Cation Exchange with Reverse-Micelles

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Abstract

Experimental and theoretical studies on the extraction of the cations K^+ and Mg^{++} from a bulk aqueous phase to an organic phase using the water/dinonylnaphthalene sulfonic acid (HD)/heptane reverse-micellar system were conducted. The counter ion of the surfactant, H^+ , was exchanged with the alkali metal cations in the aqueous phase. Two different types of experiments were conducted. The first set involved a constant total normality of ions while the second investigated the effect of varying the normality of ions. Electrolyte solutions with molarities ranging from 0 to 1 were contacted with a reverse-m cellar organic phase containing different concentrations of surfactant with different types of counter ions.

The HD reverse-micelia extraction system exhibited behavior similar to that of conventional ion-exchange resin systems. A preferential extraction for Mg^{++} over K⁺ was observed. The efficiency of the extraction was high for low salt concentrations and it was independent of surfactant concentration. The amount of water uptake was low, with W_o ranging between 4 and 10. For a wide range of salt and surfactant concentrations W_o was independent of surfactant concentration. The HD surfactant showed a low solubility in the aqueous phase.

The results of the equilibrium partition experiments were correlated using a thermodynamic model. Interaction parameters determined from binary system experimental data were used to predict the ternary system partition behavior. The ternary system predictions were compared with experimental results and found to be satisfactory.

Résumé

Des études théoriques et expérimentales sur l'extraction des cations K^+ et Mg^{++} de la phase aqueuse à une phase organique, à partir d'un système micellaire-réversible ont été réalisées. L'ion opposé du surfactif, H^+ , a été remplacé par les cations métalliques alcalins de la phase aqueuse. Deux différents types d'expériences ont été réalisés. La premiere série tenait compte d'une normalité totale d'ions constante, tandis que la deuxième série cherchait à découvrir l'effet d'une variance de la normalité d'ions. Des solutions électrolytiques, dont les molarités se trouvaient entre 0 et 1, or⁺ été mises en contact avec une phase organique micellaire-réversible contenant différentes concentrations de surfactif et differents types d'ions opposés.

Le système HD d' extraction micellaire-réversible a demontré un comportement similaire à celui des systèmes résineux conventionnels d'échangeurs d'ions. Une préférence pour l'extraction du cation Mg^{++} plutôt que du cation K^+ a été observée. L'efficacité de l'extraction s'est révélée élevée pour de basses concentrations de sel et indépendante de la concentration de surfactif. De plus, une quantité minime d'eau s'est avérée nécessaire, avec des valeurs de W_o entre 4 et 10. Pour différent es concentrations de sel et de surfactif, W_o est indépendant de la concentration de surfactif. Le surfactif HD a démontré une basse solubilité dans la phase aqueuse.

Les résultats des expériences de répartition à l'équilibre ont été corrélés à l' aide d'un modèle thermodynamique. Des paramètres d'interaction, déterminés à partir de données expérimentales d'un système binaire, ont été utilisés pour prédire le comportement de la répartition d'un système ternaire. Les prédictions du système ternaire ont finalement été comparées avec des résultats expérimentaux et se sont avérées satisfaisantes.

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Notation

Α	Debye-Hückel constant, $mol^{-1/2}kg^{1/2}$
В	Bromley adjustable parameter
a _s	Area occupied by a surfactant head group at the oil/water interface
С	Concentration of cations in aqueous phase, mol/l
$\overline{\mathbf{C}_{M^+}}$	Concentration of cation in reverse-micellar water pools, mol/l
Cos	Concentration of surfactant in organic phase, mol/l
Е	Number of experimental data points
F _b	Binary goodness of fit
Ι	Ionic strength, mol/kg
Ki	Distribution coefficient
\mathbf{K}_{j}^{i}	Thermodynamic equilibrium constant for species i
	moving from aqueous to reverse-micellar phase and
	species j moving from reverse-micellar to aqueous phase
L	Number of cations in the system
m	Molality of ions in aqueous phase, mol/kg
Μ	Molarity of ions, mol/l
M,	Cation i in the system
meq/g	Milli equivalent per gram
Ν	Normality of ions in the system
n	Aggregation number
Р	Total number of ions in the system
P _t	Ternary goodness of fit
r	The radius of the micelles
R	Surfactant molecule without counterion H ⁺
Wo	Molar ratio of water to surfactant in organic phase
X-	Anion X in the system
X,	Equivalent fraction in the aqueous phase
Yi	Equivalent fraction in the organic phase
Z	Valence number of ions (positive or negative integer)

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Greek Letters

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α	Karl Fischer reading, weight fraction of water in organic phase
γ	Activity coefficient of ions in aqueous phase
$\overline{\gamma}$	Activity coefficient of ions in reverse micellar phase
γ±	Mean ionic activity coefficient
δ	Mole ratio of surfactant to total electrolyte in the system
Λ	Wilson parameter
υ _w	Volume of an individual water molecule
ρο	Density of the organic phase, g/l

Subscripts

i, j, k	Ions i, j, and k
-	Anion
+	Cation
±	Mean ionic

Superscripts

exp	Experimental value
fit	Fitted value
pred	Predicted value
0	Function in pure electrolyte water mixture

Abbreviations

AOT	Surfactant Aerosol OT
CMC	Critical micelle concentration
ELM	Emulsion Liquid Membrane
HD	Dinonylnaphthalenesulfonic acid (DNNSA)
KD	Reverse-micelles with counterion K
KF	Karl Fischer
MgD	Reverse-micelles with counterion Mg
O/W	Oil in water microemulsion
W/O	Water in Oil microemulsion xii

Chapter 1

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Introduction

Surfactant-aided separation processes are emerging as a major class of unit operation for industrial separations. Along with traditional applications, such as mineral flotation, these separations are uniquely suited to emerging technologies. The first of these is biotechnology, where valuable products, which are easily degraded, must be recovered from dilute aqueous solutions. The need for new technologies for separating biological products from aqueous electrolyte solutions, is considered of vital importance (Rahaman et al., 1988). A second area of application is in pollution control where surfactant-aided separations to treat aqueous process streams are predicted to increase in number and importance (Wason et al., 1988). Dissolved toxic organics or heavy metals can be removed from aqueous waste waters without introducing substantial toxicity from residual surfactant. Surfactant-aided separations generally require little energy and provide an energy-efficient alternative to traditional purification methods (Scamehorn et al., 1988).

1.1 Definitions

1.1.1 Surfactants

Surfactant molecules (surface active molecules) possess a characteristic structure comprising a *lipophi.ic* hydrocarbon tail and a *hydrophilic* head. Hence they are *amphiphilic* and tend to accumulate at interfaces between polar and non-polar solvents (Eicke, 1984). Based on whether the polar group in the surfactant possesses an ionic charge or not, surfactants are classified as *ionic* and *nonicnic*, respectively. Ionic surfactants are further termed *anionic* or *cationic* based on the nature of the hydrophilic head group.

The interfacial region may contain compounds in addition to the primary surfactants. Molecules having a substantial presence within the interfacial layers are sometimes called *cosolvents* or *cosurfactants*.

1.1.2 Micelles

Micelles are aggregates formed by surfactants in polar media. The polar head groups of the surfactant molecules are directed outward toward the polar medium while the hydrocarbon tails are pointed inward. The aggregation number for most micelles is larger than 50. Micelles are formed above a certain concentration, called the critical micelle concentration (CMC). The CMC is detected by the significant change in properties with concentration near the CMC (Bourrel et al., 1988).

1.1.3 Reverse Micelles

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Reverse or Inverse-Micelles are surfactant aggregates formed in apolar media. In contrast to micelles, the polar head groups of the surfactant molecules are directed inward to form a polar core which can solubilize water as a minute water pool. The

lipophilic chains are exposed to the apolar solvent thus shielding the inner core from the apolar environment. For apolar solvents the aggregation numbers are smaller than for polar solvents, often less than 20 molecules per reverse-micelle, hence changes in the property/concentration slope are much less abrupt, and a CMC is often unobservable.

Among the surfactants which form reverse micelles, the most widely studied is *Aerosol OT (AOT)*, the sodium salt of bis-(2-ethylhexyl) sulfosuccinate (Eicke et al., 1984). Surfactants which form reverse-micelles and their aggregation numbers, are listed by Eicke (1980), Fendler (1982), and Luisi (1984).

1.1.4 Microemulsions

The term microemulsion, refers to isotropic, thermodynamically stable, clear, transparent, liquid-liquid colloidal-systems which contain significant amounts of oil, water, surfactant, and cosurfactant (Hoar and Schulman, 1943). Although not homogeneous at the molecular level, a microemulsion is effectively a one phase system. In a microemulsion, very small droplets of the dispersed phase, surrounded by an interfacial layer of surfactant, and cosurfactant, are suspended in a continuous phase. Terminology is based on whether the dispersed phase is aqueous (water-in-oil) or organic (oil-in-water). Some prefer the names swollen micellar solutions or solubilized micellar solutions to describe these systems (Bourrel et al., 1988). Emulsions are distinguished from microemulsions by the fact that the drop size grows continuously with time. Emulsions ultimately separate into two distinct phases, a manifestation of thermodynamic instability. The properties of microemulsions are time independent.

There is no clear criterion distinguishing microemulsions from micelles containing solubilizate. One definition asserts that a microemulsion is composed of





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Figure 1.1: Schematic representation of water droplets of various radii (0.7 to 300 nm) in oil with an ionized surfactant at the interface (Overbeek, 1978).

bulk isotropic organic and aqueous regions separated by an anisotropic layer. Since the assumption of isotropic bulk phases is more acceptable for large droplets than for small droplets, the bigger droplets are referred to as microemulsions. As shown in the Fig. 1.1, the diameter of droplets may range from a few nm to more than 500 nm.

Luisi et al. (1988) suggested a criterion for reverse-micelles based on the parameter W_o which is defined as the ratio of the molarity of water to the molarity of surfactant, i.e., $W_o = [H2O]/[S]$. Normally, the term *reverse-micelle* is reserved for small aggregates, e.g. when W_o is about 15 or less. For some surfactants it is possible to disperse more than 50 moles of water per mole surfactant: it is then per-haps more appropriate to describe these systems, as water-in-oil microemulsions. Luisi (1988) proposed the following equation to estimate the water core radius of a reverse-micelle, r in nm:

$$r = (3v_{\rm H_2O}/a_{\rm s})W_o$$
 (1.1)

where $v_{\rm H_2O}$ is the molecular volume of water (approximately 0.03 nm³) and a_8 is the area in nm² occupied by a surfactant head group at the surface of the reversemicelle.

