results are listed in the following table (Table 9):

*	Graphically	d-d-	and Q values	
ammonium salt	Cl	Br	ı*	Clo <sub>4</sub>
ТВАН	/ ~•• \	, c	·	$\sim 3 \times 10^{-3}$ 3.1 x 10 <sup>-10</sup>
тртан '		$10^{-5} \times 10^{-5}$ 4.0 x 10 <sup>-8</sup>	$\sim 2 \times 10^{-4}$ 2.0 x 10 <sup>-9</sup>	$\sim 3 \times 10^{-3}$ 2.7 x 10 <sup>-10</sup>
тнан	$< 10^{-5}$ 3.5 x 10 <sup>-7</sup>	$\sim 5 \times 10^{-5}$ 3.5 x 10 <sup>-8</sup>	$\sim 2 \times 10^{-4}$ 1.9 x 10 <sup>-9</sup>	$\sim 3 \times 10^{-3}$ 2.8 x 10 <sup>-10</sup>
TOAH	$< 10^{-5}$ 3.5 x 10 <sup>-7</sup>	$\sim 5 \times 10^{-5}$ 3.5 x 10 <sup>-8</sup>	$\sim 2 \times 10^{-4}$ 1.8 x 10 <sup>-9</sup>	$\sim 3 \times 10^{-3}$ 2.9 x 10 <sup>-10</sup>
TLAH	$( < 10^{-5})$ 3.5 x 10 <sup>-7</sup>	$\sim 5 \times 10^{-5}$ 3.5 $\times 10^{-8}$	$\sim 3 \times 10^{-4}$ 2.0 x 10 <sup>-9</sup>	

TABLE 9

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\*  $K_d$  approximate.  $K_d$  in mol  $\ell^{-1}$ Q in mol<sup>2</sup>  $\ell^{-2}$ 

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Kd

<u>Q</u>

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## 4. Estimation of Q and K by computation

a) General

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The preceding visual method is approximate. It is, possible to calculate directly from the data points on the log-log plot the pair of  $K_d$  and Q values fitting each system best. Each data point consists of a pair of values  $[\overline{R_3NHX}]_T$ and  $[\overline{R_3N}][H^+][X^-]$ . By an iteration method each  $[\overline{R_3NHX}]_T$  value yields a value of  $[\overline{R_3NHX}]$  for a given  $K_d$  value. Q is calculated for each point as  $[\overline{R_3N}][H^+][X^-]/[\overline{R_3NHX}]$ . If the correct value of  $K_d$  has been selected, Q should be a constant over the whole concentration range. The plot of  $[\overline{R_3NHX}]$  vs.  $[\overline{R_3N}][H^+][X^-]$ should be a straight line of slope one.

Several  $K_d$  values are tested around the approximate  $K_d$  found by the visual method. The value that minimizes the spread on Q values is selected together with the corresponding Q value. Details on the computation can be found in Appendix XI. In figures 16 to 31 the corresponding straight lines of slope one were drawn for each system.

b) The chloride series

These salts gave log-log plots which were linear and of slope one. No computation of Q or K by the preceding method was attempted. Values of Q' calculated directly for each data point were averaged over the entire concentration

range giving the following results: THAHC1, Q = 3.6 (± .2) x  $10^{-7}$ ; TOAHC1, Q = 3.3 (± .2) x  $10^{-7}$ ; TLAHC1, Q = 3.4 (± .2) x  $10^{-7}$ .

c) The bromide series

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A complete computation was attempted;  $K_d$  values ranging between 1 x 10<sup>-5</sup> to 1 x 10<sup>-4</sup> were tested. Values in this range which minimized the standard deviation on Q were found. The corresponding Q values with their standard deviations are listed in the following table together with the  $K_d$  values and their ranges.

TABLE 10

Calculated Q	and K <sub>d</sub> values for the	bromide salts
• -,	$Q \times 10^8$	κ <sub>d</sub> .x 10 <sup>5</sup>
TPTAHBr	4.2 ± .2	5 ± 3
THAHBr	3.7 ± .2	5 ± 3
TOAHBr	, 3.7 ± .2	7 ± 3
TLAHBr	3.6 ± .3	5 ± <sup>e</sup> 4

d) The iodide series

Since relatively few stable data points were found in this system and all of these in the upper concentration decade, no direct computation of  $K_{d}$  and Q was attempted but

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rather the results from the visual graphical method were believed to give a reasonable approximation on the value of Q. These appear in Table 9.

e) The perchlorate series

The results of a complete calculation are presented below in Table 11.  $K_d$  values ranging between  $10^{-3}$  and 4.5 x  $10^{-3}$  were tested.

### TABLE 11

Calculated Q and K<sub>d</sub> values for the perchlorate salts

- \	$Q \times 10^{10}$	κ <sub>d</sub> × 10 <sup>3</sup>
TBAHC104	3.0 ± .3	2.0 ± .5
TPTAHC104	2.7 ± .2	2.0 ± .5
THAHClo4	2.5 ± .3	2.0 ± .5.
TOAHC104	2.7 ± .3	2.0 ± .5
TLAHC104	$3.0 \pm .4$	°2.5 ± 1

<u>Note</u>: The partition of MX between the aqueous' medium and the nitrobenzene phase was disregarded. Conductivity measurements done on nitrobenzene phases equilibrated with 0.1 M aqueous solutions of NaClO<sub>4</sub>, KI, KBr or KCl showed the concentration of ionized inorganic salt in nitrobenzene to be in all cases negligible.

Attainment of equilibrium. Sources of error 5. In all cases attainment of equilibrium in the twophase emf titrations was verified by comparing data points on the log-log plots obtained by direct and reverse titrations (see figures 16 to 31). In general titrations of organic amine by acid and of organic ammonium salt by base in the same concentration decade gave data points that coincided (from their Q' values) within 5% or less. The difference was attributed in good part to potentiometric errors (.2/.3 mV or 1% in concentration on each potential reading). In several cases the points for one titration would lie systematically above or below the points obtained by the reverse titration (within usually less than 5% in Q' values). This could be attributed partly to the potentiometric error and to the influence of possible impurities in the constant ionic strength aqueous medium, such as dissolved  $CO_2$  or  $O_2$  in the case of the iodides. The presence of low level acidic or basic impurities in either the initial amines or ammonium salts can also be invoked. The presence of low level impurities in the constant ionic strength aqueous solution could also have the effect of shifting points significantly in the low concentration region in the log-log plots. These impurities could come not only from the water (CO<sub>2</sub>) but also from the salt dissolved in it. (The presence of carbonate has been reported in commercially available sodium perchlorate. (29)

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The assumption of constant ionic strength in the aqueous phase can be examined. The concentration of  $X^-$  as calculated by eqs. (8), (16) or (17) never deviated from .1000 M by more than 2% which would result in negligible changes in the liquid junction potential or in activity coefficients in the aqueous phase.

The assumption of constant ratio of activity coefficients for  $R_3NHX$  and  $R_3N$  in the organic phase seems to be justified by the smoothness of the plots on the log-log scale, be they plots of  $[\overline{R_3NHX}]_T$  vs.  $[\overline{R_3N}][H^+][X^-]$  or the corresponding linear plots corrected for dissociation. The activity coefficients cannot actually be proven to be unity by this method.

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In the case of iodides the accuracy of the visual method was believed to be  $\pm$  5%. To this a standard deviation of 10% was added giving a range of  $\pm$  15% around the values listed in Table 9.

## 6. Final K values and ion exchange constants

In order to obtain the thermodynamic constant K from Q values, an estimate of the activity coefficient of low concentrations of HX in 0.1 M MX is necessary. This is obtained by applying the extended form of the Debye-Hückel law (see Appendix IV) yielding  $y_{H^+}$  and  $y_{X^{\pm}}$  or  $y_{\pm HX}$ . A value of .79 for  $\sqrt{y_{H^+}y_{X^-}}$  is obtained in all cases and is seen to be

close to the values of  $y_{\pm HX}$  tabulated for  $10^{-1}$  M solutions of HX (HC1: .796, HBr: .805, HI: .818, HC10<sub>4</sub>: .803).\*

. Table 12 gives the final tabulation of log Q and log K values.



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Log Q and log K values

system	Cl .	Br	I	ClO <sub>4</sub>
		,		-9.52±.05
тван			,	-9.71±.05
	1	-7.38±.02	-8.70±.06	<sup>∨</sup> -9.57±.03
тртан		-7.58±.02	-8.90±1.06	-9.77±.03
	-6.44±.03	-7.43±.02	-8.72±.06	-9.60±.05
тнан	-6.65±.03	-7.64±.02	-8.90±.06	-9.76±.05
	-6.48±.03	-7.43±.02	-8.74±.06	-9.57±.05
ТОАН	-6.69±.03	-7.64±.02	-8.95±.06	-9.74±.05
	-6.47±.03	-7.44±.03	-8.70±.06	-9.52±.06
TLAH (	-6.67±.03	-7.65±.03	-8.90±:06 0	-9.69±.06
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log Q<sup>-</sup> log K

See reference (19), Appendix B.

The constants K can be combined for each series of salts to give ion exchange equilibrium constants. The equilibria:

$$\overline{R_3^{NHX}}_1 \stackrel{\ddagger}{\leftarrow} \overline{R_3^N} + H^+ \stackrel{+}{\neq} x_1^-$$

and

$$\overline{R_3NHX}_2 \neq \overline{R_3N} + H^+ + X_2^-$$

with constants  $K_1$  and  $K_2$ , can be combined to yield the fallowing equilibrium:

$$\overline{R_3^{NHX}}_1 + x_2^{-2} \neq \overline{R_3^{NHX}}_2 + x_1^{-2}$$

This equilibrium describes the exchange of anion  $X_1$  from the ion-paired salt in nitrobenzene  $R_3NHX_1$  for anion  $X_2$  in the aqueous solution. The constant for this ion-exchange equilibrium is  $K_{12}$  with:

$$K_{12} = \frac{[\overline{R_3NHX}_2][x_1]}{[\overline{R_3NHX}_1][x_2]} = \frac{K_1}{K_2}$$

Similarly for the salts of low to middle molecular weight for which no value of K was obtainable, K values (determined in chapter IV) can be combined to obtain the ion exchange constants:

$$K_{12} = \frac{K_{p1}}{K_{p2}}$$

In Table 13 the ion exchange constants for the couples

Cl<sup>-</sup>/Br<sup>-</sup>, Br<sup>-</sup>/I<sup>-</sup>, and I<sup>-</sup>/Clo<sup>-</sup><sub>4</sub> are listed for each trialkylammonium series.

# TABLE 13

Ion exchange	constants lo	<u>g K</u> 12 -	of trialkyl	ammonium salts
log K <sub>12</sub>	Cl <sup>-</sup> /Br <sup>-</sup>	° .	Br /I	1 <sup>-</sup> /c10 <sup>-</sup> / <sub>4</sub> °
TPRAH	1.01±.01*†	ۍ د	1.26±.03	.92±.04
ТВАН	.98±.01 <sup>*†</sup>	-	1.35±.03 <sup>*</sup>	.82±.03*
<b>ТРТАН</b>	, 1.01±.03 <sup>*</sup>		1.25±.05 <sup>*</sup> 1.32±.08	.86±.04*
ТНАН	1.10±.03 <sup>*</sup> .99±.05	• •	1.26±.02	86±.11
ТОАН	•95±•05	• • / • •	1.26±.08	.84±.11
<b>TLAH</b>	.98±.06	s.	1.25±,09	.79±.12
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Obtained from K values.

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Obtained from K values based on one concentration level

For a few salts values obtained by both methods are available. In most cases there is no significant difference between the two values. In the case of THAHC1, the value obtained by two-phase emf titration was believed to be more reliable sincé it was obtained from more experimental points.

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## H) DISCUSSION

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The technique of two-phase emf titration has been seen to yield values for the hydrolysis equilibrium constant, K, of various middle and high molecular weight trialkylammonium salts dissolved in nitrobenzene. Information on the aggregation or dissociation of these salts in the organic phase has also been collected.

### 1. Aggregation and dissociation

Dissociation constants obtained by two-phase emf titration can be compared to the ones obtained by conductometry (see Tables 2, 9, 10 and 11). The  $pK_d$  values by conductometry (chlorides  $\sim$  5.0, bromides  $\sim$  4.5, iodides  $\sim$  3.4, perchlorates  $\sim$  2.4) are in fair agreement with values from two-phase emf titrations (chlorides < 5, bromides  $\sim$  4.3, iodides  $\sim$  3.7, perchlorates  $\sim$  2.7). No significant trend with alkyl chain length can be observed in values obtained by potentiometry since they are associated with high standard deviations. No precise value was obtainable for the chloride salts by potentiometry (see section G, part 3). At this low level of dissociation deviations from the slope one line were considered to be non significant. Furthermore the influence of low level impurities in the aqueous phase would make their determination uncertain. Values of  $K_d$  for bromide salts obtained by potentiometry were seen to be associated with important standard deviations making only their order of magnitude significant. Values of iodide salt dissociation are only semi-quantitative because of iodide decomposition. The dissociation constants of perchlorate salts obtained by two-phase emf titration compare favorably with values from conductivity measurements. Again if the discrepancy is assigned in part to low level impurities in the aqueous phase it is interesting to note that  $pK_d$  values calculated by omitting the low concentration decade points in the two-phase emf titration are seen to agree better with conductivity values  $(pK_d \sim 2.4$  in both cases).

