ABSTRACT

The 'Group Solution' model, which treats a solution as a hypothetical mixture of the constituent functional groups, has been extended to predict the heats of mixing of liquid mixtures.

The model has been tested using published data for mixtures containing long-chained n-alkanes and n-alcohols at 25°C and 45°C and has been found to be satisfactory. The root-mean-square deviations of the predictions range from 3% to 17%.

Attempts were also made to predict heats of mixing of ternary systems containing hydroxyl groups and methylene groups. Surprisingly good results were also obtained for ternaries.

HEATS OF MIXING OF SOLUTIONS BY A GROUP SOLUTION MODEL

HEATS OF MIXING OF LIQUID SOLUTIONS BY A GROUP SOLUTION MODEL

A

Thesis

by

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To my mother

N.T.H.

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INTRODUCTION

The enthalpy change of mixing represents one of the few practical entry points into the network of functions relating the thermodynamic properties of functions. Vapor-liquid equilibrium data represent another commonly used entry point. Enthalpy change of mixing information is very useful in constructing theories of the liquid state.

In the last few years, data on heats of mixing have become more generally available due primarily to the improvements in calorimetric equipment. This study concerns itself with the application of a group solution model to the prediction of heats of mixing using recently published data for mixtures containing hydrocarbons and alcohols.

In dealing with mixtures of molecules in terms of their constituent groupings of atoms, it should be clear that in some way account must be taken of (1) the interactions of various groups which can occur in solutions and in the standard state, (2) the restrictions imposed upon these interactions by the organization of the groups into molecules, and (3) the organization of the molecules in the solution and in the standard state.

Even for mixtures of simple molecules, the effects are so complicated that completely satisfactory models have yet to be developed. However, what is needed are perhaps less detailed and simpler models.

One of the earliest descriptions of simple mixtures in terms of groups was given by Langmuir (1) some forty years ago. Langmuir stated that the force field around a group of radical is largely independent of the nature of the rest or the molecule.

Butler et al. (2) studied a series of solutes at infinite dilution in a given solvent and observed a simple relation between solute carbon number and its activity coefficients. He also indicated that this relation depends roughly on the nature of the polar grouping.

Some ten years later, Pierotti et al. (3), as had Butler, considered the infinitely dilute solution and determined the dependence of the limiting activity coefficients of families of systems of fixed structural type upon solute and solvent structure. Pierotti, Derr and Redlich (4) further developed a group interaction model which calculates the heats of solution as the sum of contributions from interacting groups proportional to the number of groups present, a group cross-section characteristic of each kind of group, and an interaction energy characteristic of each group pair. It provides a van Laar-like relation for the partial molar excess heats with concentrations expressed in surface fractions.

In a comparison paper, Papadopoulos and Derr (5) provided a preliminary test of this model for hydrocarbon systems. It is still not clear, however, how successful this free energy model can be in treating polar systems.

Recently an extension of the above theoretical model to polar mixtures has been done by Chao et al. (6). The interaction frequencies between groups were considered to be independent on both geometrical and energy properties. The model was tested satisfactorily on alcohol and paraffin systems.

The group solution proposed by Wilson et al. (7) does not restrict the molecular activity coefficients to a van Laar-type relation, but nonetheless estimates the partial molar excess free energy as the sum of the group contributions and provides a concentration dependency on these group contributions. In this case, a 'group' portion of the partial excess free energy is taken as the difference between contributions in solution and molecular standard state,

$$\log \gamma_i^G = \sum_k N_{ki} \left(\log \Gamma_k - \log \Gamma_k^*\right) \tag{1}$$

where the log Γ's represent the group contribution in the solution, the superscripts G and * denote the group contribution and the standard state respectively, and N_{ki} is the number of groups of type k in the solution.

Γ is taken as a function of the group composition,

$$\Gamma_k = f_k \left(X_1, X_2 \dots\right) \tag{2}$$

where

$$X_k = \frac{\sum_i x_i N_{ki}}{\sum_i \sum_k x_i N_{ki}} \tag{3}$$

The molecular activity coefficient is taken as the sum of the group contribution and a contribution concerning the size,

$$\log \gamma_i = \log \gamma_i^G + \log \gamma_i^S \qquad (4)$$

where the size contribution represents the only distribution between the environment of the same group constitution and the different molecular constitution. It is evaluated with a Flory-Huggins-like expression using only the number of groups in the respective molecules of the mixtures:

$$\log \gamma_i^S = \log \frac{N_i}{\sum_i x_i N_i} + 0.4343 \left(1 - \frac{N_i}{\sum_i x_i N_i}\right) \qquad (5)$$

Wilson applied such an approach to two fairly extreme cases - CH_2-OH and CH_2-CN mixtures - making no distinctions between methyl and methylene groups.

As this model is applied to paraffin mixtures, the values obtained are numerically too large. One may think that the size contribution has been overestimated. This conclusion leads to the modified group solution model of Ratcliff and Chao (8) which will be discussed later in detail.

Recently, Scheller (9) has used a 'solution of groups' idea to make a correlation of a broad range of mixtures. The log γ's term was calculated in terms of molar volumes rather than the group numbers. With six base systems involving hydrocarbons and alcohols and water, log γ's appeared to be generally within 10% of experimental values.

Finally, in the most recent paper, Derr (10) has used the analytical solutions of groups approach. The concentration dependencies of log Γ in binary group systems is presented. The technique is particularly attractive for handling complex systems which contain many more kinds of molecules than kinds of groups since fewer adjustable parameters are required.

Thus, it is apparent that the approach of treating liquid mixtures in terms of their constituent groupings can be of considerable practical use.

THEORY

Group Solution Model and Activity Coefficients

Ratcliff and Chao (8) have modified the group solution model of Deal and Wilson (7) to predict excess free energies of liquid mixtures. The model postulates that the non-ideal behavior of a molecule in solution may be broken down into two independent parts. One is associated with the overall skeleton of the molecule and the other with the interactions between the functional groups of the molecule and those present in the solution. In terms of activity coefficients, one can write:

$$\log \gamma_i = \log \gamma_i^S + \log \gamma_i^G \qquad (6)$$

where the subscript i identifies the molecular species, and the superscripts S and G denote the skeletal and group contribution respectively. The skeletal contribution accounts only for the differences in size of the molecules. It can be estimated using the Bronsted and Koefoed (11) correlation for mixtures of n-paraffins:

$$\log \gamma_i^S = B \left(N_i - \sum_j N_j x_j\right)^2 \qquad (7)$$

The summation is over all molecular species in the solution and represents the average size of the molecular skeletons in the solution. For binary mixtures, Equation (2) reduces to:

$$\log \gamma_1^S = B (N_1 - N_2)^2 x_2^2 \qquad (8)$$

The group contribution to log γ_i is assumed to be the sum of the individual contributions of each group present, i.e. all the groups are assumed to act independently. Each group is assumed to be an individual entity in a solution of groups.

A group activity coefficient Γ is defined in a similar manner to a molecular activity coefficient γ,

$$\log \gamma_i^G = \sum_k N_{ki} (\log \Gamma_k - \log \Gamma_k^*) \qquad (9)$$

where N_{ki} = number of groups of type k in molecular species i

and P_k^* = activity coefficient of group k at standard state

And finally, the group solution model postulates that the group activity coefficients are functions of temperature, pressure and composition:

$$\log \Gamma_k = f_k [X_1, X_2 \ . \ . \ . \ X_k, T, P] \qquad (10)$$

where

$$X_k = \frac{\sum_j x_j N_{kj}}{\sum_k \sum_j N_{kj} x_j} \qquad (11)$$

Group Solution Model and Heats of Mixing

The model has been extended to heats of mixing of liquid mixtures. The molar heats of mixing of liquid mixtures can be expressed in a similar manner to the activity coefficients:

$$\Delta H^M = \Delta H^S + \Delta H^G \qquad (12)$$

where the superscript M denotes the mixing function, and S and G denote the skeletal and group contributions as before.

The skeletal contribution to heats of mixing accounts only for the difference in size of the molecules, and could be estimated from the heats of mixing of mixtures of n-paraffins, as in this case. There are no specific group interactions.

The group contribution to ΔH^M is assumed to be the sum of the individual contributions to each group present, i.e. all the groups are again assumed to act independently and the excess enthalpy of a group, H, is defined as:

$$\overline{\Delta H_i^G} = \sum_k N_{ki} \left(H_k - H_k^*\right) \qquad (13)$$

where N_{ki} = number of groups of type k in molecular species i

and H_k^* = excess enthalpy of group k at standard state.

The standard state chosen for a group is that of the pure molecular species i under consideration. This agrees with normal practice, and assures that the partial molar heats of mixing are zero for pure compounds.

The same group must be referred to different standard states, depending on the molecular species under consideration. Thus, if aliphatic alcohols are considered to be made up of methylene and hydroxyl groups, then the standard state of the hydroxyl group in n-butanol is a state in a solution containing 20 group % hydroxyl and 80 group % methylene. The standard state of n-hexane is a state containing 100 group % methylene.

The definition of the standard state of the excess enthalpies of group k is computed by specifying the temperature and pressure. The final postulate of the group solution model is that the excess enthalpies of group k are functions only of group composition, temperature and pressure:

$$H_k = f_k (X_1, X_2 \ldots X_k, T, P) \qquad (14)$$

where X_k is given by Equation (11),

$$X_k = \frac{\sum_j x_k N_{kj}}{\sum_k \sum_j x_j N_{kj}}$$

Equations (13) and (14) assume that the molecular forces acting on a group and on a whole molecule are uniquely determined by the average group composition of the solution, i.e. are independent of how the groups are joined together in the molecules.

The importance of the group solution model is that it enables us to calculate the properties of any mixture from known data on other mixtures of similar molecular groups.

PREDICTION METHOD

Requirements for Testing the Model

The data for a test of the model should satisfy the following requirements:

1. Heat-of-mixing data should be available as a function of composition. The composition range should be as wide as possible.
2. The data should be at the same temperature and pressure.
3. The number of the groups present in the mixture must be greater than the number of molecular species, since otherwise there are insufficient equations to determine heats of mixing.

A literature survey of heat-of-mixing data for systems containing n-paraffins and aliphatic alcohols has been done, as shown in Table 1.

These mixtures could be regarded as mixtures of groups of methylene and hydroxyl. Methyl groups are regarded as equivalent to methylene so that a paraffin molecule consists entirely of methylene. Aliphatic alcohols consist partly of methylene and partly of hydroxyl groups.

TABLE 1

Data Sources on Excess Properties of Mixing

System	Range, °C	Data Source
n-hexane + n-hexadecane	20, 30, 40, 50	12
n-octane + n-tetradodecane	76	13
n-hexane + n-hexadecane	20	14
n-pentane + n-hexadecane	"	"
n-heptane + n-hexadecane	"	"
n-octane + n-hexadecane	"	"
n-nonane + n-hexadecane	"	"
n-pentane + n-decane	"	"
n-hexane + n-hexadecane	40, 51, 60, 76	15
n-octane + n-tetradodecane	51, 76	"
n-hexane + n-tetradodecane	60, 76, 96, 106	"
n-hexane + n-hexatridecane	76	"
n-octane + n-ditridecane	"	"
n-heptane + n-hexatridecane	"	"
n-nonane + n-hexatridecane	"	"
n-hexane + n-hexatridecane	"	"
n-decane + n-hexadecane	as f(T)	16
n-octane + n-hexane	"	"
n-heptane + n-hexadecane	"	"
n-hexane + n-hexadecane	"	"

TABLE 1 (cont.)

System	Range, °C	Data Source
ethanol + n-decanol	25	17
ethanol + n-hexane	30, 45	18
n-propanol + n-heptane	" "	"
ethanol + n-nonane	" "	"
n-butanol + n-heptane	" "	"
n-pentanol + n-hexane	" "	"
n-octanol + n-heptane	" "	"
n-octanol + n-nonane	" "	"
n-hexanol + n-heptane	35, 45	19
n-decanol + n-heptane	" "	"
n-butanol + n-undecane	" "	"
n-hexanol + n-undecane	" "	"
methanol + water (high dil.)	4.75, 15, 25	20
ethanol + water " "	35	"
n-propanol + water " "	"	"
i-propanol + water " "	"	"
n-butanol + water " "	"	"
t-butanol + water " "	"	"
methanol + water	25	21
2-propanol + water	"	"
ethanol + water	"	"
1-propanol + water	"	"

TABLE 1 (cont.)

System	Range, °C	Data Source
methanol + water (high dil.)	25	22
ethanol + water " "	"	"
n-propanol + water " "	"	"
n-butanol + water " "	"	"
n-pentanol + water " "	"	"
n-hexanol + water " "	"	"
methanol + n-hexane	30, 45, 64	23
ethanol + n-heptane	30, 60	"
ethanol + n-hexane	30, 35	"
ethanol + cyclohexane	25, 35	"
n-propanol + n-heptane	30, 40, 45	"
isopropanol + n-heptane	30, 45, 60	"
ethanol + n-octane	20, 25, 30	24
n-heptane + n-propanol + n-pentanol	25	"
n-tetradecane + n-propanol + n-octanol	"	"
n-heptane + n-octanol	"	"
n-heptane + n-pentanol	"	"
n-heptane + n-propanol	"	"
n-heptane + n-ethanol	"	"
n-heptane + n-decanol	"	"

TABLE 1 (cont.)

System	Range, ^{o}C	Data Source
methanol + n-hexane	45	25
ethanol + n-hexane	25, 35, 45	"
n-propnaol + n-hexane	" " "	"
n-butanol + n-hexane	" " "	"
n-hexanol + n-hexane	" " "	"
n-octanol + n-hexane	" " "	"
ethanol + n-hexane	30	6
ethanol + n-nonane	"	"
n-pentanol + n-hexane	"	"
n-butanol + n-heptane	"	"
n-octanol + n-heptane	"	"
n-octanol + n-nonane	"	"
methanol + n-hexane	25, 30, 34, 40, 45, 50	26
methanol + n-heptane	30, 45, 60	"
methanol + n-butanol	25	27
ethanol + n-butanol	"	"
n-propanol + n-butanol	"	"
n-butanol + n-hexanol	"	"
n-butanol + n-octanol	"	"
n-butanol + n-decanol	"	"
methanol + n-octanol	"	"

TABLE 1 (cont.)

System	Range, °C	Data Source
ethanol + n-octanol	25	27
n-propanol + n-octanol	"	"
n-hexanol + n-octanol	"	"
n-octanol + n-decanol	"	"
ethanol + n-heptane	20, 25, 30	28
n-propanol + n-heptane	" " "	"
n-pentanol + n-heptane	" " "	"
n-octanol + n-heptane	" " "	"
n-decanol + n-heptane	" " "	"
ethanol + n-octane	" " "	"
n-propanol + n-octane	" " "	"
n-pentanol + n-octane	" " "	"
n-decanol + n-octane	" " "	"
n-octanol + n-octane	" " "	"
n-propanol + n-tetradecane	" " "	"
n-pentanol + n-tetradecane	" " "	"
n-octanol + n-tetradecane	" " "	"
n-decanol + n-tetradecane	" " "	"
ethanol + n-propanol	" " "	"
ethanol + n-pentanol	" " "	"
ethanol + n-octanol	" " "	"
ethanol + n-decanol	" " "	"
n-propanol + n-pentanol	" " "	"

TABLE 1 (cont.)

System	Range, °C	Data Source
n-propanol + n-octanol	20, 25, 30	28
n-propanol + n-decanol	" " "	"
n-pentanol + n-octanol	" " "	"
n-pentanol + n-decanol	" " "	"

Treatments of Heat-of-Mixing Data

The greatest difficulty in fitting the heat-of-mixing data is thought to be due to the extreme skewness of the heat-of-mixing curve. It was almost impossible to achieve a good fit in the dilute-composition regions. Attempts to fit the data directly, i.e. to fit ΔH^M data against composition by power series would be very unsuccessful since the fitted curve could show inflection points, as is shown in Figure 1.

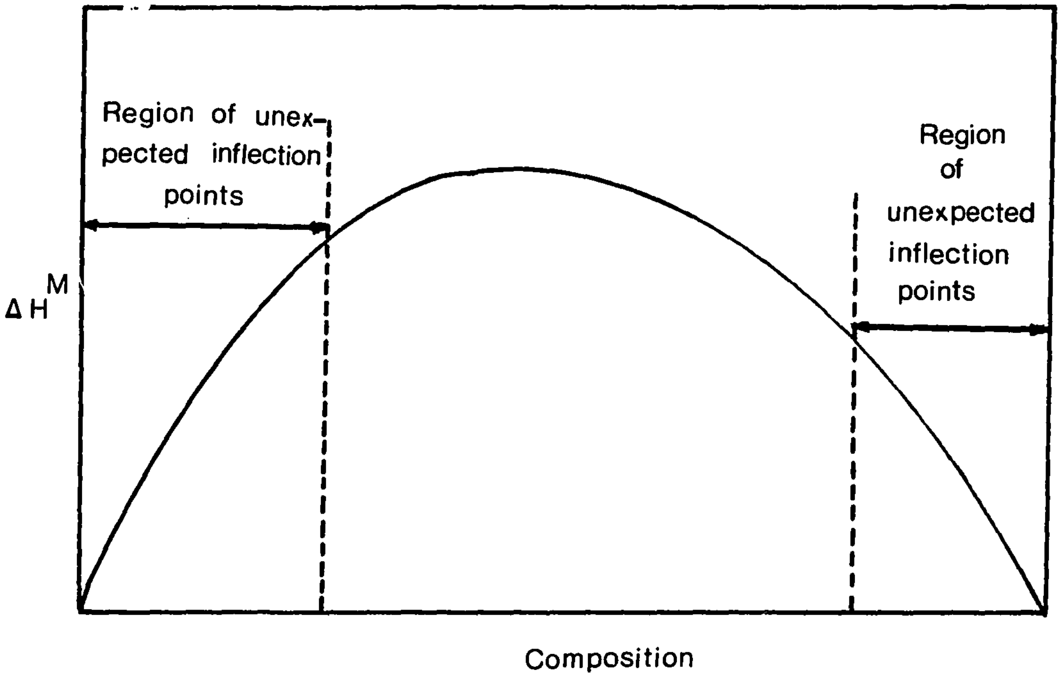


FIGURE 1

This is particularly important since the data are to be differentiated. Accuracy in representing these curves seemed to be related to the steepness of the curves in one or more parts of the composition interval as compared with other parts.

Van Ness (29) recently pointed out that one of the best ways to treat the thermodynamic excess data is the spline-fit method. This is a method for smoothing, interpolating and differentiating data. This method is very acceptable, as no unwarranted inflection points could be introduced.

The spline-fit technique was first introduced by Landis and Nelson (30). This method puts a different cubic between two successive data points such that the curves pass exactly through each of the two data points, and the first two derivatives of the curve on the right-hand side of the data point are equal respectively to the first two derivatives of the curve on the left-hand side of the data point, all derivatives being evaluated at the data point.

Since the curves pass exactly through each data point, the spline-fit accomplishes no smoothing of the data and represents random errors in the data at least as faithfully as it does the large scale trends. Van Ness (31) modified this method by defining interval boundaries in such a way that each interval may contain a number of data points. The extended method thus provides a means of smoothing the data.

For our heat-of-mixing data, the smoothed curves of $\Delta H^M/x_1 x_2$ were extrapolated to reasonable intercepts if possible, and these values were used to anchor the end point (Figure 2), although the extrapolation is not really necessary.

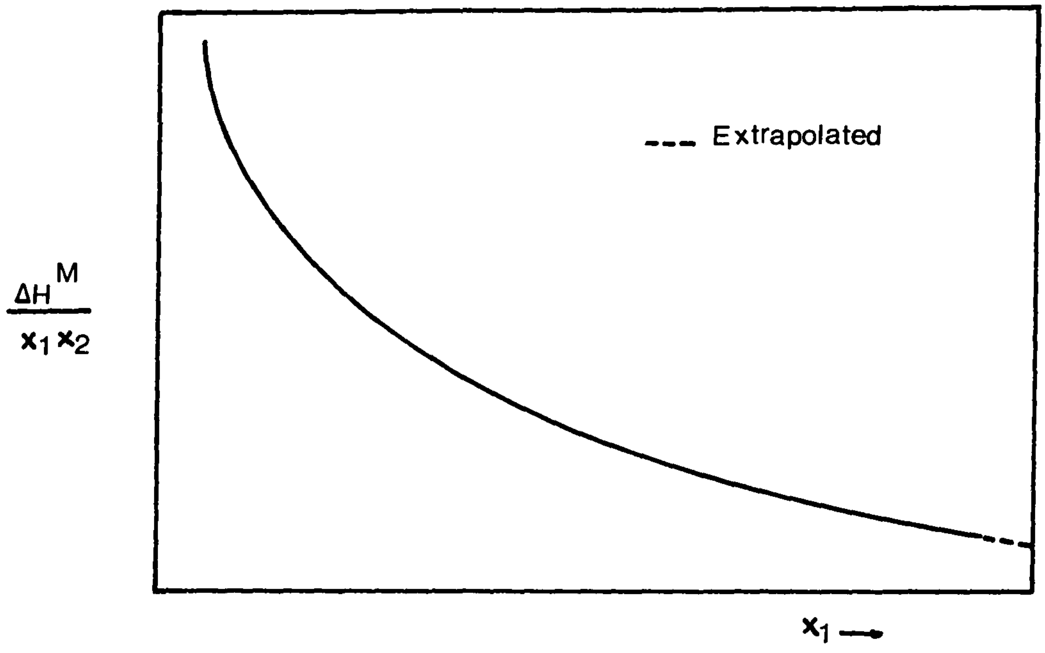


FIGURE 2

The n-butanol + n-hexane system was chosen as the base system in computing the group excess enthalpies because of the following advantages:

- The two components of the system have the shortest size lengths in the sense that the skeletal contribution of this system, i.e. the heats of mixing of the n-pentane + n-hexane system, can be easily estimated.
- The curves $\Delta H^M/x_1\ x_2$ are shown in Figure 3. No inflection point could be introduced and hence, there is a better chance of fitting them.

The partial molar heats of mixing are calculated from the first derivatives of the spline-fit of $\Delta H^M/x_1\ x_2$,

$$\overline{\Delta H}_1^M = x_2^2 \left(y + x_1 \frac{\partial y}{\partial x_1}\right) \tag{15}$$

$$\overline{\Delta H}_2^M = x_1 \left(y - \frac{\overline{\Delta H}_1^M}{1 - x_1}\right) \tag{16}$$

where

$$y = \frac{\Delta H^M}{x_1 \; x_2} \tag{17}$$

n-butanol + n-hexane system at 25 and 45°C

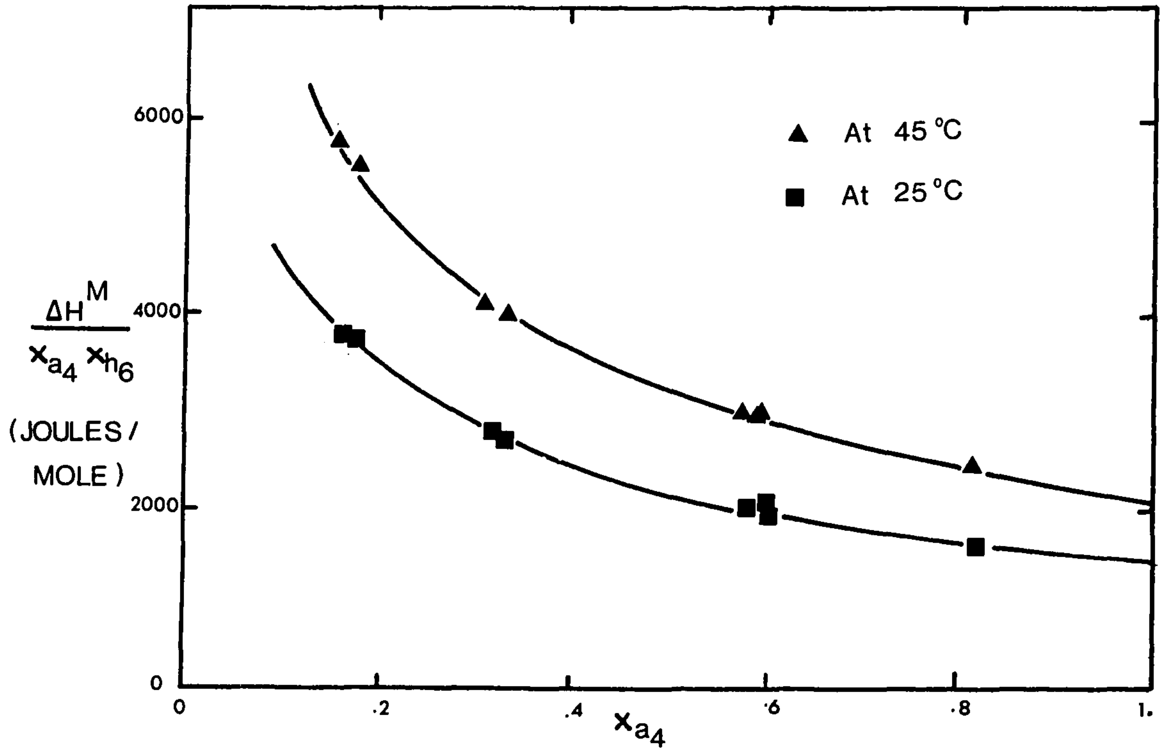


FIGURE 3

Determination of Group Excess Enthalpies from Published Data

In order to cover the whole range of group compositions, the skeletal heats of mixing of short-chained binary mixtures must be available. Heat-of-mixing data for some short-chained mixtures of n-alkanes, e.g. methane + n-propane (32), are reported at very low temperatures (- 173°C). Corrections for temperature would be very dangerous.

It was thought that one could back-calculate the skeletal contributions of these short-chained mixtures. The partial molar heats of mixing of different series of mixtures of the same one component were computed and plotted against the group fraction (Figures 4-6); for example, for n-propanol systems, $\overline{\Delta H}^M_{a_3}$, the partial molar heats of mixing of n-propanol in different n-propanol mixtures, were plotted against X_{CH_2}. These curves exhibit similar shapes and are almost congruent. From Equation (7),

$$\overline{\Delta H}^M_{a_3} = 3\ (\overline{H}_{CH_2} - H^*_{CH_2}) + (H_{OH} - H^*_{OH}) + \overline{\Delta H}^S_{a_3} \qquad (18)$$

One can see that at certain methylene group compositions, the differences among these curves must be due to the last term in Equation (18), i.e. to the skeletal heat of mixing. The same conclusion is also true for n-butanol systems.

However, for the water series (Figure 6), these curves behave differently. The curves of the partial molar heats of mixing of water, $\overline{\Delta H}^M_{OH}$, in the three water + alcohol systems have markedly odd shapes, and the skeletal contribution of these systems could be very large (e.g. $\sim 10^3$), as indicated by the differences among these curves. Thus, it is not easy to back-calculate this term. The problem of estimating the skeletal heats of mixing of short-chained systems remains unsolved.

In the present work, attempts will be made to predict heats of mixing of long-chained mixtures of n-alkanes and n-alcohols only.

FIGURE 4

Plots of $\overline{\Delta H}^{M}_{a_3}$ versus X_{CH_2} for

n-propanol systems at 25°C

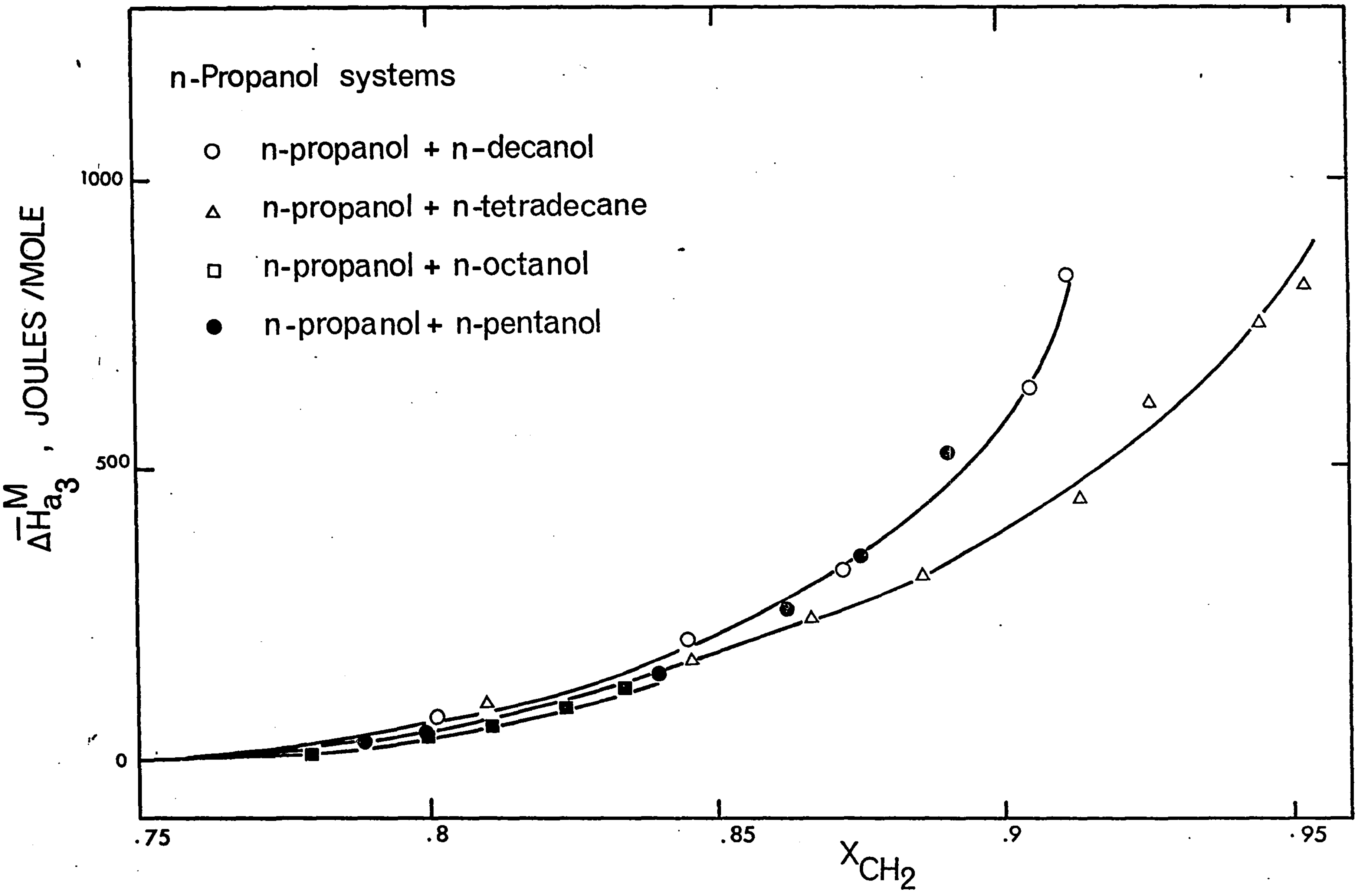

n-Propanol systems
○ n-propanol + n-decanol
△ n-propanol + n-tetradecane
□ n-propanol + n-octanol
● n-propanol + n-pentanol
$\overline{\Delta H}^{M}_{a_3}$, JOULES /MOLE
1000
500
0
.75
.8
.85
.9
.95
X_{CH_2}

FIGURE 5

Plots of $\overline{\Delta H}^{M}_{a_4}$ versus X_{CH_2} for n-butanol systems at 25°C

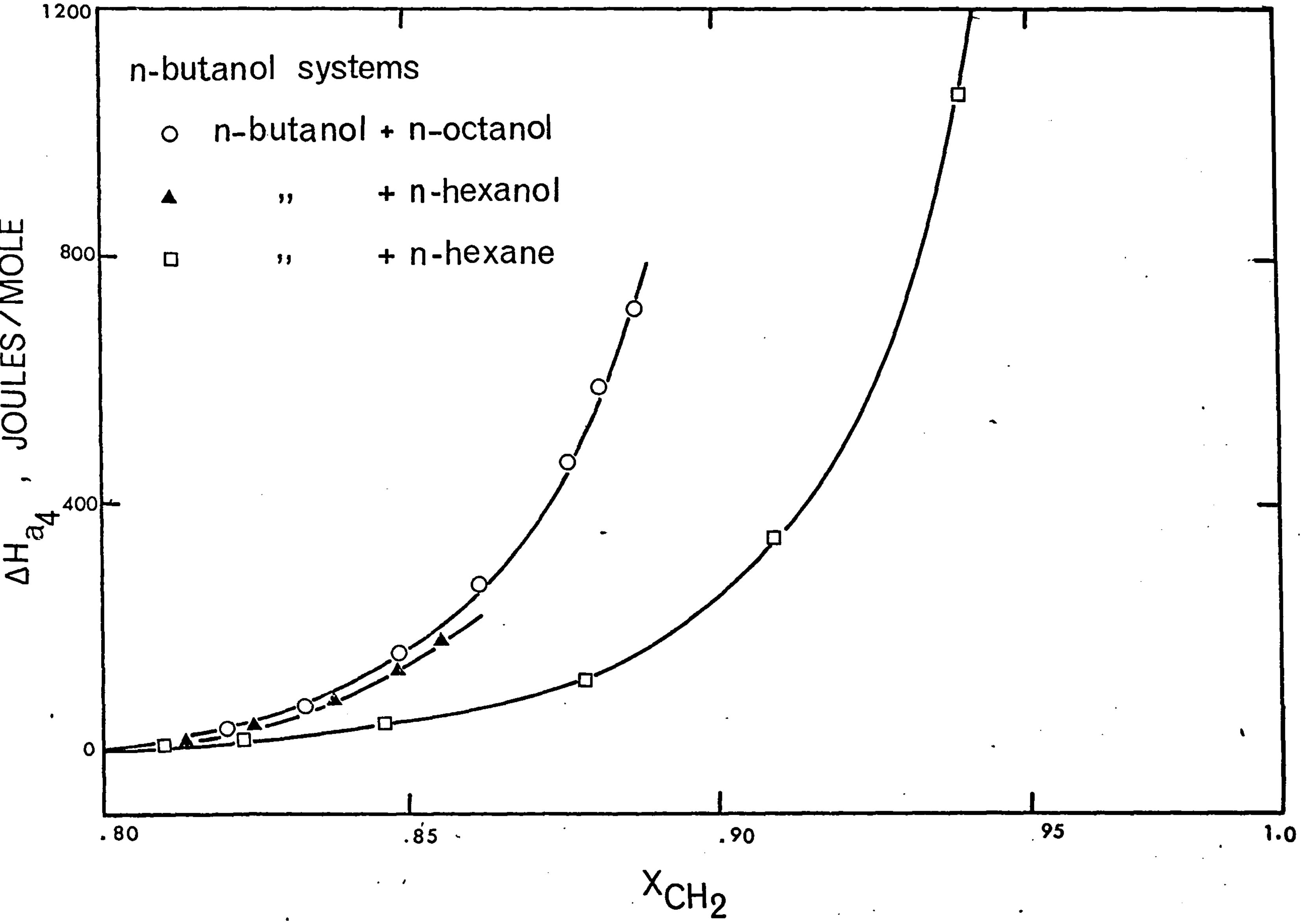
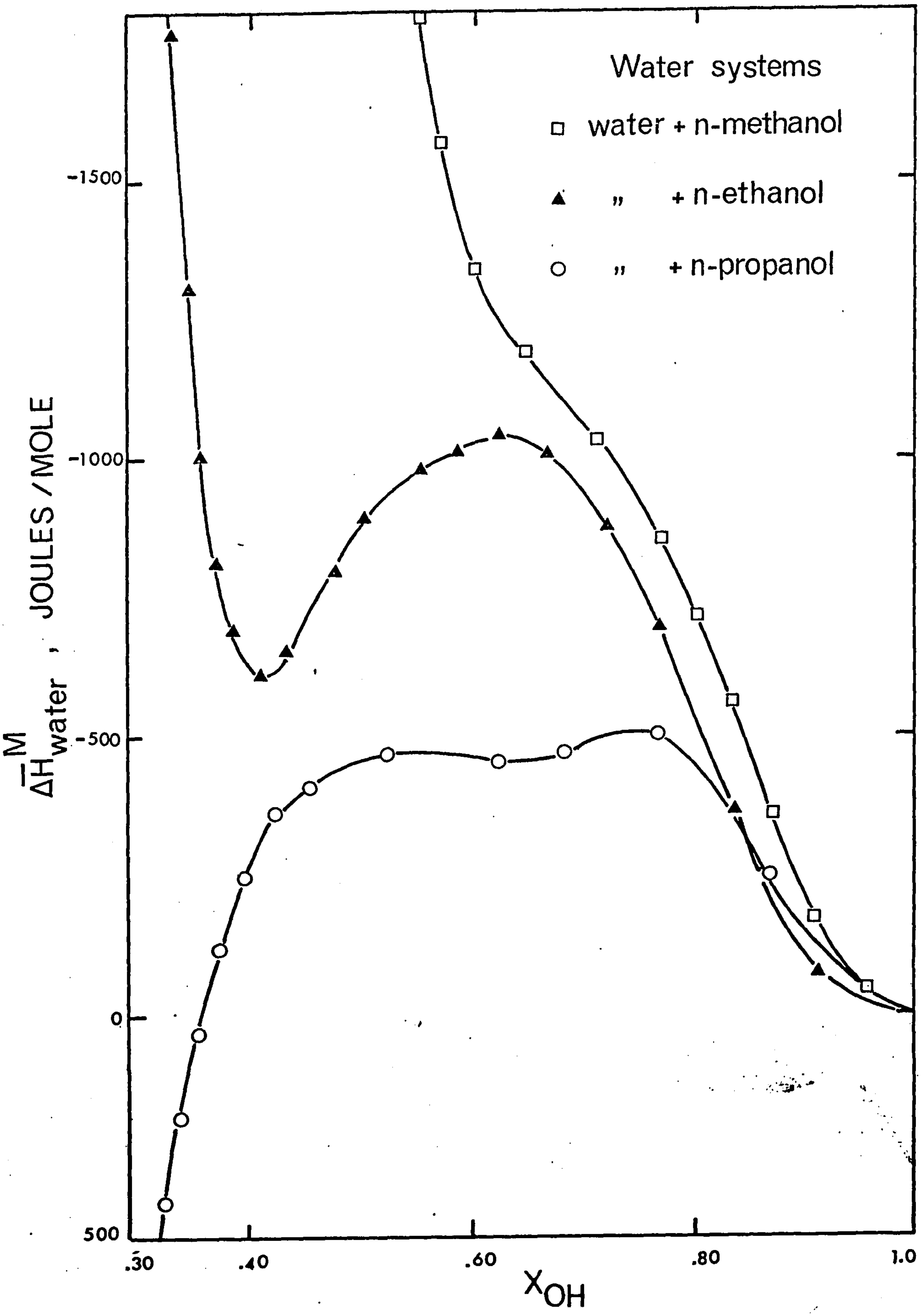

n-butanol systems
○ n-butanol + n-octanol
▲ ,, + n-hexanol
□ ,, + n-hexane
$\overline{\Delta H}_{a_4}^{M}$, JOULES/MOLE
1200
800
400
0
.80
.85
.90
95
1.0
X_{CH_2}

FIGURE 6

Plots of $\overline{\Delta H}^{M}_{H_2O}$ versus X_{OH} for water systems at 25°C


Water systems
□ water + n-methanol
▲ " + n-ethanol
○ " + n-propanol
-1500
-1000
-500
0
500
$\overline{\Delta H}^{M}_{water}$, JOULES / MOLE
.30
.40
.60
.80
1.0
X_{OH}

The group excess enthalpies for mixtures of methylene and hydroxyl groups were computed from the data of Brown, Fock and Smith (25) on the system n-butanol + n-hexane at 25°C and 45°C. The skeletal contribution is practically negligible in this mixture; for example, at 20°C, the heats of mixing of the n-pentane + n-hexane mixture are of the order of 1 to 2 joules/mole as calculated from the data of McGlashan and Morcom (12). Hence,

$$H_{CH_2} = \frac{1}{6}\,\overline{\Delta H}_{hexane} \tag{19}$$

The standard state of group excess enthalpy $H^*_{CH_2}$ is zero for a paraffin and hence does not appear in Equation (19). Computed group excess enthalpies H_{CH_2} are shown in Figure 7 for the methylene group fraction ranging from 0.80 to 1.0.

