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ANALYSIS AND INTERPRETATION OF EXCESS MOLAR PROPERTIES OF AMPHIPHILE + WATER SYSTEMS. I. EXCESS MOLAR VOLUMES V^E FOR 1-PROPANOL + WATER

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ABSTRACT

A recently developed version of the four segment composition model for analysing the excess molar properties of binary amphiphile + water systems has been applied to the excess molar volumes of 1-propanol + water, as reported by Benson and Kiyohara (J. Solution Chem., 9 (1980) 791). The model, which was found to provide a gratifying quality of fit to these excellent data, is formulated in such a way as to explore the composition dependence of excess thermodynamic properties in terms of transitions among a sequence of different metastable patterns of aggregation.

INTRODUCTION

1-Propanol may be regarded as being a primitive amphiphile. Its hydroxyl group,with its hydrogen bonding capability, is clearly hydrophilic. Its propyl group is of sufficient length to be at least moderately hydrophobic.

In studying simple amphiphile + water systems, one attempts to address a number of questions. The basic question is whether there is an essentially random pattern of distribution and orientation of the two molecular species, or a tendency for the amphiphiles to mimic, in an aqueous environment, the micellar and liquid crystalline schemes of molecular aggregation that are characteristic of non-ionic detergents. This invites a second question. Where should one look for evidence of structural order in binary liquid mixtures, if such exists?

Among the numerous means that have been adopted to search for evidence of ordered molecular aggregates in binary liquid systems is the careful scrutiny of the composition dependence of thermodynamic properties of such systems. There are to be found in the literature examples of relatively small amphiphile + water systems whose thermodynamic properties possess intriguing composition dependences that appear to reflect substantial variations in the patterns of molecular aggregation.

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Having identified a particular thermodynamic property of a given binary system as possessing an interesting type of composition dependence, one faces further questions concerned with the analysis and interpretation of the data. The analysis involves seeking equations that are capable of producing faithful replicas of the data, apart from the inevitable random errors. Interpretation implies furnishing molecular scale rationales for the form of the data. Ideally, the curve fitting equations are so formulated that their optimised parameters are of assistance in the interpretation.

A brief account of a new curve fitting strategy, which goes some way to meeting those requirements, has recently been published [1]. In this article, the rationale for that approach will be discussed in more detail together with an account of its application to a particularly nice set of data.

The excess molar volumes of 1-propanol + water at 15, 20, 25, 30 and 35 ° C, as reported by Benson and Kiyohara [2], were singled out for several reasons. The data appear to be of exceptional quality, both in terms of the level of internal consistency and the high point density (which is necessary to furnish an adequate account of the composition dependence). The data provide a challenge for any curve fitting strategy, in view of the authors' revelation that they were unable to obtain a satisfactory quality of fit using conventional approaches. They resorted to the use of two separate equations; one for the extremely water rich mixtures, the other for the remainder.

Mention should be made of the work of Dethlefsen et al. [3], who chose to analyse the apparent molar volumes of this system using a mass action model which distinguishes between hydrophobic and hydrophilic hydration. Their conclusion was that the fraction of the water molecules involved in hydrophobic hydration falls off extremely rapidly with increasing 1-propanol concentration, becoming negligible above a mole fraction of 0.1.

PRELIMINARY ANALYSIS

Before any efforts are made to select specific model equations for the excess molar property data, it is appropriate to examine plots of their dependence upon mole fractional composition.

Plots of V^E, across the total composition range, are relatively uninformative on the scale of a journal page. The plot of V^E, over the range $0 < X_A < 0.2$ (where X_A denotes the 1-propanol mole fraction), reveals an interesting variation of slope at $X_A \approx 0.07$ (Fig. 1). A more sensitive indicator of the nature of the composition dependence of V^E is the plot of dV^E/dX_A versus X_A that is shown in Fig. 2. The derivatives were estimated using a cubic splines procedure. Such curves are only meaningful if the original data sets are of high quality.