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From an examination of the log-log plots in the upper concentration region occurrence of significant aggregation could be disregarded. Confirmation of this comes from the fact that  $K_d$  values determined conductometrically for low salt concentrations where aggregation is negligible compare favorably with  $K_d$  values obtained over a wider range of concentration. Furthermore the absence of any significant general trend in  $K_p$  values measured over a decade of organic salt concentration (from  $10^{-2}$  to  $10^{-1}$  M) supports the argument against aggregation (see chapter IV and Appendix VI).

Finally, it is interesting to note that the relative standard deviations of Q oscillate around 5 and 10% for measurements performed over a three decade range of concentrations. This corresponds approximately to what should be expected knowing the reproducibility of two-phase emf titration data

between the direct and the reverse titrations.

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2. K values. Basicity of amines.

A few of the -log K values tabulated in Table 12 can be compared to values determined by other workers: TOAHC1,  $6.75^{(2)}$  vs. 6.69; TLAHC1,  $6.78^{(4)}$  vs. 6.67; TLAHBr,  $7.70^{(4)}$ vs. 7.65; TLAHI,  $9.00^{(4)}$  vs. 8.90. The agreement is good in all cases. Müller and Diamond<sup>(3)</sup> gave a value of pK = 7.45for TLAHC10<sub>4</sub> corresponding to the following equilibrium:

 $\overline{R_{3}NH^{+}} + \overline{Clo_{4}^{-}} \stackrel{\stackrel{\scriptstyle ?}{\scriptstyle \sim}}{=} \overline{R_{3}N} + H^{+} + Clo_{4}^{-}.$ 

A corresponding value from this work would be 7.0 (obtained as  $pK - pK_d$ ). The Müller and Diamond treatment however was admittedly inaccurate since consideration of the association of dissociated ions to ion-pairs is ignored.

From an examination of K values obtained in this work for a variety of salts two major elements appear, the constancy of K with increasing carbon chain length for the same anion and the marked influence of the nature of the anion.

No significant trend could be found in the K values in a given series of salts when going from tributyl or tripentylamine to tridodecylamine (Table 12). If the following acid-base reaction in the organic solvent is considered

 $\overline{R_3NHX} \neq \overline{R_3N} + \overline{HX}$ 

(12)

the equilibrium constant  $\overline{K_a}$  is directly related to K through  $\overline{K_a} = K k_{HX}$  where  $k_{HX}$  represents the partition equilibrium constant of HX corresponding to the partition reaction:

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 $H^+ + X^- \ddagger \overline{HX}$ 

For a given anion,  $k_{HX}$  is a constant and since K does not vary with alkyl chain length,  $\overline{K_a}$  is a constant too. This suggests that the basicity of trialkylamines in nitrobenzene does not change with increasing chain length.

The inductive effect should increase the basicity of trialkylamines as alkyl chain length is increased.<sup>(30)</sup> This effect has been observed in water proceeding from trimethyl to tributylamine.<sup>(31)</sup> Trémillon et al.<sup>(32)</sup> by a spectrophotometric method found that the base strength of amines in various solvents was not significantly influenced by the chain length from tributyl to trioctylamine. Grinstead<sup>(10)</sup> reported a similar affinity of THA and TOA for HCl in toluene. A higher affinity of TOA than THA for  $H_2SO_4$  in benzene was reported by Verstregen. (11) Comparison between trioctyl and tridodecylamine systems (1) usually reveals similar affinity of these amines for various acids in different solvents. The above affinity comparisons, however, may be indicative since the authors have not always considered the influence of aggregation in the organic phase and of activity corrections in the aqueous Thus the constancy of the equilibrium constant of reaction phase.

(12) for all four acids HX with increasing chain length can be attributed to the constant basicity of the amines.

### 3. Anion exchange constants

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The influence of anion nature on the values of the hydrolysis constant is large. Hydrolysis assumes increasing importance in the order  $\text{ClO}_4^- < I^- < Br^- < \text{Cl}^-$ . There is approximately an order of magnitude difference in the hydrolysis constant when going from  $\text{ClO}_4^-$  to  $I^-$ , from  $I^-$  to  $Br^-$  and from  $Br^-$  to  $\text{Cl}^-$ . Anion exchange constants (Table 13) reflect these differences. As is the case with basicity, ion exchange does not seem to be influenced significantly by alkyl chain length. (Only two values of log  $K_{12}$  differed significantly from others in their series: for the couples TBAHBr/TBAHI and TPRAHI/TPRAHClO<sub>4</sub>. This deviation may be attributed to experimental error.)

The order of anion exchange can be attributed to the nature of the aqueous and organic phases. In the organic phase cation-anion interaction through electrostatic interaction and hydrogen bonding should favor the extraction of Cl vs. Br, Br vs. I and I vs.  $Clo_4$  (see chapter III). However this interaction is believed to be less important than interactions in the aqueous phase. Hydration is more favorable in the case of a smaller more basic anion. Furthermore anions of larger diameter are also energetically more favored in the organic

phase than small anions because of the water structure breaking factor (see chapter IV, section E, part 3). These effects can be summarized in a diagram. (33)



In step I the ion-pair  $R_3$ NHX in the organic phase is dissociated. In step III the anion X is extracted in the aqueous phase. In step III anion Y from the aqueous phase is extracted in the organic phase to form an ion-pair with the organic cation in step IV. Scibona et al. applied such a cycle to study ion exchange involving tetraalkylammonium<sup>(34)</sup> and trialkylammonium<sup>(33)</sup> salts. Coulomb's law was applied for dealing with dissociation in the organic phase and the Born charging expression for the transfer of ions. In this study no such attempt was made since the simple electrostatic theory and the Born charging expression for the transfer of ions were not considered sufficient in the case of trialkylammonium salts in nitrobenzene (see chapters III and IV).

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## CHAPTER VI

# LIQUID ION EXCHANGE SELECTIVE ELECTRODES

From ion exchange constants of tertiary ammonium salts determined in nitrobenzene it was concluded that the affinity of the organic phase for  $Clo_4^-$  anions was superior to that for the other anions studied. This property suggests the use of these salts as liquid ion exchangers in electrodes that would be selective towards perchlorate.

In order to test the electrochemical response of the salts a cell was developed to measure the potential across a membrane of ion exchanger contacted on each side with aqueous solutions. In a design similar to that adopted for ion selective electrodes, the aqueous solution on one side of the exchanger was maintained at a constant concentration while on the other side concentrations could be varied. The potential response of the electrochemical cell was measured for all the trialkylammonium salts.

### A) EXPERIMENTAL

. Chemicals and solutions

The preparation of nitrobenzene saturated aqueous solutions of NaClO<sub>4</sub>, KI, KBr and KCl has been described (chapter V). Trialkylammonium salt solutions in nitrobenzene of 0.1 M concentration were prepared as described in chapter III.

### 2. Experimental cell

The electrochemical cell was designed to provide maximum flexibility and rapidity of use. Inspired by a design of Eisenman<sup>(1)</sup> it consisted of a Teflon block divided in two parts connected to each other through a machined key. Each, block contained a drilled-out compartment that could be filled with an aqueous solution (see figure 33). The two blocks and compartments were separated by a liquid ion exchanger compartment. Three Teflon o-rings sandwiched two Millipore filter membranes and could be positioned to separate the two compartments. The central space in between the two filters could be filled with liquid ion exchanger.

Two 4 cm long pieces of polyethylene "spaghetti tubing" were inserted in the top part of the central o-ring through fine holes. These allowed the injection of liquid ion exchanger by a syringe in the central space in between the two filters. The aqueous cylindrical compartments were ca. eight cm long with a one cm diameter. O-rings had a one cm internal diameter





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(Millipore XX3001201). Reference electrodes (1 M calomel electrodes Fisher 13-639-51) contacted the solutions on each side of the membrane through holes drilled in the block.

Several types of filters were tested for the central liquid ion exchanger compartment. Millipore Solvinert filters (UGHP01300) were found to be adequate to retain the nitrobenzene ion exchanger solutions. These filters are described by the manufacturer as solvent resistant hydrophobic filters of  $0.25 \mu$  pore size. They were found to swell slightly in nitrobenzene and were adjusted in the compartment after pre-soaking in the organic solutions. The volume of the exchanger compartment was estimated as 150 mm<sup>3</sup>.

The electrochemical cell was placed in a constant temperature environment. This consisted of a double-walled lucite box through the lid of which reference electrodes could be lowered. The temperature was maintained at 25° by circulation of water. This is the temperature at which all other measurements have been done in this study.

Measurements of the potential were performed by a calibrated Accument Expanded Scale Research pH-meter (model 320) in the expanded mV mode. The potentiometric error was estimated at  $\pm$  .2 to .3 mV.

Experimental procedure

For each salt tested as a liquid ion exchanger a

potential response curve was obtained. First the membranes after soaking, one minute in the organic liquid were placed in between the o-rings. The block thus formed was positioned in the cell using an external centering device. The two blocks were tightened in order to support the exchanger compartment. The 0.1 M liquid exchanger was introduced. One of the aqueous compartments was filled with a 0.1 M solution of MX, X being the anion of the salt used as exchanger (e.g. NaClO<sub>4</sub> for the TLAHClO<sub>4</sub> exchanger). In the other compartment several MX solutions were tested consecutively. Concentration levels usually were  $10^{-1}$  M,  $10^{-2}$  M,  $10^{-3}$  M and  $10^{-4}$  M. In the perchlorate series intermediate concentrations were also tested. For interference measurements the solutions tested were decimolar in KI, KBr or KCl and contained various levels of perchlorate from  $10^{-4}$  to  $10^{-1}$  M.

Solutions were removed from the compartments by drainage through a plug situated on the side of each block. Compartments were refilled from the holes provided on the top of the blocks. Reproducibility was checked by testing duplicate solutions first from dilute to concentrated then in the reverse order. All organic solutions were decimolar (within 5%) in ion exchanger except the TLAHC1 solution which was 0.06 M (saturated solution).

### B) RESULTS

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The response curves of the electrochemical cell for the four series of salts studied appear in figures 34 to 37. In figure 38 the response curve of the TLAHClO<sub>4</sub> based electrode in the presence of anion interferences is presented. The quantity E is plotted vs. the log of the anion activity. The value for E is obtained as the difference between the potential measured and the potential obtained when the two aqueous compartments contain 0.1 M MX solution. Values of E for each system are tabulated in Appendix XII. The anion activity is calculated from the concentration after a Debye-Hückel single ion activity coefficient correction (see Appendix IV). On the graphs the activity is plotted as decreasing from left to right.

Solutions of pure water tested in the electrode were not reported since they gave drifty, unstable, and nonreproducible potentials. Generally the response times increased with increasing dilution of the test solutions. Solutions at  $3 \times 10^{-4}$  M or  $10^{-4}$  M could require ten to fifteen minutes to reach a stable value. Other more concentrated solutions would reach a stable reading within a few minutes. Reproducibility varied with the concentration level and the exchanger tested. High molecular weight ammonium salts gave usually reproducible potentials while low molecular weight exchangers had generally a poor reproducibility. A vertical line extending at a value of  $\sigma$  above and below each point on the graphs represents the

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dispersion range on each potential reading.

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It was observed that for the low molecular weight salts TPRAHCIO<sub>4</sub>, TPRAHI, TBAHI, TBAHBr, and TPTAHBr potential 'values were stable only for a few minutes after which the / potential would drift to lower values. For the salts TPRAHBr, TBAHCl and TPRAHCl no stable value could be recorded. In the case of the TLAHClO<sub>4</sub> electrode, response times were found to be longer when interfering ions were present especially at low concentrations of the main ion.

## FIGURES 34 to 37

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Response curve of electrodes using trialkylammonium perchlorates, iodides, bromides and chlorides as liquid anion exchangers in nitrobenzene.

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Lines extended with dots represent theoretical Nernstian response of 59 mV per decade.









## FIGURE 38

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Response curve of the  $TLAHClO_4$  electrode in the presence of interfering anions.

Line extended with dots represents theoretical Nernstian response of 59 mV per decade.

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## C) DISCUSSION

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# 1. Respondent curves

High molecular weight ammonium salts in each series usually gave more Nernstian response curves than their low molecular weight homologues. In general, the order of increasing deviation from an ideal Nernstian response curve was  $Clo_4^ < I^- < Br^- < Cl^-$ . In the range of concentration studied all curves showed deviation from the theoretical slope at low concentrations. These deviations are usually attributed to contamination of the test aqueous phase in contact with the ion exchanger with anions coming from the exchanger, thus increasing their concentration above that of the test solution. (1,2)

Two processes were probably responsible for deviations from the ideal Nernst slope. One would be the partition of the organic ammonium salt from nitrobenzene into water. The other would be hydrolysis of the ion exchanger.

The extent of solubilization of the ion exchanger in an aqueous phase by partition is regulated by its K value corresponding to the equilibrium:

 $\overline{R_3NHX}$   $\ddagger$   $R_3NH^+ + x^-$ 

These constants have been measured for various exchangers (see chapter IV; Table 6) and are seen to be of increasing magnitude in the order: TPTAHI < THAHCL < TBAHCLO<sub>4</sub> < TPTAHBr < TBAHI <

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TPRAHC10<sub>4</sub>, TPTAHC1 < TBAHBr < TPRAHI, considering only those salts with  $K_D$  values above  $10^{-4}$ .