For the evaluation of H_{OH}, we first extrapolated H_{CH_2} to a methylene group fraction of 0.80, since this corresponds to the standard state concentration of the groups in pure n-butanol. For methylene in n-butanol, we thus find:

$$H^*_{CH_2} = 210. \tag{20}$$

Rearranging Equation (8):

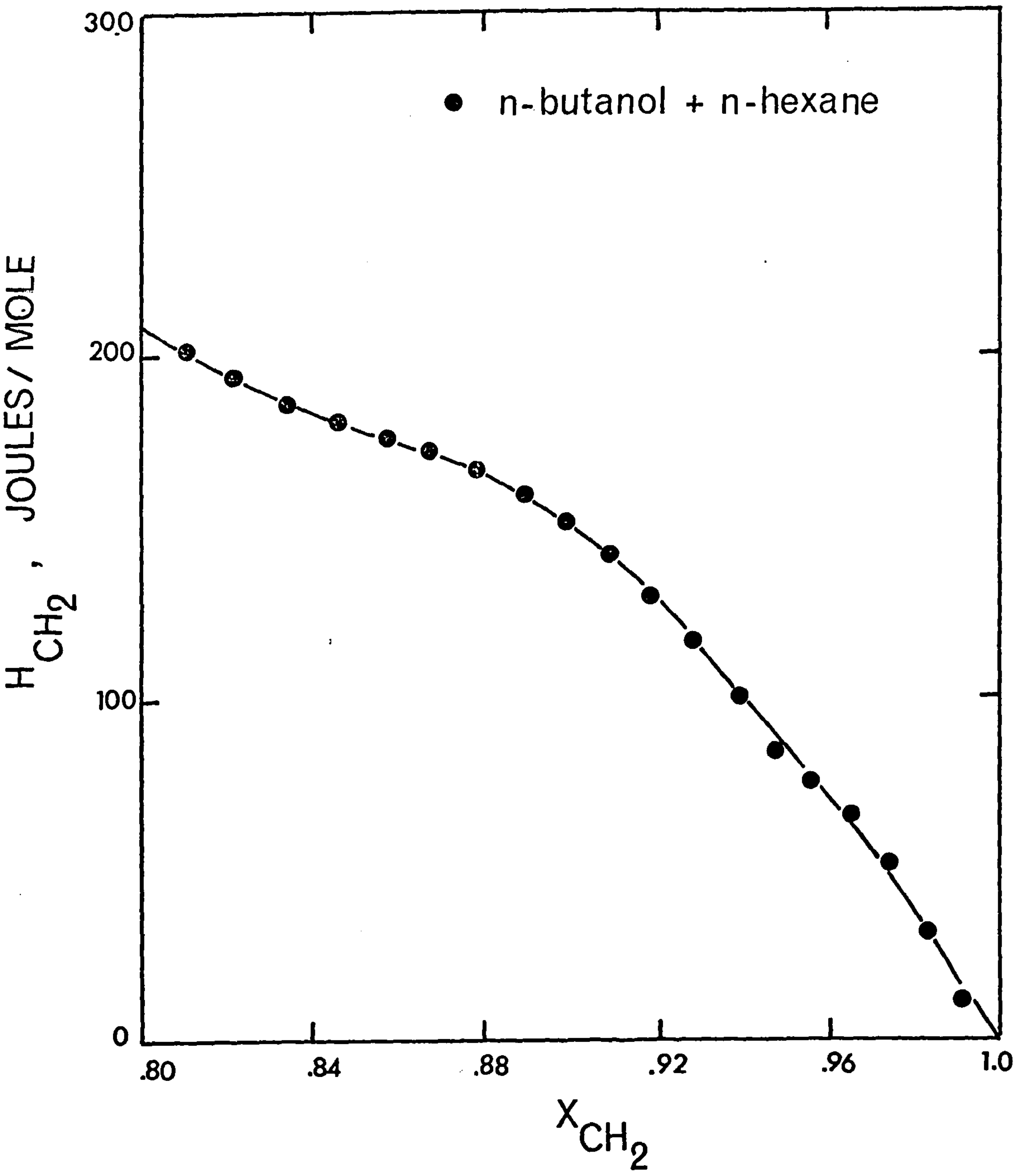
$$H_{OH} = \overline{\Delta H}_{butanol} - 4\,(H_{CH_2} - H^*_{CH_2}) \tag{21}$$

H^*_{OH} of n-butanol is chosen to be zero. Here we are concerned with the difference in group excess enthalpies; therefore the standard state chosen for the reference system is quite arbitrary.

FIGURE 7

Excess Enthalpies of CH_2 Group

at 25°C



● n-butanol + n-hexane
H_{CH_2} , JOULES/ MOLE
300
200
100
0
.80
.84
.88
.92
.96
1.0
X_{CH_2}

The computed values of H_{OH} are shown in Figure 8. Figures 7 and 8 are incomplete in the group composition range, but nevertheless could be used for testing the model on mixtures of long chains.

Data of the same system at $45^{o}C$ were used to determine the excess enthalpies of methylene and hydroxyl groups in a similar manner as at $25^{o}C$. Results are shown on Figures 9 and 10.

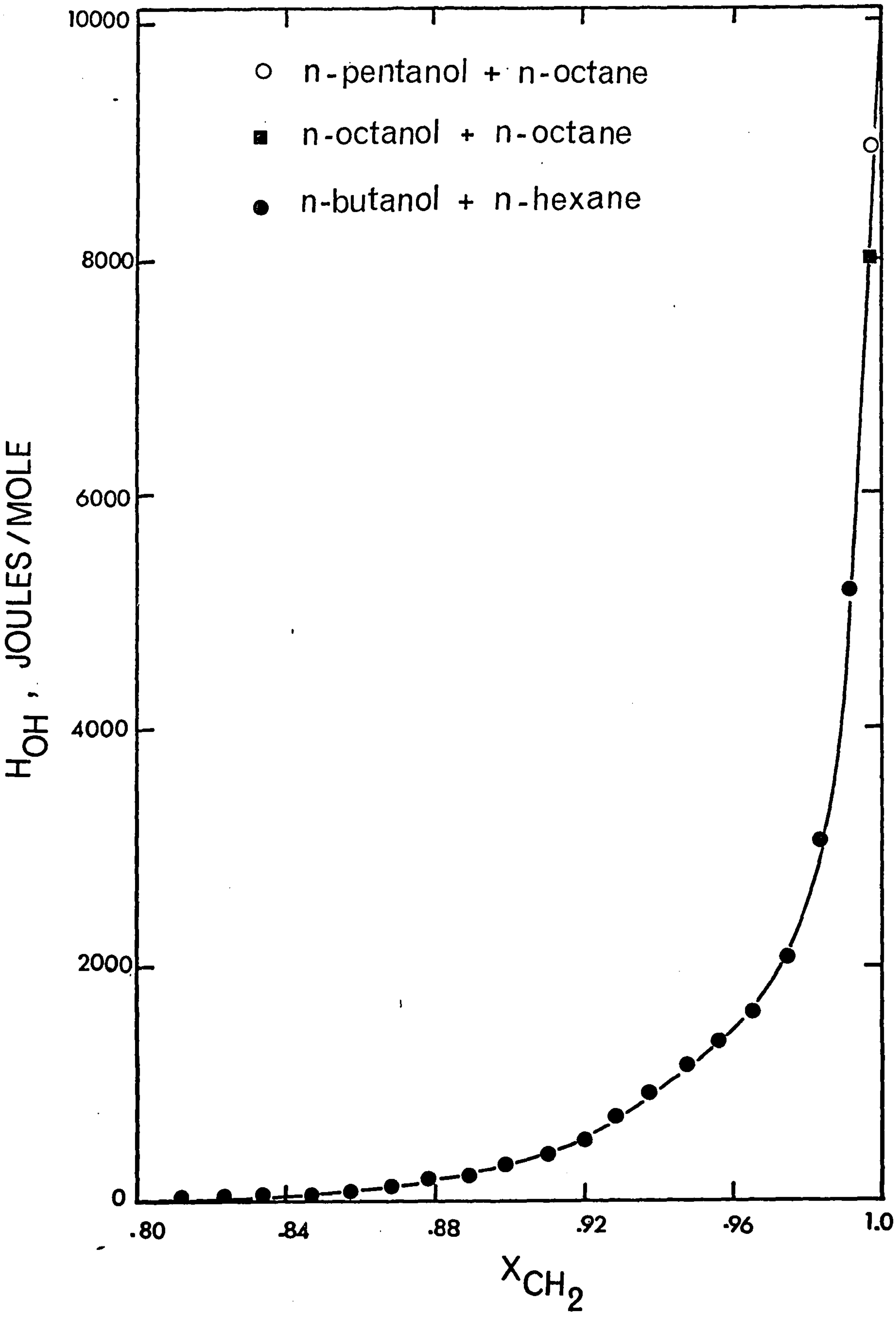
The gap in the group composition data for the reference system was filled by the data of Ramalho and Ruel (24) for the systems n-octanol + n-octane and n-pentanol + n-octane at $25^{o}C$, and by the data of Van Ness (18) for the system n-octanol + n-octane at $45^{o}C$. Fitted parameters for H_{OH} and H_{CH_2} are tabulated on Table 2, the Forsythe polynomial method (33) being used.

If the group solution model is satisfactory, these curves should represent the non-ideal behavior of long-chained paraffin and n-alcohol solutions at the two temperatures. Interpolation and slight extrapolation should be satisfactory.

FIGURE 8

Excess Enthalpies of OH Group

at 25°C

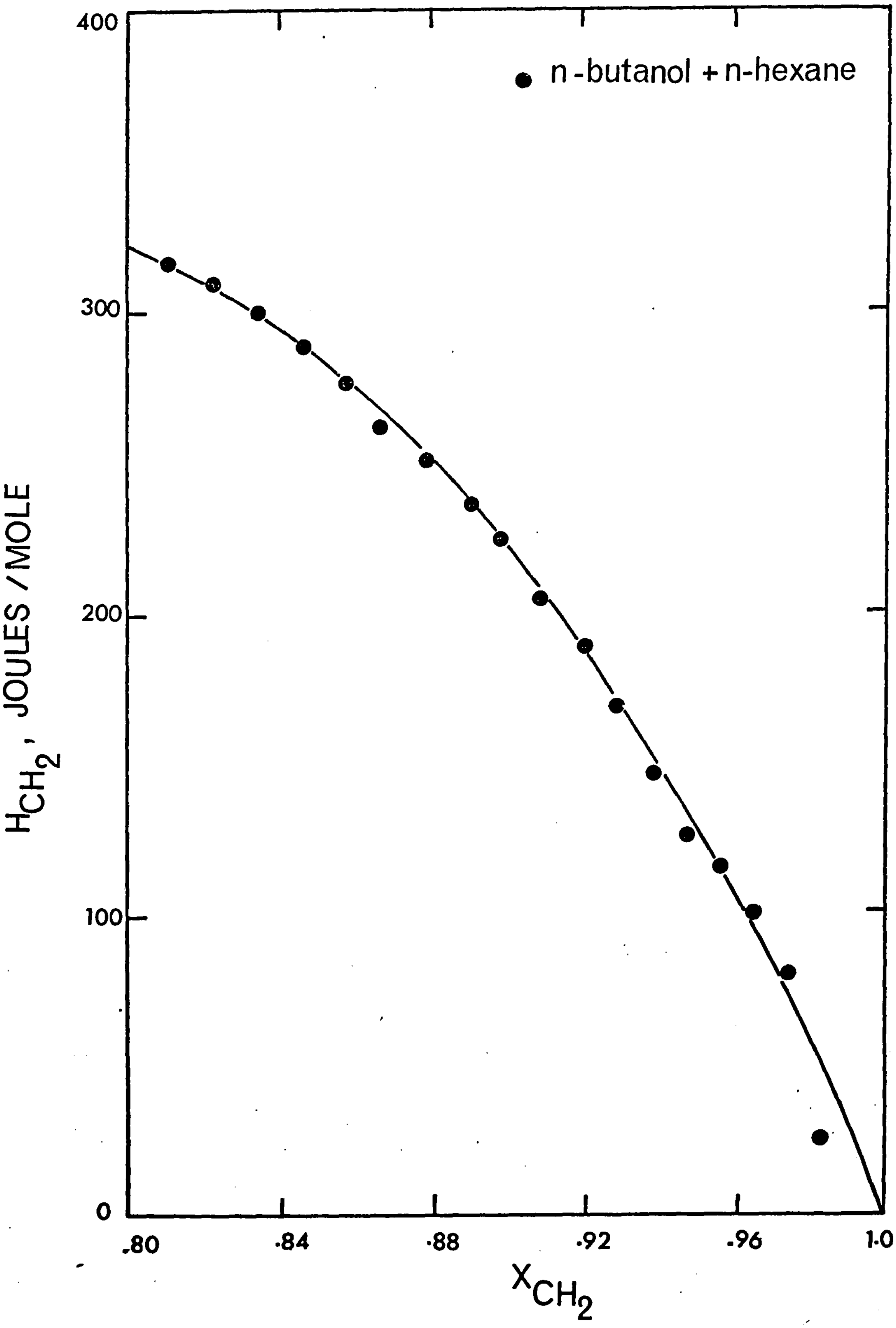


○ n-pentanol + n-octane
■ n-octanol + n-octane
● n-butanol + n-hexane
H_{OH}, JOULES/MOLE
10000
8000
6000
4000
2000
0
.80
.84
.88
.92
.96
1.0
X_{CH_2}

FIGURE 9

Excess Enthalpies of CH_2 Group

at 45°C

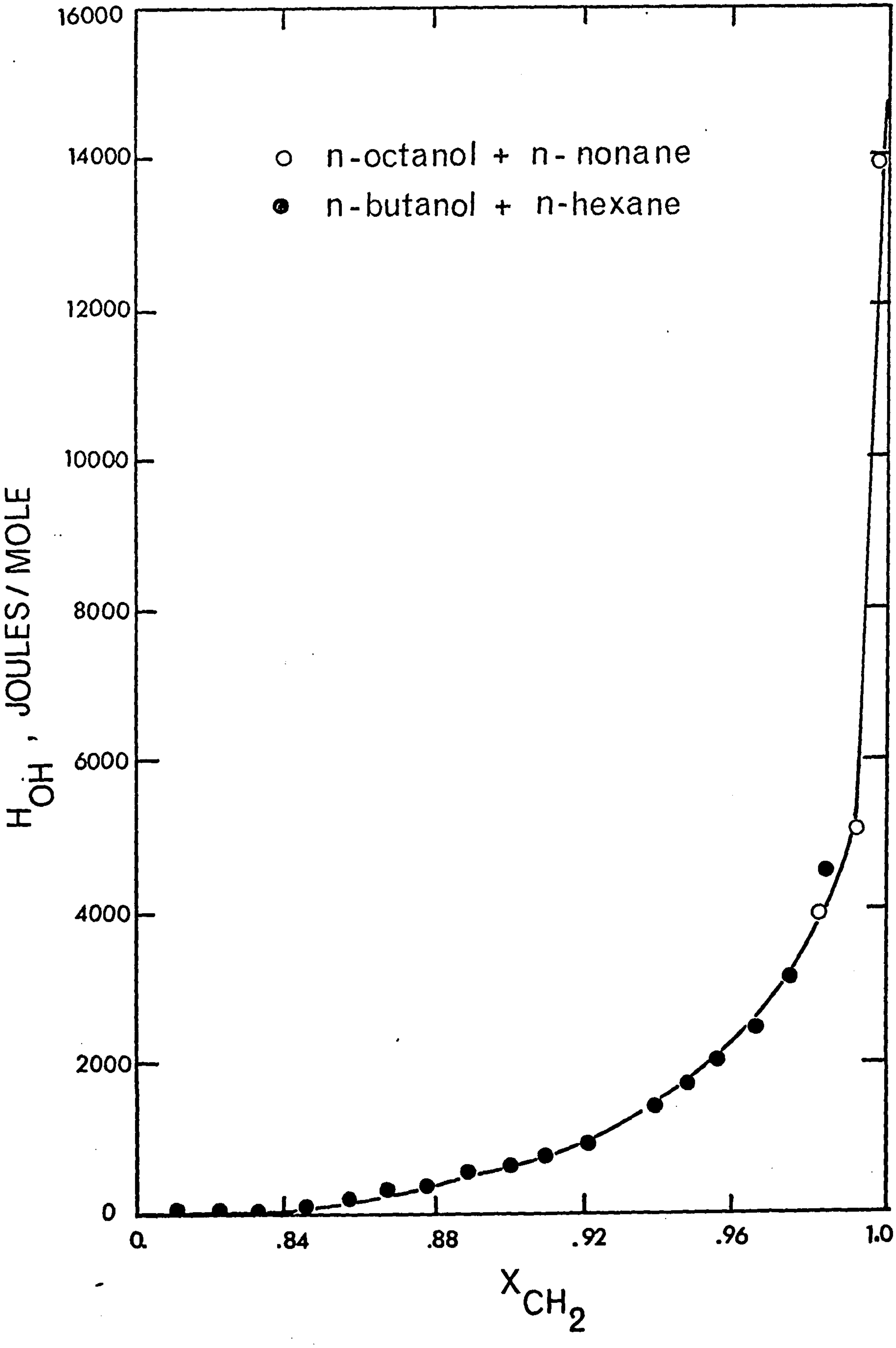


● n-butanol + n-hexane
H_{CH_2}, JOULES / MOLE
400
300
200
100
0
.80
.84
.88
.92
.96
1.0
X_{CH_2}

FIGURE 10

Excess Enthalpies of OH Group

at 45°C



16000
14000
12000
10000
8000
6000
4000
2000
0
○ n-octanol + n-nonane
● n-butanol + n-hexane
H_{OH} , JOULES / MOLE
0.
.84
.88
.92
.96
1.0
X_{CH_2}

TABLE 2

Fitted Parameters for Group Excess Enthalpies

$$y = \sum_m A_m X_{CH_2}^m$$

Coefficients	$A_0 \times 10^{-3}$	$A_1 \times 10^{-3}$	$A_2 \times 10^{-3}$	$A_3 \times 10^{-3}$	$A_4 \times 10^{-3}$
$\underline{T = 25^oC}$					
$y = H_{CH_2}$	- 2.8647449	7.6687539	- 4.80141	-	-
$y = \text{Ln } H_{OH}$ $(0.80 < X_{CH_2} < 0.9444)$	- 14.3709	64.5469	- 108.6505	81.2403	- 22.759754
$y = \text{Ln } H_{OH}$ $(0.9444 < X_{CH_2} < 0.9916)$	0.15209	- 0.33038	0.1870599	-	-
$y = H_{OH}$ $(0.9916 < X_{CH_2} < 1.0)$	659.285	- 649.285	-	-	-

TABLE 2 (cont.)

Coefficients	$A_0 \times 10^{-3}$	$A_1 \times 10^{-3}$	$A_2 \times 10^{-3}$	$A_3 \times 10^{-3}$	$A_4 \times 10^{-3}$
<u>$T = 45^oC$</u>					
$y = \text{Ln}\ H_{CH_2}$	- 3.77753	17.27207	- 29.5606	22.4841	- 64.14875
$y = \text{Ln}\ H_{OH}$ $(0.80 < X_{CH_2} < 0.9286)$	10.18123	- 49.91294	90.916313	- 73.024188	21.185534
$y = \text{Ln}\ H_{OH}$ $(0.9286 < X_{CH_2} < 1.0)$	- 1.13124	3.5962285	- 3.8078923	1.3518303	-

PREDICTION RESULTS

Binary Mixtures

The model has been tested using the data of Ramalho and Ruel (24) at 25°C, and of Brown, Fock and Smith (25) and Van Ness (26) at 45°C.

The skeletal contributions in these mixtures were evaluated from n-hexane + n-hexadecane heat-of-mixing data, using the limited principle of congruence formulated by Holleman and Hijmans (15):

$$\Delta H^S(N_1, N_2, n) = \Delta H^S(6, 16, n) - \frac{N_2-6}{16-6}\Delta H^S(6, 16, N_1) - \frac{16-N_1}{16-6}\Delta H^S(6, 16, N_2) \qquad (22)$$

Equation (22) is shown graphically in Figure 11.

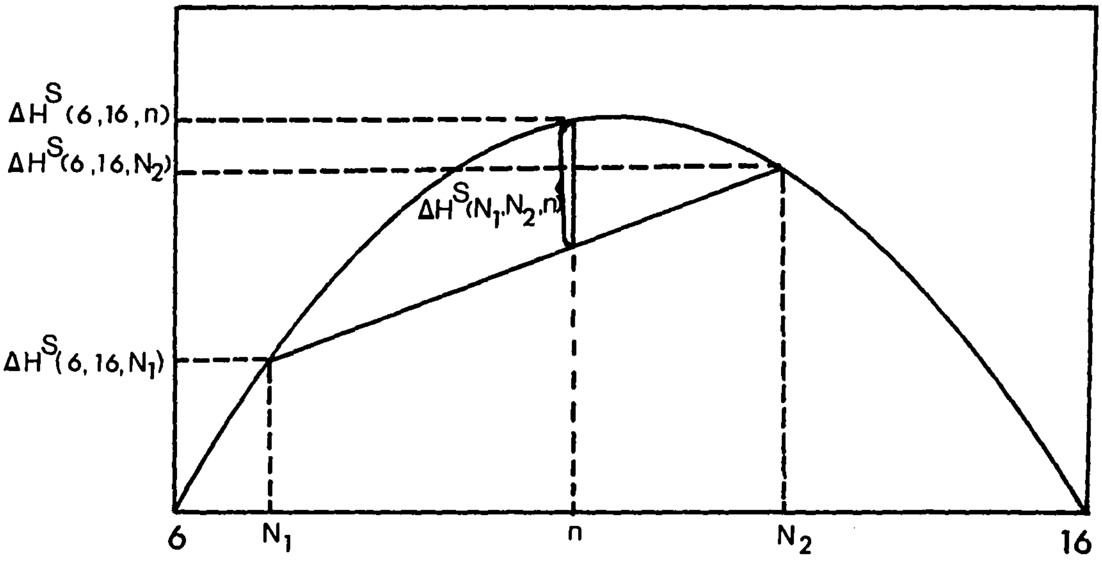


FIGURE 11

The four mixtures referred to in Equation (22) are:

1. (N_1, N_2, n) is the mixture for which the values of skeletal heats of mixing are to be computed.
2. $(6, 16, n)$ refers to a reference system having the same average number of carbon atoms equal to n.
3. $(6, 16, N_1)$ is the mixture corresponding to the reference system having an average number of carbon atoms equal to N_1.
4. $(6, 16, N_2)$ is the mixture corresponding to the reference system having an average number of carbon atoms equal to N_2.

Predicted results are shown in Figures 12-25. The root-mean-square deviations from the experimental data are tabulated in Table 3.

The model thus correctly predicts the heats of mixing of n-alcohol and n-alkane mixtures.

FIGURE 12

Heats of Mixing at 25°C for the System

n-pentanol + n-heptane

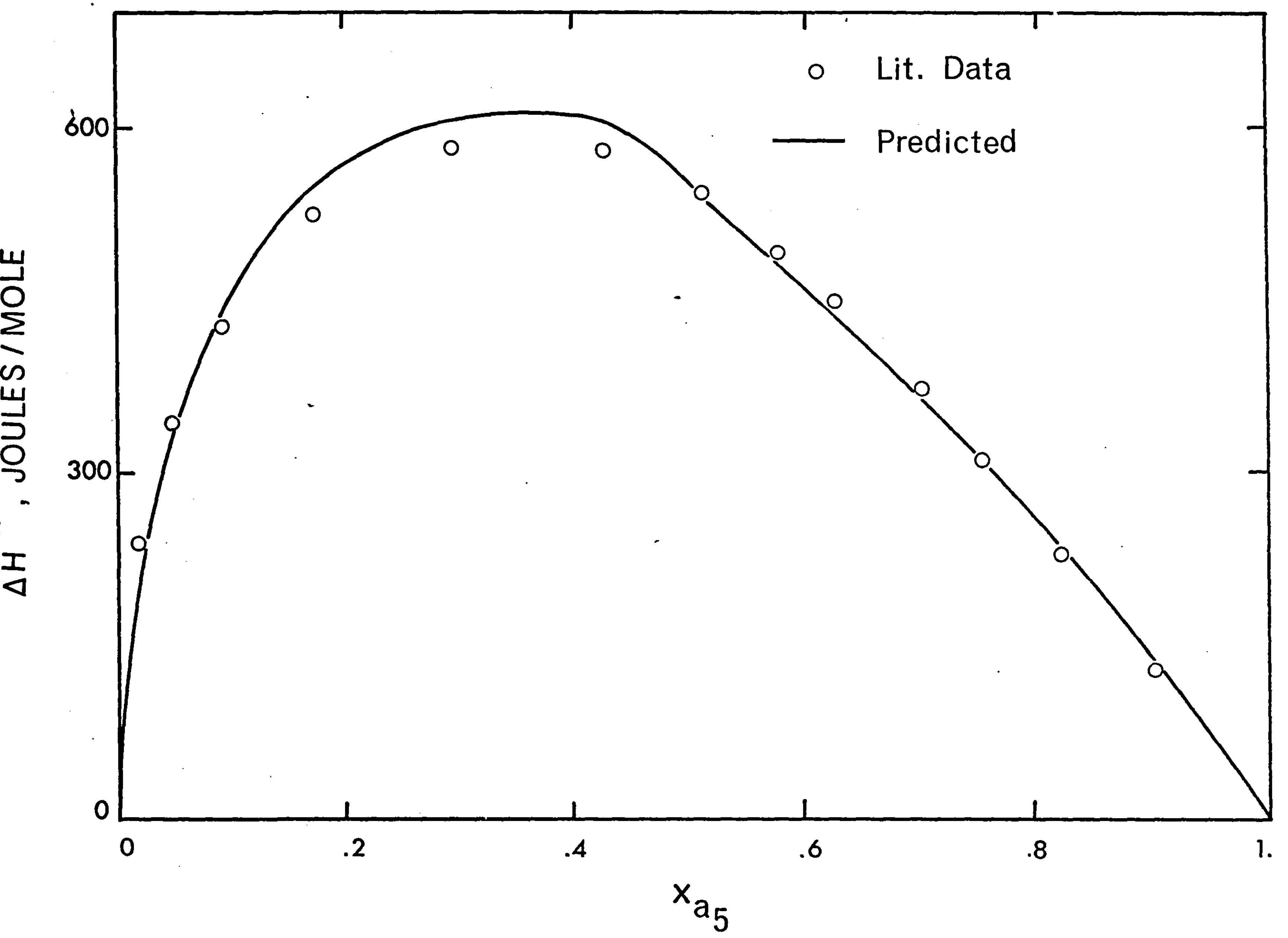
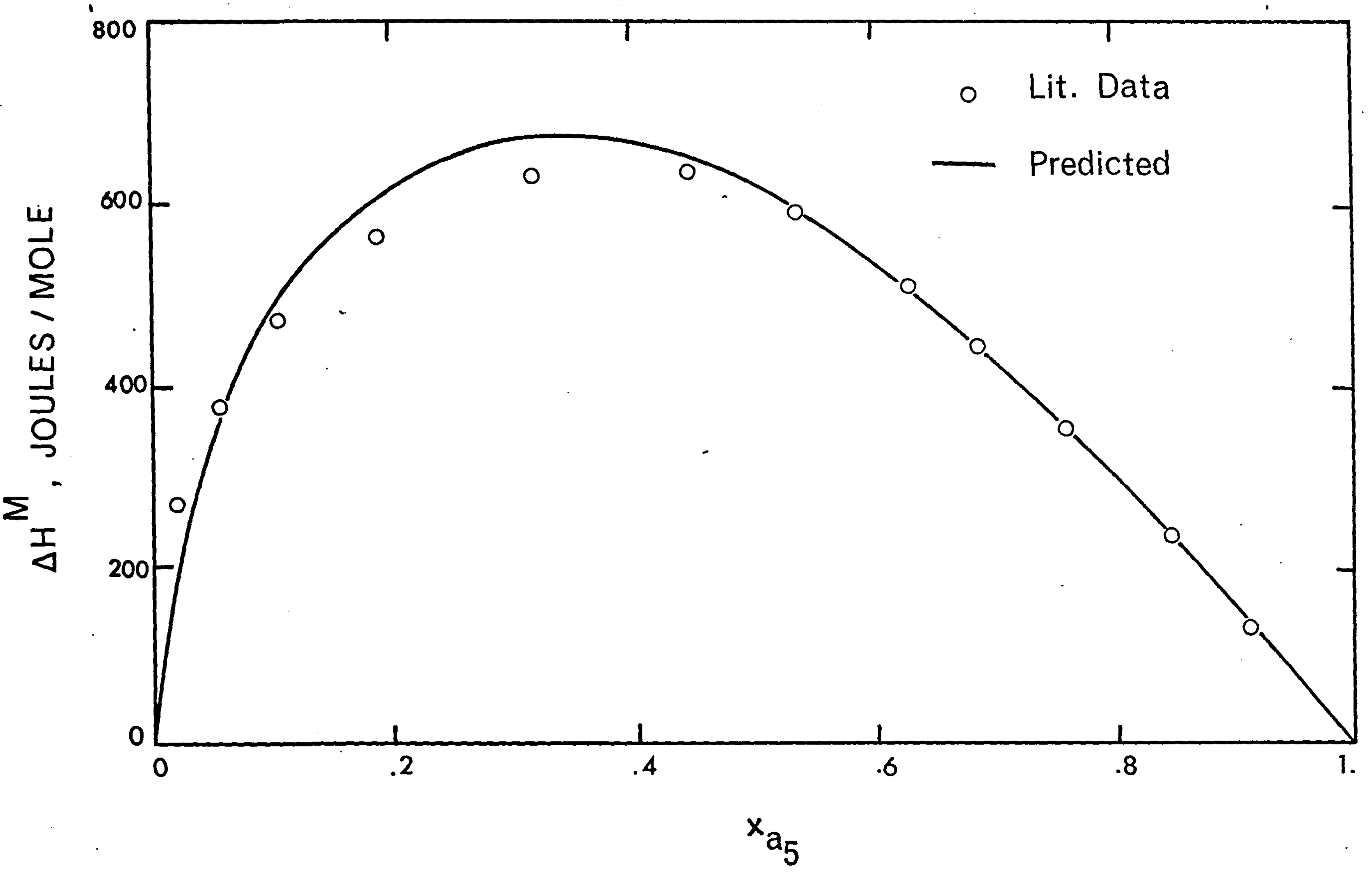

○ Lit. Data
— Predicted
600
300
0
ΔH^M, JOULES / MOLE
0
.2
.4
.6
.8
1.
x_{a_5}

FIGURE 13

Heats of Mixing at 25°C for the System

n-pentanol + n-octane



Lit. Data
Predicted
800
600
400
200
0
0
.2
.4
.6
.8
1.
ΔH^M, JOULES / MOLE
x_{a_5}

FIGURE 14

Heats of Mixing at 25°C for the System

n-pentanol + n-tetradecane

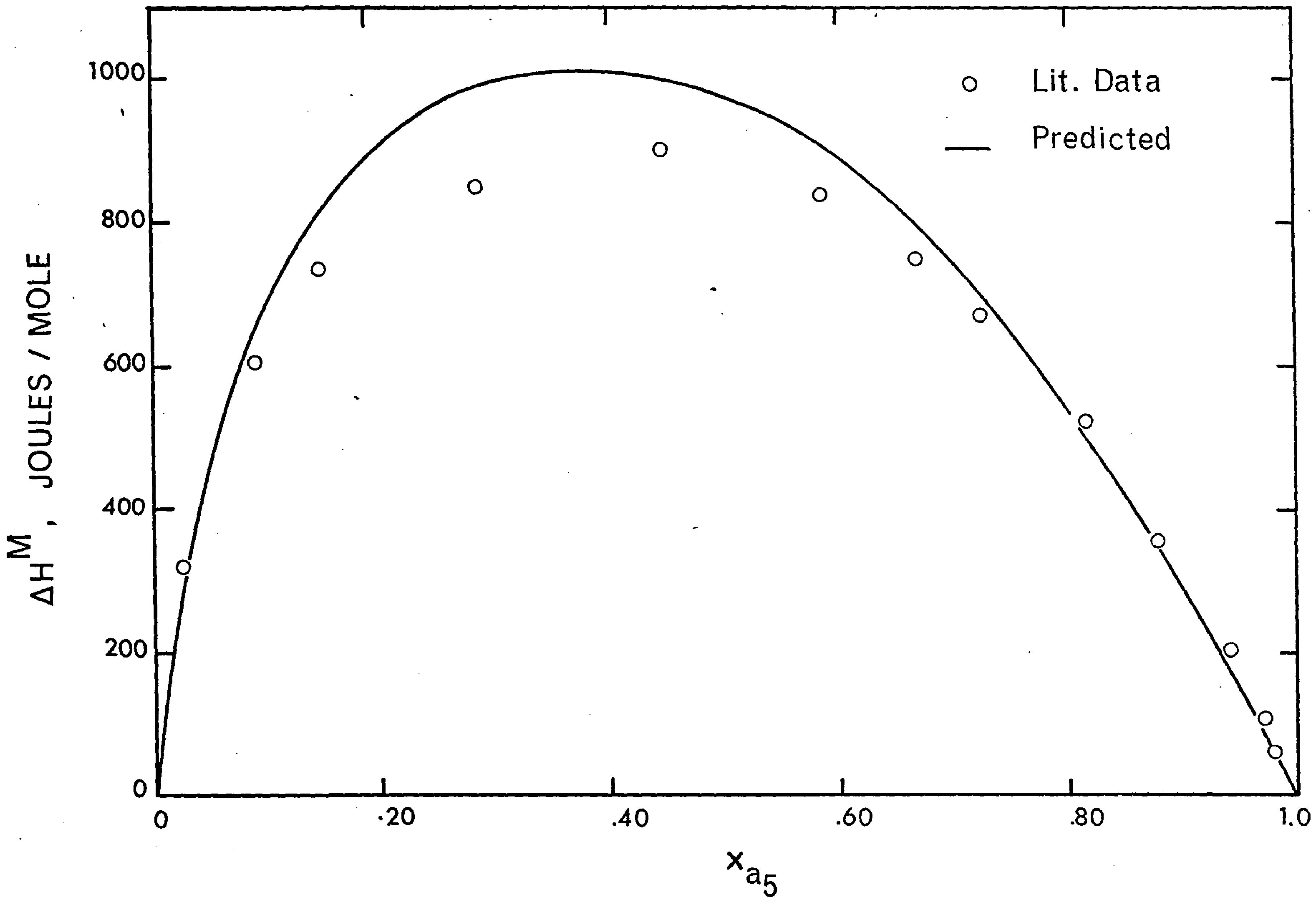

Lit. Data
Predicted
1000
800
600
400
200
0
ΔH^M, JOULES / MOLE
0
.20
.40
.60
.80
1.0
x_{a_5}