1.2 Ion Exchange Systems

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A reverse-micellar phase can act as a liquid ion exchange system. The reversemicelles, which contain the ion exchange sites, are analogues of solid ion exchange resin beads. Solid ion exchangers are insoluble polymers with active inorganic groups covalently bonded to the polymer. The fixed groups are either permanently ionized so that they always possess a formal charge, or are capable of ionization or acceptance of protons to form a charged site. Mobile ions within the resin may be exchanged with ions from an external solution. Resins capable of exchanging cations are called cation exchangers.

Ion exchange can also occur between two immiscible liquid phases. These liquid ion exchangers are prepared by dissolving compounds with ionogenic groups in organic solvents which are immiscible with water. The ionogenic compound must have hydrophobic groups in order to remain in the organic phase when the latter is contacted with aqueous solutions.

Boyd and Lindenbaum (1968) showed that solutions of dinonylnaphthalene sulfonic acid, of di-2-ethylhexylphosphoric acid, of dimethyldidodecylammonium chloride, and of tri-n-octylamine in nonpolar organic liquids serve as analogs of solid crosslinked strong-and weak-acid cation-exchangers and strong- and weakbase anion-exchangers, respectively. Liquid ion-exchangers offer several advantages over the solid ion-exchangers. Liquid ion exchangers are easily prepared,

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the concentration of the functional groups in the ion-exchanger phase is readily adjusted, high ion-exchange rates can be attained by efficient dispersion of the organic phase in the aqueous phase, and continuous countercurrent operation is simply achieved (Helfferich, 1962). Practically all of the useful liquid exchangers are organic compounds having molecular weights in the range of 250-500 and are unifunctional; i.e. they contain only one ionizable group per molecule. Some commercially available liquid cation exchangers are: phosphoric acid derivatives; monodecyl phosphoric acid; monoheptadecyl phosphoric acid; di (2-ethylhexyl) phosphoric acid; and dinonylnaphthalene sulfonic acid.

1.3 HD Surfactant

Dinonylnaphthalene sulfonic acid, abbreviated HD, is a strong acid surfactant, with a low solubility in aqueous solutions but high solubility in organic liquids. The molecular structure of HD is shown below.



Figure 1.2: Structure of dinonylnaphthalene sulfonic acid

The sulfonic acid molecules are present in the organic phase as reversemicelles and as a layer at the interface between the organic and aqueous phases (Van Dalen and Wijikstra, 1978). The hydrogen ion of the sulfonic acid can be replaced by other cations, thus the reverse micellar phase acts as a liquid cation exchanger. The acid, which is purchased in a solution of n-heptane, kerosene or other aliphatic diluent, contains various isomers resulting from the sulfonation of dinonylnaphthalene as well as small amounts of neutral impurities (Danesi et al., 1973). For the pure HD, $(C_9H_{19})_2 C_{10}H_5SO_3H$, (M.W.=460.7), the neutralization equivalent is 2.175 meq/g. If the substance is stored in air, the neutralization equivalent decreases slowly to 2.02 meq/g, corresponding to a molecular weight of 496, thus indicating the presence of 2 molecules of water of hydration (Danesi et al., 1973).

1.4 Previous work with HD

The micellar properties of oil-soluble sulfonates in moist benzene have been studied by Kaufman (1955, 1957). The dinonylnaphthalene sulfonates of barium and sodium aggregated to form micelles of 7 to 8 and 12 to 13 monomers, respectively. The sizes of these micelles were not sensitive to the water concentration. The aggregation numbers of dinonylnaphthalene sulfonates of ten cations: Li⁺, Na⁺, Cs⁺, NH4⁺, Mg⁺², Ca⁺², Ba⁺², Zn⁺², Al⁺³, and H⁺ were independent of concentration and almost independent of the water content of the system. With a specified concentration of surfactant in a solution, the smaller size of micelles is concommitant with a larger number of micelles thus giving a smaller volume of water pools and a higher ratio of ion/water. More concentrated aqueous solutions are desirable for recovery processes. Little and Singleterry (1964) found that the aggregation number of alkali dinonylnaphthalene sulfonates in different solvents



Figure 1.3: Aggregation number of alkali-dinonylnaphthalene sulfonates shown as a function of the solubility parameter of the solvent, δ .(After Little and Singleterry, 1964)

correlated with the solubility parameter of the solvent as shown in Fig. 1.3. As the solubility parameter of the solvent is increased, the reverse-micelles decreased in size. The aggregation numbers determined by Van Dalen et al., (1974a) were in general agreement with those in Fig. 1.3.

Recently it has been shown that the concentration of surfactant in either an aqueous phase or an organic phase can be measured by UV spectroscopy at 285 nm (Marc, 1989; 1990). The water-to-surfactant ratio in the organic phase was not affected by the average carbon number of the organic solvent for carbon numbers between 8 and 15 (Ladanowski, 1991).

The extraction of Co^{+2} , Zn^{+2} , Mn^{+2} , Fe^{+3} , and In^{+3} from aquecus percholoric

acid solutions into heptane containing HD, gave distribution coefficients for divalent and trivalent cations which were inversely proportional to the second power and third power, respectively, of the hydrogen ion concentration in the aqueous phase. The distribution coefficient was directly proportional to the HD concentration in the heptane phase (White et al., 1960). Extraction of Am^{+3} and Eu^{+3} by HD and its salts showed a high selectivity of HD for these ions (Khopkar et al., 1968). Some organic acids can be extracted into micelles of HD (Van Dalen et al., 1974b).

The effects of several neutral donors on the extraction of Zn^{+2} by HD and by sodium dinonylnaphthalene sulfonate was investigated by Wang et al., (1966). The decreased extraction of Zn^{+2} by mixtures of HD and the organophosphorous esters was ascribed to the formation of the hydrogen-bonded complexes: HD-TOPO and HD-TBP (TOPO=tri-n-octyl phosphine oxide and TBP=tri-n-butyyl phosphate which are two neutral donors).

1.5 Project Objectives

This thesis is concerned with the equilibrium between an aqueous phase containing different electrolytes and an organic phase containing reverse-micelles at 25 °C. The organic phase contains HD surfactant or its salts in a mixture of kerosene and heptane. The objectives are:

- 1. To determine the equilibrium compositions of the cations and the surfactant in the aqueous and organic phases for systems containing two or three cations (H⁺, K⁺, Mg⁺⁺). The independent variables are the temperature, the initial concentrations of the cations in the aqueous phase, the concentration of the surfactant in the organic phase, and the total normality of the system. The dependent variables are the amount of water solubilized in the organic phase and the distribution of the cations and the surfactant between the reverse-micellar and aqueous phases.
- 2. To predict ion exchange equilibria in a tennary system using only equilibrium data for binary systems. The parameters of a thermodynamic model, determined from the three binary systems, are to be used to predict ternary system equilibrium behavior.

Chapter 2

Experimental Methods

2.1 Materials

Dinonylnaphthalene sulfonic acid (HD) dissolved in kerosene at a concentration of approximately 50% was obtained from Pfaltz & Bauer (Waterbury, CT, U.S.A.). Heptane (HPLC grade) was obtained from ACP Chemicals Inc. (Montreal, Quebec). Reagent grade KCl was obtained from A & C American Chemicals Ltd. (Montreal, Quebec) and magnesium chloride crystals (MgCl₂.6H₂O) were obtained from Anachemia Chemicals Ltd.(Montreal, Quebec). Atomic absorption standards (K⁺ and Mg⁺⁺) were obtained from Aldrich Chemical Company, Inc. (Milwaukee, WI, U.S.A.). Karl Fischer titrant, AQUASTAR Comp 5 (pyridine free), and solvent (1-propanol) were obtained from BDH Inc (Ville St-Laurent, Quebec). Distilled water, which was deionized to a minimum resistance of 1 megohm/cm, was used for preparation of electrolyte solutions.

2.2 Analytical Methods

• Surfactant Analysis

The amounts of surfactant in the organic and aqueous phases were determined by UV spectroscopy on a Bomem-Michelson 100 spectrophotometer. Due to the presence of a naphthenic structure, the surfactant absorbs in the UV spectrum at 285 nm (Marc, 1989).

A calibration curve for surfactant measurement was prepared by making various concentrations of surfactant in a mixed solvent obtained by diluting the original HD/kerosene solution with heptane. This was done by diluting a stock solution of 0.3M HD which had been prepared by potentiometric titration as described by Danesi et al. (1973). The titration $\exp -r$, ments and the preparation of the calibration curve, which is shown in Fig. 2.1, are described in Appendix B. The same calibration curve was used for analysis of surfactant in the organic and the aqueous phases. Heptane was used as a reference for reverse-micellar phases, while distilled water was used for aqueous solutions.

Water Content

The water content of the reverse-micellar phase, in weight percent, was determined by Karl Fischer (KF) titration using a Metrohm-Brinkmann Model 701/1 KF Titrator. The KF reaction takes place in two steps: in the first step the KF titrant produces a complex with a primary alcohol. In the next step, this complex is titrated with I₂ and the H₂O in the sample. Usually, a sample containing water is added to methanol and then titrated with KF titrant. Since the organic solvents were long chain hydrocarbons which do not dissolve satisfactorily in methanol, propanol was employed. The KF titrant had an initial titer of about 5 mg H₂O/ml titrant. Since atmospheric moisture can penetrate into the reagent solution and cause gradual errors, the titer was checked on a weakly basis and before each exper-





Figure 2.1: Calibration curve for surfactant measurement.

iment. It remained constant at 5.35 (\pm 0.05) mg H₂O/ml titrant. At high water contents in the organic phase, KF measurements are consistently low (Goklen, 1986; Helou, 1991). With HD as the surfactant, the amount of water in the organic phase was so low that no correction was made to the KF measurements. In a few cases the results were checked against IR measurements. In addition, some samples were prepared by injecting a known amount of water into the organic phase. In all cases the KF readings were accurate to about $\pm 2\%$.

• Ion Analysis

The cations were K^+ , Mg^{++} , and H^+ . The concentrations of K^+ and Mg^{++} ions in the aqueous phase were determined by atomic absorption spectroscopy (AA) on a Thermo Jarrell Ash Model 757 Spectrophotometer. Since this method measures small concentrations of ions, the samples were diluted with water by a factor of several hundreds or, in the concentrated cases, several thousands. The

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concentrations of metal ions in the reverse-micellar phase were obtained by mass balance.

The concentration of H⁺ ions in the aqueous phase was measured with a Fisher Scientific pH meter with a precision of ± 0.01 in the pH scale. Most samples were diluted by a factor of 50 in order to be in the most sensitive part of the pH range (pH between 2.5 and 4.0).