If part of the deviation from Nernstian slope is due to solubilization, it is to be expected that this deviation will follow the same order as  $K_p$ .<sup>(3)°</sup> By measuring the deviation at an activity level of  $10^{-2}$  the following order of increasing deviation is found (see figures 34 to 37): TPTAHI (no deviation) < THAHC1, TBAHClO<sub>4</sub> < TBAHI < TPTAHBr < TPRAHClO<sub>4</sub>, TPTA-HC1, TBAHBr < TPRAHI.' This is essentially the same order as that of  $K_p$  values. No deviation is found for TPTAHI and other salts of higher molecular weight in each series. Thus deviations from the theoretical slope at this concentration level can be attributed confidently to the process of solubilization of the exchanger by partition into the aqueous phase.

When deviations at low concentration levels are considered  $(10^{-3} - 10^{-4} \text{ F} \text{ ion concentration})$  partition would not be sufficient to explain the trends. The salts TLAHClO<sub>4</sub>, TOAHClO<sub>4</sub> and THAHClO<sub>4</sub> give the same response curve. The same is true for TLAHI and TOAHI, TLAHBr and TOAHBr. These salts are however expected to have different water partition constants. It is also observed that the extent of deviation increases in the order  $\text{ClO}_{4}^{-} < \text{I}^{-} < \text{Br}^{-} < \text{Cl}^{-}$ . This is however the order expected if this deviation is attributed to hydrolysis of these high molecular weight salts. Two-phase hydrolysis constants have been determined (chapter V) and are known to increase when

going from perchlorate to chloride salts. Thus the high molecular weight salts cited which have very low partition constants would however hydrolyze to the same extent within each series (K values are independent of carbon chain length) and to a different extent from series to series. This would explain the observed trends.

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At all concentrations a combination of the two mentioned effects probably regulates the behaviour of the electrodes.

Reproducibility, drift and response time are better <sup>7</sup> understood if the above reactions are considered. Occurrence of important partition or hydrolysis is expected to create drift and worsen the reproducibility by changing the composition of the ion exchanger phase. The constant drift encountered in the TPRAHC1, TBAHC1, TPRAHI systems can be attributed to their very high corresponding K<sub>p</sub> values depleting the organic phase of ion exchanger immediately after introduction of the aqueous phases. For the higher molecular weight salts partition is less important. At high aqueous concentration levels since hydrolysis or partition are repressed no drift is observed and reproducibility is of the same order as the potentiometric error.

#### 2. Selectivity

The TLAHClO system was chosen for selectivity studies

since it represented the exchanger having the most Nernstian response and the best reproducibility. From the plots in figure 38 the effect of interference could be assessed. Qualitatively the iodide anion could be seen to have the most influence on the potential of the perchlorate electrode since the response curve in the presence of a constant level of iodide  $(10^{-1} \text{ M})$  deviated most from the interference free perchlorate response curve. Bromide was seen to interfere less than iodide, . while chloride gave the least interference. This is what is to be expected qualitatively from the trend in ion exchange constants determined in chapter V.

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The extent of interference on the response of ion selective electrodes is usually expressed through the insertion of a selectivity constant  $K_{S12}$  in the equation for potential response. For a monovalent anion selective electrode one has:

 $E = E'^{\circ} - \frac{RT}{F} \ln (a_1 + K_{S12} a_2)$ 

where  $a_1$  and  $a_2$  are the activities of main and interfering ion respectively, (4,5) and E'<sup>O</sup> a constant term.

The constant  $K_{S12}$  can thus be obtained as

$$K_{S12} = \frac{a_1 \times 10^{\Delta E/59} - a_1}{a_2}$$

in the case of a monovalent anion selective electrode. The

value  $\Delta E$  (in mV) is the difference in E value between the theoretical Nernstian interference free potential and the actual recorded potential in the presence of interference.

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Values for  $K_{S12}$  were computed at different  $Clo_4^$ activity levels for the interference of I<sup>-</sup>, Br<sup>-</sup> and Cl<sup>-</sup> ions on the TLAHClO<sub>4</sub> exchanger electrode (see Appendix XII). These values are seen to vary with the activity level as was often observed with ion selective electrodes. <sup>(6)</sup> The average value corresponding to activity levels below 2 x  $10^{-3}$  was selected since in this activity range the response of the electrode is Nernstian.

The selectivity constants K<sub>S12</sub> were found to be:

 $\frac{c10_{4}^{-}/1^{-}}{1^{-}} \frac{c10_{4}^{-}/Br^{-}}{1^{-}} \frac{c10_{4}^{-}/c1^{-}}{1^{-}}$   $K_{S12} \qquad 1 \qquad \sqrt{.03} \qquad \sqrt{.005}$ 

These values are only approximate and must be considered as empirical parameters<sup>(2)</sup> describing interference in the experimental conditions specified. Interference is seen to increase from Cl<sup>-</sup> to Br<sup>-</sup> to I<sup>-</sup>.

A few authors have attempted to correlate electrochemical selectivity constants with ion exchange constants. (1,3,7-9) Freiser et al.<sup>(8)</sup> studied the interference properties of electrodes using tetrahexylammonium iodide dissolved in

various organic alcohols as liquid anion exchangers. He found a good correlation between selectivity constants and ion exchange constants in this system. Scibona et al.<sup>(9)</sup> and Fabiani <sup>(10)</sup> used tetraheptylammonium salts dissolved in various solvents. Applying theoretical equations developed by Eisenman et al.<sup>(7)</sup> they related semi-quantitatively interference constants to ion-exchange constants, dissociation constants and the mobility of the anions in the organic phase. Eisenman<sup>(1,7)</sup> mentions a membrane made of dodecylamine dissolved in nitrobenzene which in an electrochemical cell was selective for I<sup>-</sup> in the presence of Br<sup>-</sup> and Cl<sup>-</sup>. In a more detailed study on di-2-ethylhexyl phosphoric acid in n-amyl alcohol the author, using the theoretical equations,<sup>(7)</sup> could predict the order of selectivities; however the agreement was only qualitative.

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For the system used in this selectivity study no theoretical equation is available which could relate the interference response curves to the chemical properties of the ion exchanger. The system does not fall in the category of a completely dissociated ion exchanger nor a strongly associated one ( $\sim$  15% of the ion exchanger is ionized). However a correlation could be found between  $K_{S12}$  values and  $K_{12}$  values. In figure 39 a plot of log  $K_{S12}$  vs. log  $K_{12}$  appears. Values of ion-exchange constants  $K_{12}$  were deduced from Table 13 in chapter V. The slope of the plot is ca. 0.6. A similar correlation with a slope of ca. 0.5 was observed by Bäck and

# FIGURE 39

Plot of log  $K_{S12}$  vs. log  $K_{12}$  for tridodecylammonium perchlorate in nitrobenzene.

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Sandblom<sup>(3)</sup> on tetraalkylammonium salts in methylene chloride. Freiser et al.<sup>(8)</sup> observed the same phenomenon but with a slope close to one.

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Finally it may be of practical interest to compare the selectivity constants obtained with those of commercial perchlorate electrodes reported.

	cl0 <sub>4</sub> /1	C104/Br	c104/c1
This work	0.1	0.03	0.005
Orion <sup>(11)</sup>	0.012	0.00956	0.00022
Corning <sup>(12)</sup>		10 <sup>-5</sup>	$4 \times 10^{-6}$
Radelkis <sup>(13)</sup>	.9	.49	.27

Thus the TLAHCIO<sub>4</sub> electrode appears to have a poorer selectivity than commercial electrodes. For a complete comparison however interference coefficients of the commercial electrodes should be redetermined under the same interference conditions as the ones used for the electrode in this work.

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#### APPENDIX I

## Parameters and expressions used in the Shedlovsky method

 $\alpha = 8.2 \times 10^{5} (\epsilon T)^{-3/2} = .774$   $\beta = 82\eta^{-1} (\epsilon T)^{-\frac{1}{2}} = 44.4$   $z = (\alpha \Lambda_{\circ} + \beta) \Lambda_{\circ}^{-3/2} \sqrt{c\Lambda}$   $S(z) = (z/2 + \sqrt{1 + (z/2)^{2}})^{2}$  $\gamma = \Lambda S(z)/\Lambda_{\circ}$ 

 $-\log y_{\pm}^2 = 3.65 \times 10^6 (\epsilon T)^{-3/2} \sqrt{c\gamma} = 3.45 \sqrt{c\gamma}$ 

 $Y = 1/\Lambda S(z)$  $X = \Lambda c y_{\pm}^{2} S(z)$ 

 $\Lambda_{\circ} = 1/I$ 

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 $K_d = I^2/S$ 

 $\sigma \Lambda_{\bullet} / \Lambda_{\bullet} = \sigma I / I$ 

 $\sigma_{K_{d}}/K_{d} = \sqrt{4 \frac{\sigma_{1}^{2}}{r^{2}} + \frac{\sigma_{s}^{2}}{s^{2}}}$ 

#### APPENDIX II

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## Conductometry data

In the following pages data points (c,  $\Lambda$ ) are tabulated for each system together with the corresponding X and Y values. For the I<sup>-</sup> and Clo<sub>4</sub><sup>-</sup> systems the X and Y values listed correspond to the initial calculation using  $\Lambda_{\circ}$  values listed in Appendix III B.

	TPRAH	<u>21</u> •			TBAHC.	Ľ	-	•
c	٨	¥ _	x ° x10 <sup>3</sup>	. c	Λ	¥ *	X. x10 <sup>3</sup>	
$1.013 \times 10^{-2}$	1:636 1.641	.586 .585	14.56 14.61	9.43 x $10^{-3}$	1.548 1.552	.620 .619	12.91 12.94	
6.08 x 10 <sup>-3</sup>	1.720 1.709	.563	9.440 9.38	5.66 $\times 10^{-3}$	1.672 1.658	.579 .584	8.57 8.51	
$4.05 \times 10^{-3}$	2.009 1.992	.484 .488	7.44 7.38	$3.77 \times 10^{-3}$	1.879	.517	6.51 6.49	
$2.026 \times 10^{-3}$	2.716 2.704	.360 .361	5.11 5.09	$1.885 \times 10^{-3}$	2.599 2.572	.376	4.57 4.52	
$1.013 \times 10^{-3}$	3.73 3.77	.2626 .2604	3.56 3.59	9.43 x $10^{-4}$	3.53 3.57	.2782 .2750	3.14 3.17	1
$6.08 \times 10^{-4}$	4.75 4.71	.2070 .2086,	2.737 2.717	5.66 $\times 10^{-4}$	4.64 4.57	.2117 .2153	2.50 2.455	

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**Sector Sector** 

	TPTAHC1	u.	,	~. ^	<u>тңанс1</u>		2
C	٨	Y	x _x10 <sup>3</sup>	c	Λ.	¥	x x10 <sup>3</sup> .
$8.57 \times 10^{-3}$	1.537 1.537	.625 .625	11.71 11.71	9.91 $\times 10^{-3}$	1.459 1.463	.656 .655	12.77 12.80
5.14 x $10^{-3}$	1.660 1.648	.583 .588	7.77 7.72	$5.95 \times 10^{-3}$	1.529 1.535	.632 .629	8.24 8.28
$3.43 \times 10^{-3}$	1.922 1.914	.506 .508	6.07 6.05	$3.96 \times 10^{-3}$	1.715 1.715	.566 .566	6.25 6.25
1.715 x $10^{-3}$	2.627 2.632	.372 .37 <u>1</u>	4.21 4.22	1.982 x 10 <sup>-3</sup>	2.291 2.336	.426 .418	4.24 4.32
8.57 x $10^{-4}$	3.67 3.73	.2673 .2626	2.972 3.03	9.91 $\times 10^{-4}$	3.25 3.27	.301 .3001	3.04 3.05
$5.14 \times 10^{-4}$	4.65 4.61	.2114 .2133	2.277 2.257	5.95 x $10^{-4}$	4.06 3.99	.2419 .246	2.297 2.258

- · · · · · · · · · · · · · · · · · · ·	TOAHC1	· · ·	, ? 0	TLAHC1	۰.
° C .	Λ ° Υ	X , , x10 <sup>3</sup>	C	<b>٨</b> . ۲.	×10 <sup>3</sup>
$1.015 \times 10^{-2}$	1.416 .676 1.407 .680	12.69 12.61	$1.043 \times 10^{-2}$	1.378 .693 1.369 .698	12.67 12.59
$6.09 \times 10^{-3}$	1.493 .647 1.487 .649	8.24 8.21	6.26 x 10 <sup>-3</sup>	1.442 .669 1.448 .666	8.17 8.20
$4.06 \times 10^{-3}$	1.633 .594 1.642 .591	6.10 6.13	4.17 $\times 10^{-3}$	1.585 .611 1.585 .611	6.07 6:07
$2.030 \times 10^{-3}$	2.207 .442 2.224 .439	4.18 4.21	$2.086 \times 10^{-3}$	2.116 .461 2.164 .450	4.12
$1.015 \times 10^{-3}$	3.14 .312 3.14 .312	3.01 3.004	$1.043 \times 10^{-3}$	2.933 .334 2.968 .330	2.889 - 2°.922
$6.09 \times 10^{-4}$	3.87 .2539 3.91 .252	2.242 2.262	$6.26 \times 10^{-4}$	3.68 .2668 3.77 .2606	2.191 2.241