FIGURE 15

Heats of Mixing at 25°C for the System

n-octanol + n-heptane

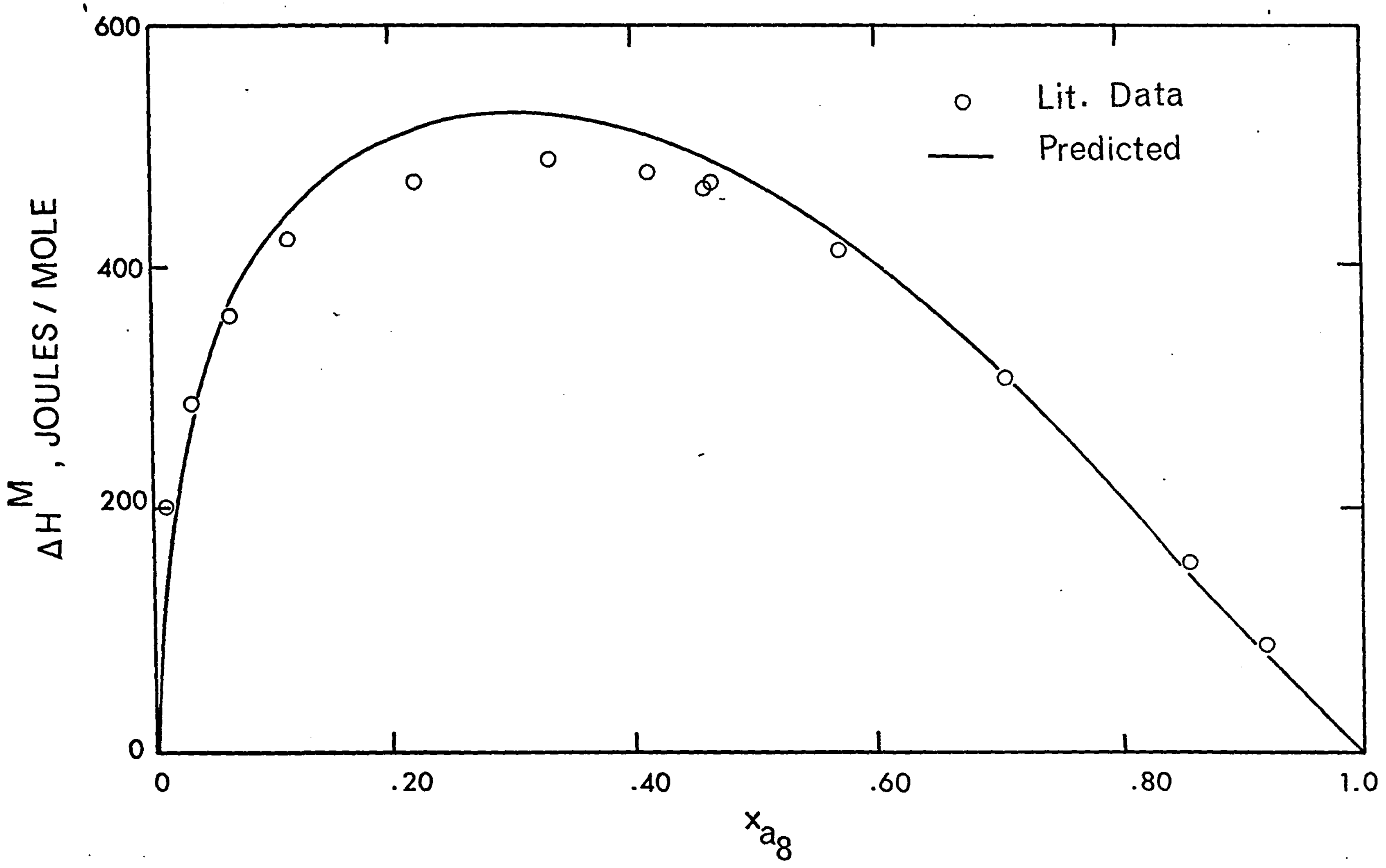
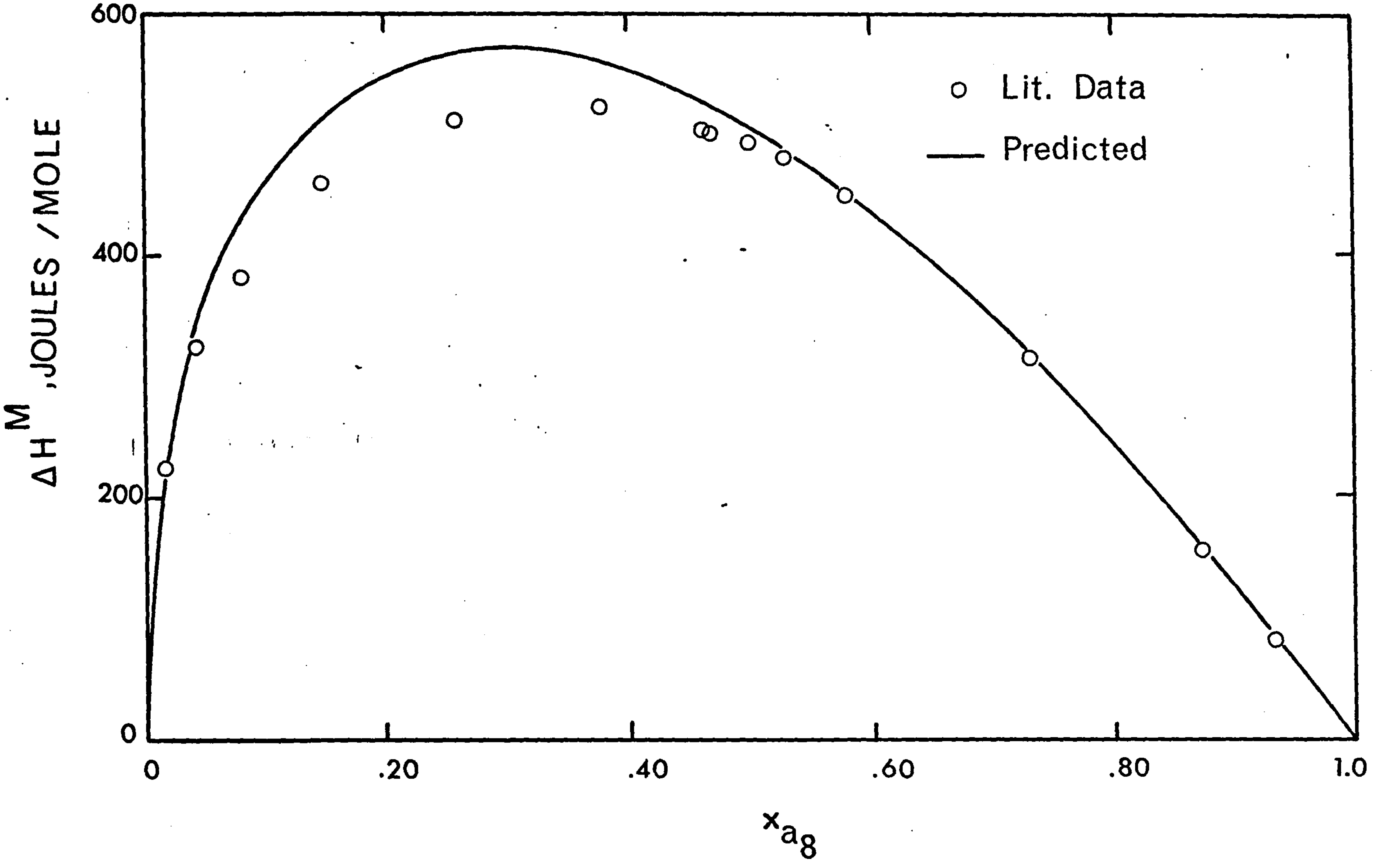

600
400
200
0
ΔH^M, JOULES / MOLE
0
.20
.40
.60
.80
1.0
x_{a_8}
Lit. Data
Predicted

FIGURE 16

Heats of Mixing at 25°C for the System

n-octanol + n-octane

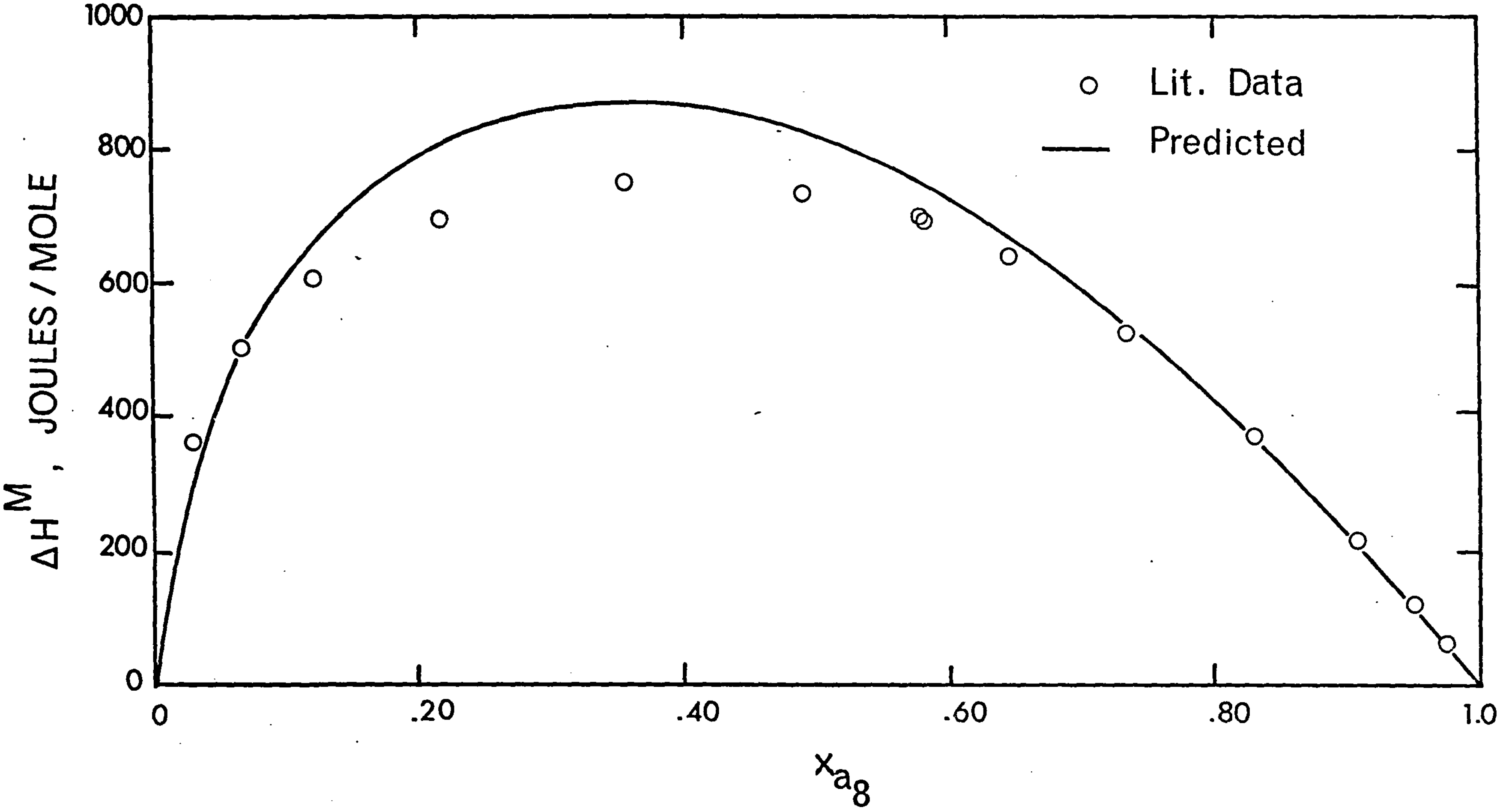


○ Lit. Data
— Predicted
ΔH^M, JOULES / MOLE
600
400
200
0
0
.20
.40
.60
.80
1.0
x_{a_8}

FIGURE 17

Heats of Mixing at 25°C for the System

n-octanol + n-tetradecane



○ Lit. Data
— Predicted
ΔH^M, JOULES / MOLE
1000
800
600
400
200
0
0
.20
.40
.60
.80
1.0
x_{a_8}

FIGURE 18

Heats of Mixing at $25^{\circ}C$ for the System

n-decanol + n-heptane

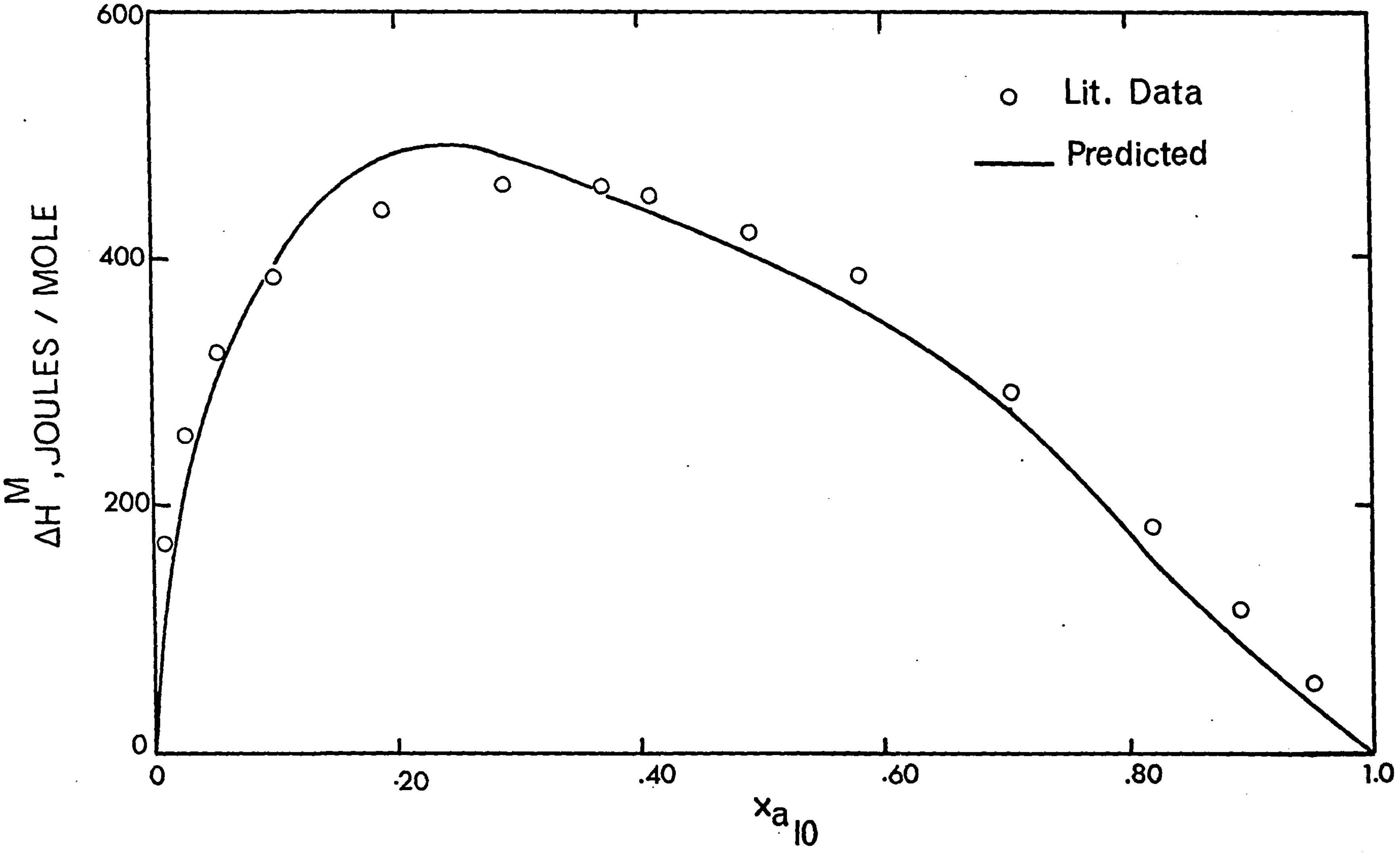
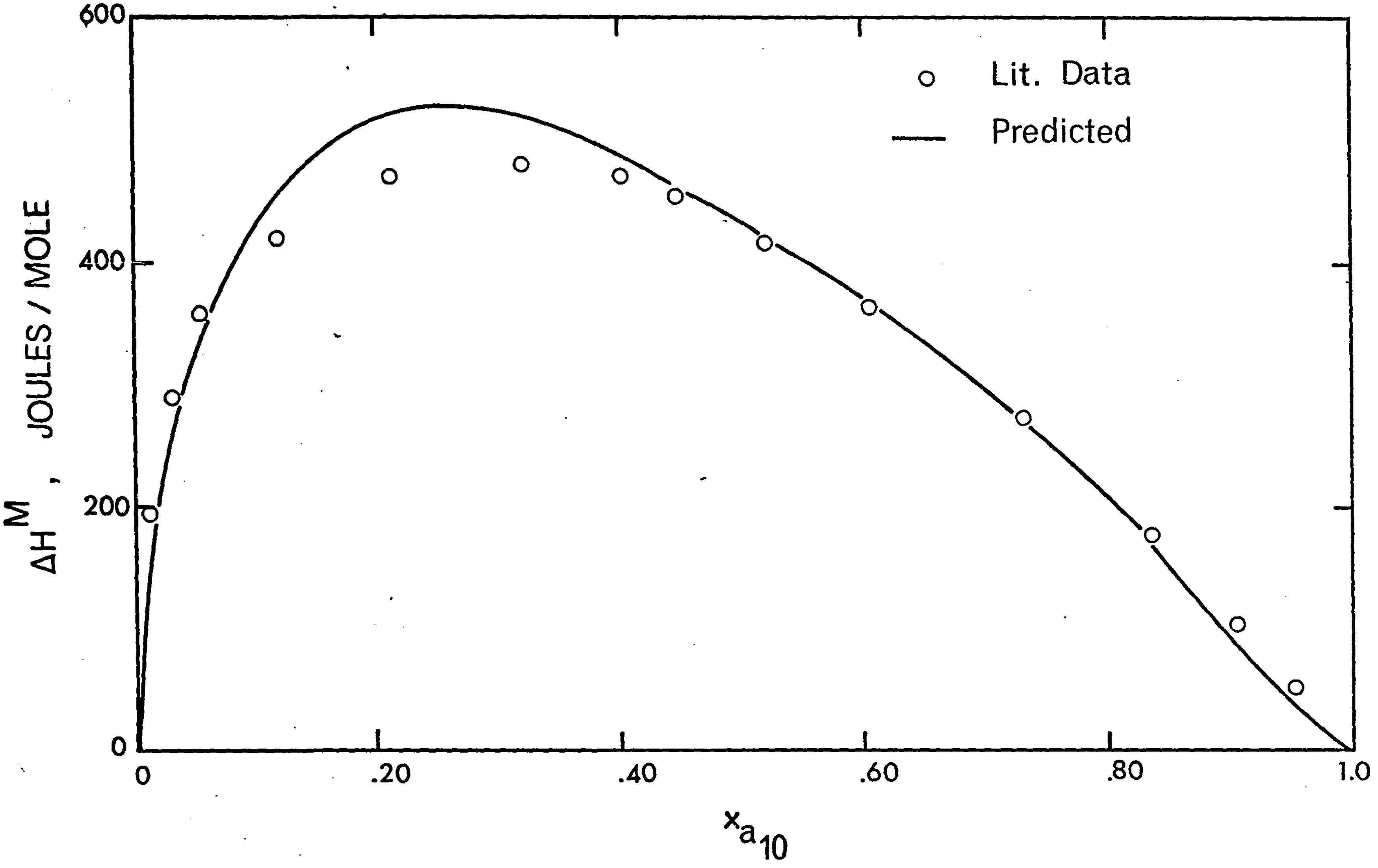

600
400
200
0
ΔH^M, JOULES / MOLE
0
.20
.40
.60
.80
1.0
$x_{a_{10}}$
○ Lit. Data
— Predicted

FIGURE 19

Heats of Mixing at 25°C for the System

n-decanol + n-octane



Lit. Data
Predicted
ΔH^M, JOULES / MOLE
600
400
200
0
0
.20
.40
.60
.80
1.0
$x_{a_{10}}$

FIGURE 20

Heats of Mixing at 25°C for the System

n-decanol + n-tetradecane

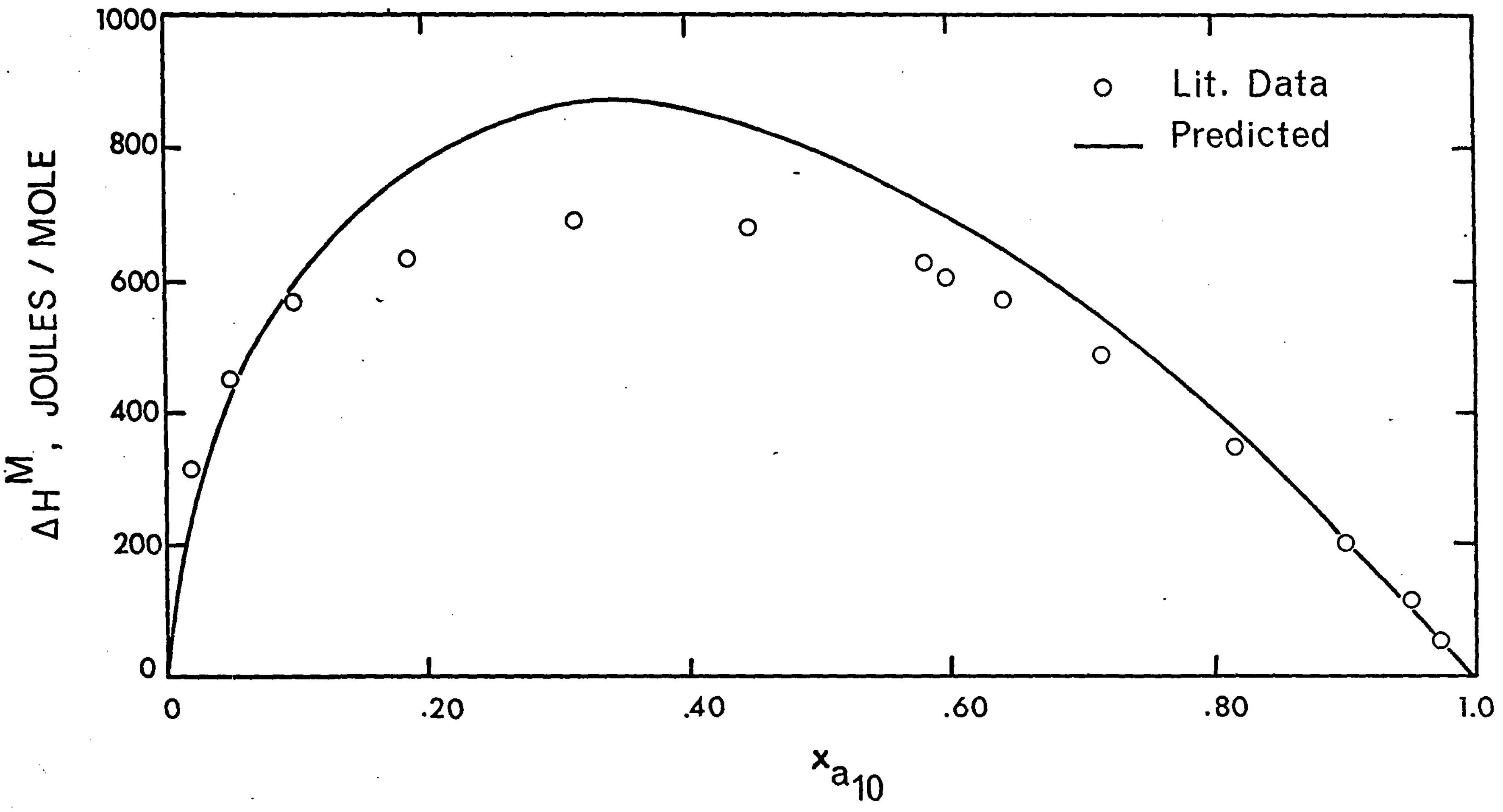

Lit. Data
Predicted
1000
800
600
400
200
0
0
.20
.40
.60
.80
1.0
ΔH^M, JOULES / MOLE
$x_{a_{10}}$

FIGURE 21

Heats of Mixing at 45°C for the System

n-pentanol + n-hexane

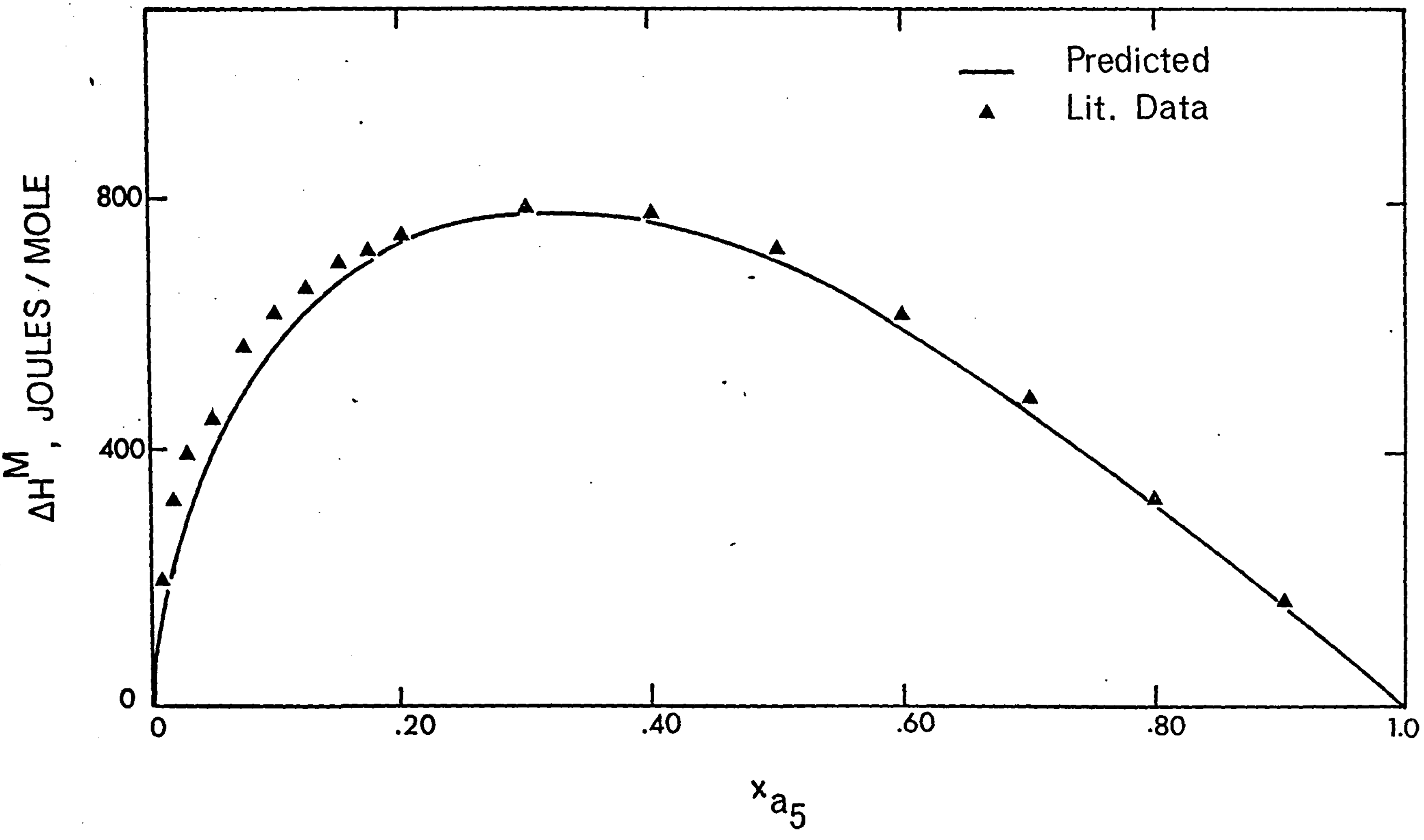

Predicted
Lit. Data
800
400
0
0
.20
.40
.60
.80
1.0
ΔH^M, JOULES / MOLE
x_{a_5}

FIGURE 22

Heats of Mixing at 45°C for the System

n-hexanol + n-hexane

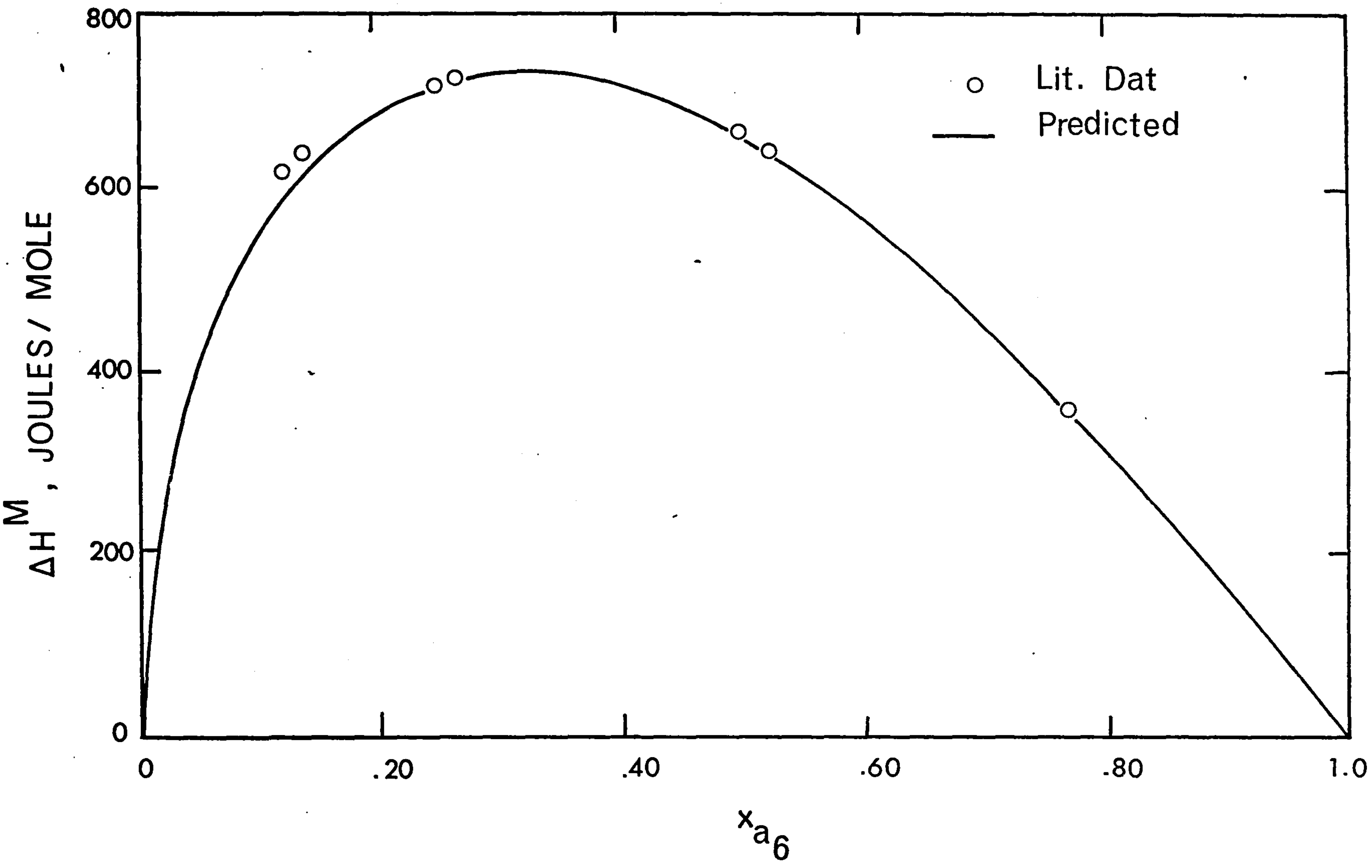
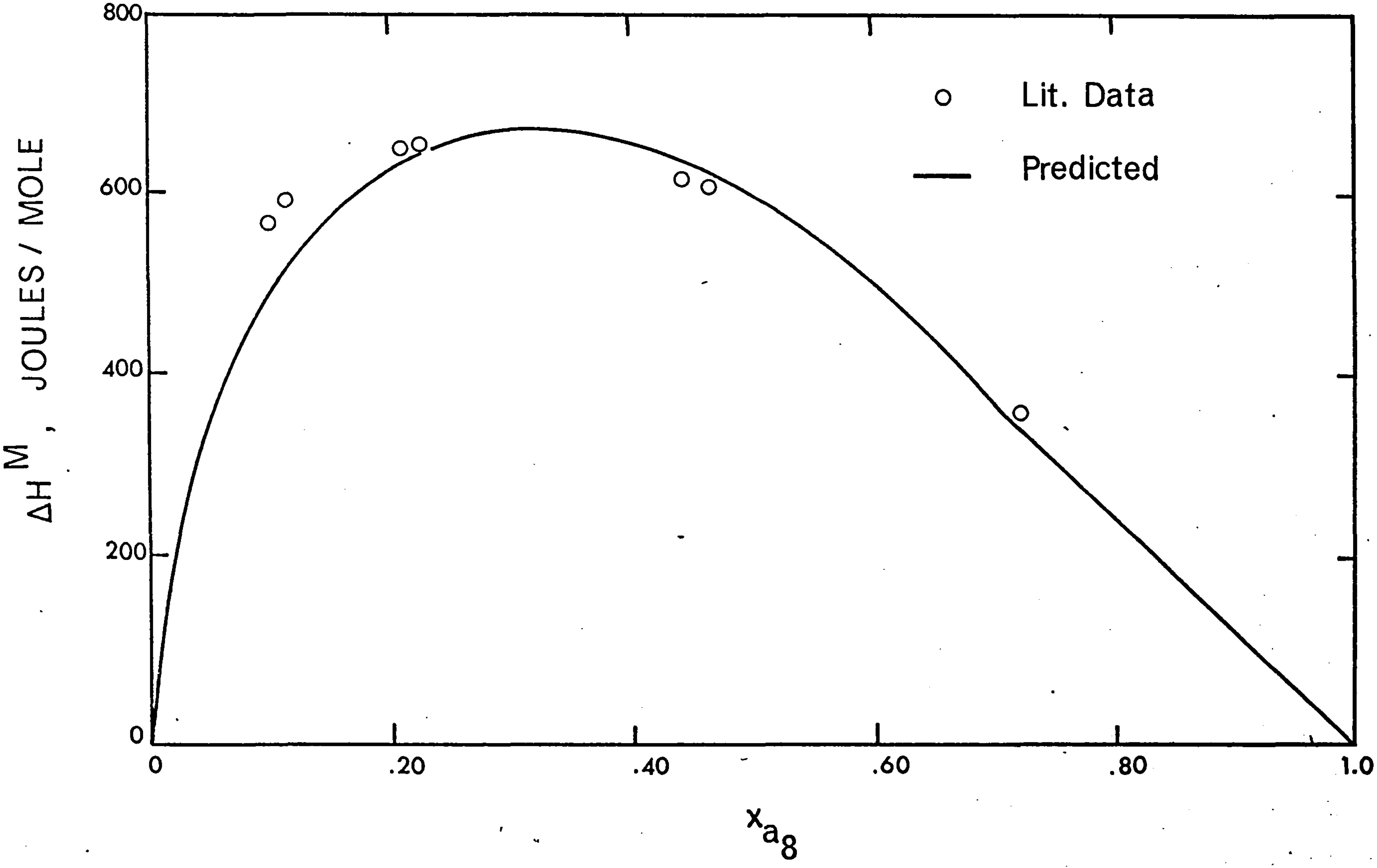

800
600
400
200
0
ΔH^M, JOULES/ MOLE
0
.20
.40
.60
.80
1.0
x_a6
○ Lit. Dat
— Predicted