2.3 Procedure

Ion exchange experiments were performed by contacting aqueous salt solutions (15 ml) of KCl, MgCl₂ and HCl with an organic solution containing the surfactantsolvent solution (15 ml). The experiments were carried out in 50 ml test tubes with gasket-tightened caps. The tubes were placed on a vibrating shaker at 200 rpm and agitated for 60 minutes in a constant temperature room at 23°C. The samples were then centrifuged at 8000 rpm for 20 minutes at 25°C on a Dupont Instruments Co. centrifuge (Sorvall RC-5B) to achieve phase separation. The samples were left to settle at 25°C for 24 hours before the phases were analyzed. Pasteur pipettes were used to collect a sample from each of the phases.

The experimental conditions such as shaking time, settling time, and the volumes of the phases were fixed through the preliminary experiments described in Appendix C.

2.4 Sample Preparation

Two types of experiments were conducted. The first type was conducted with constant normality of ions. Aqueous phases containing a combination of cations having a common anion, Cl^- , with constant normality were contacted with an

organic phase with a fixed concentration of HD surfactant at a phase volume ratio of 1. For example, in extracting Mg^{++} with the HD organic phase, the initial concentration of the Mg^{++} was varied between 0 and 1 N, while the total normality of the aqueous phase was maintained at 1 N by adding HCl. Since the concentration of the surfactant in the organic phase was constant, the total normality of the system was constant. Reverse-micelles containing only K⁺ or Mg^{++} (i.e. KD or MgD_2 reverse-micelles) were prepared following the procedure described in Appendix D. Experiments were conducted with KD and MgD reversemicellar phases using the procedure used for the HD reverse-micellar phase. When the experiments involve two cations, the system is referred to as a binary. When three cations are present, the system is called a ternary. Experiments for the three binaries, K⁺/H⁺, Mg⁺⁺/H⁺, and K⁺/Mg⁺⁺, as well as the ternary, K⁺/H⁺/Mg⁺⁺, were conducted.

In the second type of experiments organic phases with different fixed concentrations of HD surfactant (0.1, 0.2 or 0.3 M) were contacted with a series of aqueous solutions with different concentrations of K^+ and/or Mg⁺⁺ at a phase volume ratio of 1. Similar experiments for Mg⁺⁺ extraction were performed with KD reverse-micelles. In these experiments, which were binaries, the normality of the aqueous phase varied.

2.5 Calculation of Experimental Parameters

A sample calculation, which is based on mass balances for the ions and the surfactant, is described in detail in Appendix A. The following assumptions were used to derive the equations.

1. All salts dissociate completely.

2. The anion does not enter the reverse-micelles.

- 3. The organic solvent and water are immiscible.
- 4. The phase separation is complete and the concentrations in the bulk phases are uniform.

The calculation takes into account the amount of water which moves from the original aqueous phase to the reverse-micellar water pools - see Appendix A. The experimental results are reported in terms of the parameters defined below.

• Water-to-Surfactant Ratio

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The molar ratio of water to surfact at equilibrium, W_o , is defined by

$$W_o = \frac{\text{moles } H_2 \text{O in organic phase (water pools)}}{\text{moles surfactant in organic phase}}$$
(2.1)

If α is the weight fraction of water measured by KF titration, then

$$W_o = \frac{\alpha \rho_o}{18.02 C_{os}} \tag{2.2}$$

where ρ_o is the density of the organic phase and C_{os} is the concentration of surfactant in the organic phase.

• Equivalent Fractions

Equivalent ionic fractions X and Y are defined for each cation in the aqueous and organic phases, respectively. These quantities are the fraction of the total equivalents represented by a particular ion at equilibrium:

$$X_i = \frac{\text{Equivalents of cation 'i' in the aqueous phase (N)}}{\text{Total equivalents of cations in the aqueous phase (N)}}$$

$$= \frac{z_i C_i}{\Sigma z_i C_i} \tag{2.3}$$

$$Y_i = \frac{\text{Equivalents of cation 'i' in the organic phase (N)}}{\text{Total equivalents of cations in the organic phase (N)}}$$

$$= \frac{z_i \overline{C_{M^+}}}{\Sigma z_i \overline{C_{M^+}}}$$
(2.4)

Since X_i and Y_i are fractions,

$$\sum_{i=1}^{L} X_i = 1$$
 (2.5)

$$\sum_{i=1}^{L} Y_i = 1$$
 (2.6)

where L is the number of cations in the system.

• Distribution Coefficient

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A distribution coefficient is defined for cation 'i' in a binary system:

$$K_{i} = \frac{\text{concentration of cation 'i' in the reverse-micells (M)}}{\text{concentration of cation 'i' in the bulk aqueous phase (M)}}$$

$$= \frac{\overline{C_{M^+}}}{C} \tag{2.7}$$

The numerator of this expression represents the concentration of cation 'i' in the water pools of the reverse-micelles.

Chapter 3

Results and Discussion

3.1 Equilibrium with constant normality

Since ion exchange occurs with charge neutrality, equilibrium curves are plotted at constant normality. In this format, the variables are X, the equivalent fraction in the aqueous phase and Y, the equivalent fraction in the organic phase. A different Y vs X curve is obtained for each normality. Neglecting the small amounts of anions which exist in the reverse-micelles at equilibrium and the small amount of surfactant which transfers to the aqueous phase, the normalities of the aqueous and organic phases at equilibrium are identical to the normalities at preparation.

The equilibrium curves for the binaries, K^+/H^+ and Mg^{++}/H^+ , are shown in Figs. 3.1 and 3.2. Experiments for these two binary systems were carried out at constant normalities of 0.1 and 0.2 for the organic and aqueous phases, respectively. The results for Mg^{++}/K^+ binary system are shown in Fig. 3.3. For all of the sets shown in this figure, the normality of the organic phase was 0.1, while the normality of the aqueous phase was either 0.1, 0.2, or 0.5. The data points near $X_{H^+} = 0$ were obtained by starting with HD reverse-micelles while points near $X_{H^+} = 1$ were obtained by starting with KD or MgD₂ reverse-micelles. Thus, different symbols are used to present these data points in Figures 3.1 to 3.3 and an asterisk is used to distinguish them in Tables 4.2 and 4.3.

The results showed a similar behavior with the solid ion exchange extraction systems. In fact, while the ratio of the Mg^{++} in the organic phase increased with increasing the concentration of Mg^{++} in the system, for higher normalities the equilibrium curve was shifting down. The above observation means that the selectivity for Mg^{++} decreases as the normality of the system increases. The same phenomena was observed in the extraction of cations with the systems of different total normality of ions, which is described in the next section.

The equilibrium for the ternary system, $Mg^{++}/K^+/H^+$, is shown in Fig. 3.4 in a triangular diagram and the data are presented in Table 4.6. For all experiments the normalities of the organic and aqueous phases were 0.1 and 0.2, respectively. The equivalent fractions, X or Y, are plotted with each vertex corresponding to a single cation. Filled circles represent X while open circles represent Y and the compositions of the phases in equilibrium are connected by a tie line. It must be emphasized that each pair of experimental points is independent of the other pairs and for any point in the triangular diagram corresponding to the composition of one of the phases one can experimentally determine a corresponding equilibrium point giving the composition of the other phase. The pairs of points in the axes K^+/H^+ and Mg^{++}/H^+ correspond to measurements in which the initial aqueous phase had a normality of 0.2 in K^+ or Mg^{++} , respectively, and the initial organic phase had a normality of 0.1 in HD.

Each of the data points for these experiments at constant normality of ions, is an average value of three replicate samples. Since the organic phase composition is determined by mass balance closure based on aqueous phase measurements, the magnitude of relative error in the organic phase compositions depends on the

	St. Dev. aqueous ph.	St. Dev. organic ph.
Max. Std. Dev.	0.010	0.021
Min. Std. Dev.	0.003	0.007
Ave. Std. Dev.	0.007	0.015

Table 3.1: Standard deviations of the compositions for replicate runs.

normality of both phases. The error is larger for the systems with higher normality of ions in the aqueous phase. This is explained by an example in Appendix A. The standard deviations of the compositions for replicate runs, for both binary and ternary systems with an aqueous phase of 0.2 N and an organic phase of 0.1 N, are given in the Table 3.1.

Based on the average standard deviation of the organic phase composition, the average confidence interval for Y_i , equivalent fraction in the organic phase, is calculated to be 0.031. This value can be presented by a bound or error bars on the experimental data points. The same value is used in the next chapter for the comparison of experimental data with the fitted model.



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Figure 3.1: Equilibrium curve for the K^+/H^+ binary with constant normality (organic phase 0.1 N and aqueous phase 0.2 N).



Figure 3.2: Equilibrium curve for the Mg^{++}/H^+ binary with constant normality (organic phase 0.1 N and aqueous phase 0.2 N).


Figure 3.3: Equilibrium curve for the Mg^{++}/K^+ binary with constant normalities (organic phase 0.1 N and aqueous phase 0.1, 0.2, or 0.5 N).

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Figure 3.4: Triangular diagram of the ternary equilibrium, $Mg^{++}/K^{+}/H^{+}$, with constant normality (organic phase 0.1 N and aqueous phase 0.2 N).

3.2 Equilibrium with variable normalities

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In the experiments described in this section, the concentration of HD surfactant was fixed at three values, 0.1, 0.2, and 0.3 M. The effect of aqueous cation concentration on variables such as water uptake, extraction efficiency of the system, and surfactant distribution between two phases is examined. The numerical values of the experimental results for this section are given in Tables 1-9 in Appendix E.

The surfactant distribution between the two phases is an important variable for the reverse-micellar systems. The amount of HD surfactant, or its salts, which dissolves into the aqueous phase is very small. This small quantity decreases with increasing salt concentration in the aqueous phase and increases with increasing surfactant concentration in the organic phase. These results are shown in Figs. 3.5 and 3.6.

The measurement of water content through Karl Fischer (KF) readings vs the concentration of surfactant in the organic phase is shown in Fig. 3.7. The water uptake, wt%, increases linearly with the increase in surfactant concentration. The intercept of 0.03% is due to the solubility of water in pure heptane. The work of Ladanowski (1991), also using HD showed the same behavior of the Karl Fischer readings, when using a cosurfactant in the system.