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,	-	TPRAHB	r	~ ı		-	TBAHBr	-	i
-	c	۸	Ŷ	x ×10 <sup>3</sup>	•	ۍ ۲	· <b>Λ</b>	Ŷ	. x x10 <sup>3</sup>
9.01	x 10 <sup>-3</sup>	2.475 2.475	.385 .385	19.17 19.17	5	9.02 $\times 10^{-3}$	2.324 2.324	.410 410	18.08 18.08
6.01	× 10 <sup>-3</sup>	2.719 2.738	.353	14.36 14.46	-	5.41 $\times 10^{-3}$	2.720 2.745	.353 .349 。	13.01 13.12
4.51	x 10 <sup>-3</sup>	3.06 3.08	.315 .313	12.25 12.31		3.61 $\times 10^{-3}$	3.22 3.23	.2991 .2983	10.42 10.45
1.803	x 10 <sup>-3</sup>	4.67 4.68	.2079 .2072	7.68		$1.805 \times 10^{-3}$	4.44 4.47	.2183 .2168	7.32 7.37
-9.01 <sup>°</sup>	× 10 <sup>-4</sup>	~6.31 6.33	.1546 .1542	5.28 •5.29	f	9.02 x $10^{-4}$	6.06 6.07	.1610 .1606	<sup>°</sup> 5.07 5.08
6.76	x 10 <sup>-4</sup>	7.17 7.29	.1363 <sup></sup> .1340	4.52 4.60		5.41 $\times 10^{-4}$	7.58 7.70	.1290 .1270	3.85 3.91
3.61	$\times 10^{-4}$	9.53 9.74	.1030	3.24 3.31		$2.707 \times 10^{-4}$	10.18 ° 10.38	.0965 .0946	2.614 2.664

	TPTAH	Br	`	۰	THAHBr				
C	٨	<b>۲</b>	x x10 <sup>3</sup>	с 	٨	Y	x x10 <sup>3</sup>		
$1.024 \times 10^{-2}$	<b>2.16</b> 8 2.168	.437 .437	19.01 19.01	$1.023 \times 10^{-2}$	2.074	.457 .459	18.22 18.14		
6.14 $\times 10^{-3}$	2.489 2.473	.384 .387	13.46 13.38	$6.14 \times 10^{-3}$	2.399 2.399	.399 .399	12.98 12.98		
4.10 x $10^{-3}$	2.925 2.866 -	.329 .33 <u>6</u>	10.70 10.50	4.09 x $10^{-3}$	2.815 2.842	°.342 .338	10.31 - 10.40		
$2.048 \times 10^{-3}$	4.04 4.01	.2397 .2414	7.53 7.48	2.046 x $10^{-3}$	3.85 3.87	.2511 .2499	7.20		
$1.024 \times 10^{-3}$	5.50 5.45	.1769 .1786	5.22 5.17	$1.023 \times 10^{-3}$	5.28 5.28	.1843 .1843	5.01 5.01		
6.14 $\times 10^{-4}$	6.92 7.09	.1411 .1378	3.98 4.07	6.14 $\times 10^{-4}$	6.68	.1463 .1465	3.84 3.83		
$3.07' \times 10^{-4}$	9.26 9.12	.1060 .1077	2.694 2.654	$3.07 \times 10^{-4}$	8.86 -9.01	.1108 .1088	2.577		

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, C	٨	¥	x ×10 <sup>3</sup>	-	C	٨	<b>Y</b> .	X x10 <sup>3</sup>	
$1.014 \times 10^{-2}$	2.012 2.003	.471	17.55	9	$9.82 \times 10^{-3}$	1.953 1.957	.485 .484	16.55 16.98	
$6.08 \times 10^{-3}$	2.355 2.334	.406 .410	12.64 12.54	۰ _ ۲ E	5.89 x 10 <sup>-3</sup>	2.224 2.243	.430 .426	11.61 11.70	*
4.06 x $10^{-3}$	2.798 2.779	.343 .346	10.16 10.09	3	$3.93 \times 10^{-3}$	2.686	.358 .361	9.47 9.39	
$2.028 \times 10^{-3}$	3.85 3.81	.2512 .2538	7.12 7.06	ĺ	$1.964 \times 10^{-3}$	3.70 3.68	.2613 .2629	6.65 <sup>°</sup> 6.61	
$1.014 \times 10^{-3}$	5.19 5.19	.1876 .1876	4.88 4.88	9	$1.82 \times 10^{-4}$	5.02 5.02	.1937 .1937	4.58 4.58	
$6.08 \times 10^{-4}$	6.56 6.65	.1490 .1469	3.74 3.79	5	$1.89 \times 10^{-4}$	6.34 6.41	.1540 .1523	3.50 3.54	*
$3.04 \times 10^{-4}$	8.52 8.61	.1151 .1140	2.460 2.483	2	$1.945 \times 10^{-4}$	8.32 8.35	.1179 .1175	2.326	

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c	Λ .	ү x10 <sup>2</sup>	x10 <sup>2</sup>	, C	Λ	Y x10 <sup>2</sup>	x. x10 <sup>2</sup>
9.78 $\times 10^{-3}$	6.75 6.76	13.56 13.54	5.04 5.04	9.98 × 10	-3 6.40 6.38	/ 14.27 14.31	4.88 4.86
$5.87 \times 10^{-3}$	.38 8.45	11.06 10.96	3.90 3.93	5.99 x 10	-3 7.89 7.89	11.72 11.72	3.75 3.75 ·
$3.91 \times 10^{-3}$	9.92 - -9.85	- 9.42 9.49	3.16 3.14	3.99 x 10	-3 9.29 9.27	10.04 10.07	3.03 3.02
$1.957 \times 10^{-3}$	12.93 12.96	7.32 7.31	2.148 2.153	<b>1.996</b> x 10	-3 12.30 12.30	7.68 7.68	2.085 2.085
9.78 x $10^{-4}$	16.59 16.70	5.77 5.73	1.425 1.434	9.98 x 10	-4 15.83 15.67	6.04 6.10	1.387 1.374
$3.91 \times 10^{-4}$	21.70 21.66	4.47 4.47	.773 .772	3.99 x 10	-4 20.72 20.82	4.67 4.65	.753 .757
$1.957 \times 10^{-4}$	25.32 25.45	3.86 3.84	.462 .464	1.996 x 10	-4 23.90 24.00	4.08 4.06	.445 .446
9.78 x 10 <sup>-5</sup>	28.21 28.31	3.48 3.47	.2618 .2627	9.98 x 10	-5 26.74 26.83	3.67 3.66	.2532

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С	· ۸	Y x10 <sup>2</sup>	x x10 <sup>2</sup>	C	Λ	Y xl0 <sup>2</sup>	x x10 <sup>2</sup>
9.87 $\times 10^{-3}$	6.09 6.11	14.97 14.92	4.61 4.63	$1.004 \times 10^{-2}$	5.72 5.72	15:96 15.96	4.43 4 <b>a</b> 43
5.92 x $10^{-3}$	7.50 7.52	12.32 12.28	3.55 3.55	$6.02 \times 10^{-3}$	7.07 7.06	13.08 13.10	3.41 , 3.41
3.95 x 10 <sup>-3</sup>	8.86 8.85	10.52 10.53	2.867 2.864	4.02 $\times 10^{-3}$	8.47 8.40	11.01 11.10	2.794 2.774
1.975 x 10 <sup>-3</sup>	11.68 11.68	8.09 8.09	1.965 1.965	$2.008 \times 10^{-3}$	11.11 11.01	8.51 8.59	1.905 1.889
9.87 $\times 10^{-4}$	15.10 15.00	6.325 6.37	1.312 1.304	$1.004 \times 10^{-3}$	14.22 14.26	6.72 6.70	1.259 1.263
$3.95 \times 10^{-4}$	19.77 19.70	4.89 4.91	.712 .710	$4.02 \times 10^{-4}$	18.82 18.76	5.14 5.16	.691 .688
$1.975 \times 10^{-4}$	22.95 22.86	4.25 4.27	.423 .421	$2.008 \times 10^{-4}$	22.10 22.02	4.41 4.43	.414 .413
9.87 x $10^{-5}$	25.68 25.63	3.82 3.83	.2407 .2403	$1.004 \times 10^{-4}$	25.04 25.14	3.92 3.90	.2388 .2397

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C,	٨	Y x10 <sup>2</sup>	x . x10 <sup>2</sup>	` <b>C</b>	Λ	Y x10 <sup>2</sup>	x x10 <sup>2</sup>			
9.87 x 10 <sup>-3</sup>	5.42 5.41	16.85 16.88	4.16 4.15	$1.026 \times 10^{-2}$	4.99 5.01	18.26 18.18	3,99 4.00			
5.92 $\times 10^{-3}$	6.74 6.72	13.72 13.76	3.22 3.21	6.16 $\times 10^{-3}$	6.22 6.20	14.83 14.88	3.09 3.08			
3.95 x 10 <sup>-3</sup>	7.96 8.01	11.72 11.64	2.598 2.613	4.10 $\times 10^{-3}$	7.41 7.35	12.56 12.67	2.516 2.497			
$1.975 \times 10^{-3}$	10.55 10.60	8.96 8.91	1.787 1.795	$2.052 \times 10^{-3}$	9.74 9.69	9.69 9.74	1.716 1.708			
9.87 x $10^{-4}$	13.60 13.49	7.03 7.09	1.188 1.179	$1.026 \times 10^{-3}$	12.56 12.63	7.60 7.56	1.141 1.147			
$3.95 \times 10^{-4}$	17.99 17.89	<sup>9</sup> 5.38 5.41	.650 .647	4.10 $\times$ 10 <sup>-4</sup>	16.96 16.96	5.70 5.70	.637 .637			
$1.975 \times 10^{-4}$	21.62 21.50	4.51 4.53	.399 .397	$2.052 \times 10^{-4}$	20.12 20.20	4.84 4.82	.386 .387			
9.87 x $10^{-5}$	24.41 24.46	4.02 4.01	.2290	$1.026 \times 10^{-4}$	23.13 23.01	4.24 4.26	.2255 .2244			

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	TPRAHC104		,	TBAHC1	<u>5</u> 4	
C	Λ Υ ×10 <sup>2</sup>	x x10 <sup>2</sup>	c -	_ ^	Y x10 <sup>2</sup>	X xl0 <sup>2</sup>
$1.000 \times 10^{-2}$	17.64 4.96 17.57 4.98	11.28 11.24	9.66 x 10 <sup>-3</sup>	16.82 16.71	5.19 5.23	10.52 10.47
$5.68 \times 10^{-3}$	20.74 4.32 20.90 4.29	8.22 8.27	4.83 x $10^{-3}$	20.52 20.60	4.39 4.37	7.11 7.13
$2.838 \times 10^{-3}$	24.69 3.72 24.76 3.71	5.33 5.35	$3.22 \times 10^{-3}$	22.62 22.47	4.04 4.07	5.49 5.46
$2.000 \times 10^{-3}$	26.57 3.50 26.60 3.49	4.20 4.20	$1.933 \times 10^{-3}$	25.38 25.74	3.66 3.61	3.90 3.95
$1.000 \times 10^{-3}$	29.81 3.17 29.84 3.17	2.504 2.51	9.66 x 10 <sup>-4</sup>	28.56 28.14	3.31 3.36	2.328 2.297
$5.68 \times 10^{-4}$	31.61 3.03 31.38 3.05	1.569 1.558	4.83 × 10 <sup>-4</sup>	30.86 30.65	3.11 3.13	1.317 1.309
$2.000 \times 10^{-4}$	34.00 2.865 34.00 2.865	.627 .627	$1.933 \times 10^{-4}$	32.38 32.56	3.01 2.991	.578 .581
$1.419 \times 10^{-4}$	34.88 2.803 34.67 2.820	.462 .459	$1.136 \times 10^{-4}$	33.41 33.46	2.932 2.928	•.357 .357

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	- ,	THAHCLO4
x 0 <sup>2</sup>	с	Λ Υ x10 <sup>2</sup>

C	۸	Y x10 <sup>2</sup>	x x10 <sup>2</sup>	c	- Λ	Y x10 <sup>2</sup>	x x10 <sup>2</sup>
9.92 x $10^{-3}$	15.64 15.74	5.58 5.54	10.10 10.15	9.73 x	10 <sup>-3</sup> 15.45 15.40	5.64	9.82 9.80
4.96 x 10 <sup>-3</sup>	19.19 19.50	<b>4.68</b> 4.60	6.84 6.94	4.87 x	10 <sup>-3</sup> 19.03 18.96	4.72 4.73	6.67 6.65
$2.977 \times 10^{-3}$	21.81 21.81	4.20 4.20	4.96 4.96	3.24 x	10 <sup>-3</sup> 20.92 21.04	4.36 4.33	5.14 5.17
$1.984 \times 10^{-3}$	24.01 23.92	3.86 3.88	~`3.79 3.78	1.946 x	10 <sup>-3</sup> 23.16 23.42	4.00 3.96	3.60 3.64
9.92 x $10^{-4}$	26.74 27.18	3.53 3.48	2.242 2.28	9.73 x	10 <sup>-4</sup> 26.52 26.38	3.56 3.58	2.184 2.173
$4.96 \times 10^{-4}$	29.13 29.41	3.29 3.26	1.278 1.289	4.87 x	10 <sup>-4</sup> 28.83 28.67	3.33 3.34	1.242 1.235
$1.984 \times 10^{-4}$	31.31 31.47	3.11 3.09	.574 .576	1.946 x	10 <sup>-4</sup> 31.02 30.79	3.14 3.16	.558 .554
9.92 x $10^{-5}$	32.34 32.39	3.03 3.04	.303	9.73 x	10 <sup>-5</sup> 31.60 32.02	3.10 3.06	.2907 .2945

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	TOAHCL	<u>0</u> 4		•	TLAHC1	0 <sub>4</sub>	
c	Λ	x10 <sup>2</sup>	x x10 <sup>2</sup>	Ċ,	<b>Λ</b>	Y xl0 <sup>2</sup>	x x10 <sup>2</sup>
9.75 x 10 <sup>-3</sup>	14.68	5.93 5.93	9.41 9.41	9.91 $\times 10^{-3}$	13.94 13.91	6.21 6.22	9.08 9.06
4.88 × 10 <sup>-3</sup>	18.22 18.15	4.92 4.94	6.42 6.40	5.95 x $10^{-3}$	16.10 16.17	5.51 5.48	6.7 <u>9</u> 6.81
$2.925 \times 10^{-3}$	20.86 20.78	4.38 4.39	4.68 -4.66	$3.57 \times 10^{-3}$	18.60 18.69	4.86 4.85	5.00 5.02
$1.950 \times 10^{-3}$	22.35 22.51	4.14 4.11	3.49 3.51	$1.982 \times 10^{-3}$	21.52 21.65	<b>4.2</b> 9 <b>4.2</b> 6	3.41 3.43
9.75 x $10^{-4}$	25.43 25.24	3.71 3.74	2.101 2.087	9.91 $\times 10^{-4}$	24.48 24.38	3.84 3.86	2.054 2.047
4.88 x $10^{-4}$	27.79 27.96	3.45 3.43	1.200	5.95 $\times 10^{-4}$	26.05 26.00	3.66 3.66	1.358 ° 1.356
$1.950 \times 10^{-4}$	30.04 30.11	3.24 3.23	.541 .543	$1.982 \times 10^{-4}$	28.50 28.40	3.41 3.42	.522 .521
9.75 x $10^{-5}$	30.81 30.66	3.18 3.20	.2840 .2827	9.91 $\times 10^{-5}$	29.26 29.12	3.35 3.36	.2742 <sup>°</sup> .2724

## APPENDIX III

# Initial, intermediate and calculated $\Lambda_{\circ}$ and $K_{d}$ values

A. The chloride and bromide series

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Individual  $K_d$  values were calculated for each (c,  $\Lambda$ ) data point through the expression:

 $K_d = X/(Y - 1/\Lambda_o) \Lambda_o^2$ 

The average and standard deviation on  $K_d$  for each system are tabulated below together with the proper  $\Lambda_o$  value.