FIGURE 23

Heats of Mixing at $45^{\circ}C$ for the System

n-octanol + n-hexane

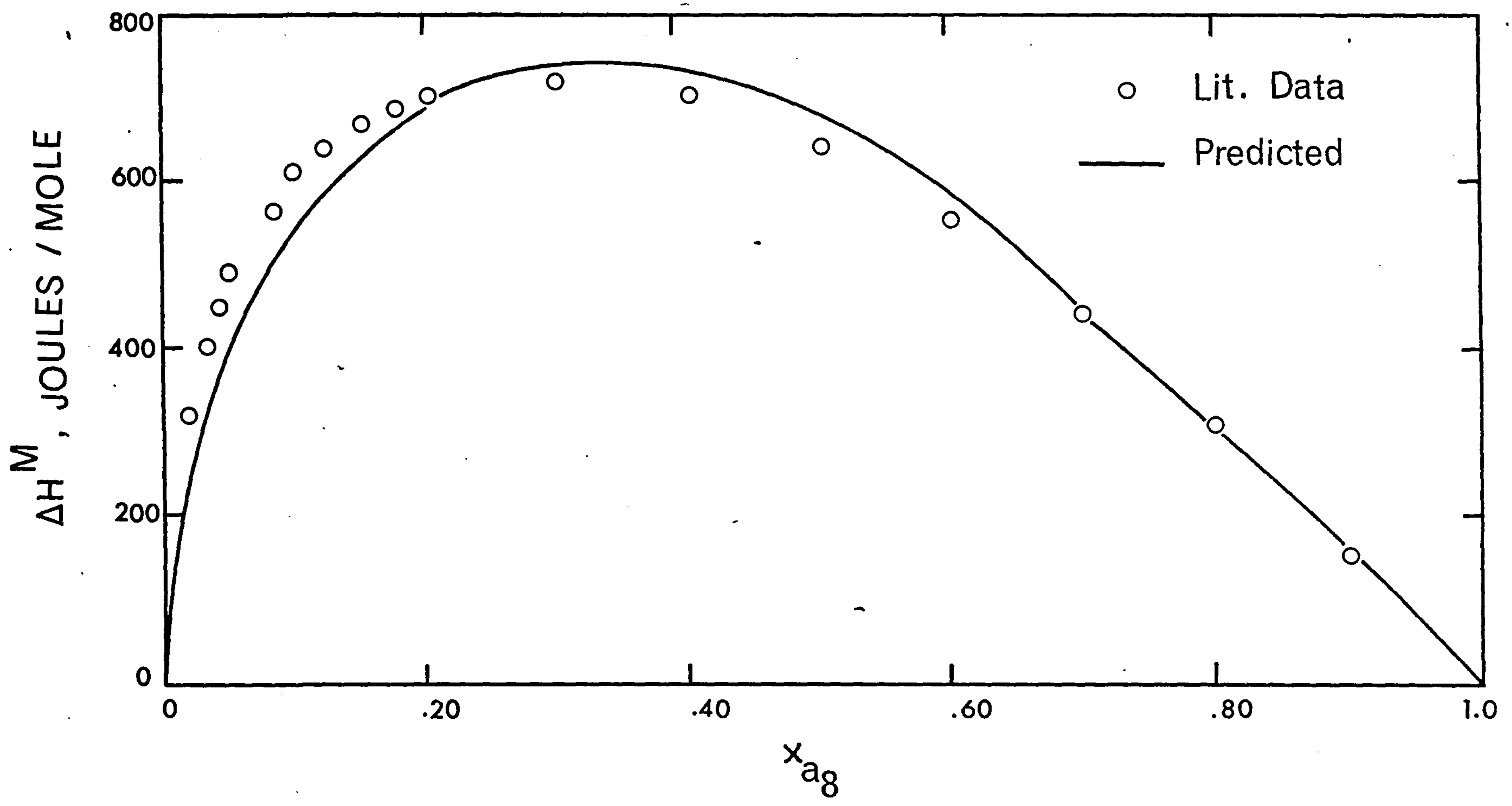


Lit. Data
Predicted
800
600
400
200
0
ΔH^M, JOULES / MOLE
0
.20
.40
.60
.80
1.0
x_{a_8}

FIGURE 24

Heats of Mixing at 45°C for the System

n-octanol + n-heptane



800
600
400
200
0
ΔH^M, JOULES / MOLE
0
.20
.40
.60
.80
1.0
x_{a_8}
Lit. Data
Predicted

FIGURE 25

Heats of Mixing at 45°C for the System

n-octanol + n-nonane

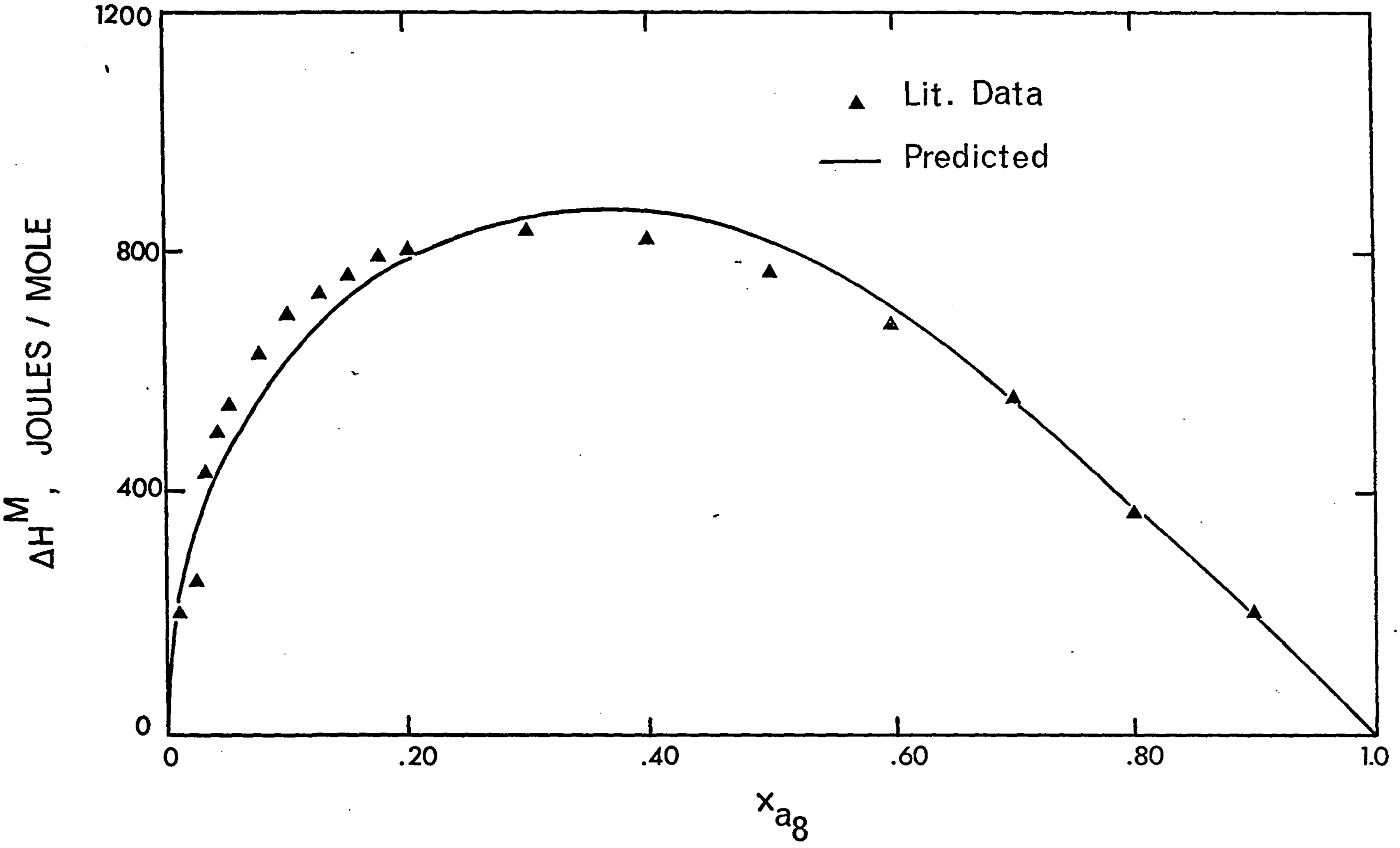
1200
800
400
0
ΔH^M, JOULES / MOLE
0
.20
.40
.60
.80
1.0
x_{a_8}
▲ Lit. Data
— Predicted

TABLE 3

Root-Mean-Square Deviations from Experimental Data

Mixture	Ref.	T, °C	R.M.D., %
n-pentanol + n-heptane	24	25	6.71
n-pentanol + n-octane	24	25	6.94
n-pentanol + n-tetradecane	24	25	8.35
n-octanol + n-heptane	24	25	9.69
n-octanol + n-octane	24	25	8.02
n-octanol + n-tetradecane	24	25	10.27
n-decanol + n-heptane	24	25	16.38
n-decanol + n-octane	24	25	15.98
n-decanol + n-tetradecane	24	25	17.11
n-pentanol + n-hexane	26	45	11.23
n-hexanol + n-hexane	25	45	3.60
n-octanol + n-hexane	25	45	7.00
n-octanol + n-heptane	26	45	11.10
n-octanol + n-nonane	26	45	12.40

Ternary Mixtures

The model has also been tested on eight ternary mixtures of n-alcohols and n-alkanes using the data of Ramalho and Ruel (28). Extrapolation of group excess enthalpies to a methylene group fraction of 0.75 is required since these mixtures contain n-propanol. This extrapolation is reasonable as shown in Figures 26 and 27.

The skeletal contributions were computed from the following formula of the Koefoed-Bronsted type (11):

$$\Delta H^S = A \left[\sum_i x_i N_i^2 - \left(\sum N_i x_i \right)^2 \right] \qquad (23)$$

where A is a constant and was calculated from binary data to be 4.6 joules/mole. Equation (23) is expected to give a reasonable estimation of the skeletal contributions at 25°C. Moreover, since the skeletal contributions of the systems studied are small in comparison with the group contributions, our results would be little affected by this term.

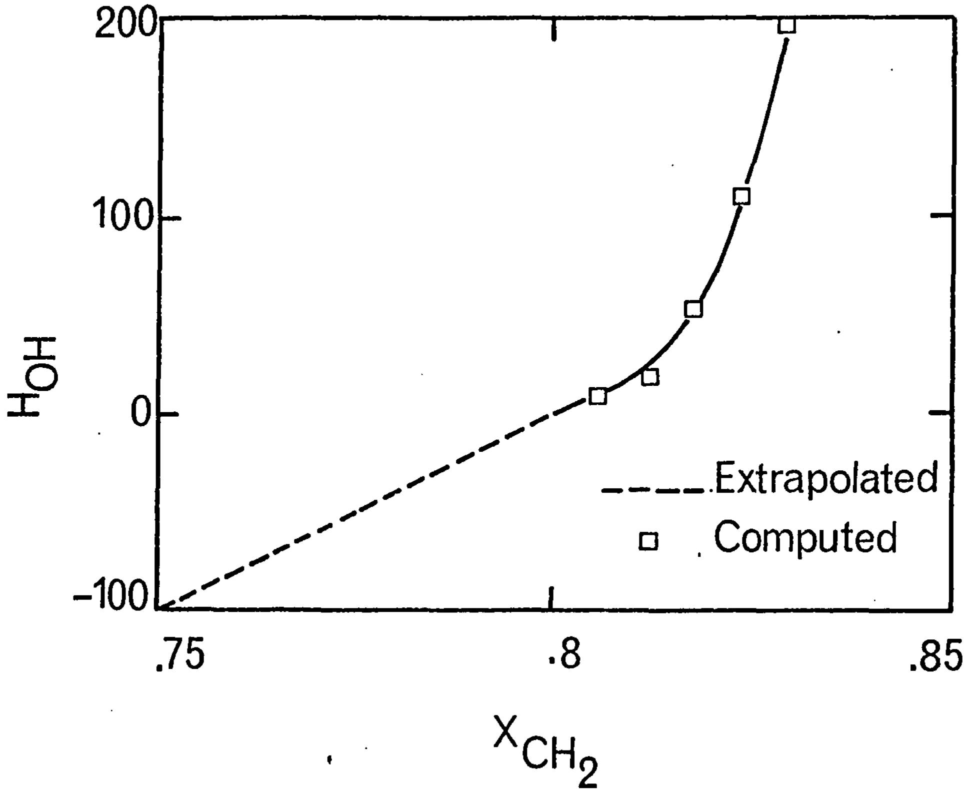
The results are surprisingly good as in the case of binary mixtures, as shown in Figures 28-35. Deviations from the published data and parameters of the extrapolated curves are tabulated in Table 4.

FIGURE 26

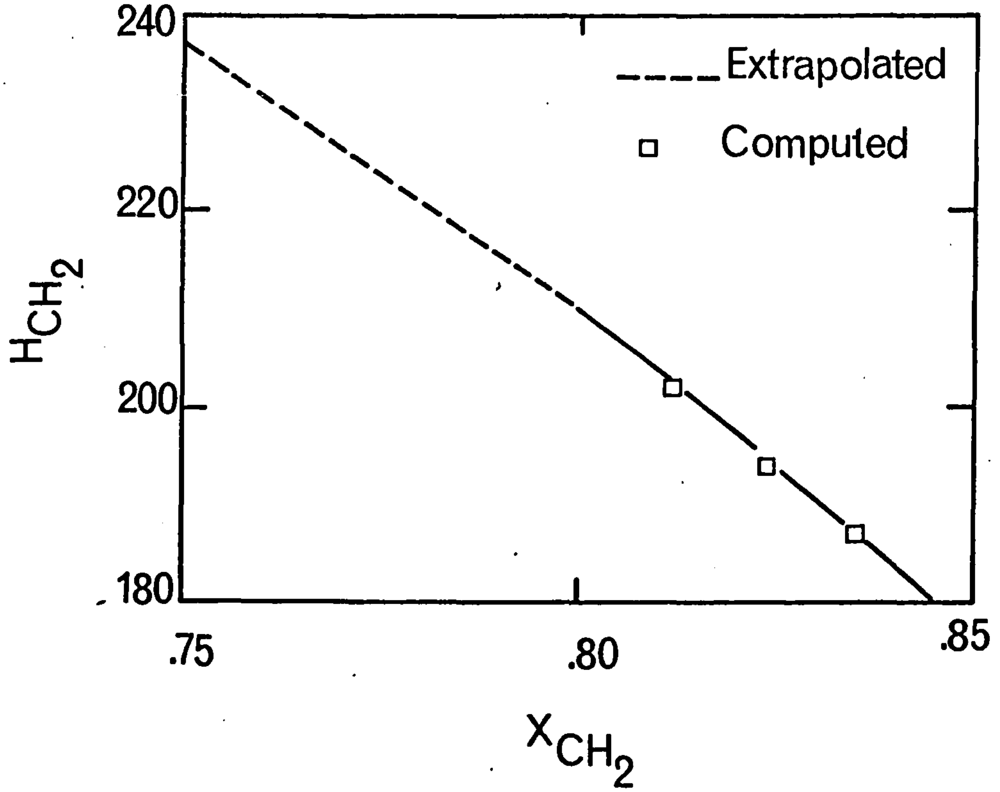
Extrapolation of H_{OH} Curve at 25°C from Methylene Group Fraction of 0.80 to 0.75

FIGURE 27

Extrapolation of H_{CH_2} Curve at 25°C from Methylene Group Fraction of 0.80 to 0.75



200
100
0
−100
H_{OH}
.75
.8
.85
X_{CH_2}
Extrapolated
Computed

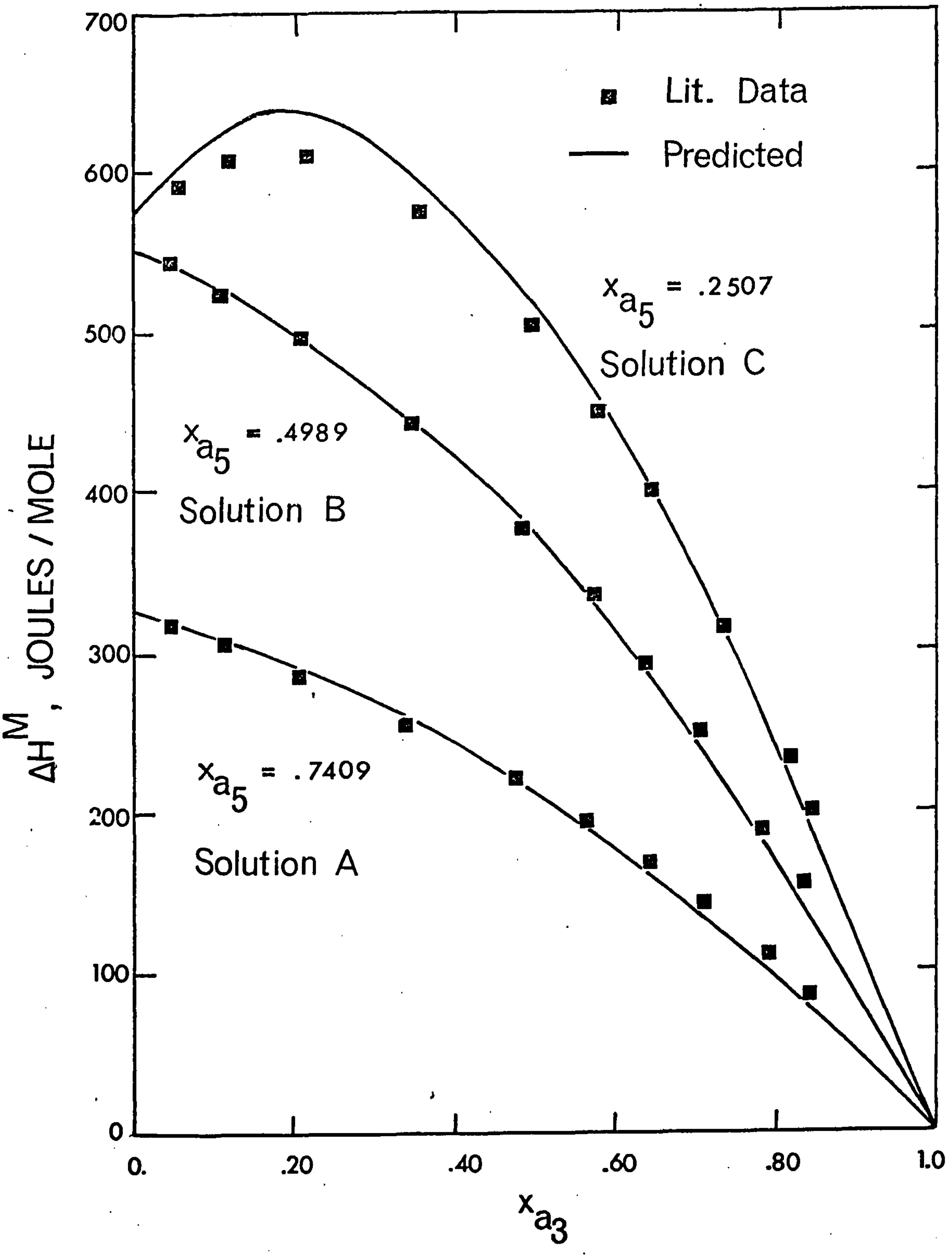


240
220
200
180
H_{CH_2}
.75
.80
.85
X_{CH_2}
Extrapolated
Computed

FIGURE 28

Heats of Mixing at 25°C for the System

n-heptane + n-propanol + n-pentanol

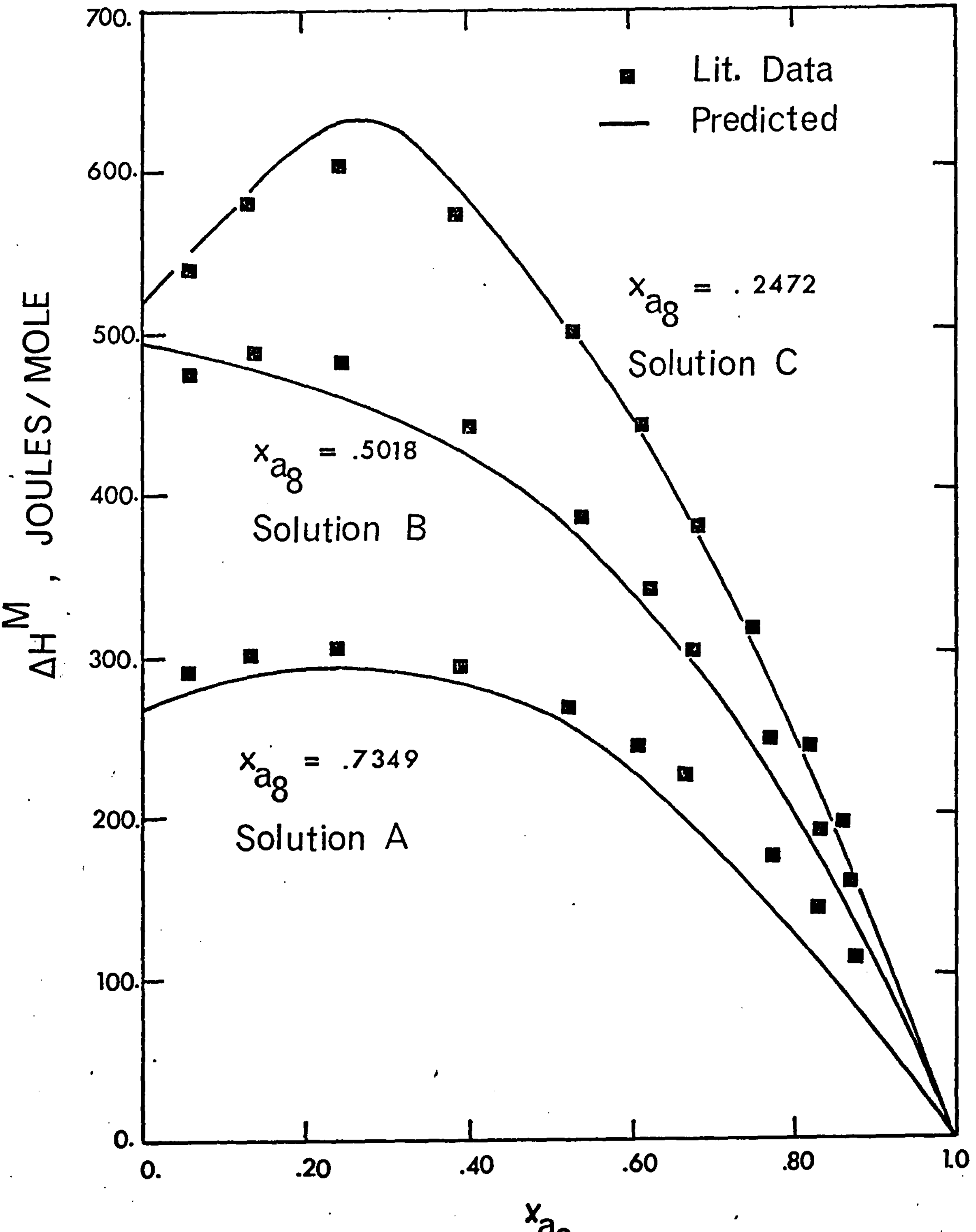


700
600
500
400
300
200
100
0
ΔH^M, JOULES / MOLE
0.
.20
.40
.60
.80
1.0
x_{a_3}
▨ Lit. Data
— Predicted
x_{a_5} = .2507
Solution C
x_{a_5} = .4989
Solution B
x_{a_5} = .7409
Solution A

FIGURE 29

Heats of Mixing at 25°C for the System

n-heptane + n-propanol + n-octanol



700.
600.
500.
400.
300.
200.
100.
0.
0.
.20
.40
.60
.80
1.0
ΔH^M, JOULES / MOLE
x_{a_3}
■ Lit. Data
— Predicted
x_{a_8} = .2472
Solution C
x_{a_8} = .5018
Solution B
x_{a_8} = .7349
Solution A

FIGURE 30

Heats of Mixing at 25°C for the System

n-heptane + n-propanol + n-decanol

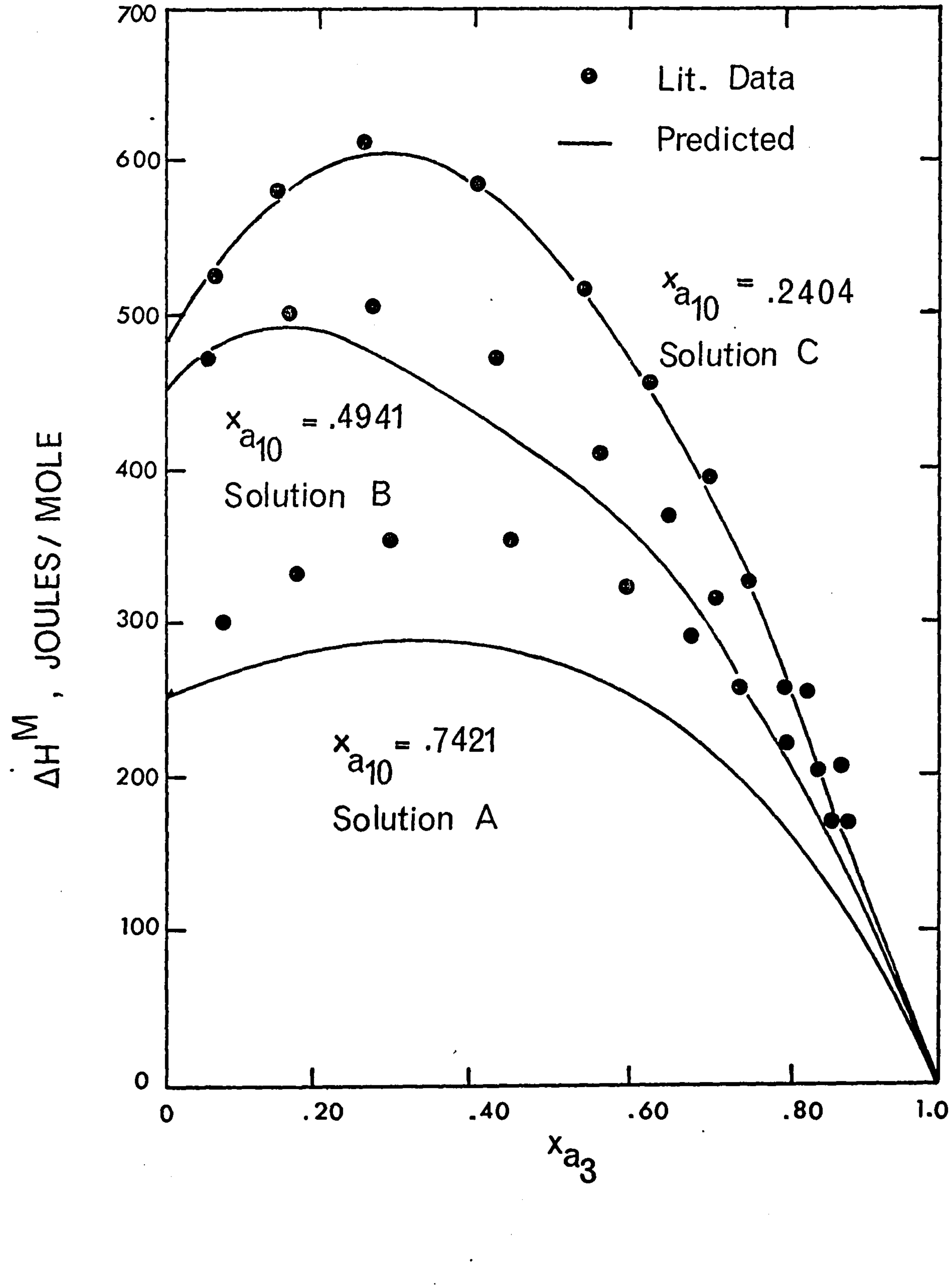

● Lit. Data
— Predicted
$x_{a_{10}} = .2404$
Solution C
$x_{a_{10}} = .4941$
Solution B
$x_{a_{10}} = .7421$
Solution A
ΔH^M, JOULES/ MOLE
x_{a_3}
0
100
200
300
400
500
600
700
0
.20
.40
.60
.80
1.0

FIGURE 31

Heats of Mixing at 25°C for the System

n-octane + n-propanol + n-pentanol

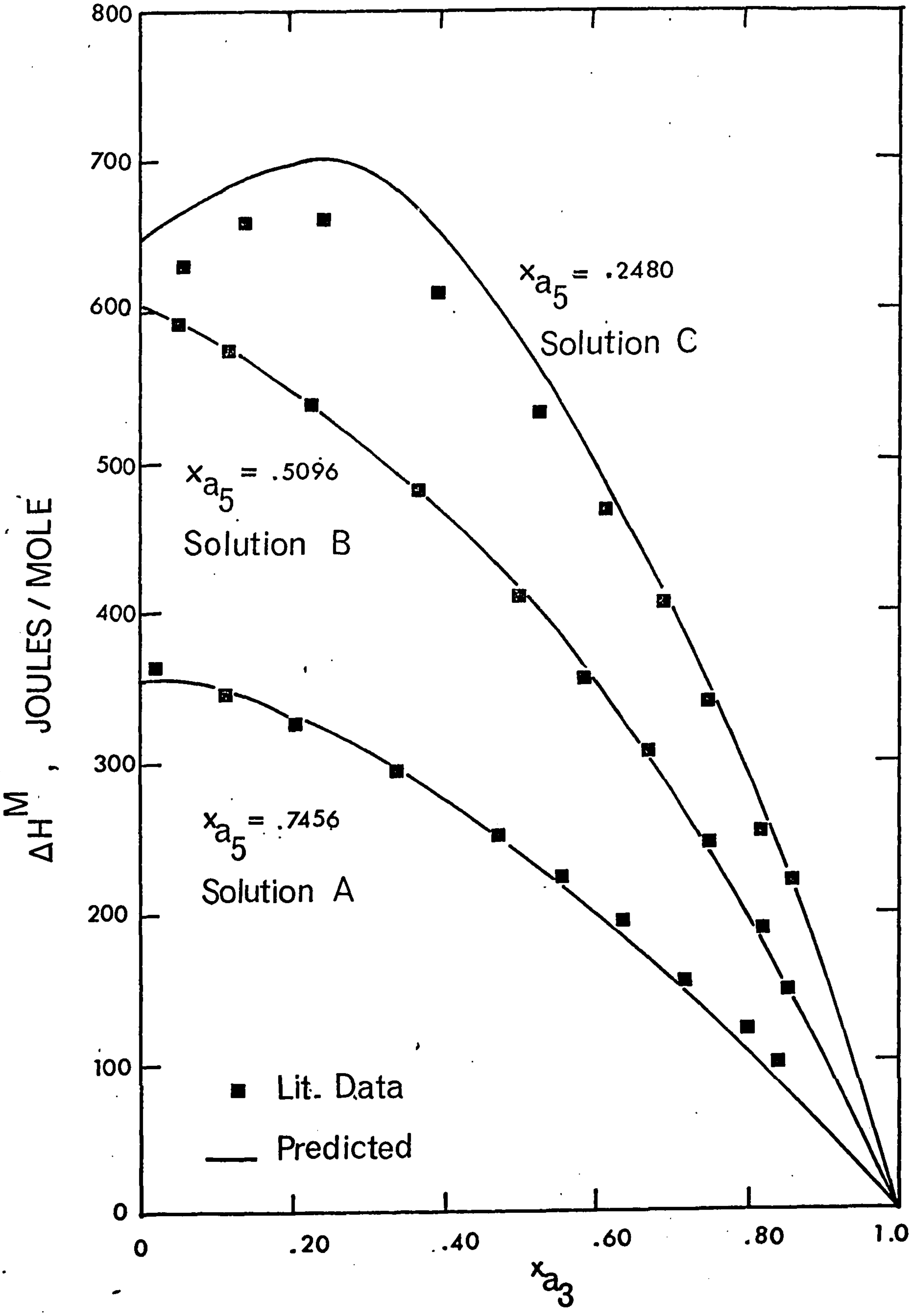
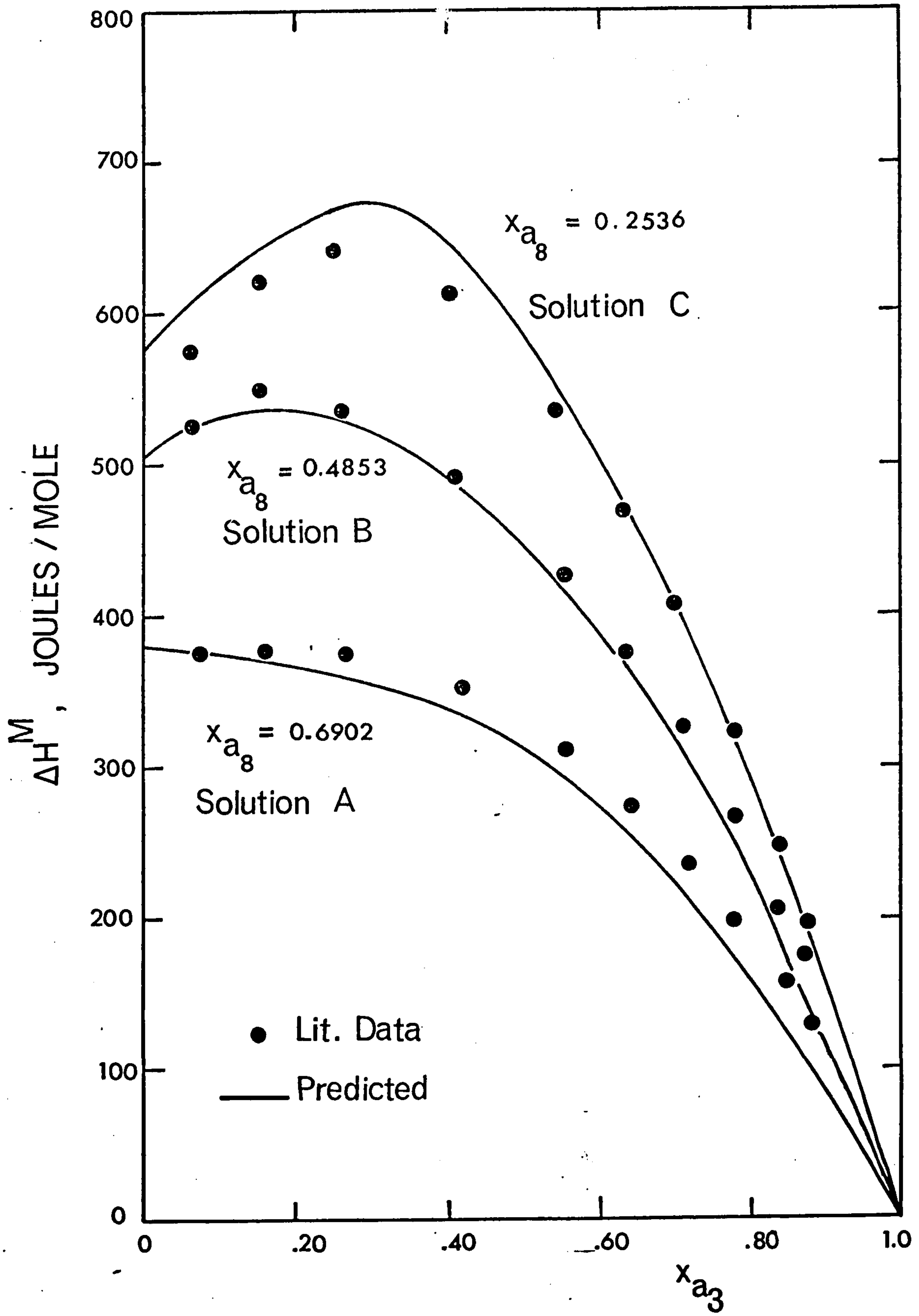

800
700
600
500
400
300
200
100
0
ΔH^M, JOULES / MOLE
0
.20
.40
.60
.80
1.0
x_{a_3}
x_{a_5} = .2480
Solution C
x_{a_5} = .5096
Solution B
x_{a_5} = .7456
Solution A
■ Lit. Data
— Predicted

FIGURE 32

Heats of Mixing at 25°C for the System

n-octane + n-propanol + n-octanol

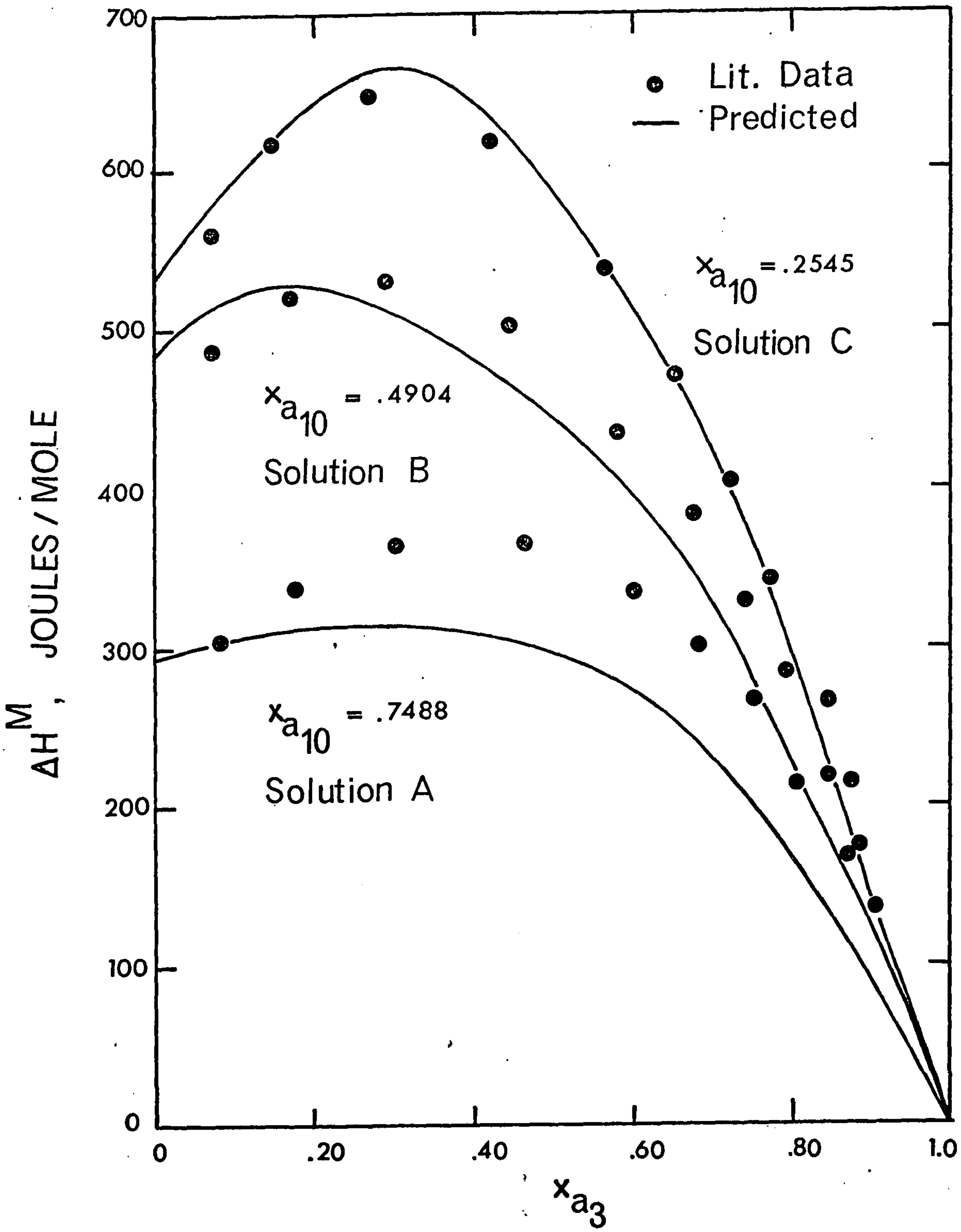


800
700
600
500
400
300
200
100
0
ΔH^M, JOULES / MOLE
x_{a_8} = 0.2536
Solution C
x_{a_8} = 0.4853
Solution B
x_{a_8} = 0.6902
Solution A
● Lit. Data
Predicted
0
.20
.40
.60
.80
1.0
x_{a_3}