The W_o , molar ratio of water to surfactant in the organic phase, vs the salt concentration in the bulk aqueous phase, is plotted for H⁺, K⁺ and Mg⁺⁺ in Fig. 3.8. The relation of water uptake to the type and the amount of salt in the system is important in many respects and has been the subject of matter for several authors. The work by Leodidis and Hatton (1989), which was of special consideration for the author of the current project, was concerned with this idea as the primary goal. Leodidis and Hatton (1989), concluded that the water uptake by an AOT reverse micellar solution in equilibrium with a bulk aqueous electrolyte is a strong function of both cation concentration and type. Based on these variables their model predicts the water uptake of the system. The general behavior of water uptake of HD reverse micellar system, for H⁺, K⁺, and Mg⁺⁺ cations, showed two major points. The HD system exhibits the same general trends as the AOT system, i.e. that the water uptake decreases with increasing amounts of salt in the initial aqueous phase but increases with increasing amounts of surfactant. However, the amount of water uptake by the HD system in comparison with other reverse-micellar and microemulsion systems is low, $W_o \leq 10$. Second, the variation of water uptake even in a wide range of salt and surfactant concentrations is small.

The value of W_o was independent of the surfactant concentration in the organic phase. For the cations H⁺, K⁺, and Mg⁺⁺, W_o showed the same trend for different surfactant concentrations.

A valuable parameter, from a cation extraction point of view, is the distribution coefficient. This coefficient is defined as the ratio of the cation concentration in the reverse micellar droplets to that in the bulk aqueous phase-see Eq. (2.7). These coefficients for the cations K^+ and Mg^{++} vs. the cation concentration in the bulk aqueous phase are shown for three different surfactant concentrations in Figs. 3.9 and 3.10. These figures are plotted on a semi-logarithmic scale to magnify the variations in the low regions of salt concentrations. It was observed that K_i decreases drastically with increasing salt concentration efficiency of HD reverse micelles, even in comparison with other micellar systems such as AOT, specially at low concentration of cations makes it promising for studies of extraction of traces of rare metals from effluent streams.



Figure 3.5: Surfactant concentration in the aqueous phase vs equilibrium concentration of K^+ in the aqueous phase for three surfactant concentrations (K^+/H^+ binary).



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Figure 3.6: Surfactant concentration in the aqueous phase vs equilibrium concentration of Mg^{++} in the aqueous phase for three surfactant concentrations $(Mg^{++}/H^+ \text{ binary})$.



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Figure 3.7: Variation of water uptake with surfactant concentration in the organic phase. The aqueous phase was 0.1 M KCl.



Figure 3.8: Water to surfactant ratio as a function of equilibrium concentration of cations in the aqueous phase for three surfactant concentrations (the curves correspond to Mg^{++}/H^{+} binary, K^{+}/H^{+} binary, and the situation that only H^{+} is present in the system).

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Figure 3.9: Distribution coefficient of K^+ vs equilibrium concentration of K^+ in the aqueous phase for three surfactant concentrations (K^+/H^+ binary).



Figure 3.10: Distribution coefficient of Mg^{++} vs equilibrium concentration of Mg^{++} in the aqueous phase for three surfactant concentrations (Mg^{++}/H^+ binary).

The equilibrium equivalent ratio in the micellar phase, Y_i , is plotted against the cation concentration in the aqueous phase for K⁺ and Mg⁺⁺ in Figs. 3.11 and 3.12, respectively. As it is shown Y_i increases with increasing salt concentration in the bulk aqueous phase. Data at higher ranges of salt concentration were difficult to obtain experimentally, but from the data available it appears that a maximum limit exists for each case. This limit is about 0.45 for K⁺ and 0.80 for Mg⁺⁺, i.e. 45% of HD molecules are electrostatically associated with K⁺, or 80% with Mg⁺⁺, and the rest are associated with the counter ion, H⁺. Furthermore, for both Mg⁺⁺ and K⁺ the value of Y_i decreased with higher concentrations of HD in the organic phase. The results also show a preferential substitution of the divalent Mg⁺⁺ for the monovalent K⁺. This higher selectivity of the system for Mg⁺⁺.



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Figure 3.11: Equivalent fraction in the organic phase, Y_{K^+} , vs equilibrium concentration of K⁺ in the aqueous phase for three surfactant concentrations (K⁺/H⁺ binary).



Figure 3.12: Equivalent fraction in the organic phase, $Y_{Mg^{++}}$, vs equilibrium concentration of Mg⁺⁺ in the aqueous phase for three surfactant concentrations (Mg⁺⁺/H⁺ binary).

Chapter 4

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Thermodynamic Modelling

4.1 Introduction

The reverse-micellar extraction system considered in this work is a two-phase system of a W/O microemulsion and an aqueous phase containing salts. Although the effect of the presence of cations in reverse-micellar systems has been considered by several authors, there is currently no theoretical model to predict the selectivity of cation extraction (Leodidis and Hatton, 1989). The approaches that have been used are, in most cases, based on electrical double layer theory.

Adamson (1961) used the osmotic pressure to treat reverse-micellar systems. He pointed out that the free energy contribution associated with the charge sheet of a monolayer can be treated in terms of a Donnan equilibrium. He proposed that the assumption of phase equilibrium requires that the mean activity of the salt be equal in both micellar and bulk aqueous phases. He expressed the higher total ionic concentration in the micelle units as compared to the external aqueous phase in the form of an osmotic pressure difference. The osmotic pressure difference is a positive quantity, so that in the presence of available water, an infinite swelling of the micellar units should occur. Where equilibrium with an external aqueous electrolyte solution is in fact present, this swelling is considered to be balanced by the Laplace pressure determined by the interfacial tension γ and the micelle radius r. Based on such a theory, he derived equations governing the distribution of electrolyte and water between the micelle and the external aqueous phase. He mentioned that errors are introduced in assuming a uniform electrolyte concentration in the interfacial region rather than considering the diffuse double layer.

Leodidis and Hatton (1989), presented a phenomenological model for the selective solubilization of cations in AOT reverse-micelles. Their primary goal was to model the large differences in water uptake by AOT microemulsions for the different cations. They used the Modified Poisson-Boltzmann (MPB) theory by making the assumption that the activity corrections for the ions can be expressed as a linear combination of a series of different interaction terms, while neglecting the ion-ion term. Their model distinguished the different cations via their charge, hydrated size, and electrostatic free energy of hydration.

Recently Vijiyalakshmi et al. (1990) and Vijiyalakshmi and Gulari, (1991), proposed a model which assumed that the adsorption of counterions onto the surfactant surface of the reverse-micelle is described by the Stern double layer model. Although their model is much simpler than the Leodidis-Hatton model, it cannot distinguish between different ions with the same charge. Moreover, they neglected the amount of water which moved from bulk to reverse-micellar phase.

4.2 Modelling

The extraction of cations using a HD reverse-micellar system, is modelled with a thermodynamic approach previously used for ionic exchange with resins (Allen and Addison, 1989). Earlier studies (Little and Singleterry, 1964; Van Dalen et al., 1974a) showed that a small number of HD surfactant molecules participate in each reverse-micelle, about 7 to 15. Experiments described in Chapter 3 showed that the water uptake of HD micelles is very low, $W_o \leq 10$. Thus the HD micelles are very small, (type 'a' in Fig. 1.1). Since one of the basic assumptions of treatments using the electrical double layer is that charged surfaces are parallel planes, the use of such treatments for small micelles is unjustified. In addition, the properties of the water in the micellar phase are unknown and probably different from the bulk aqueous phase due to the small size of the micelles.

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Most of the current work in the field of ion exchange equilibria centers on multicomponent exchange, and, in particular, the prediction of multicomponent equilibria from binary data (Allen and Addison, 1990) using the activity coefficients of ions. The first step in the development of a model to predict multicomponent systems attempts to predict ternary equilibria using binary data. Binary equilibrium data are reproduced by adjusting parameters in the model and these parameters are then used to estimate the activity coefficients of the ions in the ternary system.

Following Allen and Addison (1989), ion exchange is represented by a reversible reaction of the form,

$$z_i R_{z_j} M_j + z_j M_i^{z_i^+} \rightleftharpoons z_j R_{z_i} M_i + z_i M_j^{z_j^+}$$
 (4.1)

where the ion M_i replaces ion M_j in the reverse-micelle R, and z_i is the charge number of ion M_i . The thermodynamic equilibrium constant K'_j for this reaction is defined as:

$$K_{j}^{i} = \left(\frac{Y_{i}\overline{\gamma}_{i}}{C_{i}\gamma_{i}}\right)^{z_{j}} \left(\frac{C_{j}\gamma_{j}}{Y_{j}\overline{\gamma}_{j}}\right)^{z_{i}}$$
(4.2)

where C_i is the molar concentration of species i in the aqueous phase, Y_i is the equivalent fraction of species i in the micellar phase, γ_i is the activity coefficient of species i in the aqueous phase, and $\overline{\gamma}_i$ is the activity coefficient of species i in the micellar phase.

In this work three cations were employed, H^+ , K^+ , and Mg^{++} . The anion was Cl⁻. To evaluate the activity coefficients of the ions in the aqueous phase Allen and Addison (1989), used the extended Debye-Hückel relation with the parameters given by Robinson and Stokes (1959), and Klotz (1964), while Shallcross (1988) used the Pitzer method. Here a method proposed by Haghtalab and Vera (1992) is used. This method considers the effect of mixed ions in multielectrolyte solutions. The simplified form of the activity coefficients for two 1:1 electrolytes (HCl and KCl) has the form,

$$\ln \gamma_{\pm 1} = \ln \gamma_{\pm 1}^{\circ} - \frac{m_2}{2I} [\ln \gamma_{\pm 1}^{\circ} - \ln \gamma_{\pm 2}^{\circ}]$$
(4.3)

$$\ln \gamma_{\pm 2} = \ln \gamma_{\pm 2}^{\circ} - \frac{m_1}{2I} [\ln \gamma_{\pm 2}^{\circ} - \ln \gamma_{\pm 1}^{\circ}]$$
(4.4)