Two features of the derivative curve are of special interest. The tortuous variations over the range $0 < X_A < 0.1$ are presumed to be associated with

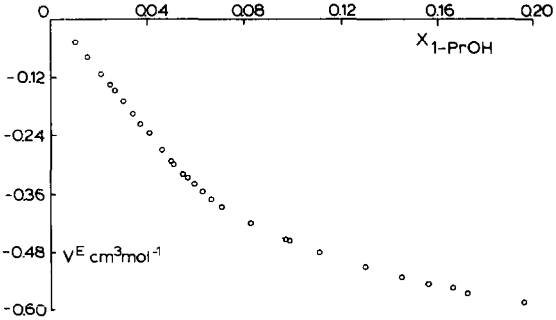

Fig. 1. Excess molar volumes of 1-propanol + water mixtures at 25 °C (ref. 2) over the composition range $0 < X_{1\text{-PrOH}} < 0.2$.

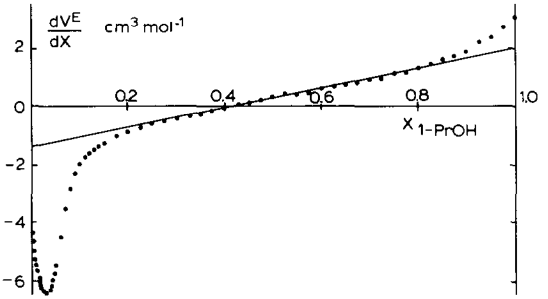

Fig. 2. dV^E/dX_A for 1-propanol + water at 25 °C over the total composition range.

radical changes in the patterns of molecular aggregation. By contrast, the essentially linear dependence of dV^E/dX_A over the range $0.3 < X_A < 0.7$ seems to indicate the existence of a consistent pattern which is either substantially ordered or totally random. The proposition that an amphiphile + water mixture could be randomly structured would be contradictory to all of the concepts that have been developed concerning hydrophobic effects.

THE ANALYTICAL MODEL

A few years ago, it was demonstrated that a reasonably satisfactory fit to the V^E data of 1-propanol + water could be obtained using a model which partitions the total composition range into four separate segments [4]. Since that time, the four-segment model has passed through several evolutionary stages [5].

The current version retains the assumption of the validity of treating the total composition range as comprising four separate segments, with junctions at mole fractions of 1-propanol denoted by X_1, X_2 and X_3. As in the earlier versions, X_2 and X_3 represent the limits of the composition range over which $\mathrm{d}V^{\mathrm{E}}/\mathrm{d}X_{\mathrm{A}}$ is closely approximated by a linear function of X_{A}. X_1 lies in the vicinity of the minimum value of $\mathrm{d}V^{\mathrm{E}}/\mathrm{d}X_{\mathrm{A}}$.

Where this version differs from its predecessors is in the formulation of the equations used to fit the two water-rich segments.

The water-rich segment: $0 < X_A < X_l$

At infinite dilution of 1-propanol in water, the solute exists as a fully hydrated monomer. The hydration cosphere is made up of two parts. One part consists of those molecules occupying sites, the characteristics of which are influenced by their proximity to the alkyl group; the other comprises molecules that are affected by their interactions with the hydroxyl group.

In the extreme low concentration limit, one may represent the excess molar volumes by

$$V_{\mathrm{mono}}^{\mathrm{E}} = a_{\mathrm{mono}} X_{\mathrm{A}} + b_{\mathrm{mono}} X_{\mathrm{A}}^2 \qquad (1)$$

As the 1-propanol concentration rises, the effects of hydrophobic aggregation come into play. These effects include greater than random contact between pairs of alkyl groups and diminished contact between the alkyl groups and water. In the case of non-ionic surfactants, this phenomenon leads to the formation of micellar aggregates. It is worth bearing in mind that critical micelle concentrations tend to be low enough for most of the water molecules to be virtually unaffected by the presence of the solute.

1-Propanol cannot be classified as a true surfactant. However, it might be termed a borderline surfactant insofar as the surface tensions of its aqueous mixtures drop dramatically with increasing 1-propanol mole fraction. A plot of surface tension against mole fraction is shown in Fig. 3 [6].