FIGURE 33

Heats of Mixing at 25°C for the System

n-octane + n-propanol + n-decanol



700
600
500
400
300
200
100
0
ΔH^M, JOULES / MOLE
0
.20
.40
.60
.80
1.0
x_{a_3}
Lit. Data
Predicted
$x_{a_{10}} = .2545$
Solution C
$x_{a_{10}} = .4904$
Solution B
$x_{a_{10}} = .7488$
Solution A

FIGURE 34

Heats of Mixing at 25°C for the System

n-tetradecane + n-propanol + n-octanol

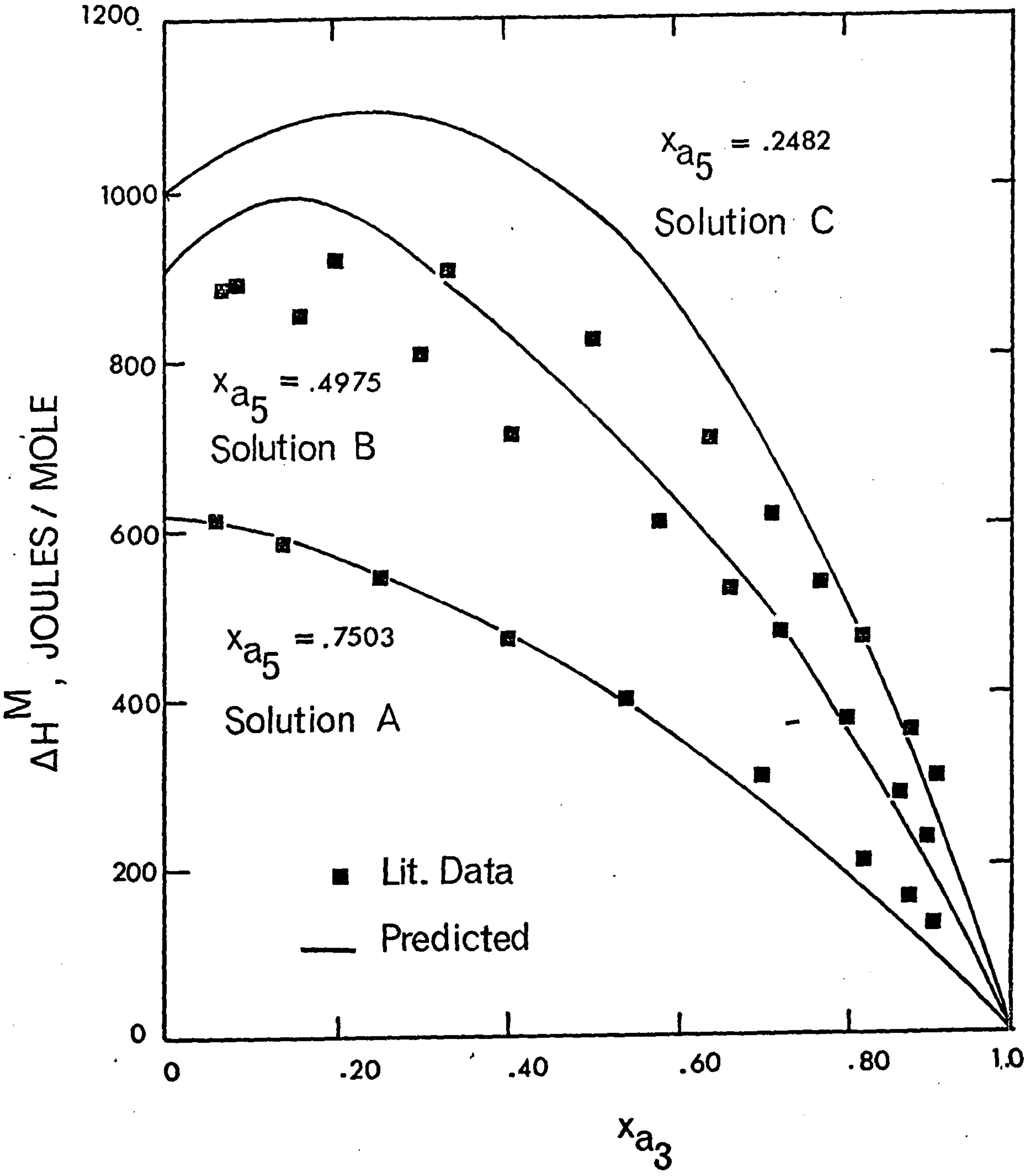

1200
1000
800
600
400
200
0
ΔH^M, JOULES / MOLE
0
.20
.40
.60
.80
1.0
x_{a_3}
x_{a_5} = .2482
Solution C
x_{a_5} = .4975
Solution B
x_{a_5} = .7503
Solution A
■ Lit. Data
Predicted

FIGURE 35

Heats of Mixing at 25°C for the System

n-tetradecane + n-propanol + n-pentanol

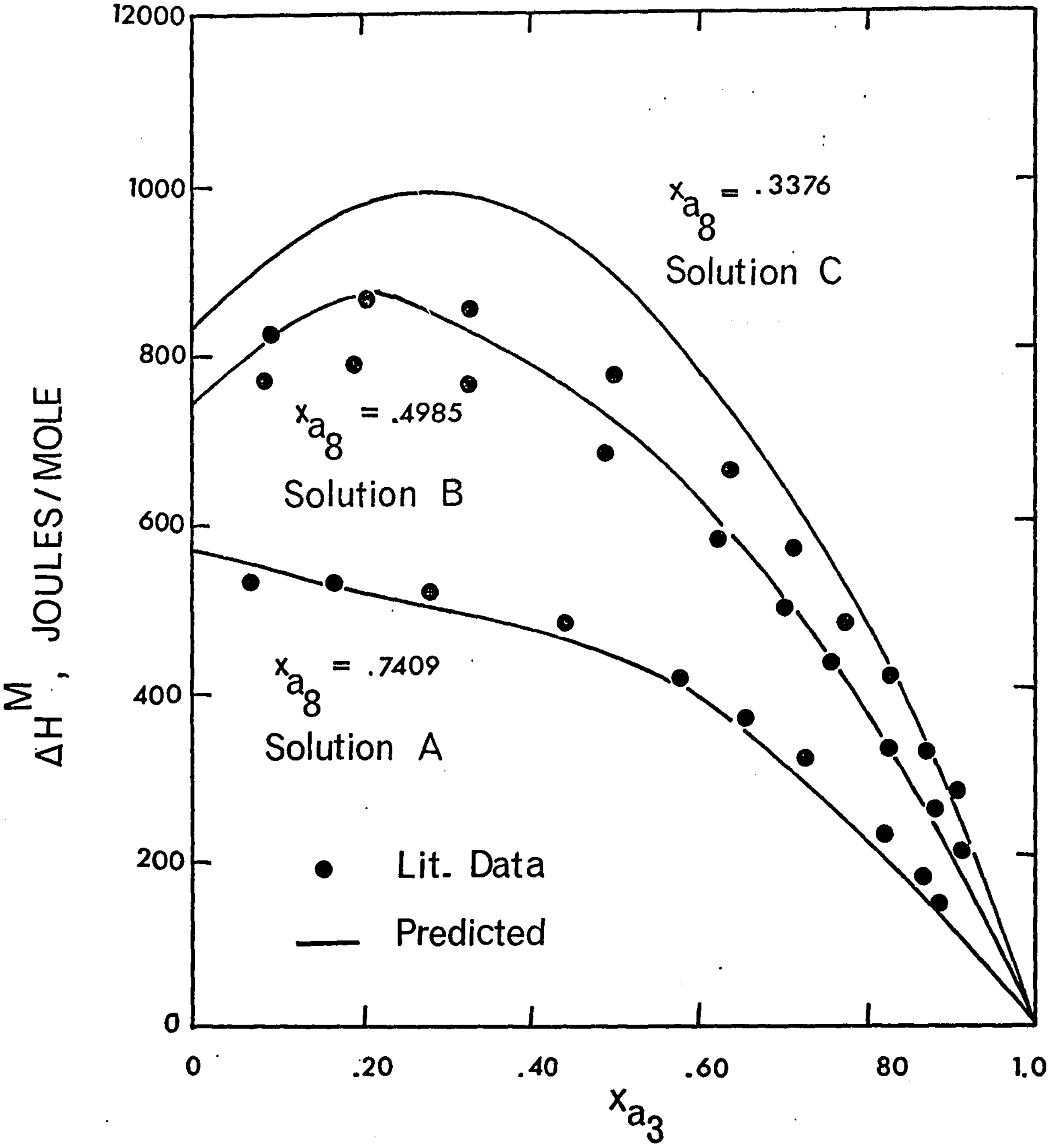

12000
1000
800
600
400
200
0
0
.20
.40
.60
80
1.0
ΔH^M, JOULES/MOLE
x_{a_3}
x_{a_8} = .3376
Solution C
x_{a_8} = .4985
Solution B
x_{a_8} = .7409
Solution A
● Lit. Data
— Predicted

TABLE 4

Fitted Parameters of the Extrapolated Curves

$$y = A_0 + A_1 X_{CH_2}$$

$$0.75 < X_{CH_2} < 0.80$$

	A_0	A_1
$y = H_{OH}$	- 1600	2000
$y = H_{CH_2}$	642	- 540

Prediction Results for Ternary Systems at 25°C

System	Solution	R.M.D., %
n-heptane + n-propanol + n-pentanol	A (x_{a_5} = 0.7409)	12.0
	B (x_{a_5} = 0.4989)	7.15
	C (x_{a_5} = 0.2507)	5.08
n-heptane + n-propanol + n-octanol	A (x_{a_8} = 0.7349)	15.4
	B (x_{a_8} = 0.5018)	12.0
	C (x_{a_8} = 0.2472)	8.1
n-heptane + n-propanol + n-decanol	A ($x_{a_{10}}$ = 0.7421)	28.3
	B ($x_{a_{10}}$ = 0.4941)	15.7
	C ($x_{a_{10}}$ = 0.2404)	10.6

TABLE 4 (cont.)

System	Solution	R.M.D., %
n-octane + n-propanol + n-pentanol	A (x_{a_5} = 0.7456)	12.6
	B (x_{a_5} = 0.5096)	5.2
	C (x_{a_5} = 0.2480)	9.2
n-octane + n-propanol + n-decanol	A ($x_{a_{10}}$ = 0.7488)	23.3
	B ($x_{a_{10}}$ = 0.4904)	12.6
	C ($x_{a_{10}}$ = 0.2545)	8.7
n-octane + n-propanol + n-octanol	A (x_{a_8} = 0.6902)	13.7
	B (x_{a_8} = 0.4853)	10.8
	C (x_{a_8} = 0.2536)	6.5
n-tetradecane + n-propanol + n-pentanol	A (x_{a_5} = 0.7503)	12.3
	B (x_{a_5} = 0.4975)	10.7
	C (x_{a_5} = 0.2482)	15.0
n-tetradecane + n-propanol + n-octanol	A (x_{a_8} = 0.7409)	11.0
	B (x_{a_8} = 0.4985)	9.3
	C (x_{a_8} = 0.3375)	11.20

Limitation of the Application of the Model

The application of this method requires heats of mixing of two reference system, one for the skeletal contributions and the other for the excess enthalpies of the groups. In our case, the n-butanol + n-hexane system was chosen as the reference system for the group excess enthalpies and the n-hexane + n-hexadecane system is for the skeletal estimations. The number of carbon atoms of the two components in the system for which the heats-of-mixing data are to be predicted must be in the range of these reference system. These conditions can be formulated as follows:

Predicted System:

$$n\ C_{n_1} H_{2n_1+1} OH + n\ C_{n_2} H_{2n_2+2}$$

Then

$$15 < n_1 < 5$$

$$16 < n_2 < 6$$

For n_1 smaller than 5, an extrapolation is necessary.

DISCUSSION OF RESULTS

The Group Solution Model here presented for heats of mixing gives a very good representation of liquid mixtures containing the methylene and hydroxyl groups. As in the case of excess free energies of mixing, the skeletal contributions are small in comparison with the group contributions. For mixtures with components of very different length, the size contributions could be as much as 7.5% of the total heats of mixing; for example, in a mixture of n-pentanol and n-tetradecane at 25°C, the maximum size contribution is 74 joules/mole whereas the predicted group contribution is 837 joules/mole at a pentanol mole fraction of 0.5884. Our predictions would be quite rough if the skeletal contributions were neglected.

The accuracy of the predictions depends very much on the accuracy of the reference system heats of mixing. Also, it is sometimes necessary to make small extrapolations, as in the case of ternaries.

Equation (22) was used to estimate the size contributions for the ternary systems at 25°C since published data on the skeletal heats of mixing for these mixtures are not available. Although Equation (22) was found to be incorrect (34) at high temperatures for many binaries when the heats of mixing become unsymmetric, it still gives a good representation of heats of mixing of n-paraffins at 25°C, and we expect that the error would be relatively small when using this formula for ternary systems.

Predictions of heats of mixing for aliphatic alcohol mixtures have been made for three systems:

n-pentanol + n-octanol (28)
n-pentanol + n-decanol (28)
n-hexanol + n-octanol (27)

The root-mean-square deviations of the predictions of the three mixtures were very high (50-100%). The results of these predictions are shown in Appendix B. However, these systems are very close to ideal and we are most interested in making predictions for highly non-ideal systems.

Finally, although the model presented is not based on rigorous thermodynamic relations, the relatively high precision as well as its intuitive sense suggests that it is basically sound. We expect that the group solution model will be applicable to mixtures of other groups, such as in ethers, aldehydes, ketones, etc. The present work offers a very good ground for further study of these groups.

NOMENCLATURE

A	constant in Equation (17)
B	constant in Equation (3)
H	group excess enthalpy
n	number of carbon atoms
N	number of carbon atoms other than hydrogen in a molecule
N_{ki}	number of groups of type k in molecular species i
P	pressure
T	absolute temperature
x	mole fraction
ΔH^M	heats of mixing

Subscripts

i	molecular species i
j	molecular species j
k	group species k

Superscripts

M	mixing function
G	group contribution
S	skeletal contribution
*	standard state

Greek Letters

γ	molecular activity coefficient
Γ	group activity coefficient

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APPENDIX A

Computational Data for the Reference System

n-butanol + n-hexane

TABLE 5

Heat-of-Mixing Data for the System n-butanol + n-hexane

At 25°C

x_{a_4}	$\Delta H / x_{a_4} x_{h_6}$
0.1634	3658
0.1772	3579
0.3151	2650
0.3323	2583
0.5817	1858
0.5960	1782
0.5971	1825
0.8173	1426
1.000	1280*

At 45°C

x_{a_4}	$\Delta H / x_{a_4} x_{h_6}$
0.1581	5605
0.1806	5371
0.3108	3959
0.3360	3823
0.5785	2850
0.5986	2805
0.5994	2803
0.8160	2258
1.000	1920*

* extrapolated

TABLE 6

Computed Excess Enthalpies of Methylene Group at 25°C
Reference System: n-butanol + n-hexane

X_{CH_2}	H_{CH_2} (joules/mole)
0.8000	210 *
0.8019	202
0.8235	194
0.8350	187
0.8462	182
0.8571	177
0.8679	173
0.8785	167
0.8889	160
0.8991	152
0.9091	142
0.9189	130
0.9286	116
0.9381	100
0.9474	85
0.9565	76
0.9655	66
0.9744	52
0.9831	32
0.9916	11
1.0000	0

* extrapolated

TABLE 7

Computed Excess Enthalpies of Hydroxyl Group at 25°C

Reference System: n-butanol + n-hexane

X_{CH_2}	H_{OH} (joules/mole)
0.8000	0
0.8119	5
0.8235	17
0.8350	36.6
0.8462	61.4
0.8571	92.1
0.8679	130
0.8785	176
0.8889	234
0.8991	308
0.9091	403
0.9189	527
0.9286	689
0.9381	898
0.9474	1137
0.9565	1337
0.9655	1587
0.9744	2051
0.9831	2969
0.9975	7948+
0.9940	8830*
1.0000	10000**

** extrapolated

* computed from n-pentanol + n-octane system

\+ computed from n-octanol + n-octane system

TABLE 8

Computed Excess Enthalpies of Methylene Group at 45°C
Reference System: n-butanol + n-hexane

X_{CH_2}	H_{CH_2} (joules/mole)
1.0000	0
0.9831	49
0.9744	80
0.9655	102
0.9565	116
0.9474	128
0.9381	148
0.9286	169
0.9189	189
0.9091	206
0.8990	222
0.8889	236
0.8680	263
0.8785	250
0.8680	263
0.8571	276
0.8462	289
0.8350	301
0.8235	310
0.8119	316

TABLE 9

Computed Excess Enthalpies of Hydroxyl Group at 45°C
Reference System: n-butanol + n-hexane

X_{CH_2}	H_{OH} (joules/mole)
1.0000	14600**
0.9978	13895*
0.9920	5050*
0.9830	4507
0.9800	3840*
0.9744	3110
0.9655	2404
0.9565	2029
0.9474	1753
0.9381	1431
0.9286	1143
0.9189	922
0.9091	750
0.8991	610
0.8889	492
0.8785	384
0.8679	292
0.8570	197
0.8460	110
0.8349	52
0.8235	13.4
0.8119	8
0.8000	0

** extrapolated

* computed from data of n-octanol + n-nonane system

APPENDIX B

Predicted Data on Heats of Mixing

Binary n-alcohol + n-alkane systems at 25°C

Binary n-alcohol + n-alkane systems at 45°C

Ternary n-alkane + two n-alcohols systems at 25°C

Binary n-alcohol + n-alcohol systems at 25°C

TABLE 10

PENTANOL + HEPTANE AT 25 DEG. C
X=MOL FRACT. OF THE ALCOHOL

X	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.0202	0.11	198.90	240.00	199.01	17.08
0.0500	0.26	322.26	344.00	322.52	6.24
0.0954	0.48	440.40	427.00	440.87	-3.25
0.1741	0.79	555.51	523.00	556.30	-6.37
0.2964	1.15	588.89	579.00	590.04	-1.91
0.4244	1.35	605.79	579.00	607.14	-4.86
0.5129	1.38	544.02	542.00	545.41	-0.63
0.5779	1.35	471.71	492.00	473.06	3.85
0.6254	1.30	440.12	449.00	441.42	1.69
0.6966	1.17	360.75	374.00	361.92	3.23
0.7536	1.03	299.47	311.00	300.50	3.38
0.8210	0.82	233.69	228.00	234.50	-2.85
0.9018	0.49	141.69	128.00	142.19	-11.08

RMS DEVIATION = 6.68

TABLE 11

PENRANOL + OCTANE AT 25 DEG,
X=MOL FRACT. OF THE ALCOHOL

X	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.0222	0.46	220.87	268.00	221.33	17.41
0.0549	1.11	363.16	380.00	364.27	4.14
0.1044	2.00	433.99	470.00	490.99	-4.47
0.1885	3.29	615.15	559.00	618.43	-10.63
0.3169	4.67	646.68	628.00	651.35	-3.72
0.4479	5.35	650.51	629.00	655.86	-4.27
0.5368	5.40	578.69	586.00	584.08	0.33
0.6011	5.21	515.41	535.00	520.62	2.69
0.6277	5.09	491.18	508.00	496.27	2.31
0.6867	4.69	430.15	444.00	434.84	2.06
0.7580	4.01	336.96	356.00	340.97	4.22
0.8457	2.86	238.84	235.00	241.69	-2.85
0.9165	1.68	140.51	129.00	142.19	-10.22

RMS DEVIATION = 6.98

TABLE 12

C5-OH+C14 AT 25 DEG. C
X=MOL. FRACT. OF THE ALCOHOL, DTH=HEATS OF MIXING

X	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.0283	7.76	304.88	322.00	312.64	2.91
0.0916	23.71	609.47	607.00	633.18	-4.31
0.1678	40.22	789.94	735.00	830.16	-12.95
0.2869	59.91	942.22	849.00	1002.13	-18.04
0.4456	73.92	915.92	898.00	989.84	-10.23
0.5844	74.04	836.93	838.00	910.97	-8.71
0.6676	68.40	740.77	752.00	809.17	-7.60
0.7263	61.74	621.45	670.00	683.19	-1.97
0.8066	48.96	451.51	523.00	500.47	4.31
0.8795	33.57	304.28	356.00	337.85	5.10
0.9359	19.14	183.69	204.00	202.83	0.57
0.9669	10.25	98.32	110.00	108.57	1.30
0.9829	5.39	47.90	58.00	53.30	8.11

RMS DEVIATION = 8.20

TABLE 13

C8-OH + C7 AT 25 DEGREE
X=MOL. FRACT. OF THE ALCOHOL, DTH=HEATS OF MIXING

X	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.0147	0.30	150.13	203.00	150.43	25.89
0.0347	0.70	264.49	287.00	265.20	7.60
0.0667	1.31	328.43	360.00	329.74	8.41
0.1248	2.29	449.56	422.00	451.85	-7.07
0.2217	3.61	513.73	471.00	517.34	-9.84
0.3325	4.63	502.22	487.00	506.84	-4.07
0.4157	5.05	472.20	476.00	477.25	-0.26
0.4606	5.16	481.73	464.00	486.89	-4.93
0.4651	5.16	484.86	468.00	490.03	-4.71
0.5702	5.07	436.24	414.00	441.31	-6.60
0.7051	4.28	292.32	308.00	296.61	3.70
0.8569	2.52	134.81	155.00	137.33	11.40
0.9231	1.45	86.76	84.00	88.21	-5.02

RMS DEVIATION = 9.69

TABLE 14

OCTANOL + OCTANE AT 25 DEG. C
X=MOL FRACT. OF THE ALCOHOL

X	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.0172	0.09	174.50	224.00	174.59	22.06
0.0434	0.21	314.65	324.00	314.86	2.82
0.0780	0.37	379.07	382.00	379.44	0.67
0.1477	0.64	514.31	460.00	514.96	-11.95
0.2571	0.97	569.89	512.00	570.86	-11.50
0.2771	1.02	569.29	523.00	570.31	-9.05
0.4637	1.26	501.52	506.00	502.78	0.64
0.4704	1.26	498.04	503.00	499.30	0.74
0.4944	1.27	512.44	494.00	513.70	-3.99
0.5291	1.26	502.00	478.00	503.27	-5.29
0.5779	1.23	453.92	450.00	455.15	-1.15
0.7326	0.99	322.40	315.00	323.39	-2.66
0.8728	0.56	149.21	156.00	149.77	3.99
0.9323	0.32	83.77	83.00	84.09	-1.31

RMS DEVIATION = 8.12

TABLE 15

```
C10-OH + C7 AT 25 DEGREE
X=MOL. FRACT. OF THE ALCOHOL, DTH=HEATS OF MIXING

     X          SIZE      GROUP    LIT.DATA    PREDICT    DEV

  0.0112        0.90     118.90     169.00     119.80     29.11

  0.0281        2.23     226.62     257.00     228.85     10.95

  0.0550        4.23     291.82     323.00     296.05      8.34

  0.1040        7.56     389.57     385.00     397.13     -3.15

  0.1883       12.34     464.79     437.00     477.13     -9.18

  0.2886       16.47     464.33     459.00     480.80     -4.75

  0.3669       18.54     436.27     458.00     454.81      0.70

  0.4101       19.26     415.77     450.00     435.03      3.33

  0.4906       19.79     372.47     429.00     392.26      8.56

  0.5790       19.20     367.23     387.00     386.43      0.15

  0.7059       16.22     254.15     292.00     270.37      7.41

  0.8200       11.44     139.26     186.00     150.71     18.97

  0.8920        7.43      72.30     115.00      79.74     30.66

  0.9494        3.69      29.01      56.00      32.70     41.60

                                RMS DEVIATION =          17.58
```

TABLE 16

OCTANOL + TETRADECANE AT 25 DEG. C
X=MOL FRACT. OF THE ALCOHOL

X	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.0271	2.75	281.59	360.00	284.34	21.02
0.0651	6.36	503.69	503.00	510.06	-1.40
0.1219	11.24	606.32	605.00	617.57	-2.08
0.2167	18.00	793.60	697.00	811.60	-16.44
0.3559	24.63	843.07	747.00	867.70	-16.16
0.4914	27.19	760.53	730.00	787.72	-7.91
0.5798	26.71	674.90	689.00	701.61	-1.83
0.6366	25.50	675.82	642.00	701.32	-9.24
0.6420	25.34	680.46	637.00	705.80	-10.80
0.7335	21.73	531.21	527.00	552.94	-4.92
0.8281	15.96	340.41	373.00	356.37	4.46
0.9060	9.61	209.96	217.00	219.57	-1.19
0.9507	5.31	98.30	118.00	103.61	12.20
0.9747	2.80	61.63	62.00	64.43	-3.92

RMS DEVIATION = 10.20

TABLE 17

DECANOL + OCTANE AT 25 DEG. C
X=MOL FRACT. OF THE ALCOHOL

X	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.0131	0.58	138.20	195.00	138.77	28.84
0.0327	1.41	261.36	289.00	262.77	9.08
0.0636	2.64	330.80	357.00	333.45	6.60
0.1194	4.65	442.32	420.00	446.98	-6.42
0.2132	7.39	518.33	468.00	525.72	-12.33
0.3215	9.56	508.14	481.00	517.71	-7.63
0.4037	10.51	471.02	471.00	481.53	-2.23
0.4482	10.77	445.74	456.00	456.51	-0.11
0.5188	10.84	401.20	417.00	412.04	1.19
0.6054	10.33	376.11	366.00	386.44	-5.58
0.7292	8.48	292.89	275.00	301.38	-9.59
0.8348	5.89	178.04	178.00	183.94	-3.34
0.9050	3.66	81.85	106.00	85.51	19.33
0.9529	1.91	28.06	53.00	29.97	43.46

RMS DEVIATION = 16.06

TABLE 18

DECANOL + TETRADECANE AT 25 DEG. C
X=MOL FRACT. OF THE ALCOHOL

X	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.0217	2.21	238.41	314.00	240.63	23.37
0.0546	5.39	456.80	456.00	462.20	-1.36
0.1039	9.77	578.28	573.00	588.06	-2.63
0.1880	16.15	754.01	635.00	770.16	-21.29
0.3162	23.15	847.73	688.00	870.88	-26.58
0.4472	26.78	796.03	682.00	822.82	-20.65
0.5810	26.70	673.71	618.00	700.40	-13.33
0.5966	26.43	657.15	606.00	683.58	-12.80
0.6396	25.41	670.62	567.00	696.03	-22.76
0.7171	22.52	545.44	484.00	567.96	-17.35
0.8160	16.81	396.11	345.00	412.93	-19.69
0.8987	10.27	215.47	201.00	225.74	-12.31
0.9467	5.72	120.12	110.00	125.84	-14.40
0.9724	3.05	53.10	57.00	56.15	1.49

RMS DEVIATION = 17.01

TABLE 19

```
PENTANOL+HEXANE AT 45 DEG.C
X=MOL. FRACT. OF THE ALCOHOL, TDTH=PREDICTED HEATS OF MIXING

   X          SIZE      GROUP     LIT.DATA    PREDICT     DEV

 0.0100       0.0      205.41     201.00      205.41     -2.19
 0.0200       0.0      260.81     325.00      260.81     19.75
 0.0300       0.0      313.69     400.00      313.69     21.58
 0.0400       0.0      360.15     455.00      360.15     20.85
 0.0500       0.0      400.38     499.00      400.38     19.76
 0.0750       0.0      486.91     572.00      486.91     14.88
 0.1000       0.0      558.11     622.00      558.11     10.27
 0.1250       0.0      613.86     662.00      613.86      7.27
 0.1500       0.0      660.42     696.00      660.42      5.11
 0.1750       0.0      696.11     722.00      696.11      3.59
 0.2000       0.0      728.72     744.00      728.72      2.05
 0.3000       0.0      803.39     785.00      803.39     -2.34
 0.4000       0.0      781.79     778.00      781.79     -0.49
 0.5000       0.0      693.61     720.00      693.61      3.67
 0.6000       0.0      583.48     619.00      583.48      5.74
 0.7000       0.0      471.84     487.00      471.84      3.11
 0.8000       0.0      327.17     333.00      327.17      1.75
 0.9000       0.0      151.36     168.00      151.36      9.91

                               RMS DEVIATION =           11.23
```

TABLE 20

SYSTEM HEXANOL + HEXANE AT 45 DEG. C
X=MOL FRACT. OF HEXANOL, TDTH=PREDICTED HEATS OF MIXING

X	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.1227	0.26	583.71	625.00	583.98	6.55
0.1398	0.29	613.64	653.00	613.93	5.98
0.2490	0.45	735.35	716.00	735.80	-2.77
0.2709	0.48	741.24	728.00	741.72	-1.88
0.5026	0.60	660.28	663.00	660.89	0.32
0.5230	0.60	636.45	648.00	637.06	1.59
0.5230	0.60	636.45	652.00	637.06	2.29
0.7689	0.43	360.19	353.00	360.62	-2.16

RMS DEVIATION = 3.59

TABLE 21

SYSTEM OCTANOL + HEXANE AT 45 DEG. C
X=MOL. FRACT. OF OCTANOL, TOTH=PREDICTED HEATS OF MIXING

X	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.1003	1.90	494.71	575.00	496.61	13.63
0.1132	2.11	522.23	593.00	524.34	11.58
0.2083	3.45	630.69	655.00	634.14	3.18
0.2270	3.67	644.67	660.00	648.34	1.77
0.4445	5.10	640.82	620.00	645.92	-4.18
0.4642	5.13	624.27	613.00	629.41	-2.68
0.4653	5.13	617.80	611.00	622.94	-1.95
0.7233	4.07	340.83	367.00	344.91	6.02

RMS DEVIATION = 7.05

TABLE 22

SYSTEM OCTANOL+HEPTANE AT 45 DEG. C
X=MOL. FRACT. OF THE ALCOHOL, TDTD=PREDICTED HEATS OF MIXING

X	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.0200	0.18	273.72	322.00	273.90	14.94
0.0300	0.26	319.57	400.00	319.83	20.04
0.0400	0.35	359.78	452.00	360.12	20.33
0.0500	0.43	397.42	491.00	397.85	18.97
0.0750	0.63	476.85	563.00	477.48	15.19
0.1000	0.81	538.13	610.00	538.94	11.65
0.1250	0.99	586.98	643.00	587.97	8.56
0.1500	1.15	625.92	667.00	627.07	5.99
0.1750	1.30	662.16	686.00	663.45	3.29
0.2000	1.44	683.59	699.00	685.03	2.00
0.3000	1.88	738.82	718.00	740.70	-3.16
0.4000	2.14	735.64	698.00	737.78	-5.70
0.5000	2.22	673.38	642.50	675.61	-5.15
0.6000	2.13	588.14	554.00	590.27	-6.55
0.7000	1.85	429.83	443.00	431.68	2.55
0.8000	1.41	287.80	307.00	289.20	5.80
0.9000	0.79	156.60	157.00	157.38	-0.24

RMS DEVIATION = 10.96

TABLE 23

SYSTEM OCTANOL+NONANE AT 45 DEG. C
X=MOL. FRACT. OF THE ALCOHOL, TDTH=PREDICTED HEATS OF MIXING

X	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.0200	0.0	325.11	346.00	325.11	6.04
0.0300	0.0	371.00	440.00	371.00	15.68
0.0400	0.0	414.25	500.00	414.25	17.15
0.0500	0.0	454.30	544.00	454.30	16.49
0.0750	0.0	542.58	629.00	542.58	13.74
0.1000	0.0	614.91	688.00	614.91	10.62
0.1250	0.0	672.66	730.00	672.66	7.85
0.1500	0.0	719.38	760.00	719.38	5.35
0.1750	0.0	758.67	784.00	758.67	3.23
0.2000	0.0	790.06	802.00	790.06	1.49
0.3000	0.0	861.13	832.00	861.13	-3.50
0.4000	0.0	871.56	816.00	871.56	-6.81
0.5000	0.0	827.08	763.00	827.08	-8.40
0.6000	0.0	719.32	677.00	719.32	-6.25
0.7000	0.0	555.76	552.00	555.76	-0.68
0.8000	0.0	373.88	365.00	373.88	-2.43
0.9000	0.0	181.64	205.00	181.64	11.39

RMS DEVIATION = 9.57

TABLE 24

SYSTEM HEPTANE+PROPANOL+PENTANOL AT 25 DEG,C, SOLUTION A
1=HEPTANE,2=PROPANOL,3=PENTANOL, x_{a5} = 0.7409

X1	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.2461	1.75	319.42	317.00	321.17	-1.32
0.2291	2.14	308.78	304.00	310.92	-2.28
0.2054	2.18	293.94	285.00	296.12	-3.90
0.1703	1.73	260.56	255.00	262.28	-2.86
0.1357	1.24	212.60	221.00	213.84	3.24
0.1128	1.34	171.45	193.00	172.79	10.47
0.0921	1.91	131.78	167.00	133.70	19.94
0.0745	2.87	93.43	142.00	96.30	32.18
0.0544	3.83	94.11	108.00	97.94	9.32
0.0411	4.69	73.98	85.00	78.67	7.45

RMS DEVIATION = 13.14

TABLE 25

SYSTEM PROPANOL+HEPTANE+PENTANOL AT 25 DEG. C, SOLUTION B
1=HEPTANE,2=PROPANOL,3=PENTANOL , $x_{a_5} = 0.4989$

X1	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.4752	1.16	543.38	543.00	544.54	-0.28
0.4412	1.33	522.41	526.00	523.74	0.43
0.3942	1.29	489.34	496.00	490.62	1.08
0.3252	0.98	431.01	442.00	431.99	2.27
0.2576	0.84	379.46	377.00	380.31	-0.88
0.2134	1.45	331.91	331.00	333.37	-0.71
0.1822	2.82	283.92	293.00	286.73	2.14
0.1473	4.81	224.64	248.00	229.45	7.48
0.1068	6.89	147.04	190.00	153.92	18.99
0.0841	8.89	139.32	155.00	148.21	4.38

RMS DEVIATION = 6.69

TABLE 26

SYSTEM HEPTANE+PROPANOL+PENTANOL AT 25 DEG, C, SOLUTION C
1=HEPTANE,2=PROPANOL,3=PENTANOL, $x_{a_5} = 0.2507$

X1	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.7076	0.40	604.26	589.00	604.65	-2.66
0.6576	0.49	615.87	609.00	616.36	-1.21
0.5860	0.48	634.50	612.00	634.98	-3.76
0.4814	0.35	583.10	573.00	583.44	-1.82
0.3767	0.50	506.30	503.00	506.80	-0.76
0.3151	1.50	460.45	446.00	461.95	-3.58
0.2688	3.47	407.33	398.00	410.80	-3.22
0.1997	6.39	310.45	316.00	316.84	-0.27
0.1382	9.14	201.14	233.00	210.27	9.75
0.1145	12.07	184.20	198.00	196.27	0.87

RMS DEVIATION = 3.82

TABLE 27

SYSTEM HEPTANE+PROPANOL+OCTANOL AY 25 DEG.C, SOLUTION A
1=HEPTANE, 2=PROPANOL, 3=OCTANOL , x_{a8} = 0.7409

X1	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.2492	10.96	268.10	291.00	279.06	4.10
0.2287	13.15	274.21	301.00	287.36	4.53
0.2011	12.87	270.38	305.00	283.25	7.13
0.1620	9.40	255.69	295.00	265.09	10.14
0.1255	5.61	228.25	269.00	233.86	13.06
0.1024	3.98	202.77	242.00	206.75	14.56
0.0883	3.78	179.66	225.00	183.45	18.47
0.0592	3.26	103.26	174.00	106.52	38.78
0.0450	3.78	95.71	143.00	99.49	30.43
0.0331	4.22	75.42	112.00	79.64	28.90