For a 1:1 and a 2:1 binary system in water with HCl or KCl as electrolyte 1 and $MgCl_2$ as electrolyte 2, Eqs. (4.3) and (4.4) become,

$$\ln \gamma_{\pm 1} = \ln \gamma_{\pm 1}^{\circ} - \frac{m_2}{I} [2 \ln \gamma_{\pm 1}^{\circ} - \ln \gamma_{\pm 2}^{\circ}]$$
(4.5)

$$\ln \gamma_{\pm 2} = \ln \gamma_{\pm 2}^{\circ} - \frac{m_1}{2I} [\ln \gamma_{\pm 2}^{\circ} - 2 \ln \gamma_{\pm 1}^{\circ}]$$
(4.6)

where m is the molality of the salts in the aqueous phase, I is the ionic strength of the solution and $\gamma_{\pm i}^{\circ}$ is the activity coefficient of electrolyte i in a solution of pure electrolyte in water. Bromley's equation (Bromley, 1973) is used for calculating this activity coefficient:

$$\log \gamma_{\pm i}^{\circ} = \frac{-A|z_{\pm}z_{-}|\sqrt{I}}{1+\sqrt{I}} + \frac{(0.06+0.6B)|z_{\pm}z_{-}|I}{(1+\frac{1.5}{|z_{\pm}z_{-}|}I)^{2}} + BI$$
(4.7)

where A is the Debye-Hückel constant (A = 0.5108 mol^{-1/2} kg^{1/2} and B is the Bromley parameter (B_{HCl} = 0.1433, B_{KCl} = 0.0240, B_{MgCl2} = 0.1129 kg/mole). Both A and B are functions of temperature. The ionic strength, I, of the solution is given by:

$$I = \frac{1}{2} \sum_{i=1}^{P} m_i z_i^2 \tag{4.8}$$

where P is the number of ionic species in the aqueous phase. For the activity coefficients of ions in the ternary-cation system, the activity coefficient of the electrolytes 1, 2 and 3, in water, $\gamma_{\pm i}$, is calculated with the same procedure as before,

$$\ln \gamma_{\pm 1} = \ln \gamma_{\pm 1}^{\circ} - \frac{m_2}{2I} [\ln \gamma_{\pm 1}^{\circ} - \ln \gamma_{\pm 2}^{\circ}] - \frac{m_3}{I} [2 \ln \gamma_{\pm 1}^{\circ} - \ln \gamma_{\pm 3}^{\circ}]$$
(4.9)

$$\ln \gamma_{\pm 2} = \ln \gamma_{\pm 2}^{\circ} - \frac{m_1}{2I} [\ln \gamma_{\pm 2}^{\circ} - \ln \gamma_{\pm 1}^{\circ}] - \frac{m_3}{I} [2 \ln \gamma_{\pm 2}^{\circ} - \ln \gamma_{\pm 3}^{\circ}]$$
(4.10)

$$\ln \gamma_{\pm 3} = \ln \gamma_{\pm 3}^{\circ} - \frac{m_1}{2I} [\ln \gamma_{\pm 3}^{\circ} - 2 \ln \gamma_{\pm 1}^{\circ}] - \frac{m_2}{2I} [\ln \gamma_{\pm 3}^{\circ} - 2 \ln \gamma_{\pm 2}^{\circ}]$$
(4.11)

Having the activity coefficients of electrolytes 1, 2, and 3, the activity coefficients for the ions are calculated assuming that the contributions of the cation and anion partition have the same form as in the Debye-Hückel model (Lewis and Randall, 1961), i.e.,

$$\ln \gamma_{i} = \frac{z_{i}^{2}}{|z_{+}z_{-}|} \ln \gamma_{\pm}$$
(4.12)

where γ_i is the activity coefficient of ion i in the aqueous solution and γ_{\pm} is the activity coefficient of salt in the same solution. Thus for the cations,

$$\ln \gamma_{+} = \frac{z_{+}^{2}}{|z_{+}z_{-}|} \ln \gamma_{\pm}$$
(4.13)

To estimate the activity coefficients of ions in the micellar phase, following Allen and Addison (1990), the Wilson equation was used:

$$\ln \overline{\gamma}_{i} = 1 - \ln\left(\sum_{j=1}^{L} Y_{j} \Lambda_{j}^{i}\right) - \sum_{k=1}^{L} \left(\frac{Y_{k} \Lambda_{i}^{k}}{\sum_{j=1}^{L} Y_{j} \Lambda_{j}^{k}}\right)$$
(4.14)

where L is the number of cations in the system and Λ_i^j is the Wilson interaction parameter, $\Lambda_i^j = 1$, and $\Lambda_i^j \neq \Lambda_j^i$. Eqs. (4.2) and (4.14) were used to fit the experimental data for three binaries. The equilibrium constant, K_i^j , and the two Wilson parameters were obtained by fitting binary data using a least squares technique. Thus these parameters are functions of the normality of ions. A Nelder-Mead Simplex algorithm (Woods, 1985) was used to minimize the average absolute deviation between the experimental and fitted Y-values.

$$F_b = \frac{\sum_{i=1}^{E} |Y_i^{exp} - Y_i^{fit}|}{E}$$
(4.15)

where E is the number of experimental points. The average absolute error between the experimental and fitted data for each binary is within the range of the uncertainties in the experimental data. As discussed in Chapter 3, the confidence interval for Y_i measurements has been estimated to be 0.03.

In another method of fitting binary data, the following constraint was imposed to the optimization,

$$\Lambda_j^i = \frac{1}{\Lambda_i^j} \tag{4.16}$$

	F _b with 3 parameters	F_b with 2 parameters
K-H	0.0276	0.0340
Mg-H	0.0150	0.0174
Mg-K	0.0245	0.0299

Table 4.1: Quality of fit for three binaries, F_b .

Then only two parameters were obtained by the fitting of each binary: K_i^j , and Λ_i^j . Equilibrium micellar fractions were calculated from

$$(K_j^i)^{1/z_j} \left(\frac{C_i \gamma_i}{\overline{\gamma}_i}\right) \left(\frac{Y_j \overline{\gamma}_j}{C_j \gamma_j}\right)^{z_i/z_j} - Y_i = 0$$
(4.17)

The comparisons between experimental and the calculated results for the three binary systems are shown in Tables 4.2 and 4.3. For each binary only Y_1 has been shown since $Y_2 = 1 \cdot Y_1$. The equilibrium constants and Wilson parameters obtained by both constrained and unconstrained optimization are shown in Tables 4.4 and 4.5. Figures 4.1, 4.2 and 4.3 show the experimental data and the fitted model for the K⁺/H⁺, Mg⁺⁺/H⁺ and Mg⁺⁺/K⁺ binaries, respectively. The solid curve shows the results obtained with the model using 3 parameters per binary and the dashed curve shows the fitted model with 2 parameters per binary.

к-н	X _K (exp)	0.09	0.18	0.28	0.34	0.43	0.50	0.57	0.74	0.83*	0.97*	0.99*
	Y _K (exp)	0.06	0.12	0.16	0.21	0.26	0.29	0.29	0.31	0.32*	0.59*	0.81*
	Y _K (fit)	0.09	0.14	0.17	0.19	0.22	0.24	0.26	0.31	0.36	0.57	0.77
[X _{Mg} (exp)	0.07	0.12	0.20	0.27	0.36	0.44	0.50	0.58	0.66	0.77*	0.89 •
Mg-H	$Y_{Mg}(exp)$	0.27	0.38	0.42	0.48	0.50	0.57	0.60	0.61	0.66	0.73*	0.86*
	$Y_{Mg}(fit)$	0.32	0.37	0.42	0.46	0.50	0.54	0.57	0.61	0.66	0.73	0.83
[X _{Mg} (exp)	0.06	0.19	0.35	0.48	0 56	0.64	0.72*	0.84*	0.91 •		I
Mg-K	$Y_{Mg}(exp)$	0.30	0.46	0.52	0.56	0.64	0.68	0.72*	0.86*	0.94*		
	$Y_{Mg}(fit)$	0.27	0.42	0.51	0.59	0.64	0.68	0.73	0.81	0.88		

Table 4.2: Experimental and fitted data with three parameters.

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*These data points are obtained by starting with KD or MgD₂ reverse micellar systems.

Table 4.5: Experimental and inter usits with two parameter	4.3: Experimental and fitted data wi	ith two parameters
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к-н	X _K (exp)	0.09	0.18	0.28	0.34	0.43	0.50	0.57	0.74	0.83*	0.97*	0.99*
	$Y_K(exp)$	0.06	0.12	0.16	0.21	0.26	0.29	0.29	0.31	0.32*	0.59*	0.81*
	Y _K (fit)	0.10	0.14	0.17	0.19	0.21	0.24	0.26	0.32	0.35	0.55	0.74
	$X_{Mg}(exp)$	0.07	0.12	0.20	0.27	0.36	0.44	0.50	0.58	0.66	0.77*	0.89*
Mg-H	$Y_{Mg}(exp)$	0.27	0.38	0.42	0.48	0.50	0.57	0.60	0.61	0.66	0.73 •	0.86*
	Y _{Mg} (fit)	0.33	0.37	0.42	0.46	0.50	0.54	0.58	0.62	0.66	0.75	0.85
	X _{Mg} (exp)	0.06	0.19	0.35	0.48	0.56	0.64	0.72*	0.84*	0.91*		T
Mg-K	$Y_{Mg}(exp)$	0.30	0.46	0.52	0.56	0.64	0.68	0.72*	0.86*	0.94*		
	Y _{Mg} (fit)	0.28	0.43	0.52	0.60	0.64	0.68	0.72	0.79	0.85		1

*These data points are obtained by starting with KD or MgD₂ reverse micellar systems.

1	2	K ¹ ₂	Λ2	Λ^1_2
K	H	0.8940	8.8413	1.3858
Mg	H	2.4504	1.7367	6.1287
Mg	K	23.4908	1.3900	0.2259

Table 4.4: Equilibrium constants and Wilson parameters with unconstrained optimization.

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Table 4.5: Equilibrium constants and Wilson parameters with reciprocal constraint.

1	2	K ¹ ₂	Λ
K	H	1.1759	5.8803
Mg	H	0.9765	0.3585
Mg	K	30.8221	1.9854



Figure 4.1: Experimental and fitted equilibrium curves for the K^+/H^+ binary system (organic phase 0.1 N and aqueous phase 0.2 N).



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Figure 4.2: Experimental and fitted equilibrium curves for the Mg^{++}/H^{+} binary system (organic phase 0.1 N and aqueous phase 0.2 N).



Figure 4.3: Experimental and fitted equilibrium curves for the Mg^{++}/K^+ binary system (organic phase 0.1 N and aqueous phase 0.2 N).

4.3 Comparison of experiment and theory

There are three ways of comparing the experimental results with theory. Two of them assume the composition in one phase known and predict the composition in the other phase. These are the equivalent of typical dew or bubble point calculations. The third possibility is to calculate the composition of both (the aqueous and the organic) phases at equilibrium assuming a known overall composition. This latter case is the equivalent of a flash calculation. In this work, calculations were performed for the most frequently encountered situation, i.e. where the composition of the aqueous phase is known. In this case, once the parameters for all three binary pairs have been obtained, the prediction of the corresponding ternary equilibrium can be made using the following equations:

$$\frac{(\overline{\gamma}_{i}Y_{i})^{z_{j}}}{(\overline{\gamma}_{j}Y_{j})^{z_{i}}} = K_{j}^{i} \frac{(\gamma_{i}C_{i})^{z_{j}}}{(\gamma_{j}C_{j})^{z_{i}}}$$
(4.18)

$$\frac{(\overline{\gamma}_i Y_i)^{z_k}}{(\overline{\gamma}_k Y_k)^{z_i}} = K_k^i \frac{(\gamma_i C_i)^{z_k}}{(\gamma_k C_k)^{z_i}}$$
(4.19)

$$Y_{i} + Y_{j} + Y_{k} = 1 \tag{4.20}$$

For the unconstrained method L^2 -1 parameters were required. The 8 parameters were two equilibrium constants and six Wilson parameters. For the constrained method 2L-1 parameters were required. The 5 parameters were two equilibrium constants and three Wilson parameters. An iterative technique was required to find the reverse micellar phase composition (Y_i, Y_j, Y_k) for a given solution composition (C_i, C_j, C_k) . The above procedure was tested against measured ternary equilibrium data.