Salt	Λ.``	$K_{d}$ av x 10 <sup>5</sup>
TPRAHCL	37.2	1.10 ± .01
TBAHCl	35.81	1.01 ± .03
TPTAHC1	34.46	1.05 ± .02
THAHCl	33.69	.96 ± .03
TOAHC1	32.98	.95 ± .03
TLAHCL	31.72	.96 ± .03
TPRAHBr	36.6	3,19 ± .08
TBAHBr	35.21	3.13 ± .05
TPTAHBr	33.86	3.09 ± .09
THAHBr	33.09	'3.00 ± .05
TOAHBr	32.38	2.99 ± .11
TLAHBr	31.12	2.94 ± .08

# B. The iodide and perchlorate series

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The initial  $\Lambda_o$  values as found by extrapolation on the phoreograms are listed below:

Amine	Iodide	Perchlorate
TPRA	35.1	37.4
тва .	33.7	35.9
TPTA	32.4	34.8
"THA	32.2	34.05
TOA	31.3	* 33.0
TLA	30.0	31.4

Two successive calculations of  $\Lambda_{\circ}$  and  $K_{d}$  were performed on the more limited range of concentration. Values did not differ by more than .5% between the first calculation and the iteration.

#### APPENDIX IV

Use of the extended form of the Debye-Hückel limiting law

 $-\log y_{\pm} = \frac{1.825 \times 10^{6} (\epsilon T)^{-3/2} \sqrt{J}}{1 + 50.3 (\epsilon T)^{-1/2} \times a \sqrt{J}}$ 

J is the ionic strength in mol  $l^{-1}$ 

A Aqueous solutions

 $-\log y_{\pm} = \frac{0.51\sqrt{J}}{1+.33 a \sqrt{J}}$ 

Organic solutions

В

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$$-\log \bar{y}_{\pm} = \frac{1.72\sqrt{J}}{1+.5a\sqrt{J}}$$

C Values of the a parameter

The a parameter in the organic and aqueous phases was estimated as the average of a values for the anion and the cation and expressed in Å. Kielland's table (reference 4 in chapter IV) was used for a values of  $H^+$  (9),  $Cl^-$  (3),  $Br^-$  (3),  $I^-$  (3),  $Clo_4^-$  (3.5) and TPRAH<sup>+</sup> (7). For trialkylammonium cations the calculated values of their van der Waals diameter was used (see Table 4): TPRAH<sup>+</sup> (7), TBAH<sup>+</sup> (7.6), TPTAH<sup>+</sup> (8.1), THAH<sup>+</sup> (8.6), TOAH<sup>+</sup> (9.4) and TLAH<sup>+</sup> (10.7). Aqueous single ion activities of halide and perchlorate anions (chapter VI) were estimated using the same limiting law.

## APPENDIX V

#### Calculation of partition constants

The following parameters are known:

 $V_{org}$ ,  $V_{aq}$ ,  $c_{org}^{o}$ ,  $c_{aq}^{o}$ ,  $K_{d}$ ,  $[\overline{R_{3}NHX}]_{T}$ , pH, a.

The following calculations are performed:

$$[x^{-}] = c_{aq}^{o} + c_{org}^{o} \frac{v_{org}}{v_{aq}} - [\overline{R_{3}NHX}]_{T} \frac{v_{org}}{v_{aq}}$$

 $[H^+] = 10^{-pH}/y_{H^+}$ 

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 $y_{H^+}$  is estimated from the Debye-Hückel law (see Appendix IV) using an ionic strength equal to  $[X^-]$ .

 $[R_3NH^+] = [X^-]^- [H^+]$ 

From the total organic salt concentration  $[\overline{R_3NHX}]_T$ the concentration of the ionized part  $[\overline{X}\overline{P}]$  can be calculated knowing the thermodynamic dissociation constant.

$$K_{d} = [\overline{X}^{-}]^{2} / ([\overline{R_{3}^{NHX}}]_{T} - [\overline{X}^{-}]) \times 10^{-3.45} / [\overline{X}^{-}] / (1 + .5 a / [\overline{X}^{-}])$$

First  $[\overline{X}_{1}]_{1}$  is calculated neglecting activity coefficient corrections:

$$[\overline{X}^{-}]_{1} = -K_{d}/2 + 1/2 \times \sqrt{K_{d}^{2} + 4K_{d}[\overline{R}_{3}^{NHX}]_{T}}$$

(13)

This low value of  $[\overline{X}^{-}]$  is then increased by 1/2% steps until right and left sides of equation (13) become equal within 1% yielding a final value  $[\overline{X}^{-}]_{2}$ .

The four constants are calculated:  $Q_{1} = [R_{3}NH^{+}][\overline{x}]/[\overline{R_{3}}NH\overline{x}]_{T}$   $Q_{2} = [R_{3}NH^{+}][\overline{x}]/([\overline{R_{3}}NH\overline{x}]_{T} - [\overline{x}]_{1})$   $Q_{3} = [R_{3}NH^{+}][\overline{x}]/([\overline{R_{3}}NH\overline{x}]_{T} - [\overline{x}]_{2})$   $K_{p} = Q_{3}Y_{\pm}^{2}$ 

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 $Y_{\pm}$  is the mean activity coefficient of  $R_{3}$ NHX in the aqueous phase and is estimated from the Debye-Hückel law.

# APPENDIX VI

# Data on the partition experiments

In the following table volumes are in ml, concentrations in mol  $l^{-1}$  and the various partition coefficients in mol  $l^{-1}$ .

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Salt	<b>v</b> org	$v_{aq}$	c <sup>o</sup> org	c <sup>o</sup> aq	corg	рH	<b>Q</b> 1	Q <sub>2</sub>	Q <sub>3</sub>	кр
TPRAHC1	50	10	0	.496	.00297	3.67	78.0	82.9	83.2	38.9
	60	10 -	0	.496	.00283	3.67	81.0	86.3	86.5	40.5
тванс1	10	50	0	.500	.1154 - .1148	3.55 3.58	1.97 1.98	1.99 2.00	1.99 2.00	.968 .974
	30	30	0	.100	.00512 .00512	3.79 3.79	1.75 1.75	1.83 1.83	1.84 - 1.84	1.155 1.155
-	60	10	0	.100	.00367 .00372	3.50 3.49	1.65 1.61	1.74 1.70	1.74 1.71	1.127 1.103
శ్			ŧ					x :	10 <sup>2</sup>	
TPTAHC1	25	ຸ 25 ັ	.0499	.0499	.0581 .0584	3.20 3.20	2.93 2.89	2`:97 2.93	2.98 2.93	2.10 2.07
	20	20	.0249	.0249	.0236 .0235	3.30 3.30	2.86 2.89	2.92 2.96	2.93 2.96	2.18 2.21
	35	<b>35</b> <sup>-</sup>	.01425	.01425	.01096 .01096	3.38 3.38	2.73 2.73	2.82 2.82	2.83 2.83	2.20 2.20
								x .	10 <sup>4</sup>	
THAHC1	25	25	.0387	0	.0339 .0339	2.92 2.91	4.92 4.88	5.01 4.96	5.02 4.97	4.35 4.31
	25	25	• <b>.</b> 0967	0	.0892 .0893	2.80 2.80	4.92 4.77 -	4.97 4.82	4.98 4.82	4.18 4.06
	17	25	.01138	0	.00789 .00784	3.13 3.14	4.79 5.05	4.96 5.23	4.98 5.24	4.48 4.72

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	Salt	V <sub>org</sub>	v <sub>aq</sub>	, corg	c <sup>o,</sup> aq	corg	pH	٥ <sub>1</sub>	۵ <sub>2</sub> ۲	۵ <sup>3</sup>	к <sub>р</sub>
		<del></del>			1			1	x 10	<sub>0</sub> 7	
-	TOAHC1	- 6	200	.1017	0	.0744 .0736	-3.13 3.13	5.98 8.93	6.05 9.04	6.06 9.05	5.7 8.5
	TPRAHBr	25	10	0,	.498	.01872 .01888 .01919	3.92 3.92 3.92	10.89 10.78 10.57	11.35 11.23 11.01	11.41 11.29 11.06	5.39 5.33 5.23
		60	20	0	.0997	.01658 .01673 .01673	4.28 4.28 4.28	5.41 5.36 5.36	6.21 6.15 6.15	6.27 6.20 6.20	3.88 3.84 3.84
	TBAHBr	30	30	.0997	.0997	.0752	3.78	.205	.209 .205	.210 .206	.127
		50	30	.01994	.0 <sup>4</sup> 99 ្	01757	3.83 . 3.83	.1642	.1712 .1686	.1721 .1694	.117 .116
	-	50	25	<u>•</u> .00997	.0399	.01015 .01022	3.85 3.85	.1532 .1511	.1619 .1597	.1628 .1605	.116 .114
۱ ۲	ı.		r	_		$\mathcal{Y}$	٠		· · · · · · · · · · · · · · · · · · ·	10 <sup>3</sup>	
	TPTAHBr	25	25	.09 <b>9</b> -7	<b>0</b>	.0850 .0852	3.41 3.41	2.47 2.41	2.52	2.52 -2.46	2.00 1.95
	,	50	50	.02493	0	.01818 .01821	3.59 3.59	2.40 2.38	2.50 2.48	2.52 2.49	2.13 2.11
	•	75	100	.01329	• 0	.00749 .00755	3.76 3.76	2.42 2.35	2.58 2.51	2.60 2.52	2.26 2.20

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Salt	Vorg	$v_{aq}$	corg	co aq	<sup>c</sup> org _	pH	Ql	°2	°3	к р
· · · · · · · · · · · · · · · · · · ·		ź		<u></u>			······································	х <u>4</u>	0 <sup>5</sup>	
THAHBr	<b>2</b> 5	100	.0998	0	.0913 .0913	3.33 3.37	3.80 3.90	3.87 3.98	3.89 3.99	3.52 3.62
	25	100	.02495	0	.02090 .02079	3.53 3.51	3.43 3.60	3.56 3.74	3.57	3.33 <sup>-</sup> 3.50
المبر_	25	100 ~	.00998 ,	0	.00741 .00744	3.62 3.63	3.45 3.35	3.68 3.57	3.70- 3.59	a 3.50 3.40
TPRAHI	30	30	.0998	.1006	.0576 <sup>-</sup> .0578	4.60 4.60	.354 .352	.385 .382	.394 .392	.228
	30	30	.03326	.1006	.03338 .03332	4.67 4.67	.302 .303	.337 .338	.347 .348	.213 .213
	28	20	.1069	.0503	.01082 .01082	4.80 4.80	. 232 . 232	.281 .281	.291 .291	.198 .198
~	¢		-	\				x 1	n <sup>3</sup> ?	
TBAHI '	30	30	.1019	0	.0795 .0795	4.38 4.38	6.30 6.30	6.75 6.75	6.90 6.90	5.23 5.23
	30	30	.03397	0	.02257 .02253	4.41 4.42	5.74- 5.79	<b>6.54</b> 6.60	6.73 6.80	5.46 5.51
	39	35	.01045	0	.00577	4.52	4.70	6.08 6.02	6.33	5.45