RMS DEVIATION = 20.44

TABLE 28

SYSTEM HEPTANE + PROPANOL + OCTANOL AT 25 DEG.C, SOLUTION B
1=HEPTANE, 2=PROPANOL,3=OCTANOL, $x_{a8} = 0.4985$

X1	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.4665	7.11	494.97	475.00	502.08	-5.70
0.4263	7.95	459.86	486.00	467.81	3.74
0.3735	7.49	444.03	479.00	451.52	5.74
0.2978	5.35	396.21	440.00	401.55	8.74
0.2295	3.35	347.64	383.00	350.99	8.36
0.1867	3.00	304.83	338.00	307.83	8.93
0.1574	3.82	271.06	301.00	274.88	8.68
0.1192	5.08	202.04	247.00	207.12	16.15
0.0807	6.11	121.01	191.00	127.12	33.44
0.0671	7.89	122.94	157.00	130.83	16.67

RMS DEVIATION = 14.27

TABLE 29

SYSTEM HEPTANE+PROPANOL+OCTANOL AT 25 DEG.C, SOLUTION C
1=HEPTANE,2=PROPANOL,3=OCTANOL , x_{a3} = 0.3376

X1	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.7076	2.24	544.93	537.00	547.17	-1.89
0.6498	2.62	567.28	580.00	569.91	1.74
0.5716	2.61	617.65	601.00	620.25	-3.20
0.4609	1.98	570.56	571.00	572.54	-0.27
0.3547	1.52	489.38	496.00	490.89	1.03
0.2922	2.22	427.15	438.00	429.37	1.97
0.2350	4.00	369.96	378.00	373.96	1.07
0.1854	6.58	296.30	316.00	302.88	4.15
0.1345	9.17	205.65	242.00	214.82	11.23
0.1043	11.54	145.50	197.00	157.04	20.28

RMS DEVIATION = 7.60

TABLE 30

SYSTEM HEPTANE+PROPANOL+DECANOL AT 25 DEG. C, SOLUTION A
1=HEPTANE, 2=PROPANOL,3=DECANOL, x_{a10} = 0.7421

X1	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.2382	22.93	238.72	302.00	261.65	13.36
0.2136	26.45	245.60	332.00	273.05	17.76
0.1824	23.64	240.88	355.00	264.52	25.49
0.1411	14.97	229.89	355.00	244.86	31.02
0.1054	7.74	215.19	324.00	223.93	30.88
0.0841	4.90	188.16	292.00	193.07	33.88
0.0662	3.66	154.51	257.00	158.17	38.46
0.0498	3.29	108.94	220.00	112.23	48.99
0.0356	3.33	60.20	172.00	63.53	63.06
0.0277	3.75	74.46	142.00	78.21	44.92

RMS DEVIATION = 37.52

TABLE 31

SYSTEM HEPTANE+PROPANOL+DECANOL AT 25 DEG. C, SOLUTION B
1=HEPTANE, 2=PROPANOL, 3=DECANOL , x_{a10} = 0.4941

X1	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.4720	13.63	443.95	471.00	457.58	2.85
0.4273	15.16	458.57	500.00	473.73	5.25
0.3699	13.96	429.18	505.00	443.14	12.25
0.2914	9.56	384.02	470.00	393.57	16.26
0.2211	5.52	348.88	411.00	354.40	13.77
0.1772	4.21	302.99	366.00	307.20	16.07
0.1415	4.33	258.33	321.00	262.65	18.17
0.1037	5.07	185.88	259.00	190.95	26.27
0.0742	6.05	116.01	201.00	122.05	39.28
0.0606	7.47	118.40	170.00	125.87	25.96

RMS DEVIATION = 20.33

TABLE 32

SYSTEM HEPTANE+PROPANOL+DECANOL AT 25 DEG.C, SOLUTION C
1=HEPTANE, 2= PROPANOL, 3=DECANOL ,x_{a10} =0.2404

X1	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.7109	4.19	511.47	524.00	515.66	1.59
0.6517	4.87	540.72	579.00	545.58	5.77
0.5708	4.81	576.54	610.00	581.35	4.70
0.4574	3.64	563.99	585.00	567.63	2.97
0.3525	2.53	488.77	516.00	491.30	4.79
0.2867	2.87	423.36	456.00	426.23	6.53
0.2296	4.39	366.26	396.00	370.66	6.40
0.1761	6.72	293.66	326.00	300.38	7.86
0.1265	9.00	197.59	256.00	206.60	19.30
0.0988	11.25	141.69	206.00	152.93	25.76

RMS DEVIATION = 11.27

TABLE 33

SYSTEM OCTANE+PROPANOL+PENTANOL AT 25 DEG.C, SOLUTION A
1=OCTANE,2=PROPANOL, 3=PENTANOL , x_{a_5} = 0.7456

X1	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.2479	1.51	346.83	366.00	348.34	4.82
0.2252	2.26	339.47	347.00	341.73	1.52
0.2020	2.34	326.31	326.00	328.65	-0.81
0.1676	1.83	290.30	291.00	292.14	-0.39
0.1337	1.13	238.79	251.00	239.92	4.41
0.1113	0.89	197.50	222.00	198.39	10.63
0.0909	1.09	151.70	192.00	152.79	20.42
0.0692	1.65	101.47	155.00	103.12	33.47
0.0510	2.39	100.10	121.00	102.49	15.30
0.0404	3.21	81.94	100.00	85.15	14.85

RMS DEVIATION = 14.67

TABLE 34

SYSTEM OCTANE+PROPANOL+PENTANOL AT 25 DEG. C, SOLUTION B
1=OCTANE, 2=PROPANOL, 3=PENTANOL , x_{a5} = 0.5096

X1	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.4633	1.28	583.67	593.00	584.96	1.36
0.4282	1.54	574.57	573.00	576.11	-0.54
0.3800	1.53	523.86	539.00	525.39	2.53
0.3100	1.11	467.13	479.00	468.25	2.24
0.2433	0.60	403.40	408.00	404.00	0.98
0.2004	0.65	354.33	355.00	354.98	0.01
0.1624	1.36	288.06	304.00	289.42	4.80
0.1220	2.62	208.90	244.00	211.52	13.31
0.0887	4.05	164.07	186.00	168.12	9.61
0.0698	5.52	133.35	151.00	138.87	8.03

RMS DEVIATION = 6.10

TABLE 34

SYSTEM OCTANE+PROPANOL+PENTANOL AT 25 DEG. C, SOLUTION B
1=OCTANE, 2=PROPANOL, 3=PENTANOL, $x_{a5} = 0.5096$

X1	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.4633	1.28	583.67	593.00	584.96	1.36
0.4282	1.54	574.57	573.00	576.11	-0.54
0.3800	1.53	523.86	539.00	525.39	2.53
0.3100	1.11	467.13	479.00	468.25	2.24
0.2433	0.60	403.40	408.00	404.00	0.98
0.2004	0.65	354.33	355.00	354.98	0.01
0.1624	1.36	288.06	304.00	289.42	4.80
0.1220	2.62	208.90	244.00	211.52	13.31
0.0887	4.05	164.07	186.00	168.12	9.61
0.0698	5.52	133.35	151.00	138.87	8.03

RMS DEVIATION = 6.10

TABLE 35

SYSTEM PROPANOL+OCTANE+PENTANOL AT 25 DEG.C, SOLUTION C
1=OCTANE, 2=PROPANOL,3=PENTANOL, x_{a5} = 0.2480

X1	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.7042	0.46	666.05	633.00	666.52	-5.29
0.6475	0.63	677.71	655.00	678.35	-3.56
0.5683	0.70	715.33	655.00	716.03	-9.32
0.4565	0,50	640.71	610.00	641.21	-5.12
0.3530	0.19	541.08	531.00	541.27	-1.93
0.2882	0.48	474.27	467.00	474.75	-1.66
0.2316	1.65	409.11	403.00	410.76	-1.93
0.1858	3.60	331.37	341.00	334.97	1.77
0.1345	5.80	227.26	264.00	233.06	11.72
0.1056	8.04	167.46	219.00	175.50	19.86

RMS DEVIATION = 8.36

TABLE 36

YSTEM OCTANE+PROPANOL+OCTANOL AT 25 DEG. C
1=OCTANE, 2=PROPANOL,3=OCTANOL, ASOLUTION A , x_{a8} = 0.6902

X1	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.2857	11.20	373.34	372.00	384.54	-3.37
0.2598	12.66	351.75	377.00	364.42	3.34
0.2275	11.80	337.73	374.00	349.59	6.53
0.1798	8.02	307.00	349.00	315.02	9.74
0.1369	4.31	270.66	308.00	274.97	10.73
0.1105	2.72	236.77	272.00	239.48	11.96
0.0880	2.15	184.85	236.00	186.99	20.77
0.0675	2.27	133.10	195.00	135.37	30.58
0.0485	2.69	109.50	158.00	112.19	29.00
0.0363	3.26	86.73	130.00	89.98	30.78

RMS DEVIATION = 18.90

TABLE 37

SYSTEM OCTANE+PROPANOL+OCTANOL, 25 DEG. C, SOLUTION B
1=OCTANE,2=PROPANOL,3=OCTANOL

X1	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.4807	6.90	525.09	526.00	531.98	-1.14
0.4442	7.65	547.11	536.00	554.76	-3.50
0.3811	7.33	509.22	533.00	516.54	3.09
0.3026	5.12	449.80	490.00	454.92	7.16
0.2315	2.80	394.56	425.00	397.36	6.50
0.1875	1.97	345.24	373.00	347.21	6.91
0.1497	2.13	290.20	324.00	292.32	9.78
0.1131	2.98	213.83	265.00	216.81	18.18
0.0814	4.08	138.17	204.00	142.26	30.27
0.0636	5.35	130.53	167.00	135.88	18.63

RMS DEVIATION = 13.62

TABLE 38

SYSTEM OC E+PROPANOL+OCTANOL AT 25 DEG.C, SOLUTION C
1=OCTANE, 2=PROPANOL, 3=OCTANOL, x_{a8}= 0.2536

X1	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.6987	2.42	602.06	574.00	604.48	-5.31
0.6382	2.90	624.24	619.00	627.14	-1.32
0.5574	2.92	691.05	641.00	693.97	-8.26
0.4452	2.16	627.83	608.00	629.99	-3.62
0.3419	1.19	534.47	532.00	535.65	-0.69
0.2775	1.11	462.20	467.00	463.31	0.79
0.2218	2.00	396.98	403.00	398.98	1.00
0.1636	3.65	299.47	320.00	303.13	5.27
0.1182	5.52	204.24	245.00	209.75	14.39
0.0924	7.45	175.39	199.00	182.84	8.12

RMS DEVIATION = 6.43

TABLE 39

SYSTEM OCTANE+PROPANOL+DECANOL AT 25 DEG.C
1=OCTANE, 2=PROPANOL, 3=DECANOL, SOLUTION A , x_{a10} = 0.7488

X1	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.2312	23.42	279.70	304.00	303.12	0.29
0.2068	25.92	291.82	340.00	318.74	6.25
0.1758	23.78	265.53	366.00	289.31	20.95
0.1353	14.74	250.09	367.00	264.83	27.84
0.1006	7.28	231.00	336.00	238.28	29.08
0.0800	4.19	206.80	302.00	210.99	30.13
0.0629	2.72	165.24	266.00	167.96	36.86
0.0457	2.08	110.02	220.00	112.10	49.05
0.0325	2.08	91.30	170.00	93.38	45.07
0.0252	2.45	75.20	138.00	77.65	43.73

RMS DEVIATION = 32.73

TABLE 40

SYSTEM OCTANE +PROPANOL+DECANOL AT 25 DEG.C, SOLUTION B
1=OCTANE, 2=PROPANOL, 3=DECANOL , x_{a10} = 0.4904

X1	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.4713	13.85	497.08	488.00	510.92	-4.70
0.4240	15.24	504.55	521.00	519.79	0.23
0.3630	13.72	473.74	531.00	487.46	8.20
0.2821	8.94	422.55	497.00	431.49	13.18
0.2115	4.61	370.03	436.00	374.64	14.07
0.1691	2.93	323.55	384.00	326.48	14.98
0.1335	2.58	275.49	332.00	278.08	16.24
0.1061	3.23	219.32	283.00	222.55	21.36
0.0757	4.03	139.12	218.00	143.15	34.33
0.0588	5.13	127.59	177.00	132.72	25.02

RMS DEVIATION = 17.92

TABLE 41

SYSTEM OCTANE+PROPANOL+DECANOL AT 25 DEG. C
1=OCTANE, 2=PROPANOL, 3=DECANOL, SOLUTION C, $x_{a_{10}} = 0.2545$

X1	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.6914	4.79	556.27	559.00	571.06	-2.16
0.6295	5.54	594.39	617.00	599.93	2.77
0.5447	5.40	640.12	647.00	645.53	0.23
0.4292	3.86	607.81	616.00	611.68	0.70
0.3257	2.11	510.56	537.00	512.67	4.53
0.2625	1.66	452.10	471.00	453.76	3.66
0.2085	2.30	385.87	405.00	388.17	4.16
0.1668	3.87	314.26	345.00	318.13	7.79
0.1188	5.61	214.50	265.00	220.10	16.94
0.0923	7.48	152.79	215.00	160.27	25.45

RMS DEVIATION = 10.29

TABLE 42

SYSTEM TETRADECANE+PROPANOL+PENTANOL AT 25 DEG. C, SOLUTION A
1=TETRADECANE,2=PROPANOL,3=PENTANOL , x_{a5}=0.7503

X1	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.2336	2.99	541.61	609.00	544.59	10.58
0.2135	4.64	532.19	578.00	536.83	7.12
0.1865	6.02	480.15	537.00	486.17	9.47
0.1492	6.79	424.49	469.00	431.28	8.04
0.1143	6.06	350.01	394.00	356.07	9.63
0.0931	4.45	289.94	341.00	294.39	13.67
0.0745	2.82	231.49	293.00	234.32	20.03
0.0440	1.25	144.50	203.00	145.75	28.20
0.0311	0.45	106.95	156.00	107.40	31.15
0.0241	0.10	85.05	127.00	85.15	32.95

RMS DEVIATION = 19.62

TABLE 43

YSTEM TETRADECANE+PROPANOL+PENTANOL AT 25 DEG.C, SOLUTION B =TETRADECANE,2=PROPANOL,3=PENTANOL, x_{a5} = 0.4975

X1	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.4653	2.60	888.99	878.00	891.59	-1.55
0.4187	4.88	909.86	852.00	914.74	-7.36
0.3525	8.02	831.44	796.00	839.45	-5.46
0.2722	10.22	694.90	709.00	705.13	0.55
0.2098	9.92	569.56	602.00	579.48	3.74
0.1681	7.43	496.74	524.00	504.17	3.78
0.1403	4.79	435.24	467.00	440.03	5.78
0.1000	2.45	311.83	367.00	314.28	14.37
0.0714	0.92	207.33	284.00	208.25	26.67
0.0555	0.20	180.00	232.00	180.20	22.33

RMS DEVIATION = 12.51

TABLE 44

SYSTEM TETRADECANE+PROPANOL+PENTANOL AT 25 DEG.C, SOLYTION C
=TETRADECANE, 2=PROPANOL,3=PENTANOL, x_{a5} = 0.2482

X1	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.6846	1.53	979.77	838.00	981.30	-11.13
0.6029	4.36	997.55	913.00	1001.91	-9.74
0.5029	8.77	967.18	899.00	975.95	-8.56
0.3775	13.51	880.63	818.00	894.14	-9.31
0.2753	13.44	727.27	701.00	740.71	-5.67
0.2168	9.97	614.57	612.00	624.54	-2.05
0.1689	6.25	504.98	526.00	511.23	2.81
0.1382	3.31	428.16	470.00	431.47	8.20
0.0965	1.23	296.03	362.00	297.26	17.88
0.0743	0.26	214.01	295.00	214.27	27.37

RMS DEVIATION = 12.49

TABLE 45

STEM TETRADECANE+PROPANOL+OCTANOL AT 25 DEG. C, SOLUTION A
=TETRADECANE, 2=PROPANOL,3=OCTANOL, $x_{a_8} = 0.7409$

X1	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.2401	12.91	525.98	531.00	538.89	-1.49
0.2165	16.35	477.73	531.00	494.08	6.95
0.1858	16.87	447.91	519.00	464.77	10.45
0.1449	14.02	405.08	478.00	419.10	12.32
0.1089	9.80	346.44	416.00	356.24	14.37
0.0873	6.49	305.79	365.00	312.28	14.44
0.0698	3.88	253.66	316.00	257.55	18.50
0.0460	1.64	153.95	234.00	155.59	33.51
0.0332	0.61	124.75	181.00	125.35	30.74
0.0272	0.19	105.89	152.00	106.07	30.21

RMS DEVIATION = 20.12

TABLE 46

YSTEM TETRADECANE+PROPANOL+P OCTANOL AT 25 DEG.C, SOLUTION 8
=TETRADECANE ,2=PROPANOL,3=OCTANOL, $x_{a_8} = 0.4985$

X1	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.4618	8.98	761.44	773.00	770.42	0.33
0.4093	12.06	811.06	787.00	823.12	-4.59
0.3384	14.43	743.40	758.00	757.83	0.02
0.2576	14.62	640.02	680.00	654.64	3.73
0.1898	11.96	531.24	576.00	543.20	5.69
0.1502	8.34	451.69	499.00	460.03	7.81
0.1176	5.05	381.28	426.00	386.33	9.31
0.0838	2.42	272.54	336.00	274.96	18.17
0.0596	0.88	178.16	258.00	179.04	30.60
0.0463	0.21	153.73	210.00	158.93	24.32

RMS DEVIATION = 14.40

TABLE 47

STEM TETRADECANE+PROPANOL+OCTANOL AT 25 DEG.C, SOLUTION C
TETRADECANE,2=PROPANOL,3=OCTANOL , x_{a8} = 0.3376

X1	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.6021	5.45	880.22	820.00	885.68	-8.01
0.5299	8.62	885.84	860.00	894.46	-4.01
0.4416	12.15	926.30	853.00	938.45	-10.02
0.3314	14.86	739.36	774.00	804.21	-3.90
0.2410	13.38	650.47	657.00	663.85	-1.04
0.1894	9.60	543.94	567.00	553.54	2.37
0.1474	5.89	457.14	483.00	463.03	4.13
0.1214	3.12	388.86	419.00	391.97	6.45
0.0850	1.15	266.03	317.00	267.18	15.72
0.0725	0.29	218.49	279.00	218.78	21.58

RMS DEVIATION = 9.87

TABLE 48

SYSTEM PENTANOL + OCTANOL AT 25 DEG. C
X=MOL. FRACT. OF PENTANOL, TOTH=PREDICTED HEATS OF MIXING

X	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.8848	0.11	19.18	4.50	23.68	-2.96
0.8812	0.19	20.01	7.36	27.37	27.97
0.8754	0.33	27.72	10.39	38.11	29.43
0.8689	0.46	30.37	11.82	42.19	33.04
0.8628	0.57	34.06	11.73	45.80	28.44
0.8624	0.58	30.55	11.69	42.24	35.02
0.8588	0.64	26.91	11.07	37.98	37.74
0.8534	0.73	26.39	9.58	35.97	33.39
0.8474	0.82	18.51	7.27	25.78	38.62
0.8414	0.90	12.54	4.42	16.97	34.75
0.8377	0.95	4.56	2.46	7.02	53.22

RMS DEVIATION = 34.19

TABLE 49

SYSTEM PENTANOL + DECANOL AT 20 DEG. C
X=MOL. FRACT. OF PENTANOL, TOTH=PREDICTED HEATS OF MIXING

X	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.9064	0.06	-11.11	7.33	-3.78	111.13
0.9038	0.12	-10.55	13.05	2.49	95.77
0.8992	0.22	-10.84	20.94	10.10	89.37
0.8916	0.35	4.26	28.66	32.92	74.87
0.8830	0.49	23.57	31.62	55.19	62.71
0.8766	0.58	30.93	31.06	61.99	57.83
0.8717	0.64	24.80	29.46	54.26	62.06
0.8686	0.68	39.34	28.04	67.38	51.17
0.8612	0.76	34.76	23.61	58.36	52.16
0.8522	0.85	25.78	16.88	42.66	53.12
0.8441	0.92	20.77	9.95	30.72	45.14
0.8391	0.96	10.72	5.43	16.15	47.90
0.8363	0.98	6.76	2.84	9.59	43.56

RMS DEVIATION = 68.29

TABLE 50

SYSTEM HEXANOL+OCTANOL AT 25 DEG. C
X=MOL. FRACT OF HEXANOL, TDTH=PREDICTED HEATS OF MIXING

X	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.8876	0.05	9.81	1.04	10.85	-80.78
0.8863	0.10	-0.10	1.88	1.78	82.35
0.8847	0.16	2.81	2.82	5.64	61.63
0.8827	0.24	15.47	3.73	19.20	-1.04
0.8805	0.31	16.28	4.44	20.73	8.29
0.8783	0.39	-1.44	4.92	3.47	86.11
0.8761	0.46	3.19	5.15	8.34	68.03
0.8740	0.53	3.59	5.17	8.76	66.30
0.8721	0.59	-4.06	5.03	0.97	96.15
0.8716	0.61	-0.16	4.96	4.80	80.47
0.8695	0.67	-0.54	4.63	4.09	82.45
0.8672	0.73	6.38	4.07	10.45	50.01
0.8649	0.80	4.10	3.38	7.47	57.05
0.8629	0.85	2.07	2.64	4.71	65.61
0.8610	0.90	0.34	1.82	2.16	76.97
0.8593	0.95	-8.74	1.07	-7.67	232.24
0.8582	0.97	-3.74	0.54	-3.20	214.16

RMS DEVIATION = 100.56

APPENDIX C

Fortran Programs

Spline-fit program

Forsythe polynomial program

Programs for prediction of heats of mixing

TABLE 51

Spline-Fit Program

Input-Output Format

Card	Column	Format	Variable	Data
1, 2	2-80	80H	--	Any alphameric information (e.g. headings of output)
3	1-10	I10	IANCHOR	Anchor option 0 = do not anchor the end points 1 = anchor the first and last points
	1-20	I10	NINTS	Number of intervals
	21-30	I10	IPUNOP	Punch option 0 = do not punch 1 = punch
	31-40	I10	INTEOP	Interpolation option 0 = do not interpolate 1 = interpolate
4	1-10	I10	NPTS	Number of data points
5 to 5+I	1-20	F20.0	X(I)	X_i value
	21-40	F20.0	Y(I)	Y_i value
6+I	--	--	--	Blank
7+I to 7+I+NINTS	0-21	F20.0	XINT	Value of independent variables which are to be interval boundaries
	21-40	F20.0	DXINT	XINT (I) - XINT (I-1)

TABLE 51 (cont.)

Nomenclature of Output

Variable	Data
X	X_i values
Y	Y_i values
YCALC	Fitted values of Y_i
DEV(PTC)	Percentage deviation of YCALC from Y
DER1	First derivative of Y with respect to X
DER2	Second derivative of Y with respect to X