The results for the prediction of the ternary cation system, using parameters from the best fit of the binary systems are given in Table 4.6 for the unconstrained

X (exp)			Y _{Mg}		Y	ĸ	Y _H	
Mg	K	H	exp	pred	exp	pred	exp	pred
0.00	0.74	0.26	0.00	0.00	0.31	0.3 1	0.69	0.69
0.09	0.69	0.22	0.24	0.29	0.19	0.25	0.57	0.46
0.21	0.54	0.25	0.37	0.39	0.16	0.19	0.47	0.42
0.31	0.45	0.24	0.42	0.44	0.11	0 .15	0.48	0.41
0.38	0.37	0.25	0.45	0.48	0.09	0.13	0.46	0.39
0.52	0.20	0.28	0.52	0.55	0.05	0.08	0.43	0.37
0.60	0.12	0.28	0.57	0.59	0.02	0.05	0.41	0.36
0.69	0.00	0.31	0.66	0.66	0.00	0.00	0.34	0.34

Table 4.6: Prediction of ternary with eight parameters.

 $P_t = 0.037$

method and in Table 4.7 for the constrained method. In each case the quality of prediction, P_t , which is calculated by the following equation, is given in the bottom of the table.

$$P_{t} = \frac{\sum_{i=1}^{E} \sum_{j=1}^{L} |y_{j}^{exp} - y_{j}^{pred}|_{i}}{LE}$$
(4.21)

The magnitude of P_t shows that the quality of prediction is of about the order of the uncertainties in the experimental data which has been estimated to be 0.031.

X (exp)		Y _{Mg}		Y	ĸ	Y _H		
Mg	К	Н	exp	pred	exp	pred	exp	pred
0.00	0.74	0.26	0.00	0.00	0.31	0.32	0.69	0.68
0.09	0.69	0.22	0.24	0.29	0.19	0.26	0.57	0.45
0.21	0.54	0.25	0.37	0.38	0.16	0.20	0.47	0.42
0.31	0.45	0.24	0.42	0.42	0.11	0.18	0.48	0.40
0.38	0.37	0.25	0.45	0.46	0.09	0.16	0.46	0.38
0.52	0.20	0.28	0.52	0.52	0.05	0.11	0.43	0.37
0.60	0.12	0.28	0.57	0.57	0.00	0.08	0.43	0.35
0.69	0.00	0.31	0.66	0.66	0.00	0.00	0.34	0.34

Table 4.7: Prediction of ternary with five parameters.

 $P_t = 0.043$

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Figure 4.4: Equilibrium triangular diagram for ternary system (organic phase 0.1 N and aqueous phase 0.2 N). The prediction points are calculated with 8 parameters.



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Figure 4.5: Equilibrium triangular diagram for ternary system (organic phase 0.1 N and aqueous phase 0.2 N). The prediction points are calculated with 5 parameters.

Chapter 5

Conclusions & Recommendations

5.1 Conclusions

The counter-ion of an anionic surfactant in the reverse-micellar phase was partially substituted with cations from the aqueous phase. The selectivity was greater for Mg^{++} than for K^+ and H^+ . This phenomenon can be used to separate ions with different charge numbers. For ions with same charge, K^+ and H^+ , the extent of exchange is governed by other ionic parameters. Complete substitution of one counter-ion by another was possible only after several contacts of the reverse-micellar phase with fresh aqueous phases containing high concentrations of the desired cations.

The partition coefficients for the K^+/Mg^{++} binary system were lower for higher normalities of the cations. Moreover, the same equilibrium curve was obtained using either a KD reverse-micellar phase in contact with a $MgCl_2$ solution or MgD micellar phase in contact with a KCl solution. This behavior is similar to that of conventional ion-exchange resins.

The distribution coefficient for an organic phase containing HD reverse-

micelles, was high for both K^+ and Mg^{++} at low salt concentrations. The surfactant concentration, had no effect on the distribution coefficient.

The concentration of surfactant in the aqueous phase varied with both salt and surfactant concentrations in the system, but the surfactant concentration in the aqueous phase was always less than 2 mM. Higher salt concentrations decreased the concentration of surfactant in the aqueous phase.

The water uptake of the system was low, with W_o varying between 4 and 10 for a wide range of salt concentrations (0 to 1 M). The value of W_o decreased with salt concentration but it was independent of surfactant concentration. Observed W_o values followed the trend W_o (H⁺) > W_o (Mg⁺⁺) > W_o (K⁺).

The Wilson equation satisfactorily fit the experimental binary data in the reverse-micellar phase. The method proposed by Haghtalab and Vera for the activity coefficients of ions in a multielectrolyte aqueous phase improved the results of the prediction with respect to the use of Bromley's equation for ions in single salt solutions (Allen and Addison, 1990). The accuracy of the prediction of the ternary system was about of the precision of the experimental data.

5.2 Recommendations

The determination of the concentration of ions in the organic phase was not undertaken in this study. This can be important for the verification of the results of concentration measurements in the aqueous phase. Further research is needed to find a satisfactory procedure to measure accurately the concentration of ions in the organic phase.

In order to provide a better understanding of the difference in the extraction behavior of the system for cations with different charge numbers, cations other than K^+ and Mg^{++} should be examined. A trivalent cation should also be used. The quality of the model prediction should be checked with more experimental systems. Measured binary equilibrium data should be collected as a reference for any further research in this area.

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Appendix A

Sample Calculation

Since many symbols are used in this appendix, some of which only appear here, a separate notation is given at the end of this appendix.

The experimental situation is described as follows

• Initial state

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Aqueous Phase (V_a^i) : H₂O, cation $(C_{M^+}^i)$, anion $(C_{X^-}^i)$. Organic Phase (V_o^i) : heptane and kerosene¹, surfactant (C_{os}^i) .

• Final state (at equilibrium)

Aqueous Phase (V_a) : H₂O, surfactant (C_s) , cation (C_{M^+}) , anion (C_{X^-}) . Organic Phase (V_o) : heptane and kerosene, surfactant (C_{os}) , cation $(\overline{C_{M^+}})$ and H₂O (in reverse-micelles).

¹The purchased HD surfactant was approximately 48.5 % HD in kerosene. The composition of each new bottle was measured as described in Appendix B.

Mass balances are made on surfactant and cations:

$$V_o^i C_{os}^i = V_o C_{os} + V_a C_s \tag{A.1}$$

$$V_a^i C_{M^+}^i = V_a C_{M^+} + V_o C_{os} W_o \overline{v_w} \overline{C_{M^+}}$$
(A.2)

where $\overline{v_{\omega}}$ is the molar volume of the water in the reverse-micelles.

$$V_a^{i}C_{M^+}^{i} = V_a C_{M^+} + V_o C_{oM^+} \tag{A.3}$$

Defining Q as the concentration of water in moles per liter of organic phase:

$$V_{a}^{i} - V_{a} = 0.0181 Q V_{o} \tag{A.4}$$

where the density of the aqueous phase was taken as 997 g/l. Finally,

$$V_o - V_o^i = V_a^i - V_a \tag{A.5}$$

There are 5 equations and 14 variables; V_o^i , C_{os}^i , V_o , C_{os} , V_a , C_s , V_a^i , $C_{M^+}^i$, C_{M^+} , C_{M^+} , C_{oM^+} , W_o , $\overline{v_w}$, $\overline{C_{M^+}}$, and Q. In an experiment 5 variables are fixed: V_o^i , C_{os}^i , V_a^i , $C_{M^+}^i$, \overline{v}_w and 4 others are measured: C_{os} , C_s , C_{M^+} , and Q. The remaining 5 variables, V_o , V_a , W_o , C_{oM^+} , and $\overline{C_{M^+}}$ are then calculated.

With α as the weight fraction of water in the organic phase,

$$Q = \frac{\alpha \rho_o}{18.02} \tag{A.6}$$

To complete the calculation, the density of the organic phase, ρ_o , is required. At equilibrium there are several compounds in the organic phase: heptane, kerosene, surfactant and water. The following assumptions are made:

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1. The weight of cation in the organic phase (water pools), and the weight

of surfactant in the aqueous phase are negligible.

- 2. \overline{v}_w is equal to the molar volume of pure water, $18.02/\rho_w$.
- 3. The solution of HD in kerosene and heptane, exhibits no volume change on mixing.

The density of the original mixture of HD and kerosene, which was measured several times by pycnometer at 25 °C, was 905 g/l. The densities of water and heptane at this temperature are 997 and 668 g/l, respectively. The density of the organic phase is

$$\rho_{o} = \frac{m_{o}}{V_{o}} = \frac{m_{h} + m_{w} + m_{hk}}{V_{h} + V_{w} + V_{hk}}$$
(A.7)

$$\rho_o = \frac{668V_h + 997V_w + 905V_{hk}}{V_h + V_w + V_{hk}} \tag{A.8}$$

$$V_h + V_{hk} = V_o^i \tag{A.9}$$

$$V_h = V_o^t - V_{hk} \tag{A.10}$$

$$V_{hk} = \frac{m_{hk}}{\rho_{hk}} = \frac{m_{HD}}{905\beta} \tag{A.11}$$

where β is the weight fraction HD in the original kerosene solution. Since the molecular weight of HD is 460.7,

$$m_{HD} = 460.7(C_{os}^{i}V_{o}^{i}) \tag{A.12}$$

Combining Eqs.(A.11) and (A.12) yields

$$V_{hk} = \frac{0.509C_{os}^{i}V_{o}^{i}}{\beta}$$
(A.13)

Equations (A.10) and (A.13) are substituted into Eq. (A.8) and, after rearrangement,

$$\rho_o = \frac{997V_w + 668V_o^i + 237(\frac{0.509(C_o^i,V_o^i)}{\beta})}{V_o^i + V_w}$$
(A.14)

The system of equations is solved by iteration among Eqs. (A.6), (A.8), (A.5), and (A.4). First V_w is estimated, then ρ_o is calculated from Eq. (A.14). From Eq. (A.6) Q is then evaluated. Finally, using Eqs. (A.5) and (A.4), V_o , V_a , and V_w are calculated. When the calculated value of V_w is equal to the estimated value of V_w , the calculation is terminated.