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Salt	Vorg	<b>v<sub>aq</sub></b>	corg	coaq	corg	рH	Q <sub>1</sub>	, Q <sub>2</sub>	Q <sub>3</sub>	κ
4	<b>"</b> ¢							x 1	04	· · · · · · · · · · · · · · · · · · ·
TPTAHI	10	30	.1004	0	.0902	4.19 4.19	1.256 1.256	1.341 1.341	1.369 1.369	1.21 1.21
;	15	30	.03347	0	.02977 .02962	4.22 4.22	1.110	1.244 1.356	1.278 1.393	1.16
	22	50	.00913	0	.00724 .00724	4.31 4.31	.898 .898	1.130 1.130	1.172 1.172	1.10 1.10,
					-	ł		x 1	06	
THAHI	5	200	.1010	0	.0838 .0835	4.28 4.28	1.931 2.011	2.064 2.150	2.106 2.194	2.01 2.09
	10	200 <sup>°</sup>	.505	0	.0440	4.18 4.17	1.903 1.891	2.086 2.073	2.136 2.123	2.05 2.04
					•	£		x 1	0 <sup>2</sup>	-
TPRAHCÍO 4	20	50	.1015	.0406	.0856 .0858	4.99 4.99	- 2.58 2.56	3.22 3.19	3.62 3.59	2.51 2.49
	30	50	• <b>.</b> 0338°3	.02031	.02779 .02779	5.01 5.01	2.06	3.03	3.51 3.51	2.64 2.64
	28	30	.01087	.01015	.00957 .00959	5.02 5.02	1.35 1.34	2.58 2.56	-3.06 3.09	2.48

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Salt	Vorg	v <sub>aq</sub>	<pre>corg</pre>	$-c_{aq}^{o}$	corg	рH	Ql	°2	Q <sub>3</sub>	к р
·			-				x 10 <sup>4</sup>			
TBAHC104	15 ·	30	.1004	0	.0855 .0851	4.50 4.51	6.50 6.86	8.03 8.48	9.00 9.49	7.55 7.95
	<sup>°</sup> 15	30	.03347	0	-02588 .0259	4.67 4.67	5.53 5.50	8.12 8.07	9.36 9.30	8.22 8.17
	22	35	.00 <b>9</b> 13	0	.00661 .00661	4.82 4.82	3.75 3.75	7.90 7.90	9.35 9.35	8.57 8.57
		•	4		-		x 10 <sup>5</sup>			
_ <b>TPTAHC10</b> 4	4 10	100	.1008	<b>0</b>	.0898 .0901	4.38 4.38	1.295 1.219	1.578 1.486	1.747 1.645	1.62 1.53
	15	125	.0336	0 /	.02891 .02884	4.55 4.54	1.039 1.073	1.472 1.520	1.674 1.729	1.59 1.64
	28	200	.01080	0	.00884 .00885	4.70 4.70	.7924 .7759	1.477 1.445	1.723 1.685	1.66 1.62
	-	a			•	x 10 <sup>7</sup>				
THAHC104	4	200	.09983	<sup>ه»</sup> 0	.0875 .0873	4.30 4.31	5.51 5.76	6.72 7.03	7.43 7.77	7.17 7.50

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#### APPENDIX VII

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# Potential response of the glass-calomel electrode system. Ionization product of water.

In a given constant ionic medium, the potential response of the glass electrode - reference calomel electrode system described in chapter V and depicted in figure 14 should conform to the following equations in acidic and basic solutions respectively (1,2)

$$E = E_{\lambda}^{O} + 59.16 \log[H^{+}] + J_{\lambda}[H^{+}]$$
 (14)

$$E = E_{B}^{O} - 59.16 \log[OH] + J_{B}[OH]$$
(15)

The terms  $E_A^O$  and  $E_B^O$  are constants in a given medium and include potentials of reference electrodes and liquid junction potentials. The terms in  $J_A$  and  $J_B$  stem from the fact that potentials at liquid junctions in contact with solutions of varying acidity or basicity vary linearly with H<sup>+</sup> or OH<sup>-</sup> concentration. <sup>(3,4)</sup>

Different techniques can be used to verify whether the electrode system conforms to eqs. (14) and (15). In the procedure used here constant ionic strength acidic and basic solutions were added to a known volume of constant ionic strength solution. The potential was recorded and plots were prepared of the quantities E - 59.16  $\log[H^+]$  and E + 59.16 log[OH<sup>-</sup>] vs. [H<sup>+</sup>] and [OH<sup>-</sup>] respectively. The intercepts should give  $E_A^O$  and  $E_B^O$  and the slopes  $J_A$  and  $J_B$  respectively. The solutions were (HX, 1.000 x  $10^{-2}$  N; MX, 9.00 x  $10^{-2}$  M) and (MOH, 1.000 x  $10^{-2}$  N; MX; 9.00 x  $10^{-2}$  M). They were added to 25 ml of MX, 1.000 x  $10^{-1}$  M.

In Table (14) values of E in mV are listed for a typical experiment in each ionic medium. Corresponding plots can be found in figures (40) to (43). Duplicates of each experiment were run. In the four ionic media studied the plots were linear. The high value of  $J_B$  found in the case of the NaClO<sub>4</sub> medium and the deviation from linearity at high [OH<sup>-</sup>] values are attributed to the sodium ion error of the glass electrode.<sup>\*</sup> Values of  $E_A^O$  and  $E_B^O$  (intercepts) could vary from day to day due to temperature conditions and aging of the calomel electrodes.

Once  $E_A^O$  and  $E_B^O$  were obtained consecutively for the same ionic medium the ionization product of water  $K_W$  could be calculated by:

$$E_{W}^{C} = (E_{A}^{O} - E_{B}^{O}) / 59.16$$

with  $K_w = [H^+][OH^-]$ .

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Values of  $J_A$  and  $J_B$  can be found on the graphs. The value of  $J_B$  in the case of the KI ionic medium was unusually small. A possible reason for this might be the presence of trace impurities in the solution.

# FIGURES 40 to 43

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Plots of E - 59.16  $\log[H^+]$  and E + 59.16  $\log[OH^-]$  vs.  $[H^+]$ and  $[OH^-]$  in the four constant ionic strength media.



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FIGURE 42



Values of  $pK_w$  are listed below with literature values

	рК <sub>W</sub>	рК <sub>w</sub>
medium	obtained	literature
KC1 .1000 M	13.775	13.78 <sup>(5)</sup> , 13.79 <sup>(6)</sup>
KBr .1000 M	13.77	13.79 <sup>(6)</sup>
KI .1000 M	۲ 13.75	, , ,
NaClO4 .1000 M	13.72	13.78 <sup>(5)</sup>

Linearity of the plots and fair agreement of  $pK_w$ with literature values establish the validity of eqs. (14) and (15) as working equations and the conformity of the slope of the electrode with the theoretical Nernstian slope. In eqs. (14) and (15) the  $J_A$  and  $J_B$  terms are seen to be negligible for solutions of  $H^+$  or  $OH^-$  concentrations not exceeding ca.  $10^{-3}$  M.

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TABLE 1	4
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## Potential calibration in each ionic medium

	[H <sup>+</sup> ]´		E		~ 
V	or [OH]	ксі	KBr	KI	NaClO4
3.00	1.071×10 <sup>-3</sup>	211.4 252.0	210.45 252.15	209.7 252.3	215.3 243.8
5.00	$1.667 \times 10^{-3}$	222.7 263.15	221.7 263.6	221.0 263.7	226.6 254.1
8.00	$2.424 \times 10^{-3}$	232.2 272.8	231.2 273.1	230.5 273.3	236.1 262.7
12.00	$3.24 \times 10^{-3}$	239.75 280.1	238.65 280.4	237.95 280.8	243.5 269.0
16.00	3.90 x10 <sup>-3</sup>	244.4 284.7	243.45 285.0	242.7 285.5	248'.1 273.1
20.00	4.44 x10 <sup>-3</sup>	247.7 288.0	/ ∞246.75 247.4	246.0 288.8	251.5 275.9
25.00	5.00 x10 <sup>-3</sup>	250:7 C	249.7 291.15	248.9 291.8	254.4 278.3
37.00	5.97 x10 <sup>-3</sup>	255.1 295.4	254.0 295.75	253.4 296.3	258.9 282.3
50.00	6.67 x10 <sup>-3</sup>	257.95 298.2	256.9 298.35	256.1 299.3	261.7 284.3
	1.000×1e <sup>-2</sup>	268.1 308.0	267.05 308.2	266.3 309.7	271.9 292.4

V:, volume of acidic or basic solution added.

E: potential in the case of acid addition (upper line) or base addition (lower line, all negative values).

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### APPENDIX VIII

Two-phase emf titrations. Values for  $[\overline{R_3NHX}]_T$  and  $[X^-]$  corrected for middle to low molecular weight salts.

In the case of the titration of the organic amine by the aqueous acid the following results are found:

$$[\overline{R_{3}}NH\overline{X}]_{T} = \frac{n_{H^{+}} - V_{aq}([H^{+}] - [OH^{-}])}{V_{org}} \times \frac{1}{1 + \frac{K_{p}}{y_{\pm}^{2}} \frac{V_{aq}}{V_{org}c}}$$

$$[X^{-}] = c + n_{H^{+}}/V_{aq} - [\overline{R_{3}}NH\overline{X}]_{T} V_{org}/V_{aq}$$
(16)

In the reverse case of a titration of amine salt by aqueous base the following expressions hold:

$$\frac{[R_{3}NHX]}{[R_{3}NHX]}_{T'} = \frac{c_{A}^{O} V_{org} - n_{OH^{-}} - V_{aq}([H^{+}] - [OH^{-}])}{V_{org}} \times \frac{1}{1 + \frac{K_{p}}{y_{+}^{2}} \frac{V_{aq}}{V_{org} c}}$$

$$[X^{-}] = c - n_{OH} / V_{aq} + (c_{A}^{O} - [\overline{R_{3}NHX}]_{T}) V_{org} / V_{aq}$$
(17)

#### APPENDIX IX

Limitations to the calculation of log-log plot data points for lower molecular weight salts

In the preceding Appendix modified equations were given to allow the calculation of log-log plot data points for the case of salts that partition significantly into the aqueous phase. In deriving these equations the assumption was made that the salt was not dissociated in the organic. phase (see section F, part 3). If no such assumption was made these equations could be modified to include  $K_{n}$  (1 -  $\alpha$ ) instead of  $K_{p}$ . However  $\alpha$ , the degree of dissociation, depends on  $K_d$  and on the salt concentration in the organic phase. The value of  $K_{d}$  may be considered unknown since it is obtainable from the log-log plot. The value of the salt concentration in the organic phase is also unknown at the time of the computation. For this reason the equations developed in the preceding Appendix are expected to be valid only for the less dissociated salts and those for which the correction through K<sub>p</sub> is smaller.

The range of error introduced by the approximation can be calculated a posteriori using theoretical  $\alpha$  values calculated over the whole concentration range  $(10^{-1} \text{ M to } 2 \text{ x})$  $10^{-4} \text{ M}$  from the dissociation constants obtained by conductometry (see chapter III). Use is made of Table 4 for K<sub>p</sub> values. The results are collated in the following list giving the range of relative error for each salt system: THAHC1, 0 to < 1%; TPTAHBr, 0 to 4%; TBAHC10<sub>4</sub>, 1 to 6%. Other salts of lower molecular weight in each series would be associated with more important errors: TPTAHC1, 0 to 12%; TBAHBr, 2 to 40%; TPRAHI, 20 to 300%; TPRAHC10<sub>4</sub>, 20 to 400%. For the latter salts loglog plots were not calculated.

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## APPENDIX X

### Two-phase emf titration data

In the following tabulation of two-phase emf titration data the various headings designate the following quantities:

c<sup>o</sup> is the initial amine or ammonium salt concentration in the organic phase;

 $c_{tit}$  is the H<sup>+</sup> or OH<sup>-</sup> concentration of the titrant;  $E_A^{O}$  is a constant applicable in the potential - [H<sup>+</sup>] relation (see eq. (14) in Appendix VII). It is obtained as:  $E_A^{O}$  =  $E'^{O}$  + 177.6.  $E'^{O}$  is the potential of the glass electrode system in a reference solution  $10^{-3}$  M in HX and 9.90 x  $10^{-2}$  M in MX. This potential is measured before and after each titration and averaged;

 $E_1$ ,  $E_2$ ,  $E_4$ ,  $E_6$  and  $E_8$  are the values of the potential of the glass electrode system after addition of 1, 2, 4, 6 and 8 ml of titrant respectively. In the few cases when the value of the volume of titrant is different, it is indicated below the corresponding value of the potential.

For each salt six titrations were performed; these<sup>3</sup> are designated by numbers: (1), (2) and (3) represent the titration of organic amine of initial concentration .1 M, .01 M and .001 M respectively with aqueous acid; (4), (5) and (6) are

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the corresponding titrations starting from ammonium salt in the organic phase and titrating with aqueous base. A sample calculation of a log-log plot data point is given after the tables.