TABLE 52

Spline-Fit Program

Fortran Statement

```
C     THIS DRIVER MAY BE USED TO SPLINE-FIT Y VS X. DATA OVER SPECIFIE
C     INTERVALS.
C     THIS PROGRAM ALSO HAS THE OPTION OF PUNCHING THE OUTPUT OF THE
C     BASIC CALCULATIONS FOR USE IN OTHER PROGRAMS
C     THE CURVE WILL BE A CUBIC EXCEPT IN THE FIRST AND LAST INTERVALS
C     WHERE IT WILL BE A PARABOLA. THE CURVE WILL GO AS CLOSE AS
C     POSSIBLE TO EVERY POINT IN A LEAST SQUARES SENSE
C     BUT THERE IS NO PROTECTION AGAINST INFLECTION POINTS. FIRST AND
C     SECOND DERIVATIVES WILL MATCH AT ALL INTERVAL BOUNDARIES TWO
C     HEADERS INTERVAL BOUNDARIES,AND INTERPOLATION INTERVALS ARE READ
C     X AND Y ARE READ IN FROM CARDS IN THE FORMAT (2F20.6) UNTIL A
C     A GIVEN CASE. THE PROGRAM PRINTS OUT X,Y AND THE FIRST TWO DERI-
C     VATIVES AT ALL THE DATA POINTS AND INTERVAL BOUNDARIES
C     THIS DRIVER ALSO INTERPOLATES THE DATA DEPENDING ON THE
C     VALUES STORED IN XBASE(5) AND XDELT(5).THE LATTER TWO ARRAYS
C     CONTAIN NUMBERS WHICH FORM THE BASE NUMBERS AND INTERPOLATION
C     INTERVALS. THE PROGRAM FIRST CALLS XSETUT TO SET UP VALUES
C     OF XNEW WHICH ARE THE POINT TO BE INTERPOLATED. IT THEN CALLS
C     IINTSP TO PERFORM THE ACTUAL INTERPOLATION
C     Z(I)=GROUP CH2 FRACTION
C     HS2 = SKELETAL PARTIAL HEAT OF MIXING
C     B=CONSTANT WHERE HS2=B*((N1-N2)X1)**2
C
      DIMENSION HXCH2(101)
      DIMENSION XBASE(5),XDELT(5)
      DIMENSION XNEW(101),YNEW(101),D2NEW(101),NFLAG(101)
      DIMENSION XINT(101),DXINT(101),YCALC(101)
      DIMENSION X(101),Y(101),DER2(101),DER2Y(101),D1NEW(101)
      DIMENSION DTHB1(101),DTHB2(101)
      DIMENSION XCH2(101)
      DIMENSION B(101),HS2(101),F(101)
      DIMENSION  HOH1(101),HOH2(101)
      EQUIVALENCE (DER2Y(1),D2NEW(1))
      H(Z)=-2.6647449E 03 +7.6687539E 03*Z -4.8014063E 03*Z*Z
      INP=5
      IOUTP = 6
      NC=0
      N1=1
      N2=2
      N80=80
      N101 = 101
      ERROR=5.E-6
  888 READ(5,1000,END=9999)
 1000 FORMAT(1X,79H
     1
     2  /1X,79H
     3                                                                  )
      READ(INP,200) IANKOR,NINTS,IPUNOP,INTEOP
  200 FORMAT(4I10)
C NI#NUMBER OF CARBON ATOMS IN ALCOHOL MOLECULE
C NJ#NUMBER OF CARBON ATOMS IN HYDROCARBON ATOM
      READ(INP,221) NI,NJ,NK
  221 FORMAT(3I10)
      NINTS1=NINTS+1
      READ(5,3000) NPTS
 3000 FORMAT(I10)
```

```
      READ(5,220)(X(I),Y(I),I=1,NPTS)
  220 FORMAT(2F20.0)
      IF(NINTS)17,17,15
   15 DO 16 I=1,NINTS1
   16 READ(INP,210) XINT(I)
  210 FORMAT(F16.0)
   17 IF(INTEOP) 18,19,18
   18 DO 20 I=1,5
      READ(INP,270) XBASE(I),XDELT(I)
 270  FORMAT(2F20.0)
   20 CONTINUE
   19 IF(NINTS) 41,41,43
   41 DO 42 I=1,NPTS
   42 XINT(I)=X(I)
      NINTS=NPTS-1
      NINTS1=NPTS
   43 DO 44 I=2,NINTS1
   44 DXINT(I)=XINT(I)-XINT(I-1)
      DXINT(1)=0.
      WRITE(IOUTP,1050)
 1050 FORMAT('1SPLINE FIT PROGRAM--  HUONG T. H. ')
      WRITE(IOUTP,1000)
      CALL SPLAG(IANKOR,X,Y,NPTS,XINT,DXINT,NINTS,YCALC,DER2)
         WRITE(IOUTP,3050)
 3050 FORMAT('0INPUT POINTS (* INDICATES INTERVAL BOUNDARY)'/)
      CALL XBLEND(X,Y,N101,XINT,NINTS1,NFLAG,NPTS)
      IF(IANKOR) 46,46,45
   45 WRITE(IOUTP,1045)
 1045 FORMAT(' END POINT ANCHORED ')
   46 CALL I2NTSP(DXINT,XINT,YCALC,DER2,X,YNEW,DER2Y,NINTS1,NPTS,D1NE
      WRITE(IOUTP,6050)
 6050 FORMAT(13X,1HX,19X,1HY,17X,6HY CALC,14X,'DEV(PCT)',14X,4HDER1,
     1  16X,4HDER2//)
      DO 100 I=1,NPTS
      IF(NFLAG(I)) 70,70,80
   70 STORE=100.*(YNEW(I)-Y(I))
      IF(Y(I)) 71,72,71
   71 STORE=STORE/ABS(Y(I))
   72 WRITE(IOUTP,1070) X(I),Y(I),YNEW(I),STORE,D1NEW(I),DER2Y(I)
 1070 FORMAT(6E20.6)
      IF(NFLAG(I)) 90,100,100
   80 WRITE(IOUTP,1080) X(I),YNEW(I),D1NEW(I),DER2Y(I)
 1080 FORMAT(E20.6,20X,E20.6,20X,2E20.6)
   90 WRITE(IOUTP,1090)
 1090 FORMAT(1H+,5X,1H*)
      IF(IPUNOP)95,100,95
   95 WRITE(IPUNCH,1095) X(I),YNEW(I),D1NEW(I),DER2Y(I)
 1095 FORMAT(4E15.6)
  100 CONTINUE
      IF(XDELT(1))888,888,65
   65 CALL XSETUP(XBASE,XDELT,XNEW,NPTNEW,ERROR)
      CALL I2NTSP(DXINT,XINT,YCALC,DER2,XNEW,YNEW,D2NEW,NINTS1,
     1  NPTNEW,D1NEW)
      DO 101 I=1,NPTNEW
      DTHB1(I)=(1.-XNEW(I))*(1.-XNEW(I))*(YNEW(I)+XNEW(I)*D1NEW(I))
```

```
  101 DTHB2(I) = XNEW(I)*(YNEW(I)-(DTHB1(I)/(1.-XNEW(I))))
      ANI=NI
      ANJ=NJ
      IF(NK) 6,6,7
    6 DO 102 I=1,NPTNEW
      XS1=ANI/(1.+ANI)
      XS2=ANJ/(1.+ANJ)
      HXCH2(I) = DTHB2(I)/ANJ
      XCH2(I)=(NI*XNEW(I)+NJ*(1.-XNEW(I)))/((NI+1.)*XNEW(I) +
     1NJ*(1.-XNEW(I)))
      F(I)=0.
      HOH1(I)=DTHB1(I)-ANI*(H(XCH2(I))-237.)
  102 HOH2(I)=0.0
      GO TO 104
    7 DO 103 I=1,NPTNEW
      ANI=NI
      XS1=ANI/(1.+ANI)
      XS2=ANJ/(1.+ANJ)
      XCH2(I)=(NI*XNEW(I)+NJ*(1.-XNEW(I)))/((NI+1.)*XNEW(I) +
     1 (NJ+1.)*(1.-XNEW(I)))
      F(I)=H(XCH2(I))
      HXCH2(I)=0.
      HOH1(I)=DTHB1(I)-ANI*(F(I)-H(XS1))
  103 HOH2(I)=DTHB2(I)-ANJ*(F(I)-H(XS2))
  104 WRITE(IOUTP,1050)
      WRITE(IOUTP,1000)
      WRITE(IOUTP,4050)
 4050 FORMAT ('0INTERPOLATED POINTS'/)
      WRITE(IOUTP,5050)
 5050 FORMAT(13X,1HX,19X,1HY,17X,4HDER1,16X,4HDER2,16X,5HDTHB1,15X,
     1 5HDTHB2//)
      WRITE(IOUTP,2050)  (XNEW(I),YNEW(I),D1NEW(I),D2NEW(I),DTHB1(I),
     1 DTHB2(I),I=1,NPTNEW)
 2050 FORMAT(6E20.6)
      WRITE(IOUTP,2049)
 2049 FORMAT(13X,1HX,19X,4HXCH2,13X,5HHXCH2,15X,4HHOH1,15X,4HHOH2//)
      WRITE(6,2051)(XNEW(I),XCH2(I),HXCH2(I),HOH1(I),HOH2(I),F(I),
     1  I=1,NPTNEW)
 2051 FORMAT(6E20.6)
      GO TO 888
 9999 STOP
      END


      FUNCTION SPLDR1(ARG,XHI,DELX,DER21,DER22,DELY)
C     VN-FS017.1
C     THIS FUNCTION CALCULATES FIRST DERIVATIVES IN A SPLINE-FITTING
C     ALGORITHM GIVEN THE SECOND DERIVATIVES, AN ARGUMENT, AND Y-INCR
C     MENTS
C     ARG=ARGUMENT. THIS MUST BE LESS THAN XHI BUT GREATER THAN XHI
C     MINUS DELX
C     DER21 = SECOND DERIVATIVE AT (XHI - DELX)
C     DER22 = SECOND DERIVATIVE AT XHI
C     DELY = Y(XHI) - Y(XHI-DELX)
```

```
C
      DOUBLE PRECISION STOR1,STOR2
      STOR1=DER21*(XHI-ARG)*(XHI-ARG)*0.5/DELX
      STOR2=DER22*(ARG-XHI+DELX)*(ARG-XHI+DELX)*0.5/DELX
      STOR1=STOR2-STOR1
      STOR2=DELY/DELX
      STOR1=STOR1+STOR2
      STOR2=DELX*(DER22-DER21)/6.
      STOR1=STOR1-STOR2
      SPLDR1=STOR1
      RETURN
      END


      SUBROUTINE SPLAG(IANKOR,X,Y,NPTS,XINT,DXINT,NINTS,YCALC,DER2)
C     THIS ROUTINE PERFORMS A SPLINE FIT OF DATA OVER SPECIFIED INTE--
C     VALS. IT MATCHES FIRST AND SECOND DERIVATIVES AT THE INTERVAL
C     BOUNDARIES AND GOES AS CLOSELY AS POSSIBLE THROUGH THE DATA
C     POINTS (I. E. MINIMIZES LEAST SQUARES DEVIATIONS)
C     IANKOR=ANCHORING OPTION. 0=DO NOT ANCHOR ANY POINT. 1=ANCHOR THE
C     FIRST AND THE LAST POINTS AND PUT A CUBIC IN THOSE TWO INTERVALS
C     IF POSSIBLE
C     X,Y=ARRAYS CONTAINING RESPECTIVELY THE INDEPENDENT AND DEPENDENT
C     VARIABLES TO BE FITTED.
C     NPTS= NUMBER OF THE DATA POINTS IN THE CALCULATION.
C     XINT= ARRAY CONTAING THE VALUES OF THE INDEPENDENY
C     XINT=ARRAY CONTAINING THE VALUES OF THE INDEPENDENT VARIABLES
C     WHICH ARE TO BE INTERVAL BOUNDARIES.
C     DXINT=ARRAY CONTAINING IN LOCATION I XINT(I)-XINT(I-1)
C     NINTS=NUMBER OF INTERVALS
C     YCALC=ARRAY CONTAINING THE CALCULATED VALUES OF THE INDEPENDENT
C     YCALC=ARRAY CONTAINING THE CALCULATED VALUES OF THE DEPENDENY
C     YCALC=ARRAY CONTAINING THE CALCULATED VALUES OF THE DEPENDENT
C     VARIABLE AT THE INTERVAL BOUNDARIES
C     DER2=ARRAY CONTAINING THE CALCULATED VALUES OF THE SECOND
C     DERIVATIVES AT THE INTERVAL BOUNDARIES
      DIMENSION X(101),Y(101)
      DIMENSION XINT(50),YCALC(50),DER2(50),DXINT(50)
      DIMENSION AHEX(9,101,3),CONSTS(101,3),ANS(101,3)
      DOUBLE PRECISION STOR1,STOR2,STOR3,STOR4,STOR5,FAC,STOR6,STOR7
      DOUBLE PRECISION S(11),STOR8,STOR9
      REAL*8 DBLE,DABS
      IOUTP=6
      N1=1
      N2=2
      NITS=20
      ERROR=5.E-6
      NINT=0
      NX=1
      STOR3=0.D0
      STOR4=0.D0
      STOR5=0.D0
      STOR6=0.D0
```

```
      STOR7=0.D0
      STOR8=0.D0
      STOR9=0.D0
      IF(NINTS)10,10,20
   10 WRITE(IOUTP,1010) NINTS
 1010 FORMAT('0NINTS=',I3,5X,'SPLAG BY-PASSED')
      RETURN
   20 NINTS1=NINTS+1
      DO 25 I=1,3
      DO 25 J = 1,3
      AHEX(I,1,J)=0.
   25 AHEX(I+6,NINTS1,J)=0.
   30 NIN=1
      DO 40 I=1,11
   40 S(I)=0.D0
      NBASE=NINT+1
      BASE=XINT(NBASE)
   50 NINT=NINT+1
   60 STORE=X(NX)-XINT(NINT+1)
      STOR1=DBLE(X(NX)-BASE)
      IF(ABS(STORE)-5.E-6) 100,100,70
   70 NEND=0
      IF(STORE)90,80,80
   80 IF(NINT-NINTS)170,120,120
   90 IF(DABS(STOR1)-5.D-6)110,120,120
  100 NEND=1
  110 FAC=1.D0
      GO TO 130
  120 FAC=2.D0
  130 S(1)=S(1)+FAC
      STOR2=FAC*DBLE(Y(NX))
      S(8)=S(8)+STOR2
      DO 135 I=2,4
      FAC=FAC*STOR1
      STOR2=STOR2*STOR1
      S(I)=S(I)+FAC
  135 S(I+7)=S(I+7)+STOR2
      DO 140 I=5,7
      FAC=FAC*STOR1
  140 S(I)=S(I)+FAC
      IF(NEND) 150,150,170
  150 IF(NX-NPTS)160,170,170
  160 NX=NX+1
      NIN=NIN+1
      GO TO 60
  170 NINT1=NINT+1
      IF(S(1))180,180,190
C     ROUTINE IS NOT YET EQUIPPED TO HANDLE EMPTY INTERVALS
  180 WRITE(IOUTP,1080)
 1080 FORMAT('0EMPTY INTERVAL DETECTED BY SPLAG, JOB ABORTED')
      CALL EXIT
  190 STOR1=DBLE(DXINT(NINT1))
```

```
      STOR2=0.5D0/STOR1
      AHEX(1,NINT1,1)=(S(2)-S(3)/STOR1)/STOR1
      AHEX(2,NINT1,1)=-S(3)/3.D0+(0.5D0*S(4)-S(5)/6.D0/STOR1)/STOR1
      AHEX(3,NINT1,1)=-STOR2
      AHEX(4,NINT,1)=STOR5+(S(3)/STOR1-2.D0*S(2))/STOR1+S(1)
      STOR5=S(3)/STOR1/STOR1
      AHEX(5,NINT,1)=STOR3+5.D0*S(3)/6.D0-S(2)*STOR1/3.D0-(4.D0*S(4)-
     1  S(5)/STOR1)/6.D0/STOR1
      STOR3=(S(5)/STOR1/STOR1-S(3))/6.D0
      AHEX(6,NINT,1)=STOR2
C     THE SIXTH POSITION IS INCREMENTED LATER PROVIDED NINT IS
C     GREATER THAN 1.
      AHEX(7,NINT,1)=(S(2)-S(3)/STOR1)/STOR1
      AHEX(8,NINT,1)=(S(3)-S(2)*STOR1+(S(4)-S(5)/STOR1)/STOR1)/6.D0
      AHEX(9,NINT,1)=-STOR2
      CONSTS(NINT,1)=STOR4+S(8)-S(9)/STOR1
      CONSTS(NINT,2)=0.D0
      STOR4=S(9)/STOR1
      AHEX(1,NINT1,3)=S(3)-S(2)*STOR1+(S(4)-S(5)/STOR1)/STOR1
      AHEX(2,NINT1,3)=(-S(5)-STOR1*(3.D0*S(4)-2.D0*S(3)*STOR1)+(3.D0*
     1  S(6)-S(7)/STOR1)/STOR1)/6.D0
      STOR2=0.5D0*STOR1
      AHEX(3,NINT1,3)=STOR2
      AHEX(4,NINT,3)=STOR7+5.D0*S(3)-2.D0*S(2)*STOR1+(S(5)/STOR1-4.D0
     1  S(4))/STOR1
      STOR7=S(5)/STOR1/STOR1-S(3)
      AHEX(5,NINT,3)=(STOR8+13.D0*S(5)+STOR1*(4.D0*STOR1*S(3)-12.D0*S
     1 )+(S(7)/STOR1-6.D0*S(6))/STOR1)/6.D0
      STOR8=S(7)/STOR1/STOR1-2.D0*S(5)+S(3)*STOR1*STOR1
      AHEX(6,NINT,3)=STOR1+STOR6
      AHEX(7,NINT,3)=-2.D0*S(3)+(3.D0*S(4)-S(5)/STOR1)/STOR1
      AHEX(8,NINT,3)=AHEX(2,NINT1,3)
      AHEX(9,NINT,3)=0.5D0*STOR1
      CONSTS(NINT,3)=STOR9-2.D0*S(9)*STOR1+3.D0*S(10)-S(11)/STOR1
      STOR9=S(11)/STOR1-S(9)*STOR1
      IF(NINT-1) 195,195,290
  195 IF(NIN-2)180,197,196
  196 IF(IANKOR)202,202,199
  197 DO 198 I=4,9
  198 AHEX(I,1,3)=0.D0
      CONSTS(1,3)=0.D0
      AHEX(5,1,3)=1.D0
      AHEX(8,1,3)=-1.D0
  199 AHEX(6,1,1)=1.D0
      DO 201 I=4,9
      AHEX(I,1,2)=AHEX(I,1,3)
      AHEX(I,1,3)=AHEX(I,1,1)
  201 AHEX(I,1,1)=0.D0
      AHEX(4,1,1)=1.D0
      CONSTS(1,2)=CONSTS(1,3)
      CONSTS(1,3)=CONSTS(1,1)
      CONSTS(1,1)=Y(1)
      GO TO 300
```

```
202   DO 203 I=4,9
      AHEX(I,1,2)=AHEX(I,1,3)
203   AHEX(I,1,3)=0.D0
      AHEX(6,1,3)=1.D0
      CONSTS(1,2)=CONSTS(1,3)
      CONSTS(1,3)=0.D0
      GO TO 300
290   AHEX(1,NINT,2)=-1.D0/STOR6
      AHEX(2,NINT,2)=STOR6/6.D0
      AHEX(3,NINT,2)=0.
      AHEX(4,NINT,2)=1.D0/STOR6+1.D0/STOR1
      AHEX(5,NINT,2)=(STOR6+STOR1)/3.D0
      AHEX(6,NINT,2)=0.
      AHEX(7,NINT,2)=-1.D0/STOR1
      AHEX(8,NINT,2)=STOR1/6.D0
      AHEX(9,NINT,2)=0.
      AHEX(6,NINT,1)=AHEX(6,NINT,1)+0.5D0/STOR6
      IF(NINT-NINTS)300,310,310
300   STOR6=STOR1
      GO TO 30
310   AHEX(4,NINT1,1)=STOR5
      AHEX(5,NINT1,1)=STOR3
      AHEX(6,NINT1,1)=0.5D0/STOR6
      CONSTS(NINT1,1)=STOR4
      AHEX(4,NINT1,3)=STOR7
      AHEX(5,NINT1,3)=STOR8/6.D0
      AHEX(6,NINT1,3)=STOR6
      CONSTS(NINT1,3)=STOR9
      IF(NIN-2)180,312,311
311   IF(IANKOR)318,318,316
312   DO 313 I=1,6
313   AHEX(I,NINT1,3)=0.D0
      CONSTS(NINT1,3)=0.D0
      IF(NINTS-1)315,315,314
314   AHEX(2,NINT1,3)=1.D0
315   AHEX(5,NINT1,3)=-1.D0
316   AHEX(6,NINT1,1)=1.D0
      DO 317 I=1,6
      AHEX(I,NINT1,2)=AHEX(I,NINT1,3)
      AHEX(I,NINT1,3)=AHEX(I,NINT1,1)
317   AHEX(I,NINT1,1)=0.D0
      AHEX(4,NINT1,1)=1.D0
      CONSTS(NINT1,2)=CONSTS(NINT1,3)
      CONSTS(NINT1,3)=CONSTS(NINT1,1)
      CONSTS(NINT1,1)=Y(NPTS)
      GO TO 400
318   DO 319 I=1,6
      AHEX(I,NINT1,2)=AHEX(I,NINT1,3)
319   AHEX(I,NINT1,3)=0.D0
      AHEX(6,NINT1,3)=1.D0
      CONSTS(NINT1,2)=CONSTS(NINT1,3)
      CONSTS(NINT1,3)=0.D0
```

```
 400  CALL INV3SP(AHEX,CONSTS,ANS,NINTS1,NITS,ERROR)
      DO 410 I=1,NINTS1
      YCALC(I)=ANS(I,1)
 410  DER2(I)=ANS(I,2)
      RETURN
      END


      SUBROUTINE INV3SP(ARRAY,CONSTS,ANS,NSIZ,MAXITS,ERROR)
C     THIS ROUTINE INVERTS A MATRIX WHICH HAS NO MORE THAN 9 NON ZER
C     DIAGONALS
C     ARRAY=ARRAY CONTAINING THE ELEMENTS OF THE ARRAY TO BE INVERTE
C     CONSTS=ARRAY CONTAINING THE CONSTANTS ON THE RIGHT SIDE OF THE
C     EQUATION
C     ANS=ARRAY CONTAING THE ANSWERS
C     NSIZ=NUMBER OF SIMULATION EQUATIONS BEING SOLVED
C     MAXITS=MAXIMUM NUMBER OF ITERATIONS PERMITTED IN THE IERATER
C     GAUSSIAN ELEMINATION.
C     ERROR TOLERANCE PERMITTED BETWEEN TWO SUCCESSIVE ITERATIONS IN
C     ORDER TO DEFINE CONVERGENCE
      DIMENSION ARRAY(9,101,3),CONSTS(101,3),ANS(101,3)
      DIMENSION ASTOR(9,101,3),CONSTR(101,3),DELANS(101,3)
      IOUTP=6
      DO 10 NROW=1,NSIZ
      DO 10 I=1,3
      ANS(NROW,I)=0.0
 10   CONSTR(NROW,I)=CONSTS(NROW,I)
      DO 250 NIT=1,MAXITS
      DO 20 NROW=1,NSIZ
      DO 20 NCOL=1,9
      DO 20 I=1,3
 20   ASTOR(NCOL,NROW,I)=ARRAY(NCOL,NROW,I)
      DO 70 NIND=2,NSIZ
      DO 40 I=2,3
      NM1=NIND-1
      FAC=ASTOR(4,NM1,I)/ASTOR(4,NM1,1)
      DO 30 NCOL=5,9
 30   ASTOR(NCOL,NM1,I)=ASTOR(NCOL,NM1,I)-FAC*ASTOR(NCOL,NM1,1)
 40   CONSTR(NM1,I)=CONSTR(NM1,I)-FAC*CONSTR(NM1,1)
      FAC=ASTOR(5,NM1,3)/ASTOR(5,NM1,2)
      DO 50 NCOL=6,9
 50   ASTOR(NCOL,NM1,3)=ASTOR(NCOL,NM1,3)-FAC*ASTOR(NCOL,NM1,2)
      CONSTR(NM1,3)=CONSTR(NM1,3)-FAC*CONSTR(NM1,2)
      DO 70 I=1,3
      J1 = I+1
      DO 70 J=1,3
      FAC=ASTOR(I,NIND,J)/ASTOR(I+3,NM1,I)
      DO 60 K=J1,6
 60   ASTOR(K,NIND,J)=ASTOR(K,NIND,J)-FAC*ASTOR(K+3,NM1,I)
 70   CONSTR(NIND,J)=CONSTR(NIND,J)-FAC*CONSTR(NM1,I)
      DO 90 I=2,3
      DO 90 J=I,3
      FAC=ASTOR(I+2,NSIZ,J)/ASTOR(I+2,NSIZ,I-1)
```

```
      DO 80 K=I,3
80    ASTOR(K+3,NSIZ,J)=ASTOR(K+3,NSIZ,J)-FAC*ASTOR(K+3,NSIZ,I-1)
90    CONSTR(NSIZ,J)=CONSTR(NSIZ,J)-FAC*CONSTR(NSIZ,I-1)
      DELANS(NSIZ,3)=CONSTR(NSIZ,3)/ASTOR(6,NSIZ,3)
      DELANS(NSIZ,2)=(CONSTR(NSIZ,2)-DELANS(NSIZ,3)*ASTOR(6,NSIZ,2))/
     1 ASTOR(5,NSIZ,2)
      DELANS(NSIZ,1)=(CONSTR(NSIZ,1)-DELANS(NSIZ,3)*ASTOR(6,NSIZ,1)-
     1 DELANS(NSIZ,2)*ASTOR(5,NSIZ,1))/ASTOR(4,NSIZ,1)
      DO 130 NINC=2,NSIZ
      NROW=NSIZ+1-NINC
      NROW1=NROW+1
      DO 130 I=1,3
      I1=4-I
      STORE=CONSTR(NROW,I1)
      DO 100 J=7,9
100   STORE=STORE-DELANS(NROW1,J-6)*ASTOR(J,NROW,I1)
      IF(I-1)130,130,110
110   STORE=STORE-DELANS(NROW,3)*ASTOR(6,NROW,I1)
      IF(I-2)130,130,120
120   STORE=STORE-DELANS(NROW,2)*ASTOR(5,NROW,I1)
130   DELANS(NROW,I1)=STORE/ASTOR(I1+3,NROW,I1)
      DO 140 I=1,3
      DO 140 NROW=1,NSIZ
140   ANS(NROW,I)=ANS(NROW,I)+DELANS(NROW,I)
      IF (NIT-1) 170,170,150
150   DO 160 J=1,2
      DELMAX=0.0
      BASMAX=0.0
      DO 155 I=1,NSIZ
      IF(ABS(ANS(I,J))-BASMAX) 152,152,151
151   BASMAX= ABS(ANS(I,J))
152   STORE=ABS(DELANS(I,J))
      IF(STORE-DELMAX)155,155,153
153   DELMAX=STORE
 155   CONTINUE
      IF(BASMAX)156,157,156
156   IF(DELMAX/BASMAX-ERROR)160,170,170
157   IF(DELMAX-ERROR) 160,170,170
160   CONTINUE
      RETURN
170   DO 250 NROW=1,NSIZ
      IF(NROW-1) 190,190,200
190   I1=2
      GO TO 220
200   I1=1
      IF(NROW-NSIZ)220,210,210
210   I2=2
      GO TO 230
220    I2=3
230   DO 250 J=1,3
      STORE=0.0
      DO 240 K=I1,I2
      I=NROW-2+K
```

```
      DO 240 L=1,3
      M=3*(K-1)+L
 240  STORE=STORE+ARRAY(M,NROW,J)*ANS(I,L)
 250  CONSTR(NROW,J)=CONSTS(NROW,J)-STORE
      WRITE(6,1250)
1250  FORMAT('0NO CONVERGENCE IN INV3SP'/)
      RETURN
      END


      SUBROUTINE XBLEND(X,Y,MAX,XINT,NINTS1,NFLAG,NPTS)
C     THIS ROUTINE BLENDS TOGETHER TWO ARRAYS X AND XINT WHICH ARE
C     BOTH ORIGINALLY IN ASCENDING ORDER. IT ARRANGES THE ARRAY X SO
C     AS TO INCLUDE BOTH AND MOVES ENTRIES IN Y TO CORRESPOND WITH
C     THE ORIGINAL ENTRY IN X.
C     X,Y=ARRAYS CONTAINING ORIGINAL INDEPENDENT AND DEPENDENT VARIABLES
C     MAX=MAXIMUM ALLOWABLE SIZE OF X AND Y.
C     XINT=ARRAY CONTAINS ADDITIONAL VALUES OF X TO BE BLENDED
C     NINTS1=NUMBER OF ENTRIES IN XINT
C      NFLAG=ARRAY CONTAINING FLAGS WHICH, AT A GIVEN LOCATION, INDICATE
C       THE SOURCE OF THE FINAL ENTRY IN X. 0=FROM X, 1=FROM XINT,
C     -1=EQUAL VALUE FROM X AND XINT  TWO VALUES ARE TAKEN TO BE EQUAL
C     IF THEY ARE AGREE TO WITHIN 5.E-6. THE X-VALUES(AND CORRESPONDING
C      ARE USED.
C     NPTS=ON INPUT, THE NUMBER OF ENTRIES IN X. ON OUTPUT, THE NUMBER O
C      ENTRIES IN THE BLENDED X ARRAY.
      DIMENSION X(101),Y(101),XINT(101),NFLAG(101)
      NEND=0
      NSKP=0
      IND=1
      DO 60 I=1,NPTS
   10 DO 30 J=IND,NINTS1
      STORE=XINT(J)-X(I)
      IF(ABS(STORE)-5.E-6) 50,20,20
  20  IF(STORE) 30,30,40
   30 CONTINUE
      J=NINTS1+1
   40 NFLAG(I)=J-IND
      NSKP=NSKP+NFLAG(I)
      IND=J
      IF(IND-NINTS1) 60,60,70
   50 NFLAG(I)=IND-J-1
      NSKP=NSKP+J-IND
      IND=J+1
      IF(IND-NINTS1) 60,60,70
   60 CONTINUE
      NUMB=NINTS1-J+1
      GO TO 90
   70 I=I+1
      IND=NINTS1
      IF(I-NPTS) 75,75,85
   75 DO 80 J=I,NPTS
   80 NFLAG(J)=0
   85 NUMB=0
```

```
   90 LOC=NPTS+NSKP+NUMB+1
      NPTS1=NPTS+1
      NPTS=LOC-1
      DO 250 I=1,NPTS1
       IF(NUMB) 140,140,100
  100 DO 130 K=1,NUMB
      LOC=LOC-1
      IF(LOC-MAX) 110,110,120
  110 X(LOC)=XINT(IND)
      NFLAG(LOC)=1
  120 IND=IND-1
      IF(IND) 260,260,130
  130 CONTINUE
  140 LOC=LOC-1
      IF(LOC) 260,260,150
  150 J=NPTS1-I
      IF(LOC-MAX) 170,170,160
  160 IF(NFLAG(J)) 210,240,190
  170 X(LOC)=X(J)
      Y(LOC)=Y(J)
      IF(NFLAG(J)) 200,230,180
  180 NFLAG(LOC)=0
  190 NUMB=NFLAG(J)
      GO TO 250
  200 NFLAG(LOC)=-1
  210 IND=IND-1
      IF(IND) 260,260,220
  220 NUMB=-NFLAG(J)-1
      GO TO 250
  230 NFLAG(LOC)=0
  240 NUMB=0
  250 CONTINUE
C       THERE SHOULD NEVER BE A NORMAL EXIT FROM THIS DO LOOP.
  260 RETURN
      END


      SUBROUTINE XSETUP(XBASE,XDELT,XNEW,I,ERROR)
C     THIS ROUTINE SETS UP THE XNEW ARRAY FOR A LATER INTERPOLATION.
C     IT BEGINS  SUCCESSIVELY WITH THE NUMBERS IN THE FIRST FOUR LOCA-
C     TIONS OF THE ARRAY XBASE AND ADDS THE INCREMENTS FOUND IN THE
C     CORRESPONDING LOCATION OF N XDELT. RESULTS ARE STORED IN THE NEXT
C     AVAILABLE LOCATION IN XNEW. THIS PROCESS CONTINUES UNTIL THE NEXT
C     VALUES OF XBASE IS EXCEEDED OR EQUALED TO WITHIN THE AMOUNT SPECI-
C     FIED BY ERROR. THE FIFTH LOCATION IN XBASE IS THE MAXIMUM VALUE
C     WHICH WILL BE STORED IN XNEW. THE FIFTH LOCATION  OF XDELT IS
C     IGNORED. THE CALCULATION AUTOMATICALLY TERMINATES IF XNEW IS
C     FILLED UP OR IF A ZERO IS DETECTED IN EITHER XDELT OR XBASE AT ANY
C     POINT IN THE CALCULATION
      DIMENSION XBASE(5),XDELT(5),XNEW(101)
      I=0
      DO 80 N=1,4
```

```
      IF(XDELT(N)) 85,85,30
   30 J=0
   40 I=I+1
      XNEW(I)=XBASE(N)+FLOAT(J)*XDELT(N)
      J=J+1
      STORE=XNEW(I)-XBASE(N+1)
      IF(STORE) 50,70,70
   50 IF(STORE+ERROR) 60,60,70
   60 IF(I-100) 40,90,90
   70 I=I-1
   80 CONTINUE
      N=5
   85 I=I+1
      XNEW(I)=XBASE(N)
   90 RETURN
      END


      SUBROUTINE I2NTSP(DELX,XOLD,YOLD,D2OLD,XNEW,YNEW,D2NEW,NPTOLD,
     1   NPTNEW,D1NEW)
C     THIS ROUTINE INTERPOLATES THE DATA FOUND IN XOLD VS.YOLD BASED
C     ON THE ABSISSAS SUPPLIED IN XNEW. THE INTERPOLATION METHOD IS
C     BASED ON THE DERIVATIVES CALCULATED BY THE SLINE FITTING METHOD.
C     DELX=ARRAY CONTAINING IN LOCATION I, XOLD(I)-XOLD(I-1).
C     XOLD,YOLD=ARRAYS CONTAINING RESPECTIVELY THE ORIGINAL INDEPEN-
C        DENT AND DEPENDENT VARIABLES.
C     D2OLD= ARRAY CONTAINING THE ORIGINAL SECOND DERIVATIVES,
C     XNEW,YNEW,D2NEW= ARRAYS CONTAINING THE INTERPOLATED INDEPENDENT,
C       AND DEPENDENT VARIABLES AND THE SECOND DERIVATIVES.
C     NPTOLD= ORIGINAL NUMBER OF DATA POINTS.
C     NPTNEW= NUMBER OF INTERPOLATED DATA POINTS.
C     D1NEW= CALCULATED VALUES OF THE FIRST DERIVATIVE AT THE INTERPO-
C       LATED POINTS.
C
C
C
      DIMENSION DELX(101),YOLD(101),D2OLD(101),XOLD(101)
      DIMENSION XNEW(101),YNEW(101),D2NEW(101),D1NEW(101)
      IOLD=1
      DO 50 I=1,NPTNEW
    5 IF(XNEW(I)-XOLD(IOLD)) 35,30,10
   10 IF(IOLD-NPTOLD+1)20,40,40
   20 IOLD=IOLD+1
      GO TO 5
   30 YNEW(I)=YOLD(IOLD)
      D2NEW(I)=D2OLD(IOLD)
      GO TO 50
   35 IF(IOLD-1) 40,40,37
   37 IOLD=IOLD-1
   40 STOR1=XOLD(IOLD+1)-XNEW(I)
      STOR2=XNEW(I)-XOLD(IOLD)
      YNEW(I)=STOR1*(D2OLD(IOLD)*STOR1*STOR1/6.0/DELX(IOLD+1)+
     1 (YOLD(IOLD)/DELX(IOLD+1)-DELX(IOLD+1)*D2OLD(IOLD)/6.0))+
     2 STOR2*(D2OLD(IOLD+1)*STOR2*STOR2/6.0/DELX(IOLD+1)+
```

```
     3 (YOLD(IOLD+1)/DELX(IOLD+1)-DELX(IOLD+1)*D2OLD(IOLD+1)/6.0))
      D2NEW(I)=(D2OLD(IOLD)*(XOLD(IOLD+1)-XNEW(I))+D2OLD(IOLD+1)*
     1  (XNEW(I)-XOLD(IOLD)))/DELX(IOLD+1)
 50   D1NEW(I)=SPLDR1(XNEW(I),XOLD(IOLD+1),DELX(IOLD+1),D2OLD(IOLD),
     1     D2OLD(IOLD+1),YOLD(IOLD+1)-YOLD(IOLD))
      RETURN
      END
```

TABLE 53

Spline-Fit Program

Sample of Output

```
SPLINE FIT PROGRAM--
BUTANOL+HEXANE AT 45 DEG. C
X=MOL.FRACT.OF BUTANOL, Y=DELTAH/X1X2

INPUT POINTS (* INDICATES INTERVAL BOUNDARY)


END POINT ANCHORED
         X                  Y             Y CALC           DEV(PCT)         DER1            DER2

  * 0.158100E 00     0.560500E 04     0.560500E 04     0.000000E 00    -0.173895E 05    0.120181E 06
    0.180600E 00     0.527100E 04     0.524302E 04    -0.530912E 00    -0.148375E 05    0.106657E 06
    0.310800E 00     0.395900E 04     0.399408E 04     0.886066E 00    -0.604564E 04    0.283951E 05
  * 0.336000E 00     0.382300E 04     0.384914E 04     0.683843E 00    -0.552093E 04    0.132477E 05
    0.578500E 00     0.285000E 04     0.284093E 04    -0.318376E 00    -0.303718E 04    0.723693E 04
    0.598600E 00     0.280500E 04     0.278131E 04    -0.844666E 00    -0.289672E 04    0.673871E 04
    0.599400E 00     0.280300E 04     0.277899E 04    -0.856504E 00    -0.289134E 04    0.671888E 04
  * 0.816000E 00     0.225800E 04     0.226836E 04     0.458807E 00    -0.201747E 04    0.135009E 04
  * 0.100000E 01     0.192000E 04     0.192000E 04    -0.508626E-04    -0.176905E 04    0.135009E 04
```

```
SPLINE FIT PROGRAM--  HUONG T. H.
N-BUTANOL+N-HEXANE AT 25 DEG. C, REF.(2)
X=MOL.FRACT. OF BUTANOL, Y=DELTAH/X1X2 IN J/MOLE

INTERPOLATED POINTS

          X                    Y                  DER1                 DER2


    0.500000E-01         0.549107E 04        -0.223503E 05        0.124934E 06
    0.100000E 00         0.452099E 04        -0.166274E 05        0.103983E 06
    0.150000E 00         0.381087E 04        -0.119521E 05        0.830318E 05
    0.200000E 00         0.330833E 04        -0.832425E 04        0.620807E 05
    0.250000E 00         0.296099E 04        -0.574399E 04        0.411295E 05
    0.300000E 00         0.271647E 04        -0.421129E 04        0.201785E 05
    0.350000E 00         0.252278E 04        -0.366135E 04        0.654878E 04
    0.400000E 00         0.234779E 04        -0.334064E 04        0.627969E 04
    0.450000E 00         0.218849E 04        -0.303338E 04        0.601059E 04
    0.500000E 00         0.204422E 04        -0.273958E 04        0.574150E 04
    0.550000E 00         0.191431E 04        -0.245923E 04        0.547240E 04
    0.600000E 00         0.179808E 04        -0.219234E 04        0.520331E 04
    0.650000E 00         0.169485E 04        -0.193890E 04        0.493421E 04
    0.700000E 00         0.160396E 04        -0.169892E 04        0.466512E 04
    0.750000E 00         0.152474E 04        -0.147239E 04        0.439602E 04
    0.800000E 00         0.145650E 04        -0.125931E 04        0.412693E 04
    0.850000E 00         0.139858E 04        -0.105970E 04        0.385783E 04
    0.900000E 00         0.135031E 04        -0.873531E 03        0.358874E 04
    0.950000E 00         0.131100E 04        -0.700822E 03        0.331964E 04
```

TABLE 54

Forsythe Polynomial Program

Input-Output Format

Card	Column	Format	Variable	Data
1, 2	2-80	80H	--	Any alphameric information (e.g. headings of output)
3	1-10	I10	NPTS	Number of data points
4 to I+4	1-20	F20.0	X(I)	X_i value
	21-40	F20.0	Y(I)	Y_i value

(I = No. of data points to be fitted; $I < 50$)

Power series degrees for comparison of fitted curve with data are specified by NCOM (I) = N where I = 1 - 4, $1 < N < 6$. I and N are to be specified in the program.

TABLE 55

Forsythe Polynomial Program

Fortran Statement

```
      DIMENSION X(100),Y(100),NCOM(4)
  100 READ(5,1,END=500)
    1 FORMAT(1X,79H
     1
     2  /1X,79H
     3
      READ(5,10) NPTS,HCHS
   10 FORMAT(I10,F20.0)
   15 FORMAT(2F20.0)
      READ(5,15) (X(I),Y(I),I=1,NPTS)
      WRITE(6,2)
    2 FORMAT(1H1)
        WRITE(6,1)
      NDEGRE=6
      NCOM(1)=3
      NCOM(2)=4
      NCOM(3)=5
      NCOM(4)=6
      CALL CURFIT(NDEGRE,NCOM,NPTS,X,Y)
      DO 40 I=1,NPTS
   40    Y(I)=ALOG(Y(I))
      CALL CURFIT(NDEGRE,NCOM,NPTS,X,Y)
      GO TO 100
  500 STOP
      END
C
C       SUBROUTINE CURFIT(NDEGRE,NCOM,NPTS,X,Y)
      SUBROUTINE CURFIT(NDEGRE,NCOM,NPTS,X,Y)
      DIMENSION X(100),Y(100),A(12),B(12),C(12),D(12),E(3,12),
     1 F(12,12),P(3,100),NCOM(4),DI(4),Z(4),SDI(4)
      EQUIVALENCE  (F,P), (A,DI), (B,Z),(C,SDI)
      I = NPTS
    3 FORMAT(1H0,20X,'ORTHOGONAL REPRESENTATION BY FORSYTHE METHOD'//)
      C(2) = 0.0
      DO 14 J=1,I
      P(1,J) = 0.0
      P(2,J) = 1.0
   14 C(2) = C(2) + Y(J)
      KA = 3
      KP = 1
      KC = 2
      A(2) = 1.0
      B(2) =0.0
      D(1) = 1.0
      D(2) = I
      C(2) = C(2)/D(2)
      NORTHO = NDEGRE + 2
      DO 15 K=3,NORTHO
       A(K) = 0.0
      B(K) = 0.0
      C(K) = 0.0
      D(K) = 0.0
```

```
      KA = KA + 1
      KB = KB + 1
      KC = KC + 1
      IF (KA-3) 16,16,17
17    KA = 1
      GO TO 20
16    IF (KB-3) 18,18,19
19    KB = 1
      GO TO 20
18    KC = 1
 20   DO 99 J = 1,I
      A(K) = A(K)+Y(J)*P(KB,J)*P(KB,J)
99    B(K) = B(K) + X(J)*P(KA,J)*P(KB,J)
      A(K) = A(K)/D(K-1)
      B(K) = B(K)/D(K-2)
      DO 22 J = 1,I
      P(KC,J) = (X(J)-A(K))*P(KB,J)-B(K)*P(KA,J)
      D(K) = D(K) + P(KC,J)*P(KC,J)
22    C(K) = C(K) + P(KC,J)*Y(J)
      C(K) = C(K)/D(K)
15    CONTINUE
      WRITE(6,3)
      WRITE(6,30)
   30 FORMAT(1H0,37X,'POWER SERIES COEFFICIENTS')
      E(1,1) = 1.0
      E(3,1) = 0.0
      KA = 2
      KB = 3
      KC = 1
      DO 47 J = 1,NORTHO
      E(J,J) = 0.0
47    E(1,J) = 0.0
      DO 31 K=2,NORTHO
      KDEG=K-2
      IF(KDEG-5) 205,206,207
 207  IF(KDEG-9) 205,206,208
 208  IF(KDEG-12) 205,206,205
 206  WRITE(6,3)
 205  WRITE(6,32) KDEG
32    FORMAT(1H0,'POWER SERIES OF DEGREE',I3,10X,
     1'POWER OF X',10X,'COEFFICIENT'//)
      KDEG = K-1
      KA = KA + 1
      KB = KB + 1
      KC = KC + 1
      IF(KA-3) 33,33,34
 34   KA = 1
      GO TO 37
 33   IF(KB-3) 35,35,36
36    KB = 1
      GO TO 37
35    KC = 1
37     DO 31 J=1,KDEG
      IF(J-1)39,39,40
39    E(KC,J)=A(K)*E(KB,J) - B(K)*E(KA,J)
      GO TO 41
```

```
 40    IF(J-K+2)42,80,43
 80    E(KC,J) = E(KB,J-1) + A(K)*E(KB,J)
       GO TO 41
 43    E(KC,J) = E(KB,J-1)
       GO TO 41
  42   E(KC,J) = E(KB,J-1) + A(K)*E(KB,J)-B(K)*E(KA,J)
 41    TA = (J+K)/2
       TB = J + K
       TB = TB/2.0
       IF(TA - TB) 44,45,44
 45    G = -1.0
       GO TO 46
 44    G = 1.0
 46    F(K,J) = F(K-1,J)+G*C(K)*E(KC,J)
       JA = J - 1
       WRITE(6,305) JA,F(K,J)
 305   FORMAT(I41,1PE26.7)
 31    CONTINUE
   52 WRITE(6,59)
 59    FORMAT(1H0,21X,'COMPARISION OF POWER SERIES REPRESENTATION
     1WITH FITTED DATA'//)
   58 WRITE(6,60) (NCOM(I),I=1,4)
  60  FORMAT(1H0,11X,'GIVEN DATA',21X,'Y VALUES COMPUTED FROM POWER
     1SERIES OF DEGREE N'/42X,'--------------------------------------
     2------'/50X,'PERCENT DEVIATION FROM GIVEN Y'//8X,'X',14X,'Y',5X,4(9X
     3X,'N=',I3))
       DO 65 N = 1,4
       Z(N) = 0.0
       DI(N) = 0.0
 65    SDI(N) = 0.0
       DO 67 I = 1,NPTS
       DO 61 N = 1,4
       IF(NCOM(N)) 64,64,63
 63    K = 2 + NCOM(N)
       Z(N) = F(K,K-1)
       KB = K-1
       DO 62 J = 2,KB
       JA = K-J
 62    Z(N) = Z(N)*X(I) + F(K,JA)
       DI(N) = (Y(I)-Z(N))/Y(I)*100.
       SDI(N) = SDI(N) + DI(N)*DI(N)
 61    CONTINUE
  64 WRITE(6,66) X(I),Y(I),(Z(N),N=1,4),(DI(N),N=1,4)
 66    FORMAT(1H0, 1P2E15.6,3X,4E15.6/33X,4E15.7)
 67    CONTINUE
       FNPT = NPTS
       DO 68 N = 1,4
 68    DI(N) = SQRT(SDI(N)/FNPT)
       WRITE(6,69) (DI(N),N=1,4)
 69    FORMAT(1H0,'RMS DEVIATIONS =',16X, 1P4E15.2)
       RETURN
       END
```