The cation concentrations in the organic phase, C_{oM^+} and $\overline{C_{M^+}}$ were obtained from Eqs. (A.3) and (A.2). The W_o quantity was determined from Eq. (2.2). The distribution coefficient K₁, and the equivalent fractions X₁ and Y₁ were determined from Eqs (2.3) to (2.7).

If it is assumed that the amount of water in the reverse micellar phase is negligible, i.e. $V_w = 0$, Eqs. (A.1) to (A.5) become:

$$V_o = V_o^* \tag{A.15}$$

$$V_a = V_a^* \tag{A.16}$$

$$V_a C_{M^+}^i = V_a C_{M^+} + V_o C_{oM}^+ \tag{A.17}$$

$$V_o C_{os}^i = V_o C_{os} + V_a C_s \tag{A.18}$$

This set of equations was used for preliminary estimates to start the iteration.

As discussed in the sample calculation, the determination of organic phase compositions is based on the measurement of concentrations in the aqueous phase. Thus errors in the calculation of organic phase compositions depend on the normality of both phases. This is illustrated by the following example. Consider two samples, 1 and 2, both with a phase volume ratio of 1. The concentration of ions in both the aqueous and organic phases is equal to 100 mM for sample 1. For sample 2, the concentrations of ions in the aqueous and organic phases are 1000 and 100 mM, respectively. If the concentration of ions in aqueous phase measured by AA results in a 5 percent error, then the error for sample 1 is equal to 5 mM (when the phase volume ratio is 1, the concentrations are relative to the number of moles) and that for sample 2 is equal to 50 mM. This error for sample 1 is equal to 5 percent of the concentration of organic phase, while it is equal to 50 percent for the sample 2. Therefore the calculation of the organic phase composition for sample 1 may be acceptable while for sample 2 is unacceptable. Thus the relative concentration of both phases is important in estimating the errors introduced in the determination of the organic phase composition.

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Notation

C _M +	Concentration of cation in aqueous phase, M
$C_{M^+}^i$	Initial concentration of cation in aqueous phase, M
$\overline{\mathbf{C}_{M^+}}$	Concentration of cation in reverse-micellar water pools, M
CoM+	Concentration of cation in organic phase, M
Cos	Concentration of surfactant in organic phase, M
C ⁱ os	Initial concentration of surfactant in organic phase, M
C,	Concentration of surfactant in aqueous phase, M
C_{X-}^{i}	Initial concentration of anion in aqueous phase, M
Cx-	Concentration of anion in aqueous phase, M
m _h	Weight of heptane in the organic phase, g
m _{HD}	Weight of HD surfactant in the organic phase, g
m _{hk}	Weight of HD and kerosene in the organic phase, g
mo	Weight of the organic phase, g
m _w	Weight of the water in the reverse-micelles, g
Q	Moles of water per liter of organic phase
Va	Volume of aqueous phase, l
V ⁱ _a	Initial volume of aqueous phase, l
V _h	Volume of heptane in the organic phase, l
V _{hk}	Volume of HD and kerosene in the organic phase, l
Vo	Volume of organic phase, l
V ⁱ _o	Initial volume of organic phase, l
$\mathbf{V}_{\boldsymbol{w}}$	Volume of the water in organic phase, l

Greek Letters

α	Weight fraction of water in organic phase
β	Weight fraction of HD in the purchased surfactant solution
Phk	Density of the purchased HD solution (HD + kerosene), g/l
$ ho_w$	Density of water, g/l
ρο	Density of the organic phase, g/l
\overline{v}_w	Molar volume of the water in the reverse-micelles, l/mole

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Appendix B

Surfactant Calibration

The HD surfactant was purchased as a mixture of HD in kerosene. The procedure of Danesi et. al. (1973), which involves a potentiometric titration with NaOH employing alcohol as diluent, was used to measure the neutralization equivalent of the original HD solution. A weighed amount of surfactant solution, about 2 ml in volumetric basis, was dissolved in 10 ml of ethanol. The diluent was then titrated by 0.5 M NaOH. A pH meter was used to measure the pH of the solution. At the neutralization point a drastic increase in pH was observed. A sample calculation follows

Weight of HD/kerosene sample = 1.808 g

Volume of 0.5 M NaOH used in titration = 3.8 ml

meq HD = $3.8 \times 10^{-3} \times 0.5 = 1.9 \times 10^{-3}$

Weight of HD in the sample = $1.9 \times 10^{-3} \times 460.7 = 0.875 \text{ g}$

%HD in the sample = $\frac{0.875}{1.808}$ X 100 = 48.4

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Using this result, stock solutions with different concentrations of HD in the range 0 - 0.3 M were prepared by dilution with heptane. The *IVV* absorbance was measured at 285 nm. The absorbance exhibited a linear relation with surfactant concentration - see Fig. 2.1. The same calibration curve was used to measure the concentrations of surfactant for all cations.

Appendix C

Preliminary Experiments

The results of preliminary experiments with the micellar extraction system, which were performed in the 25 ml Erlenmeyer flasks, were inconsistent. This was assumed to be due to two reasons: First, the cap of the flasks was not completely sealed which allowed heptane to evaporate and caused a significant error in the concentrations of ions. Second, when the concentration of salt in the aqueous phase was low, an interlayer between the two phases was observed. To remove both deficiencies, gasket-sealed test tubes (50 ml) were used as the sample containers. The same containers were used as centrifuge vessels. Subsequent experiments showed complete phase separation and a satisfactory consistency in the results.

The next goal was to find an optimum for both shaking and settling times. Several identical samples were prepared and tested at different shaking and settling times. A set of results is shown in Table C.1. For several sets of experiments the results did not change after 1 hour of shaking and 24 hours of settling, hence these conditions were fixed in all subsequent experiments.

Run No.	1	2	3	4	5	6	7	8	9
shaking time (hr)	1	2	4	1	2	4	1	2	4
settling time (hr)	24	24	24	48	48	48	72	72	72
C _{os} (mM)	98.2	98.3	99.3	98.6	97.9	98.5	100.3	98.8	99.6
C(m M)	1.8	2.1	2.6	1.7	1.9	2.1	1.9	2.2	2.3
% difference in	0.79	0.40	-1.1	0.50	0.99	0.20	-1.4	-0.2	-1.1
HD closure									
% water in	1.99	1.94	1.95	1.89	1.95	1.98	1.91	1.99	1.97
organic phase									
Wo	7.85	7.64	7.61	7.42	7.72	7.79	7.38	7.80	7.66
C _{K+} (mM)	21.8	21.8	22.0	21.8	21.6	22.0	21.7	21.9	22.0
C _{oK} + (mM)	18.6	18.6	18.4	18.6	18.8	18.4	18.7	18.5	18.4
К _{<i>К</i>+}	61.5	63.1	61.0	64.4	63.5	60.1	64.4	60.4	60.7

Table C.1: Effect of shaking and settling time on metal extraction.

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Initial conditions: aqueous phase 41.6 mM of K⁺ and organic phase 100.8 mM HD.

To examine the equilibrium of the system with 1 hour of shaking and 24 hours of settling, another set \pm experiments was conducted. Two identical 100 ml samples, denoted samples 1 and 2, with the phase-volume ratio of 1 were prepared (each phase 50 ml). The initial aqueous phase was a solution of 0.04 M KCl, and the initial organic phase was 0.1 M HD surfactant in kerosene/heptane. At equilibrium the phases of the both samples were collected and analyzed. With the aqueous and organic phases of sample 1, three samples with different aqueous to organic volume ratios of 2/1, 1/2, and 1/1 were prepared, samples 3, 4, and 5. With the same procedure, samples 6, 7, and 8 were prepared from sample 2. The six latter samples were shaken and settled and the phases were collected and analyzed. The same results were obtained for the original samples 1 and 2, as for the later prepared samples 3 to 8. The water uptake and the concentration of K⁺ in the aqueous phase after settling are shown in Table C.2. The results are essentially identical f i all samples indicating no change with several equilibrations.

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Table C.2: Examining the equilibrium by conducting further experiments.

Run No.	1	2	3	4	5	6	7	8
Aq volume (ml)	50	50	20	10	10	20	10	10
Org volume (nıl)	50	50	10	20	10	10	20	10
% water in	1.87	2.06	1.93	2.00	1.97	1.95	1.91	1.90
organic phase								
C _{K+} (mM)	22.2	22.0	21.9	21.9	21.5	21.9	21.7	21.8
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Initial conditions: aqueous phase 41.6 mM of K⁺ and organic phase 100 mM of HD

To examine the equilibrium behavior of the system under different volume ratios, several procedures can be employed. The method of Leodidis and Hatton (1989) is used here. They defined a ratio, δ , which is equal to $N_{\bullet}/2N_{MCl_z}$, where N_{\bullet} is the total number of moles of surfactant in the system, and N_{MCl_z} is the total number of moles of electrolyte introduced in the initial aqueous phase. When the ratio of the concentration of surfactant counterion, H^+ , to the cation, K^+ , in the final aqueous solution is plotted against the parameter δ , the data of different experiments collapse onto a single curve. The value of δ may be changed in the following ways: (i) by changing the initial KCl concentration in the aqueous phase, while keeping the surfactant concentration in the organic phase constant, and setting $V_a^i/V_o^i = 1$; (ii) by varying V_a^i/V_o^i while keeping the surfactant concentration in the organic phase and initial KCl in the aqueous phase constant.

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Several sets of experiments were conducted, in each set the concentrations of organic and aqueous phases were constant, only the volume ratio of the phases was varied. The organic phase was 0.1 M HD surfactant. The initial aqueous phase was one of the 0.02, 0.04, 0.06, 0.08, or 0.10 M KCl for each set. The samples were prepared with different volume ratios of aqueous to organic phase of 3/1, 2/1, 1.4/1, 1/1, 1/1.4, 1/2, and 1/3. These data sets collapse onto one curve-see Fig. C.1. This indicates that the cation distribution is not affected by the ratio of the phase volumes. The phase-volume ratio of 1, was chosen for subsequent experiments.



Figure C.1: Universal curve for extraction of K^+ . Ratio of final concentrations of H^+ and K^+ in the bulk aqueous phase vs the parameter δ with variation of [KCl], and phase volume ratio.