It is envisioned that there exists some type of growth pattern which culminates, at X_1, with the formation of metastable pseudomicellar aggregates. While X_1 might be regarded as an analog of a critical micelle

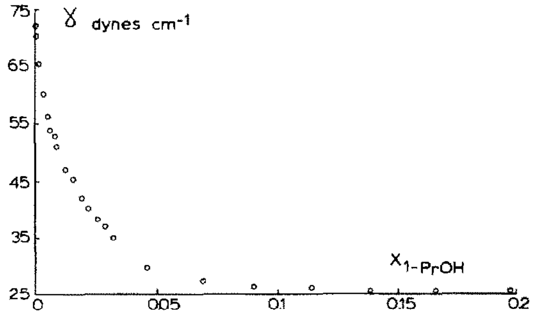

Fig. 3. Surface tension γ of 1-propanol + water mixtures at approximately 25 °C, over the composition range $0 < X_{1\text{-PrOH}} < 0.2$.

concentration, its value is such that virtually all of the water molecules occupy sites which are influenced by the presence of the solute.

For the pseudomicellar scheme of aggregation, the following equation has been adopted

$$V^{E}_{\text{Pmic}} = q_{\text{Pmic}} X_{\text{W}} + a_{\text{Pmic}} X_{\text{A}} + b_{\text{Pmic}} X_{\text{A}}^{2} \tag{2}$$

The fractional growth pattern from monomers to pseudomicellar solute aggregates is represented by a function f_{W}. The excess molar volumes of the mixtures of the water rich segment are represented by

$$V^{E}_{(\text{W})} = V^{E}_{\text{mono}}(1 - f_{\text{W}}) + \left\{ V^{E}_{\text{Pmic}} - (1 - X_{\text{A}}/X_{1}) q_{\text{Pmic}} X_{\text{W}} \right\} f_{\text{W}} \tag{3}$$

The form that was selected to represent the function f_{W} was

$$f_{\text{W}} = [\exp(X_{\text{A}}) - (1 + X_{\text{A}})]/[\exp(X_{1}) - (1 + X_{1})] \tag{4}$$

This function has the characteristics that both f_{W} and $\mathrm{d}f_{\text{W}}/\mathrm{d}X_{\text{A}}$ are zero at $X_{\text{A}} = 0$ and $f_{\text{W}} = 1$ at $X_{\text{A}} = X_{1}$. It is noted that eqn. (3) makes allowance for the fact that, for $X_{\text{A}} < X_{1}$, a proportion of the water molecules is envisaged as occupying sites which are characteristic of the pure liquid.

The secondary segment: $X_1 < X_A < X_2$

At $X_{\text{A}} = X_{1}$, it is envisioned that the 1-propanol molecules form metastable pseudomicellar aggregates. $X_{\text{A}} = X_{2}$ is the water rich end of the range of compositions for which $\mathrm{d}V^{E}/\mathrm{d}X_{\text{A}}$ is a linear function of X_{A}. In the development of concepts dealing with the patterns of aggregation that might exist in small amphiphile + water mixtures, it seems reasonable to expect these systems to mimic, to some extent, non-ionic surfactant + water systems. Certain alkoxy-polyethoxyethanol + water systems are known to possess, at different ranges of composition and temperature, three distinct liquid crystalline phases [7]. The cubic phase consists of close packed spherical micelles. The hexagonal phase consists of close packed extended rod shaped micelles. The lamellar phase consists of alternating layers of water and amphiphile, with the latter being of the membrane bilayer type.

The pseudomicellar scheme is considered to be a metastable analog of the cubic liquid crystalline phase. The opinion was offered some years ago that mixtures with composition in the range where $\mathrm{d}V^{E}/\mathrm{d}X_{\text{A}}$ varies linearly with X_{A} contain some type of metastable pseudolamellar aggregates [8].

In a lamellar aggregation scheme, the distinction between solute and solvent does not exist and the quadratic dependence of V^{E} upon X_{A} is best expressed by

$$V^{E}_{\text{Plam}} = q_{\text{W}} X_{\text{W}} + q_{\text{A}} X_{\text{A}} + b_{\text{L}} X_{\text{A}} X_{\text{W}} \tag{5}$$

The secondary segment is envisaged as involving a transition from pseudomicellar to pseudolamellar aggregation. An interesting feature of this segment was recently pointed out concerning the 2-butoxyethanol + water system; namely that its limits, at 25 ° C, correspond quite closely to the maximum span of the miscibility gap that exists at elevated temperatures [1].