TABLE 56

Forsythe Polynomial Program

Sample of Output

```
SYSTEM BUTANOL+HEXANE AT 25 DEG. C
X= CH2 GROUP FRACTION, Y= GROUP CH2 CONT. TO DELTA H MIXING

                    ORTHOGONAL REPRESENTATION BY FORSYTHE METHOD


                                POWER SERIES COEFFICIENTS

POWER SERIES OF DEGREE  0        POWER OF X          COEFFICIENT


                                     0              1.4122272E 02
POWER SERIES OF DEGREE  1        POWER OF X          COEFFICIENT


                                     0              9.7758594E 02
                                     1             -9.3528198E 02
POWER SERIES OF DEGREE  2        POWER OF X          COEFFICIENT


                                     0             -2.8647449E 03
                                     1              7.6687539E 03
                                     2             -4.8014063E 03
POWER SERIES OF DEGREE  3        POWER OF X          COEFFICIENT


                                     0              6.3750195E 03
                                     1             -2.3353801E 04
                                     2              2.9847277E 04
                                     3             -1.2873398E 04
POWER SERIES OF DEGREE  4        POWER OF X          COEFFICIENT


                                     0              2.5880969E 05
                                     1             -1.1538160E 06
                                     2              1.9255270E 06
                                     3             -1.4236620E 06
                                     4              3.9315419E 05
```

```
                COMPARISION OF POWER SERIES REPRESENTATION        WITH FITTED DATA


        GIVEN DATA                       Y VALUES COMPUTED FROM POWER     SERIES OF DEGREE N
                                       -------------------------------------------   -----
                                                PERCENT DEVIATION FROM GIVEN Y

       X              Y                N=  1          N=  2          N=  3          N=  4

  8.118809E-01    2.024680E 02      2.182485E 02   1.965200E 02   1.991445E 02   2.033125E 02
                                 -7.7940941E 00  2.9377317E 00  1.6414719E 00 -4.1710919E-01

  8.235269E-01    1.940840E 02      2.073542E 02   1.943826E 02   1.948984E 02   1.946875E 02
                                 -6.8373680E 00 -1.5383476E-01 -4.1963160E-01 -3.1094801E-01

  8.349520E-01    1.875530E 02      1.966704E 02   1.910210E 02   1.902148E 02   1.885625E 02
                                 -4.8612471E 00 -1.8490782E 00 -1.4192514E 00 -5.3825116E-01

  8.461540E-01    1.822250E 02      1.861936E 02   1.865076E 02   1.850156E 02   1.835000E 02
                                 -2.1778631E 00 -2.3501587E 00 -1.5314217E 00 -6.9968921E-01

  8.571430E-01    1.774530E 02      1.759158E 02   1.809116E 02   1.792266E 02   1.791875E 02
                                  8.6626667E-01 -1.9490414E 00 -9.9946147E-01 -9.7744870E-01

  8.679250E-01    1.726140E 02      1.658315E 02   1.742910E 02   1.727813E 02   1.740625E 02
                                  3.9292612E 00 -9.7154152E-01 -9.6893370E-02 -8.3915627E-01

  8.785050E-01    1.671320E 02      1.559363E 02   1.667080E 02   1.656289E 02   1.676875E 02
                                  6.6987209E 00  2.5368011E-01  8.9933830E-01 -3.3237886E-01

  8.888890E-01    1.605010E 02      1.462241E 02   1.582239E 02   1.577227E 02   1.608750E 02
                                  8.8951883E 00  1.4187536E 00  1.7310390E 00 -2.3302543E-01

  8.990830E-01    1.523070E 02      1.366899E 02   1.488862E 02   1.490195E 02   1.525000E 02
                                  1.0253661E 01  2.2459641E 00  2.1584425E 00 -1.2672323E-01

  9.090910E-01    1.422510E 02      1.273296E 02   1.387461E 02   1.394883E 02   1.420000E 02
                                  1.0489488E 01  2.4638824E 00  1.9421377E 00  1.7644292E-01
```

```
 9.189190E-01   1.301690E 02      1.181377E 02   1.278545E 02   1.291055E 02   1.308750E 02
                                 9.2428265E 00  1.7780714E 00  8.1703174E-01 -5.4237843E-01

 9.285710E-01   1.160580E 02      1.091104E 02   1.162544E 02   1.178477E 02   1.187500E 02
                                 5.9863567E 00 -1.6922212E-01 -1.5420361E 00 -2.3195305E 00

 9.380530E-01   1.001000E 02      1.002419E 02   1.039873E 02   1.057031E 02   1.055000E 02
                                -1.4181066E-01 -3.8834305E 00 -5.5975361E 00 -5.3946142E 00

 9.565000E-01   7.571999E 01      8.298877E 01   7.765063E 01   7.871484E 01   7.668750E 01
                                -9.5995541E 00 -2.5497208E 00 -3.9551744E 00 -1.2777519E 00

 9.655000E-01   6.645000E 01      7.457129E 01   6.361646E 01   6.382813E 01   6.237500E 01
                                -1.2221658E 01  4.2641706E 00  3.9456310E 00  6.1324253E 00

 9.831000E-01   3.248000E 01      5.811035E 01   3.391772E 01   3.117578E 01   3.512500E 01
                                -7.8911194E 01 -4.4265051E 00  4.0154381E 00 -8.1434841E 00

RMS DEVIATIONS =                     2.10E 01       2.48E 00       2.53E 00       2.99E 00

                    ORTHOGONAL REPRESENTATION BY FORSYTHE METHOD


                                       POWER SERIES COEFFICIENTS

POWER SERIES OF DEGREE  0           POWER OF X            COEFFICIENT


                                        0              4.8601017E 00

POWER SERIES OF DEGREE  1           POWER OF X            COEFFICIENT


                                        0              1.2424594E 01
                                        1             -8.4591608E 00

POWER SERIES OF DEGREE  2           POWER OF X            COEFFICIENT
```

```
                                          0            -5.3066208E 01
                                          1             1.3819287E 02
                                          2            -8.1837830E 01

POWER SERIES OF DEGREE  3            POWER OF X            COEFFICIENT

                                          0             4.4691895E 02
                                          1            -1.5405105E 03
                                          2             1.7930840E 03
                                          3            -6.9660986E 02

POWER SERIES OF DEGREE  4            POWER OF X            COEFFICIENT


                                          0            -2.2044773E 03
                                          1             1.0333074E 04
                                          2            -1.8117809E 04
                                          3             1.4121320E 04
                                          4            -4.1294141E 03

                         COMPARISION OF POWER SERIES REPRESENTATION       WITH FITTED DATA


                GIVEN DATA                           Y VALUES COMPUTED FROM POWER     SERIES OF DEGREE N
                                                   -------------------------------------   -----
                                                          PERCENT DEVIATION FROM GIVEN Y

             X              Y                  N=  1          N=  2          N=  3          N=  4

        8.118809E-01   5.310582E 00        5.556763E 00   5.186493E 00   5.328369E 00   5.288086E 00
                                        -4.6356592E 00  2.3366404E 00 -3.3493459E-01  4.2361093E-01

        8.235289E-01   5.268291E 00        5.458231E 00   5.237213E 00   5.264893E 00   5.266357E 00
                                        -3.6053333E 00  5.8991271E-01  6.4516068E-02  3.6711153E-02

        8.349520E-01   5.234061E 00        5.361601E 00   5.265381E 00   5.221436E 00   5.239258E 00
                                        -2.4367237E 00 -5.9838068E-01  2.4122173E-01 -9.9283695E-02

        8.461540E-01   5.205242E 00        5.266842E 00   5.272278E 00   5.191650E 00   5.207520E 00
                                        -1.1834164E 00 -1.2878485E 00  2.6111686E-01 -4.3751530E-02
```

```
8.571430E-01   5.178706E 00     5.173884E 00   5.259064E 00   5.167725E 00   5.173584E 00
                               9.3107700E-02 -1.5516911E 00  2.1205217E-01  9.8908544E-02

8.679250E-01   5.151058E 00     5.082677E 00   5.226913E 00   5.145264E 00   5.134277E 00
                               1.3275194E 00 -1.4726143E 00  1.1249191E-01  3.2577485E-01

8.785050E-01   5.118784E 00     4.993179E 00   5.176865E 00   5.118408E 00   5.096436E 00
                               2.4537973E 00 -1.1346569E 00  7.3405616E-03  4.3659580E-01

8.888890E-01   5.078300E 00     4.905340E 00   5.109909E 00   5.082764E 00   5.053955E 00
                               3.4058685E 00 -6.2242407E-01 -8.7887526E-02  4.7940016E-01

8.990830E-01   5.025898E 00     4.819107E 00   5.027023E 00   5.034180E 00   5.001465E 00
                               4.1145067E 00 -2.2390734E-02 -1.6478062E-01  4.8614442E-01

9.090910E-01   4.957593E 00     4.734447E 00   4.929108E 00   4.969238E 00   4.940430E 00
                               4.5010843E 00  5.7457906E-01 -2.3489857E-01  3.4620178E-01

9.189190E-01   4.868834E 00     4.651311E 00   4.816986E 00   4.884766E 00   4.865723E 00
                               4.4676533E 00  1.0648842E 00 -3.2722586E-01  6.3893795E-02

9.285710E-01   4.754090E 00     4.569663E 00   4.691498E 00   4.777832E 00   4.770752E 00
                               3.8793393E 00  1.3166027E 00 -4.9939561E-01 -3.5046965E-01

9.380530E-01   4.606170E 00     4.489453E 00   4.553375E 00   4.645996E 00   4.651855E 00

                               2.5339136E 00  1.1461678E 00 -8.6463130E-01 -9.9183840E-01

9.565000E-01   4.327042E 00     4.333407E 00   4.242477E 00   4.300049E 00   4.320313E 00
                              -1.4711607E-01  1.9543180E 00  6.2381625E-01  1.5551329E-01
 9.655000E-01   4.196449E 00     4.257275E 00   4.070572E 00   4.082031E 00   4.096191E 00
                              -1.4494476E 00  2.9996157E 00  2.7265434E 00  2.3891115E 00

 9.831000E-01   3.480624E 00     4.108394E 00   3.696121E 00   3.547852E 00   3.503662E 00
                              -1.8036102E 01 -6.1913319E 00 -1.9314737E 00 -6.6188979E-01

RMS DEVIATIONS =                      5.40E 00       2.09E 00       9.03E-01       7.23E-01
```

TABLE 57

Program for Prediction of Heats of Mixing of Binaries (n-alcohol + n-alkane)

Input-Output Format

Card	Column	Format	Variable	Data
1, 2	2-80	80H	--	Any alphameric information (e.g. headings of output)
3	1-20	F20.0	NI	Number of carbon atoms in alcohol molecule
	21-40	F20.0	NJ	Number of carbon atoms in hydrocarbon molecule
	41-60	F20.0	NK	0 = when NI = NJ + 1 1 = when NI ≠ NJ + 1
4	1-20	I10	NPTS	Number of data points
5 to 5+I	1-20	F20.0	X(I)	X_i value (composition)
	21-40	F20.0	Y(I)	Published data of Y_i for comparison with predicted data

TABLE 57 (cont.)

Nomenclature for Output of All Prediction Programs

Variable	Data
X	Mole fraction
SIZE	Predicted size contributions to heats of mixing
GROUP	Predicted group contributions to heats of mixing
LIT.DATA	Published data
PREDICT	Predicted heats of mixing
DEV	Percentage deviation of predicted heats of mixing from published data

TABLE 58

Program for Prediction of ΔH^M for n-alkane + n-alcohol Systems at 25^oC

Fortran Statement

```
C      A PROGRAM TO PREDICT HEATS OF MIXING
C      HXCH2 = CH2 GROUP CONTRIBUTION TO HEATS OF MIXING
C      HOHS = STANDARD STATE OF OH GROUP
C      HXCH2S = STANDARD STATE OF CH2 GROUP OF THE ALKANE MOLECULE
       DIMENSION ANBAR(50),HES(50),TOTH(50),F(50)
       DIMENSION XCH2(50),X(50),HXCH2(50),HOH(50),DTH(50)
       DIMENSION DTHB1(50),DTHB2(50)
       DIMENSION Y(50)
       DIMENSION DEVP(50)
       REAL NI,NJ,NK
       GG(Z) = 659285.*Z  - 649285
       H(Z)=-2.8647449E 03 +7.6587539E 03*Z -4.8014063E 03*Z*Z
       AK(Y) = 4.473*(Y-6.)*(16.-Y) + (39.5/500)*(Y-5.)*(15.-Y)*(11.-Y)
       GK(Z)=1.5208971E 02 -3.303801E 02*Z + 1.8705989E 02*Z*Z
       G(Z)=    (-1.4370887E 04 + 6.4546875E 04*Z -1.086505E 05*Z*Z +
      1 8.1240313E 04*Z*Z*Z -2.2759754E 04*Z*Z*Z*Z)
1000   READ(5,10,END=500)
  10   FORMAT(1X,79H
      1
      2  /1X,79H                                                            )
      3
       READ(5,20) NI,NJ,NK
  20   FORMAT(3F10.0)
       READ(5,24)NPTS
  24   FORMAT(I10)
       READ(5,25)(X(I),Y(I),I=1,NPTS)
  25   FORMAT(2F20.0)
       SDI = 0.0
       FNPTS = NPTS
       ANI=NI
       ANJ=NJ
       SX1=ANI/(1. + ANI)
       DO 50 I=1,NPTS
       AI=I
  50   XCH2(I) = (X(I)*ANI+(1.-X(I))*NJ)/((1.+ANI)*X(I)+(1.-X(I))*NJ)
C      CALCULATION THE GROUP HEATS OF MIXIMG
       DO 80 I=1,NPTS
 80    HXCH2(I)=H(XCH2(I))
       HXCH2S=H(SX1)
       IF(SX1-0.94444)29,29,28
  29   HOHS=EXP(G(SX1))
       GO TO 55
  28   HOHS=EXP(GK(SX1))
  55   DO 54 I=1,NPTS
       IF(XCH2(I)-0.9916) 53,53,52
 52    HOH(I)=GG(XCH2(I))
       GO TO 54
   53  IF(XCH2(I)-0.9444)49,49,48
  48   HOH(I)=EXP(GK(XCH2(I)))
       GO TO 54
  49   HOH(I)=EXP(G(XCH2(I)))
  54   CONTINUE
       DO 120 I=1,NPTS
       DTHB1(I) = ANI*(HXCH2(I) - HXCH2S) + (HOH(I)-HOHS)
       DTHB2(I) = NJ*HXCH2(I)
```

```
C     A PROGRAM TO PREDICT HEATS OF MIXING
C     HXCH2 = CH2 GROUP CONTRIBUTION TO HEATS OF MIXING
C     HOHS = STANDARD STATE OF OH GROUP
C     HXCH2S = STANDARD STATE OF CH2 GROUP OF THE ALKANE MOLECULE
      DIMENSION ANBAR(50),HES(50),TOTH(50),F(50)
      DIMENSION XCH2(50),X(50),HXCH2(50),HOH(50),DTH(50)
      DIMENSION DTHB1(50),DTHB2(50)
      DIMENSION Y(50)
      DIMENSION DEVP(50)
      REAL NI,NJ,NK
      GG(Z) = 659285.*Z  - 649285
      H(Z)=-2.8647449E 03 +7.6587539E 03*Z -4.8014063E 03*Z*Z
      AK(Y) = 4.473*(Y-6.)*(16.-Y) + (39.5/500)*(Y-6.)*(16.-Y)*(11.-Y)
      GK(Z)=1.5208971E 02 -3.303801E 02*Z + 1.8705989E 02*Z*Z
      G(Z)=   (-1.4370887E 04 + 6.4545875E 04*Z -1.086505E 05*Z*Z +
     1 8.1240313E 04*Z*Z*Z -2.2759754E 04*Z*Z*Z*Z)
1000  READ(5,10,END=500)
  10  FORMAT(1X,79H
     1
     2  /1X,79H
     3
      READ(5,20) NI,NJ,NK
  20  FORMAT(3F10.0)
      READ(5,24)NPTS
  24  FORMAT(I10)
      READ(5,25)(X(I),Y(I),I=1,NPTS)
  25  FORMAT(2F20.0)
      SDI = 0.0
      FNPTS = NPTS
      ANI=NI
      ANJ=NJ
      SX1=ANI/(1. + ANI)
      DO 50 I=1,NPTS
      AI=I
  50  XCH2(I) = (X(I)*ANI+(1.-X(I))*NJ)/((1.+ANI)*X(I)+(1.-X(I))*NJ)
C     CALCULATION THE GROUP HEATS OF MIXIMG
      DO 80 I=1,NPTS
 80   HXCH2(I)=H(XCH2(I))
      HXCH2S=H(SX1)
      IF(SX1-0.94444)29,29,28
  29  HOHS=EXP(G(SX1))
      GO TO 55
  28  HOHS=EXP(GK(SX1))
  55  DO 54 I=1,NPTS
      IF(XCH2(I)-0.9916) 53,53,52
 52   HOH(I)=GG(XCH2(I))
      GO TO 54
  53  IF(XCH2(I)-0.9444)49,49,48
  48  HOH(I)=EXP(GK(XCH2(I)))
      GO TO 54
  49  HOH(I)=EXP(G(XCH2(I)))
  54  CONTINUE
      DO 120 I=1,NPTS
      DTHB1(I) = ANI*(HXCH2(I) - HXCH2S) + (HOH(I)-HOHS)
      DTHB2(I) = NJ*HXCH2(I)
```

```
 120  DTH(I) = X(I)*DTHB1(I) + (1.-X(I))*DTHB2(I)
C      CALCULATION OF THE SIZE CONTRIBUTION
      ANI = ANI + 1.
      IF(NK ) 69,96,69
 69   DO 71 I=1,NPTS
      ANBAR(I) = X(I)*ANI+(1.-X(I))*ANJ
  71  HES(I) = AK(ANBAR(I))-(ANJ-ANBAR(I))*AK(ANI)/(ANJ-ANI)
     1 -(ANBAR(I)-ANI)*AK(ANJ)/(ANJ-ANI)
      GO TO 79
 96   DO 98 I=1,NPTS
 98   HES(I)=0.
C      TOTAL HEATS OF MIXING TOTH(I)
  79  DO 72 I=1,NPTS
      TOTH(I)=HES(I)+DTH(I)
      DEVP(I)=100.*(Y(I)-TOTH(I))/Y(I)
      SDI = SDI + DEVP(I)*DEVP(I)
  72  CONTINUE
      SDI = SQRT(SDI/FNPTS)
      WRITE(6,1)
   1  FORMAT(1H1)
      WRITE(6,10)
      WRITE(6,300)
 300  FORMAT(//T8,'X',T17,'SIZE',T26,'GROUP',T34,'LIT.DATA',T45,
     1 'PREDICT',T55,'DEV'//)
      WRITE(6,310)(X(I),HES(I),DTH(I),Y(I),TOTH(I),DEVP(I),
     1 I=1,NPTS)
 310  FORMAT(F10.4,5F10.2/)
      WRITE(6,131) SDI
 131  FORMAT(1H0,T35,'RMS DEVIATION = ',F10.2)
      GO TO 1000
 500  STOP
      END
```

TABLE 59

Program for Prediction of ΔH^M for n-alkane + n-alcohol Systems at 25°C

Sample of Output

TABLE 59

SYSTEM HEXANOL + HEXANE AT 45 DEG. C
X=MOL FRACT. OF HEXANOL, IDTH=PREDICTED HEATS OF MIXING

X	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.1227	0.26	583.71	625.00	583.98	6.56
0.1398	0.29	613.64	653.00	613.93	5.98
0.2490	0.45	735.35	716.00	735.80	-2.77
0.2709	0.48	741.24	728.00	741.72	-1.88
0.5026	0.60	660.28	663.00	660.89	0.32
0.5230	0.60	636.45	648.00	637.05	1.69
0.5230	0.60	636.45	652.00	637.06	2.29
0.7689	0.43	360.19	353.00	360.62	-2.16

RMS DEVIATION = 3.59

TABLE 60

Program for Prediction of ΔH^M for n-alkane + n-alcohol Systems at 45°C

Fortran Statement

```
C PREDICTION OF HEATS OF MIXING
C       A PROGRAM TO CALCULATE THE HEATS OF MIXING OF ALCOHOL
C       AND HYDROCARBON MIXTURES USING THE GROUP SOLUTION MODEL
C       OF RATCLIFF AND CHAO
C       NI= NUMBER OF CARBON ATOMS IN THE ALCOHOL MOLECULE
C       NJ = NUMBER OF CARBON ATOMS IN THE HYDROCARBON MOLECULE
C       HOH = OH GROUP CONTRIBUTION TO HEATS OF MIXING
C       HXCH2 = CH2 GROUP CONTRIBUTION TO HEATS OF MIXING
C       HOHS = STANDARD STATE OF OH GROUP
C       HXCH2S= STANDARD STATE OF CH2 GROUP OF THE ALKANE MOLECULE
        DIMENSION ANRAP(50),HES(50),TOTH(50),F(50)
        DIMENSION XCH2(50),Y(50),HXCH2(50),HOH(50),DTH(50)
        DIMENSION DTHP1(50),DTHP2(50)
        DIMENSION Y(50)
        DIMENSION DEVP(50)
        REAL NI,NJ,NK
        H(Z)=-3.777527E 03 +1.727207E 04*Z -2.956065 04*Z*Z +
      1 2.24841E 04*Z*Z*Z -6.414875E 03*Z*Z*Z*Z
        GK(Z)=-1.131324E 03 +3.5962285E 03*Z -3.8078923E 03*Z*Z
      1  +1.3518303E 03*Z*Z*Z
        G(Z)=1.013123E 04 -4.9912938E 04*Z +09.0916313E 04*Z*Z -
      1 7.3024188E 04*Z*Z*Z +2.185534E 04*Z*Z*Z*Z
        AK(Y) = 1.837*(Y-6.)*(16.-Y) + (21.5/500)*(Y-6.)*(16.-Y)*(11.-Y)
        GG(Z) = 659285.*Z  - 649285
 1000   READ(5,10,END=500)
   10   FORMAT(1X,79H
      1
      2  /1X,79H
      3
        READ(5,20) NI,NJ,NK
   20   FORMAT(3F10.0)
        READ(5,24)NPTS
   24   FORMAT(I10)
        READ(5,25)(X(I),Y(I),I=1,NPTS)
   25   FORMAT(2F20.0)
        SDI = 0.0
        FNPTS = NPTS
        ANI=NI
        ANJ=NJ
        SX1=ANI/(1. + ANI)
        DO 50 I=1,NPTS
        AI=I
   50   XCH2(I) = (X(I)*ANI+(1.-X(I))*NJ)/((1.+ANI)*X(I)+(1.-X(I))*NJ)
C       CALCULATION THE GROUP HEATS OF MIXIMG
        DO 80 I=1,NPTS
  80    HXCH2(I)=EXP(H(XCH2(I)))
        HXCH2S=EXP(H(SX1))
        IF(SX1-0.9286)52,52,51
   52   HOHS=EXP(G(SX1))
        GO TO 55
   51   HOHS=EXP(GK(SX1))
   55   DO 54 I=1,NPTS
        IF(XCH2(I)-0.9286)42,42,41
   42   HOH(I)=EXP(G(XCH2(I)))
```

```
      GO TO 54
   41 HOH(I)=EXP(GK(XCH2(I)))
   54 CONTINUE
      DO 120 I=1,NPTS
      DTHR1(I) = ANI*(HXCH2(I) - HXCH2S) + (HOH(I)-HOHS)
      DTHR2(I) = NJ*HXCH2(I)
      X(I) = NJ*(1.-XCH2(I))/((NJ-NI) + (NI-NJ+1.)*XCH2(I))
  120 DTH(I) = X(I)*DTHR1(I) + (1.-X(I))*DTHR2(I)
C      CALCULATION OF THE SIZE CONTRIBUTION
      ANI = ANI + 1.
      IF(NK ) 69,96,69
   69 DO 71 I=1,NPTS
      ANBAR(I) = X(I)*ANI+(1.-X(I))*ANJ
   71 HES(I) = AK(ANBAR(I))-(ANJ-ANBAR(I))*AK(ANI)/(ANJ-ANI)
     1 -(ANBAR(I)-ANI)*AK(ANJ)/(ANJ-ANI)
      GO TO 79
   96 DO 98 I=1,NPTS
   98 HES(I)=0.
C      TOTAL HEATS OF MIXING TOTH(I)
   79 DO 72 I=1,NPTS
      TOTH(I)=HES(I)+DTH(I)
      DEVP(I)=100.*(Y(I)-TOTH(I))/Y(I)
      SDI = SDI + DEVP(I)*DEVP(I)
   72 CONTINUE
      SDI = SQRT(SDI/FNPTS)
      WRITE(6,1)
    1 FORMAT(1H1)
      WRITE(6,10)
      WRITE(6,300)
  300 FORMAT(//T8,'X',T17,'SIZE',T26,'GROUP',T34,'LIT.DATA',T45,
     1 'PREDICT',T55,'DEV'//)
      WRITE(6,310)(X(I),HES(I),DTH(I),Y(I),TOTH(I),DEVP(I),
     1I=1,NPTS)
  310 FORMAT(F10.4,5F10.2/)
      WRITE(6,131) SDI
  131 FORMAT(1H0,T35,'RMS DEVIATION = ',F10.2)
      GO TO 1000
  500 STOP
      END
```

TABLE 61

Program for Prediction of ΔH^M for n-alkane + n-alcohol Systems at 45°C

Sample of Output

TABLE 61

PENTANOL + HEPTANE AT 25 DEG. C
X=MOL FRACT. OF THE ALCOHOL

X	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.0202	0.11	195.00	240.00	195.11	18.71
0.0500	0.26	327.96	344.00	328.22	4.59
0.0954	0.48	440.40	427.00	440.87	-3.25
0.1741	0.79	555.51	523.00	556.30	-6.37
0.2964	1.15	588.89	579.00	590.04	-1.91
0.4244	1.35	605.79	579.00	607.14	-4.86
0.5129	1.38	544.02	542.00	545.41	-0.63
0.5779	1.35	471.71	492.00	473.06	3.85
0.6254	1.30	440.12	449.00	441.42	1.69
0.6966	1.17	360.75	374.00	361.92	3.23
0.7536	1.03	299.47	311.00	300.50	3.38
0.8210	0.82	233.69	228.00	234.50	-2.85
0.9018	0.49	141.69	128.00	142.19	-11.08

RMS DEVIATION = 6.91

TABLE 62

Program for Prediction of Heats of Mixing of n-alcohol + n-alcohol mixtures at 25°C

Input-Output Format

Card	Column	Format	Variable	Data
1, 2	2-80	80H	--	Any alphameric information (e.g. headings of output)
3	1-20	F10.0	NI	Number of carbon atoms in the first molecule
	21-40	F10.0	NJ	Number of carbon atoms in the second molecule
4	1-10	I10	NPTS	Number of data points
5 to 5+I	1-20	F20.0	X(I)	X_i value (composition)
	21-40	F20.0	Y(I)	Published data of Y_i for comparison with predicted data

TABLE 63

Program for Prediction of ΔH^M for n-alcohol + n-alcohol Systems at $25^\circ C$ Fortran Statement

```
C     A PROGRAM TO PREDICT HEATS OF MIXING OF ALCOHOL + ALCOHOL MIXT
C     USING RATCLIFF AND CHAO MODEL
C     NI=NUMBER OF CARBON ATOMS IN MOLECULE 1
C     NJ=NUMBER CARBON ATOMS IN MOLECULE 2
C     HOH=OH GROUP CONTRIBUTION TO HEATS OF MIXING
C     HXCH2=CH2 GROUP CONTRIBUTION TO HEATS OF MIXING
C     HOHS1= STANDARD STATE OF OH GROUP  IN MOLECULE 1
C     HOHS2= STANDARD STATE OF OH GROUP  IN MOLECULE 2
C     HCH21=STANDARD STATE OF CH2 GROUP IN MOLECULE 1
C     HCH22=STANDARD STATE OF CH2 GROUP IN MOLECULE 2
      DIMENSION DTHG(50) ,Y(50)
      DIMENSION ANBAR(50),HES(50),TDTH(50),F(50)
      DIMENSION DEVP(50)
      DIMENSION XCH2(50),X(50),HXCH2(50),HOH(50),DTH(50)
      DIMENSION DTHB1(50),DTHB2(50)
      REAL NI,NJ,NK
      AK(Y) = 4.473*(Y-6.)*(16.-Y) + (39.5/500)*(Y-6.)*(16.-Y)*(11.-Y
      H(Z)=-2.8647449E 03 +7.6687539E 03*Z -4.8014063E 03*Z*Z
      GK(Z)=1.5208971E 02 -3.303801E 02*Z + 1.8705989E 02*Z*Z
      G(Z)=   (-1.4370887E 04 + 6.4546875E 04*Z -1.086505E 05*Z*Z +
     1 8.1240313E 04*Z*Z*Z -2.2759754E 04*Z*Z*Z*Z)
      GG(Z) = 587857.*Z - 578257.
1000  READ(5,101,END=500)
  101 FORMAT(1X,79H
     1
     2  /1X,79H
     3
      READ(5,10) NI,NJ
  10  FORMAT(2F10.0)
      READ(5,20) NPTS
  20  FORMAT(I10)
      READ(5,15) (X(I),Y(I),I=1,NPTS)
  15  FORMAT(2F20.0)
      SDI = 0.0
      FNPTS = NPTS
      SX1=NI/(1.+NI)
      SX2=NJ/(1.+NJ)
      DO 40 I=1,NPTS
  40  XCH2(I) = (X(I)*NI+(1.-X(I))*NJ)/((1.+NI)*X(I)+(1.-X(I))*(1.+NJ)
      HCH21=H(SX1)
      HCH22=H(SX2)
C     CALCULATION OF THE GROUP HEATS OF MIXING
      IF(SX1-0.9444)52,52,51
 52   HOHS1=EXP(G(SX1))
      GO TO 55
 51   HOHS1=EXP(GK(SX1))
      GO TO 55
 55   IF(SX2-0.9444)53,53,54
 53   HOHS2=EXP(G(SX2))
      GO TO 57
  54  HOHS2=EXP(GK(SX2))
 57   DO 56  I=1,NPTS
      IF(XCH2(I)-0.9916)42,42,41
  41  HOH(I)=GG(XCH2(I))
```

```
      GO TO 56
   42 IF(XCH2(I)-0.9444)49,49,48
   48 HOH(I)=EXP(GK(XCH2(I)))
      GO TO 56
   49 HOH(I) = EXP(G(XCH2(I)))
  56  CONTINUE
      DO 60 I=1,NPTS
      HXCH2(I) = H(XCH2(I))
       DTHB1(I)=NI*(HXCH2(I)-HCH21) + (HOH(I)-HOHS1)
      DTHB2(I)=NJ*(HXCH2(I)-HCH22)+(HOH(I)-HOHS2)
   60 DTHG(I) = X(I)*DTHB1(I)+(1.-X(I))*DTHB2(I)
C     X=MOLE FRACTION OF THE FIRST MOLECULE
C     CALCULATION OF THE SIZE HEATS OF MIXINF
      NI=NI+1.
      NJ=NJ+1.
      DO 80 I=1,NPTS
      ANI=NI
      ANJ=NJ
      ANBAR(I) = X(I)*ANI+(1.-X(I))*ANJ
   80 HES(I) = AK(ANBAR(I))-(ANJ-ANBAR(I))*AK(ANI)/(ANJ-ANI)
     1 -(ANBAR(I)-ANI)*AK(ANJ)/(ANJ-ANI)
C     CALCULATION OF THE TORAL HEATS OF MIXING TOTH(I)
      DO 120 I=1,NPTS
      TOTH(I) = HES(I) + DTHG(I)
      DEVP(I)=100.*(Y(I)-TOTH(I))/Y(I)
      SDI = SDI + DEVP(I)*DEVP(I)
  120 CONTINUE
      SDI=SQRT(SDI/FNPTS)
      WRITE(6,1)
    1 FORMAT(1H1)
      WRITE(6,101)
      WRITE(6,300)
  300 FORMAT(//T8,'X',T17,'SIZE',T26,'GROUP',T34,'LIT.DATA',T45,
     1 'PREDICT',T55,'DEV'//)
      WRITE(6,310)(XCH2(I),X(I),DTHG(I),HES(I),TOTH(I),DEVP(I),
     1  I=1,NPTS)
  310 FORMAT(F10.4,5F10.2/)
      WRITE(6,131) SDI
  131 FORMAT(1H0,T35,'RMS DEVIATION = ',F10.2)
      GO TO 1000
  500 STOP
      END
```

TABLE 64

Program for Prediction of ΔH^M for n-alcohol + n-alcohol Systems at 25°C

Sample of Output

```
SYSTEM PENTANOL + OCTANOL AT 25 DEG. C
X=MOL. FRACT. OF PENTANOL, TDTH=PREDICTED HEATS OF MIXING

     X          SIZE       GROUP    LIT.DATA    PREDICT     DEV

  0.8848        0.11       19.18      4.50       23.68     -2.96
  0.8812        0.19       20.01      7.36       27.37     27.97
  0.8754        0.33       27.72     10.39       38.11     29.43
  0.8689        0.46       30.37     11.82       42.19     33.04
  0.8628        0.57       34.06     11.73       45.80     28.44
  0.8624        0.58       30.55     11.69       42.24     35.02
  0.8588        0.64       26.91     11.07       37.98     37.74
  0.8534        0.73       26.39      9.58       35.97     33.39
  0.8474        0.82       18.51      7.27       25.78     38.62
  0.8414        0.90       12.54      4.42       16.97     34.75
  0.8377        0.95        4.56      2.46        7.02     53.22

                                   RMS DEVIATION =        34.19
```

TABLE 65

Program for Prediction of Heats of Mixing of Ternaries

Input-Output Format

Card	Column	Format	Variable	Data
1, 2	2-80	80H	--	Any alphameric information (e.g. headings of output)
3	1-10	I10	NPTS	Number of data points
4	1-10	F10.0	NI	Number of carbon atoms in the hydrocarbon molecule
	11-20	F10.0	NJ	Number of carbon atoms in the short alcohol molecule
	21-30	F10.0	NK	Number of carbon atoms in the long alcohol molecule
5 to 5+I	1-20	F20.0	X2(I)	Mole fraction of alcohol molecule with number of carbon atoms = NJ
	21-40	F20.0	X3(I)	Mole fraction of the second alcohol molecule
	41-60	F20.0	Y(I)	Published data of heats of mixing for comparison with predicted data

TABLE 66

Program for Prediction of ΔH^M for Ternary Systems at 25°C

Fortran Statement

```
C     PREDICTION HEATS OF MIXING OF TERNARY SYSTEMS AT 25 DEG. C
C     USING GROUP SOLUTION MODEL OF RATCLIFF AND CHAO
      DIMENSION X1(50),X2(50),X3(50),Y(50),XCH2(50),HOH(50),DTHG(50)
      DIMENSION DTHB1(50),DTHB2(50),DTHB3(50),X12(50),X13(50),X23(50)
      DIMENSION H12(50),H23(50),H13(50),HES(50),TOTH(50)
      DIMENSION X121(50),X122(50),X131(50),X133(50),X232(50),X233(50)
      DIMENSION HXCH2(50)
      DIMENSION AA(50),BB(50)
      DIMENSION DEVP(50)
      REAL NI,NJ,NK
      H(Z)=-2.8647449E 03 +7.6687539E 03*Z -4.8014063E 03*Z*Z
      GK(Z)=1.5208371E 02 -3.303801E 02*Z + 1.8705989E 02*Z*Z
      G(Z)=    (-1.4370887E 04 + 6.4545875E 04*Z -1.086505E 05*Z*Z +
     1 8.1240313E 04*Z*Z*Z -2.2759754E 04*Z*Z*Z*Z)
      GG(Z)=2000.*Z -1600.
      HH(Z)=-540.*Z + 642.
 1000 READ(5,10,END=500)
   10 FORMAT(1X,79H
     1
     2  /1X,79H
     3
      READ(5,24)NPTS
   24 FORMAT(I10)
      READ(5,11)NI,NJ,NK
   11 FORMAT(3F10.0)
      READ(5,30)(X2(I),X3(I),Y(I),I=1,NPTS)
   30 FORMAT(3F20.0)
      SDI = 0.0
      FNPTS = NPTS
      ANI=NI
      ANJ=NJ
      SX3=NK/(1.+NK)
   22 HOHS3=EXP(G(SX3))
      HCHS3=H(SX3)
      DO 50 I=1,NPTS
      X1(I)=1.-X2(I)-X3(I)
   50 XCH2(I)=(NI*X1(I)+NJ*X2(I)+NK*X3(I))/
     1(NI*X1(I) +(1.+NJ)*X2(I)+(1.+NK)*X3(I))
C     CALCULATION OF THE GROUP HEATS OF MIXING
   55 DO 54 I=1,NPTS
      IF(XCH2(I)-0.9444)42,42,41
   41 HOH(I)=EXP(GK(XCH2(I)))
      HXCH2(I)=H(XCH2(I))
      GO TO 54
   42 IF(XCH2(I)-0.8)39,39,38
   38 HOH(I)=EXP(G(XCH2(I)))
      HXCH2(I)=H(XCH2(I))
      GO TO 54
   39 HOH(I)=GG(XCH2(I))
      HXCH2(I)=HH(XCH2(I))
   54 CONTINUE
      DO 60 I=1,NPTS
      DTHB1(I)=NI*HXCH2(I)
      DTHB2(I)=NJ*(HXCH2(I)-237.) + (HOH(I)+100.)
```

```
      DTHB3(I)=NK*(HXCH2(I)-HCHS3) +(HOH(I)-HOHS3)
 60   DTHG(I)=X1(I)*DTHB1(I) +X2(I)*DTHB2(I) +X3(I)*DTHB3(I)
C     CALCULATION OF THE SIZE HEATS OF MIXING
      DO 100 I=1,NPTS
      B=4.6
      X121(I)=(1.+X1(I)-X2(I))/2.
      X122(I)=1.-X121(I)
      X131(I)=(1.+X1(I)-X3(I))/2.
      X133(I)=1.-X131(I)
      X232(I)=(1.+X2(I)-X3(I))/2.
      X233(I)=1.-X232(I)
      NJ=NJ+1.
      NK=NK+1
      H12(I)=B*(NI-NJ)*(NI-NJ)*X121(I)*X122(I)
      H13(I)=B*(NI-NK)*(NI-NK)*X131(I)*X133(I)
      H23(I)=B*(NJ-NK)*(NJ-NK)*X232(I)*X233(I)
 100  HES(I)=X1(I)*X2(I)*H12(I)/X121(I)*X122(I)
     1  + X1(I)*X3(I)*H23(I)/X131(I)*X133(I)
     2   + X2(I)*X3(I)*H23(I)/X232(I)*X233(I)
C     CALCULATION OF THE TOTAL HEATS OF MIXING
      DO 200 I=1,NPTS
 200  TOTH(I)=HES(I)+DTHG(I)
      DO 72 I=1,NPTS
      DEVP(I)=100.*(Y(I)-TOTH(I))/Y(I)
      SDI = SDI + DEVP(I)*DEVP(I)
 72   CONTINUE
      SDI = SQRT(SDI/FNPTS)
      WRITE(6,9)
  9   FORMAT(1H1)
      WRITE(6,10)
      WRITE(6,300)
  300 FORMAT(//T8,'X1',T17,'SIZE',T26,'GROUP',T34,'LIT.DATA',T45,
     1 'PREDICT',T57,'DEV'//)
      WRITE(6,310)(X1(I),HES(I),DTHG(I),Y(I),TOTH(I),DEVP(I),
     1 I=1,NPTS)
 310  FORMAT(F10.4,5F10.2/)
 131  FORMAT(1H0,T35,'RMS DEVIATION = ',F10.2)
      WRITE(6,131) SDI
      GO TO 1000
 500  STOP
      END
```

TABLE 67

Program for Prediction of ΔH^M for Ternary Systems at 25°C

Sample of Output

TABLE 67

SYSTEM HEPTANE+PROPANOL+PENTANOL AT 25 DEG, C, SOLUTION C
1=HEPTANE,2=PROPANOL,3=PENTANOL

X1	SIZE	GROUP	LIT.DATA	PREDICT	DEV
0.7076	0.40	604.26	589.00	604.65	-2.66
0.6576	0.49	615.87	609.00	616.36	-1.21
0.5860	0.48	634.50	612.00	634.98	-3.76
0.4814	0.35	583.10	573.00	583.44	-1.82
0.3767	0.50	506.30	503.00	506.80	-0.76
0.3151	1.50	460.45	446.00	461.95	-3.58
0.2688	3.47	407.33	398.00	410.80	-3.22
0.1997	6.39	310.45	316.00	316.84	-0.27
0.1382	9.14	201.14	233.00	210.27	9.75
0.1145	12.07	184.20	198.00	196.27	0.87

RMS DEVIATION = 3.82