Appendix D

Preparation of KD and MgD_2 Reverse-Micelles

In order to conduct the experiments with KD reverse-micelles, it was necessary to substitute K⁺ for the surfactant counterion H⁺ in the reverse-micellar phase. To make KD reverse-micelles the organic HD phase was contacted with a concentrated aqueous solution of 2 M KCl at a volume ratio of 1. The same procedure as described for extraction experiments was used to contact the phases. At equilibrium both phases were collected and the organic phase was contacted three times with another fresh aqueous phase. To ensure complete removal of the cation H⁺ from the micellar phase, the organic phase was contacted with an aqueous phase containing KCl and a small amount of KOH with a pH of about 10. It was assumed that any remaining trace amounts of H⁺ ion reacted with OH⁻ ion producing water. After each contact, the pH of the equilibrium aqueous phase was measured. The total amounts of the H⁺ ion measured at equilibrium were within 1% of the initial amount of H⁺ ion in the original organic phase. The results of pH measurements of a typical experiment are given in the Table D.1.

Aqueous Phase	first contact	second contact	third contact	total
Conc. of H (mM)	77.44	15.45	4.26	97.15
Percent replacement after each contact	79.0	94.8	99.1	

Table D.1: Concentration of H⁺ in the washing aqueous phase

In the calculation, the small amount of water which moves into organic phase has been neglected

The initial HD micellar phase was 98 mM. Considering the small amounts of surfactant that move into the aqueous phase through each contact, the final concentration of the new KD micellar phase was found to be equal to 97 mM. Moreover, after contacting this new micellar phase with an electrolyte solution, $MgCl_2$ solution, the concentration of H⁺ in the aqueous phase at equilibrium did not increase more than 0.2 % which confirmed the nearly complete substitution of H⁺ by K⁺.

The same procedure was used to prepare MgD_2 reverse-micelles. Contacting the original HD micellar phase with the concentrated $MgCl_2$ solution for four times replaced more than 99 percent of H⁺ counterion with Mg^{++} .

Appendix E

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Data for Experiments with Variable Normalities

0.1 N	1 HD	0.2 M HD		0.3 M HD	
Conc. of K ⁺	Conc. of HD	Conc. of K ⁺	Conc. of HD	Conc. of K ⁺	Conc. of HD
(M)	(mM)	(M)	(mM)	(M)	(mM)
0.007	1.35	0.003	1.67	0.004	1.96
0.020	1.03	0.015	1.40	0.008	1.82
0.033	0.88	0.025	1.24	0.019	1.58
0.048	0.81	0.036	1.15	0.029	1.50
0.071	0.78	0.052	1.11	0.081	1.45
0.111	0.68	0.097	1.02	0.121	1.33
0.164	0.62	0.142	1.02	0.202	1.22
0.257	0.55	0.227	0.93	0.291	1.14
0.364	0.52	0.332	0.88	0.460	1.01
0.539	0.46	0.498	0.75	0.651	0.91
0.734	0.43	0.686	0.69		

Table E.1: Surfactant concentration in the aqueous phase vs equilibrium concentration of K^+ in the aqueous phase for three surfactant concentrations.

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0.1	M HD	0.2	0.2 M HD		M HD
Conc. of	Conc. of HD	Conc. of	Conc. of HD	Conc. of	Conc. of HD
Mg ⁺⁺ (M)	(mM)	Mg ⁺⁺ (M)	(mM)	Mg ⁺⁺ (M)	(mM)
0.001	0.87	0.0001	1.79	0.0001	2.05
0.013	0.60	0.001	1.22	0.001	1.51
0.028	0.52	0.003	1.09	0.002	1.37
0.048	0.50	0.013	0.95	0.006	1.15
0.067	0.49	0.029	0.87	0.023	1.11
0.098	0.47	0.046	0.83	0.042	1.03
0.142	0.46	0.086	0.78	0.072	1.00
0.178	0.42	0.113	0.76	0.114	0.94
0.383	0.39	0.146	0.73	0.145	0.92
0.486	0.37	0.366	0.62	0.356	0.83
0.604	0.35	0.571	0.57	0.568	0.74
0.801	0.32	0.794	0.52	0.782	0.68
1.002	0.29	0.994	0.46	0.994	0.58

Table E.2: Surfactant concentration in the aqueous phase vs equilibrium concentration of Mg^{++} in the aqueous phase for three surfactant concentrations.

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0.1 M HD		0.2 M HI	D	0.3 M HD	
Conc. of H ⁺	Wo	Conc. of H ⁺	Wo	Conc. of H+	W _o
(M)		(M)		(M)	
0.02	10.1	0.02	10.2	0.04	10.2
0.04	9.95	0.04	10.1	0.10	9.87
0.10	9.91	0.10	9.91	0.20	9.63
0.20	9.52	0.20	9.70	0.40	9.02
0.40	9.15	0.40	9.05	0.60	8.75
0.60	8.70	0.60	8.60	0.80	8.31
0.80	8.48	0.80	8.34		

Table E.3: Water to surfactant ratio as a function of equilibrium concentration of H^+ in the aqueous phase for three surfactant concentrations.

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0.1 M HI)	0.2 M HI)	0.3 M HI)
Conc. of K ⁺	W.	Conc. of K+	Wo	Conc. of K ⁺	Wo
(M)		(M)		(M)	
0.071	6.36	0.003	7.76	0.008	7.50
0.111	6.05	0.015	7.25	0.043	6.90
0.164	5.89	0.025	6.94	0.081	6.51
0.257	5.65	0.036	6.55	0.121	6.34
0.364	5.54	0.096	6.34	0.202	6.07
0.539	5.34	0.142	6.07	0.291	5.78
0.734	5.28	0.227	5.92	0.460	5.46
		0.332	5.67	0.651	5.41
		0.498	5.42		
		0.686	5.39		

Table E.4: Water to surfactant ratio as a function of equilibrium concentration of K^+ in the aqueous phase for three surfactant concentrations.

0.1 M HD		0.2 M HD	I	0.3 M HD	
Conc. of Mg ⁺⁺	Wo	Conc. of Mg ⁺⁺	Wo	Conc. of Mg ⁺⁺	Wo
(M)		(M)		(M)	
0.104	7.89	0.004	7.96	0.0001	8.24
0.178	7.75	0.200	7.50	0.072	7.67
0.383	7.42	0.081	7.67	0.145	7.51
0.604	7.33	0.366	7.27	0.356	7.23
0.801	7.16	0.571	7.10	0.568	7.05
1.000	6.90	0.794	6.95	0.782	6.85
		0.994	6.78	0.994	6.62

Table E.5: Water to surfactant ratio as a function of equilibrium concentration of Mg^{++} in the aqueous phase for three surfactant concentrations.

0.1 M HI)	0.2 M HD		0.3 M HI)
Conc. of K ⁺	K _K	Conc. of K+	K _K	Conc. of K ⁺	K _K
(M)		(M)		(M)	
0.007	163	0.003	158	0.004	123
0.020	113	0.015	63.1	0.008	95.5
0.033	77.7	0.025	52.4	0.019	69.1
0.046	92.4	0.036	49.3	0.029	58.1
0.065	55.2	0.052	36.6	0.043	44.3
0.071	42.2	0.097	23.0	0.083	28.0
0.111	30.0	0.142	22.3	0.094	6.61
0.164	27.6	0.227	12.7	0.121	21.4
0.257	13.2	0.332	10.2	0.202	13.1
0.364	11.7	0.498	9.68	0.291	10.6
0.539	10.0	0.686	7.18	0.460	9.73
0.734	6.16			0.651	7.03

Table E.6: Distribution coefficient of K^+ vs equilibrium concentration of K^+ in the aqueous phase for three surfactant concentrations.

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0.1 M HD		0.2 M HD		0.3 M HD	
Conc. of Mg ⁺⁺	K _{Mg}	Conc. of Mg ⁺⁺	K _{Mg}	Conc. of Mg ⁺⁺	K _{Mg}
(M)		(M)		(M)	
0.013	184	0.013	153	0.006	200
0.028	98.8	0.029	78.8	0.023	57.3
0.048	61.5	0.046	51.7	0.042	32.7
0.067	44.5	0.081	25.5	0.072	19.3
0.098	28.2	0.086	23.1	0.114	12.0
0.104	23.3	0.113	22.9	0.145	11.8
0.142	18.6	0.146	17.0	0.156	7.33
0.170	15.8	0.366	6.43	0.356	5.35
0.178	12.7	0.571	5.37	0.568	4.06
0.383	7.51	0.794	2.82	0.782	2.63
0.486	6.63	0.914	2.51	0.994	2.04
0.604	4.64				
0.801	3.68				
1.000	3.22				

Table E.7: Distribution coefficient of Mg^{++} vs equilibrium concentration of Mg^{++} in the aqueous phase for three surfactant concentrations.

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0.1 M HD		0.2 M HD		0.3 M HD	
Conc. of K ⁺	Y _K	Conc. of K+	Yĸ	Conc. of K ⁺	Yĸ
(M)		(M)		(M)	
0.007	0.12	0.003	0.08	0.004	0.05
0.020	0.19	0.015	0.12	0.008	0.10
0.033	0.25	0.025	0.16	0.019	0.13
0.048	0.27	0.036	0.21	0.029	0.16
0.065	0.29	0.142	0.35	0.043	0.17
0.071	0.32	0.227	0.40	0.081	0.22
0.111	0.36	0.498	0.47	0.121	0.29
0.400	0.47	0.686	0.48	9.202	0.29
<u></u>	0.50			0.291	0.32
				0.460	0.44
				0.651	0.45

Table E.8: Equivalent fraction, Y_K , "s equilibrium concentration of K⁺ in the aqueous phase for three surfactant concentrations.

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0.1 M HD		0.2 M HD		0.3 M HD	
Conc. of Mg++	Y _{Mg}	Conc. of Mg ⁺⁺	Y _{Mg}	Conc. of Mg ⁺⁺	Y _{Mg}
(M)		(M)		(M)	
0.001	0.37	0.0004	0.19	0.0002	0.12
0.013	0.53	0.003	0.36	0.0008	0.18
0.028	0.62	0.013	0.45	0.001	0.24
0.048	0.65	0.029	0.50	0.006	0.34
0.067	0.66	0.046	0.54	0.023	0.36
0.104	0.68	0.081	0.57	0.072	0.38
0.144	0.71	0.113	0.59	0.145	0.46
0.383	0.81	0.366	0.63	0.356	0.50
0.604	0.79	0.794	0.59	0.568	0.56
0.801	0.81	0.994	0.62	0.782	0.51
1.000	0.86			0.994	0.48

Table E.9: Equivalent fraction, Y_{Mg} , vs equilibrium concentration of Mg^{++} in the aqueous phase for three surfactant concentrations.

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