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System		Vorg	c <sup>o</sup>	<sup>c</sup> tit	E <sup>O</sup> A	El	<sup>E</sup> 2	<sup>E</sup> 4	<sup>E</sup> 6	<sup>E</sup> 8 ⊸
THAHC1	(1)	9.92	.0965	.1000	385.6	10.5	30.8	55.1	75.4	103.2 (8.04)
	(2)	10.00	.00965	.01000	386.0	7.9	29.2	5,5 . 2	76.9	104.4 (8.02)
-	(3)	10.00	.000965	.001000	386.0		28.0	52,9	72.9	93.2
	(4)	10.00	.0991	.1000	398.1	128.0	108.1	83.7	63.1	36.9
	(5)	10 <sub>%</sub> 00	.00885	.00995	398.1	124.9	104.9	79.0	54.6	39.8 (7.0)
_	(6)	10.00	.000991	.00995	398.5	114.0 (0.1)	102.9 (0.2)	82.8 (0.4)	62.9 (0.6)	37.0 (0.8)
TOAHC1	(1)	9.87	.0969	.1000	412.4		56.0	80.1	100.8	128.2
	(2)	9.94	.00969	.01000	412.6		55.0	80.0	101.1	128.2
	(3)	9,91	.000969	.001000	412.9		54.2	79.2	99.3	120.6
	(4)	10.00	.1003	.1000	386.4	115.2	95.7	71.8	51.9	27.8
	(5)	10.00~	.01003	.01000	386.2	- 114.4	96.7	72.5	52.3	27.9
	(6)	20.00	.001003	.01000	386.2	106.0 (0.2)	92.1 (0.4)	70.2 (0.8)	49.9 (1.2)	23.7 (1.6)

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System	-	v <sub>org</sub>	c <sup>o</sup>	<sup>c</sup> tit	EA	. <sup>E</sup> l	<sup>~ E</sup> 2	E4	E6	E8
TLAHCl	(1)	9.99	.0983	.1000	413.8	38.5	58.3	82.9	- L	
-	(2)	9.91	.00983	.01000	413.5		53 <b>.9</b>	79.9	101.0 (6.01)	127.1
	(3)	9.99	.000983	.001000	413.1		53.2	78.0	98.2	119.0 (8.02)
	(4)	10.00	.0580	.0499	412.1	139.4	119.0	92.8	66.9 (6.03)	·
	(5)	10.00	.00979	.00997	411.6	141.0	122.3	98.2	78.1	54.0
	(6) -	10.00	.000832	.000997	411.1	127.4	118.0	100.8	84.8	67.8
TPTAÌIBr	/ (1)	9.84	.1000	.1000	386.4	-52.0	-30.9	-5.3	15.1	40.4
-	(2)	10.00	.01000	.01000	386.5	-56.0	-34.7	-7.9	13.6	38.4
	(3)	10.00	.001000	.001000	386.5		-42.9 (2.07)	-15.6	7.2	31.9
	(4)	, 8.39	.0997	.1000	387.4	52.8	32.0	7.1	-20.9	-40.1 (7.0)
	(5)	9.86	.00997	.01000	387.4	57.1	37.1	12.7	-9.9	-37.9
	(6)	19.88	.000997	.01000	387.3	54.2 (0.2)	34.9 (0.4)	9.9 (0.8)	-14.9 (1.2)	-43.9 (1.6)
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System	,	v <sub>org</sub>	່ເວ	ctit	EA _	El	E <sub>2</sub>	E4	E <sub>6</sub>	E8'.
THAHBr	(1)	9.96	.0965	.1000	387.4	-48.4	-28.2	-2.6	19.1	47.2
	(2)	10.00	.00965	.01000	386.7	-53.6	-32.7	-5.8	17.8	46.0
	(3)	10.00	.000965	.001000	386.9	,	-40.1	-12.2	12.1	39.3
	(4)	9.97	.0998	.1000	386.6	61.0	39.7	13.8	-7.8	-32.5
	(5)	10.00	.°0 <b>0998</b>	.01000	386.6	58.2	37.8	12.3	-10.9	37.7
	(6)	20,00	.000998	.01000	. 386.6	53.8 (0.2)	34.0 (0.4)	7.9 (0.8)	-16.0 (1.2)	-44.2 (1,6)
TOAHBr	(1)	9.82	.0968	.1000	387.2	-47.8	-27.6	-2.2	19.9	50.0
	(2)	10.00	.00968	.01000	387.1	-	-34.1	-6.9	16.9	45.8
	(3)	10.00	.000968	.001000	387.2	0	-41.2 (2.03)	-13.4	11.0	38.0
,	(4)	. 10.00	.1014	.1000	390.5	66.2	45.6	20.5	-0.8	-26.7
-	(5)	10.00	.01014	.00997	391.5	64.8	44.5	18.5	-2.8	-30.6
۰ .	(6) ,	10.00	.001014	.00997	390.5	57.3 (0.1)	37.3 (0.2)	10.3 (0.4)	-11.0 (0.6)	-38.3 (0.8)

	6			المعتر					<u>,</u>	
System		v <sub>org</sub>	c <sup>o</sup>	~ c <sub>tit</sub>	EA	<sup>E</sup> 1 —	E2	E <sub>4</sub>	E6	E8
TLAHBr	(1)	9.94	.0983	.1000	387.1	-48/.0	-28.2	-2.4	18.3	44.8
	(2)	10.00	.00983	.01000	387.3	-54.9	-35.0	-8.2	14.9	41.7
	(3)	10.00	.000983	.001000	387.2		-42.3	-14.2	9.3	35.0
	(4)	10.00	.0982	.1000	392.2	67.0	45.8	19.9	-2.6	-29.0
	(5)	10.00	.00982	.00997	391.8	63.5	42.1	15.8	~-6.4	-34.5
• •	(6)	10.00	.000982	.00997	· 391.8	54.0 (0.1)	36.8 (0.2)	11.9 (0.4)	-10.1 (0.6)	-35.9 (0.8)
,				•	R					
TPTAHI	(1)	10.06	.0994	.1052	388.8	-123.8	-102.9	-77.9	-56.7	-29.0
*5	(2)	10.00	.01000	.1055	390.1	-132.1 (0.1)	-110.5	-83.3 (0.4)	d (0.6)	d (0.8)
۰. ۲	(3)	¥0.00	.001000	.01028.	389.8		-118.0	-96.5	đ	đ
L	(4)	10.00	.1038	.0997	388.3	đ	-36.8	-59.0	-78.0	-100.8
	(5)	10.00	.01038	.0997	389.7	d (0.1)	đ (0.2)	-59.5 (0.4)	-82.4 (0.6)	-105.8 (0.8)
-	~ (6)	10.00	.001038	.00980	390.0	d (0.1)	d (0.2)	d (0.4)	-90.0 (0.6)	-111.5 (0.8)

Scottle 1983

System		Vorg	c	c <sub>tit</sub>	EA	E1	E2	E <sub>4</sub>	<sup>E</sup> 6	<sup>E</sup> 8
THAHI	(1)	9.98	.0990	.1052	388.8	-124.7	-103.9	-78.8	-57.0	-26.7
-	(2)	10.00	.00994	.1055	389.9	-133.8 (0.1)	-113.2 (0.2)	-85.7 (0.4)	d (0.6)	d (0.8)
	(3)	10.00	.000994	.01028	389.8	o	-116.0 (0.2)	-92.0 (0.4)	d (0.6)	d (0.8)
-	- (4)	10.00	0990	.0997	388.3	đ	-38.6	-63.1	-83.0	-109.0
	(5)	10.00	.00990	*.0997	389.7	đ (0.1)	d (0.2)	d (0.4)	-88.2 (0.6)	-115.4 (0.8)
(6)	(6)	10.00	.000990	.00980	390.0	d (0.1)	• <sup>^</sup> a (0.2)	đ (0.4)	-96.0 (0.6)	-119.2 (0.8)
TOAHI	(1)	10.Ó2	.0996	.1052	389.6	-125.6	-104.1	-78.8	-57.4°	-27.4
¢	(2)	10.00	.01003	.1055	389.9	-135.1 (0.1)	-113.3 (0.2)	-86.6 (0.4)	d (0.6)	d (0.8)
	(3)	10,00	.001003	.01028	389.8	4 1	-119.7 (0.2)	-96.0 (0.4)	d (0.6)	d (0.8 <u>)</u>
	(4)	10.00	.1015	.0997	388.3	đ.	-37.1	-61.7	-82.0	-107.2
	(5)	10.00	.01015	.0997	389 <b>.</b> 7	đ (0.1)	d (0.2)	d (0.4)	-89.0 (0.6)	-115.3 (0.8)
	(6)	10.00	.001015	.00980	390.0	d (0.1)	d (0.2)	d (0.4)	-94.5 (0.6)	-115.0 (0.8)

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٥	-									
System		Vorg	c <sup>o</sup>	ctit	EA	E1,	<sup>E</sup> 2	E4	E <sub>6</sub>	E8
TLAHI ,	(1)	9.99	.0983	.1000	386.3	-126.4	-105.9	-81.3 (4.01)	-61.2	-34.1
	(2)	10.00	.00983	.1000 ′	386.3-	-138.4 (0.1)	-117.0 (0.2)	-89.5 (0.4)	d (0.6)	d (0.8
, 0	(3)	20.00	.00098 <del>3</del>	.01000	385.6		-126.0 (0.4)	-103.0 (0.8)	d (1.2)	đ (1.6)
	(4)	10.00	.1040	.0997	388.3	ď	-36.8	-59.2	-78.0	-100.4
,	(5)	10.00	່.01040	.0997	389.7	d (0.1)	đ (0.2)	đ (0.4)	-85.9 (0.6)	-110.0
	(6)	10.00	.001040	<b>,.</b> 00980	390.0	d (0.1)	d (0.2)	, d (0.4)	-95.9 (0.6)	-117.0
	٩	-			•		1	۵		
TBAHClO4	<b>(1)</b>	10.00	.0991	.1000	389.8	-182.0	-159.0	-131.5	-110.0	-84.8
	(2)	10.00	.01032	.01000	390.6	-191.5	-176.0	-149.2	-126.4	-100.8
	(3)	10.00	.001032	.001000	390.6	-175.0	-169.2	-156.1	-139.0	-114.9
-	(4) <sup>´</sup>	10.00	.1002	.1105	391.7	-67.3	-88.8	-115.4	-139.1	-175.0
_	(5)	10.00	.01002	.00980	391.7	-72.9	-94.9	-121.8	-144.7	-169.2
D	(6)	10.00	.001002	.00980	391.7	,	-112 (0.2)	-136 (0,4)	-154	-167 (0.8)

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ģ						-		' 、 -		$\otimes$
System $V_{org}$ $c^{0}$ $c_{tit}$ $E_A^{0}$ $E_1$ $E_2$ $E_4$ $E_6$ TPTAHClo <sub>4</sub> (1)         9.91         .0989         .1000         389.8         -182.9         -160.5         -133.6         -112.           (2)         10.00         .00989         .01000         389.8         -192.3         -176.8         -150.0         -126.           (3)         10.00         .00989         .001000         389.8         -175.2         -169.3         -156.0         -138.           (4)         10.00         .1002         .1105         391.6         -67.7         -89.0         /-115.9         -139.           (5)         10.00         .01002         .0098         391.7         -72.3         -94.5         -121.0         -144.           (6)         10.00         .001002         .0098         391.7         -111         -135         -153.1         (0.4)         .00.4         .00.4         .00.7         .00.4         .00.7         .00.4         .00.7         .00.4         .00.7         .00.4         .00.7         .00.4         .00.7         .00.4         .00.7         .00.7         .00.7         .00.7	-			, ,	, , ,	÷	c				۰.
System $V_{org}$ $c^{0}$ $c_{tit}$ $E_A^{0}$ $E_1$ $E_2$ $E_4$ $E_6$ NPTAHClO4(1)9.91.0989.1000389.8-182.9-160.5-133.6-112.(2)10.00.00989.01000389.8-192.3-176.8-150.0-126.(3)10.00.00989.001000389.8-175.2-169.3-156.0-138.(4)10.00.1002.1105391.6-67.7-89.0/-115.9-139.(5)10.00.01002.0098391.7-72.3-94.5-121.0-144.(6)10.00.001002.0098391.7-111-135153.(0.4)(2)10.00.001002.0098391.5-182.0-160.0-133.1-111.(2)10.00.001002.0098391.5-191.3-176.1-149.5-125.(3)10.00.00990.001000391.5-174.3-168.6-155.0-137.(4)10.00.1033.1105391.5-65.9-88.3-115.3-138.	æ	-	-			`	•		<u>,</u>	-	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	<sup>Е</sup> 8	≠ <sup>E</sup> 6	E4	E <sub>2</sub>	<sup>-</sup> El	EA	ctit	c <sup>0</sup>	Vorg		<b>}ystem</b>
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	L -85.8	-112.1	-133.6	-160.5	-182.9	389.8	.1000	.0989	9.91	(1)	PTAHC104
(3) $10.00$ .00989 .001000 $389.8$ -175.2 -169.3 -156.0 -138. (4) $10.00$ .1002 .1105 $391.6$ -67.7 -89.0 /-115.9 -139. (5) $10.00$ .01002 .0098 $391.7$ -72.3 -94.5 -121.0 -144. (6) $10.00$ .001002 .0098 $391.7$ -111 $_{(0.2)}$ -135 $_{(0.4)}$ -153 $_{(0.4)}$ (0.4) HAHClo <sub>4</sub> (1) 9.89 .0990 .1000 391.5 -182.0 -160.0 -133.1 -111. (2) $10.00$ .00990 .04000 391.5 -191.3 -176.1 -149.5 -125. (3) $10.00$ .00990 .001000 391.5 -174.3 -168.6 -155.0 -137. (4) $10.00$ .1033 .1105 391.5 -65.9 -88.3 -115.3 -138.	3 -98.9	-126.3	-150.0	-176.8	-192.3	389.8	.01000	.00989	10.00	(2) -	
(4) $10.00$ $.1002$ $.1105$ $391.6$ $-67.7$ $-89.0$ $/-115.9$ $-139.$ (5) $10.00$ $.01002$ $.0098$ $391.7$ $-72.3$ $-94.5$ $-121.0$ $-144.$ (6) $10.00$ $.001002$ $.0098$ $391.7$ $-111$ $-135$ $-153$ (6) $10.00$ $.001002$ $.0098$ $391.7$ $-111$ $-135$ $-153$ (1) $9.89$ $.0990$ $.1000$ $391.5$ $-182.0$ $-160.0$ $-133.1$ $-111.$ (2) $10.00$ $.00990$ $.04000$ $391.5$ $-191.3$ $-176.1$ $-149.5$ $-125.3$ (3) $10.00$ $.000990$ $.001000$ $391.5$ $-174.3$ $-168.6$ $-155.0$ $-137.4$ (4) $10.00$ $.1033$ $.1105$ $391.5$ $-65.9$ $-88.3$ $-115.3$ $-138.5$	-110.8	-138.3	-156.0	-169.3	-175.2	389.8	.001000	.00989	10.00	(3)	- 1
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	-174.6	-139.0	<i>⊢</i> 115.9	-89.0	-67.7	391.6	.1105	.1002	10.00	(4)	a
(6) $10.00$ .001002 .0098 391.7 $-111$ (0.2) $-135$ (0.4) $-153$ (0.4) (0.4) $-153$ (0.4) $-153$ (0.4) $-153$ (0.4) $-153$ (0.4) $-153$ (0.4) $-153$ (0.4) $-153$ (0.4) $-153$ (0.4) $-$	-169.0	-144.3	-121.0	-94.5	-72.3	391.7	.0098	.01002	10.00	(5)	
HAHClo <sub>4</sub> (1) 9.89 .0990 .1000 391.5 $-182.0$ $-160.0$ $-133.1$ $-111.$ (2) 10.00 .00990 .0 $\pm$ 000 391.5 $-191.3$ $-176.1$ $-149.5$ $-125.$ (3) 10.00 .000990 .001000 391.5 $-174.3$ $-168.6$ $-155.0$ $-137.6$ (4) 10.00 .1033 .1105 391.5 $-65.9$ $-88.3$ $-115.3$ $-138.5$	-167 ) (0.8)	-153 ) (0.6)	-135 (0.4)	-111 (0.2)		391.7	<b>.0098</b>	.001002	10.00	(6)	• * *
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		Ś					1000	` 	0 00		нансіо
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-85.0	111.4	-133.1.	-160.0	-182.0	391.5	.1000, ,	.0990	3.03		4
(3) $10.00$ .000990 .001000 391.5 $-174.3$ $-168.6$ $-155.0$ $-137.$ (4) $10.00$ .1033 .1105 391.5 $-65.9$ $-88.3$ $-115.3$ $-138.2$	-98.5	-125.7	-149.5	-176.1	-191.3	391.5	.01000	.00990	10.00	(2)	
(4) 10.00 .1033 .1105 391.5 -65.9 -88.3 -115.3 -138.	-110.3	-137.6	-155.0	-168.6	-174.3	391.Š	.001000	.000990	10.00	(3)	
	-159.9	-138.1	-115.3	-88.3	-65.9	391.5	.1105	.1033	10.00	(4)	0
(5) 10.00 .01033 .00980 391.5 -74.0 -96.9 -123.6 -146.	-169.8	-146.1	-123.6	-96.9	-74.0	391.5 <sup>.</sup>	.00980	.01033	10.00	(5)	
(6) 10.00 .001033 .00980 391.5 -109.0 -136.1 -152. (0.2) (0.4) (0.4)	-164.4 ) (0.8)	-152.7 (0.6)	-136.1 (0.4)	-109.0 (0.2)		391.5	.00980	.001033	10.00	(6)	,

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۰ . به .	· ·	۲. ۲	-	Ŧ	• •	<i>d</i>		-	y	
Šystem	۵ ۵	v <sub>org</sub> .	c <sup>O</sup>	c <sub>tit</sub>	EA	E1	. <sup>E</sup> 2	E4	<sup>E</sup> 6	E8
TOAHC104	(1)	° <b>9.</b> 96	. <b>0961</b>	.1000	390.8	-181.6	-159.0	-131.8	-109.6	-79.8
er 3ª	(2)	10.00	.00958	.01000	388.5	-192.1 (1.01)	-176.8	-149.6 <u> </u>	-124.9	-93.7
	(3)	10.00	.000958	.001000	390.5	-174.0	-168.1	-154.2	-135.6	-102.9
· _ ·	(4)	. 10.00°	.0981	<sup>Ø</sup> .1105	392.7	-66.0	-87.7	-115.2	°-140.3	-165.1 (7.5)
, ,	(5^)	' 10 <b>.</b> 00	.00981	• <b>. 1</b> 405	392.7~	-76.8	-99.3	-129.7	-155.0	-177.8 (7.5)
. ę	(6)	10.00	.000981	.00980	392.7		-108.6 <sup>°</sup> (0.2)	-135.0 (0.4)	-152.5 (0.6)	-168.0 (0.8)
~ \$				^	•	, <b>*</b>	2	-	``	-
TLAHC104	(1)	- 9.98	.0983	.1000	389.8	-180.7 . (1.01)	-158.2	-131.1	-109.6	-82.9
. 1	(2)	10.00	.00983	.0100 <sup>°</sup> J	389.8	-191.7	-176.3	-150.0		-97.7
	(3)	10.00	.000983	.001000	389.8	-175.8	-170.0	-156.8	-139.0 °	-110.4
i a	(4)	10.00	.1000	.1105	391.2	-63.8	-86.2	-113.1	-136.9	-172.1
, <b>k</b>	(5)	10.00	.01000	01000	391.2	-75.1	-98.2	-126.0	-148.8	-173.0
•, .	(6)	10.00	.00100	.01000	391.2	-82.7 . (0.1)	-108.0 (0.2)	-135.0 (0.4)	-150.9 (0.6)	-163.2 (0.8)
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New Article

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## Sample calculation

In the titration THAHCl(1), after addition of 1 ml 'of titrant to the organic phase the potential read was 10.5 mV. The following computations are performed:

$$[H^+] = 10^{(10.5 - 385.6)/59.16} - 4.57 \times 10^{-7}$$

$$[OH^-] = 1.68 \times 10^{-14} / 4.57 \times 10^{-7} = 3.68 \times 10^{-14}$$

$$n_{H^+} = V_{add} c_{tit} = .1000$$
  
 $[\overline{R_3N}] = .0965 - .1000/9.92 + (4.57x10^{-7} - 3.68x10^{-8}) 50/9.98$   
 $= .0864$ 

$$x_{p}/y_{\pm}^{2} = 4.35 \times 10^{-4} \times 10^{-323/(1+.104\times6)} = 6.88 \times 10^{-4}$$

$$[\overline{R_{3}}NH\overline{X}]_{T} = \frac{.1000-50(4.57\times10^{-4}-3.68\times10^{-8})}{9.92} \times \frac{1}{1+\frac{6.88\times10^{-4}\times50}{9.92\times.1}}$$

$$[\overline{R_{3}}NHX]_{T} = 9.74 \times 10^{-3}$$

$$[X^{-}] = .1000 + .1000/50 - 9.74x10^{-3} \times 9.92/50 = .10007$$

$$[\overline{R_3N}][H^+][X^-] = 3.95 \times 10^{-9}$$

$$Q' = 3.95 \times 10^{-9} / 9.74 \times 10^{-3} = 4.06 \times 10^{-7}$$

## APPENDIX XI

# Calculation of Q and K<sub>d</sub> from log-log plots

A test value of  $K_d$  is selected. From the known value of  $[\overline{R_3NHX}]_T$  the value of  $[\overline{R_3NHX}]$  is calculated by iteration (see Appendix V). Then Q is computed as  $[\overline{R_3N}][H^+]$ :  $[x^-]/[\overline{R_3NHX}]$ . Values of Q obtained for all data points in one log-log plot are averaged and the standard deviation calculated. The test  $K_d$  value is incremented and the calculations repeated until  $K_d$  reaches a value where  $\sigma_Q/Q$  is minimized. The corresponding points fit best a straight line of slope one on the log-log plot. To the values  $Q - \sigma_Q$ and  $Q + \sigma_Q$  correspond  $K_d$  values considered as the limits of the dispersion range of  $K_d$  and tabulated as  $K_d \pm \sigma_{K_d}$  in Tables 10 and 11.

### Sample calculation

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In the following table are listed values of Q and  $\sigma_Q$  corresponding to various test values of K<sub>d</sub> from 10<sup>-5</sup> to 8 x 10<sup>-5</sup> for the system TPTAHBr.

K <sub>a</sub> × 10 <sup>5</sup>	Q (±σ <sub>Q</sub> ) x 10 <sup>8</sup>	σ <sub>Q</sub> /Q in %
1	3.79 (±.34)	ġ
2 `	3.92 <sup>°</sup> (±.25)	·6.5
, 3	4.02 (±.22)	5.5
4	4.10 (±.19)	4.6
`5	4.18 (±.18)	4.3
<b>6</b> "••••••••••••••••••••••••••••••••••••	4.26 (±.19)	4.5
7	4.32 (±.22)	5.0
, <b>8</b> ,	4.39 (±.25)	5.6

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The value  $K_d = 5 \times 10^{-5}$  minimizes  $\sigma_Q/Q$ . The corresponding value of Q is 4.18 (±.18)  $\times 10^{-8}$ . To the values Q = 4.0  $\times 10^{-8}$  and Q = 4.36  $\times 10^{-8}$  correspond  $K_d$  values of  $\sim 3$  and 8  $\times 10^{-5}$  and the value of  $K_d$  is given as  $K_d = 5$  (±3)  $\times 10^{-5}$ .

## APPENDIX XII

# Electrode response and selectivity constants

# I Perchlorate electrodes response (E in mV)

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			C10	concent			
ion exchanger	10-1	3x10 <sup>-2</sup>	10 <sup>-2</sup>	3x10 <sup>-3</sup>	10 <sup>-3</sup>	3x10 <sup>-4</sup>	10-4
TPRAHC104	-	17.5	31.5	46.2	60.1	72.5	80.
TBAHC104	,	26.0	47.8	65.1	80.2	93.5	104.0
TPTAHC104	1	28.3	53.8	84.1	105.1	115.5 ′	120.4
THAHClo4	o	28.4	54.0	84.0	105.8	121.6	129 <b>.</b> 5
TOAHCIO4		28.3	<b>54.5</b>	84.3	105.7	121.5	1293
TLAHC104		28.2	54.6	84.6	106.0	121.9	130.0
TLAHClO <sub>4</sub> with KCl 0.1 M	۰ ه 2.1	31.0	59.1	84.3	104.0.	111.5	114.7
TLAHClO <sub>4</sub> with KBr 0.1 M	2.0	31.5	56.4	70.5	81.1	89.5	96.2
TLAHC104 with KI 0.1 M	1.1	21.2	40.8	55.0	64.2	68.5	72.3

-	hali	de concentra	tion
ion exchanger	10-2	10 <sup>-3</sup>	10-4
TPRAHI	20	40.5	52
TBAHI	41.8	70.5	86
TPTAHI	54.0	90	. 99
THAHI	53.8	96.3	112.5
TOAHI	54.8	106.7	120
TLAHI	54.2	106.1	119.5
TBAHBr	32	58	63.5
TPTAHBr	39 <b>.</b> 5, , ,	67	74.5
THAHBr	53.6	<b>、90</b>	91.5
TOAHBr	53.6	94.7	97.5
TLAHBr	54.0	95.1	98
TPTAHC1	33	56.5	65
THAHC1	48.5	68	70
TOAHC1	52.6	73	74.5
TLAHC1	53.0	78	80.5
			•

# II Halide electrodes response (E in mV)

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III <u>Selec</u>	ctivity cor	vity constants K <sub>S12</sub> - Calculated at varie				ous cio4 ion activity revers			
	,	 , •			activity of $Clo_4^-$		,		
	2x10 <sup>-2</sup>	_ 10 <sup>-2</sup>	4x10 <sup>-3</sup>	2x10 <sup>-3</sup>	10 <sup>-3</sup>	4x10 <sup>-4</sup>	2×10 <sup>-4</sup>	10-4	
c104/c1		ŕ.,		.005	.0063	.0087	.0094	.0095	
C104/Br		•	.028	.031	.033	.028	026	.023	
C104/1	.125	.114	.092	.081	.072	.066	.069	.058	

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## Claims To Original Research

(1) Dissociation constants of 24 tertiary ammonium salts in water-saturated nitrobenzene are reported.

(2) Partition constants between nitrobenzene and water were evaluated for a series of tertiary ammonium salts.

(3) A method is described to calculate dissociation constants in the organic phase from two-phase emf titration data.

(4) Two-phase hydrolysis constants were measured for a variety of trialkylammonium salts in nitrobenzene and were shown to be essentially independent of alkyl chain length.

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(5) Tertiary ammonium salts dissolved in nitrobenzene were evaluated as liquid ion exchangers in ion-selective electrodes.

#### SUGGESTIONS FOR FURTHER WORK

K.

(1)

(5)

This study has focused on various equilibria prevalent in a two-phase system involving tertiary ammonium salts, nitrobenzene and water. The importance of hydrogen bonding between cation and anion in the organic phase has been pointed out. No steric effects could be found when the chain length was varied.

> A valuable contribution would be to study: similar equilibria involving secondary and primary ammonium salts, branched tertiary ammonium salts and quaternary ammonium salts;

- (2) the influence of the diluent dielectric constant and solvating power on the dissociation and aggregation of the salts by changing diluent or using mixed diluents;
- (3) the magnitude of the various constants for other anions of widely differing size and basicity (e.g., fluoride and tetraphenyl boron);

(4) the hydration equilibria prevalent in the organic phase and their dependence on alkyl chain length and nature of the anion;

> the influence of liquid ion exchanger concentration on the response curves of the electrodes.