For this segment, the excess molar volumes are represented by

$$V^{\mathrm{E}}_{(\mathrm{s})} = V^{\mathrm{E}}_{\mathrm{Pmic}}(1 - f_{\mathrm{s}}) + V^{\mathrm{E}}_{\mathrm{Plam}} f_{\mathrm{s}} \tag{6}$$

where the function f_{s} describes the fractional transformation from the one type of aggregate to the other as X_{A} increases from X_1 to X_2.

The form of f_{s} that was found to be suitable was

$$f_{\mathrm{s}} = \frac{\tanh[3(X_{\mathrm{A}} - X_1)/(X_2 - X_1)]}{\tanh 3} \tag{7}$$

This function rises rapidly with X_{A} for low $X_{\mathrm{A}} - X_1$ but has a very modest slope as X_{A} approaches X_2; f_{s} is zero at $X_{\mathrm{A}} = X_1$ and unity at $X_{\mathrm{A}} = X_2$.

The pseudolamellar segment: $X_2 < X_A < X_3$

The functional dependence of V^{E} upon X_{A} across this segment has already been given in eqn. (5).

The organic rich segment: $X_3 < X_A < 1$

Pure 1-propanol is assumed to be a fairly well structured liquid in which the stability derived from hydrogen bonding leads to appropriate alignments of neighboring pairs of hydroxy groups. Hydrogen bonding is also presumed to result in solute water molecules preferentially occupying sites close to the hydroxy groups of the alkanol.

From Fig. 2 it appears that V^{E} possesses at least cubic dependence upon mole fraction. Imposition of the conditions that both V^{E} and $\mathrm{d}V^{\mathrm{E}}/\mathrm{d}X_{\mathrm{A}}$ are continuous at $X_{\mathrm{A}} = X_3$ leads to

$$\begin{aligned} V^{\mathrm{E}}(a) = {} & q_{\mathrm{W}} X_{\mathrm{W}} (2y - y^2) + q_{\mathrm{A}} \left[y^2 (1 + 2X_3) - y^3 (1 + X_3) \right] \\ & + b_{\mathrm{L}} X_{\mathrm{W}} \left[y(1 + X_3) - y^2 \right] + a_{\mathrm{A}} X_{\mathrm{W}} (1 - y)^2 \end{aligned} \tag{8}$$

where

$$y = X_{\mathrm{W}}/(1 - X_3) \tag{9}$$

a_{A} is the apparent molar excess volume of water at infinite dilution in 1-propanol. It is noted that eqn. 8 differs from that adopted in ref. 1.

Equations (1)–(9) collectively provide a means of fitting an analytical curve to the excess molar volume data across the entire composition range. Evaluation of the fitted curve involves the location of the three segment junction compositions and optimisation of nine model parameters.

For a specific set of values of X_1, X_2 and X_3, the model parameters can be optimised by a relatively simple linear least squares computer program. Optimising the values of the segment junction compositions is considerably less straightforward. The most satisfactory approach seems to be that of simplex optimization. The simplex procedure is tedious and apt to locate false minima. Nevertheless, with patience and adequate safeguards it attains its purpose.

RESULTS

The optimised segment junctions for the five excess molar volume data sets were pleasingly consistent.

$X_1 = 0.038 \pm 0.006$

$X_2 = 0.260 \pm 0.020$

$X_3 = 0.735 \pm 0.015$

where the uncertainties are the magnitudes of the largest deviations from the representative values.

There were no trends of temperature dependence that could be treated as being significant.

The model equations furnished an agreeable quality of fit, with standard deviations in V^E spanning the range 0.93–1.30 mm^3 mol^{-1}. Each of the nine model parameters appeared to exhibit reasonably well defined temperature dependence. Table 1 gives values of the model parameters for V^E and for $(\delta V^E/\delta T)_P$, at 25 °C. These values were obtained on the assumption that each of the model parameters for V^E possesses quadratic temperature dependence. The uncertainties listed are the standard deviations from the quadratic functions of temperature.

TABLE 1

Four-segment model parameters for the excess molar volumes V^E and the excess molar isobaric expansivities $(\delta V^E/\delta T)_P$ for 1-propanol + water at 25 °C

	V^E (cm^3 mol^{-1})	$(\delta V^E/\delta T)_P$ (mm^3 K^{-1} mol^{-1})
a_{mono}	-4.70 ± 0.02	-40.8 ± 1.9
b_{mono}	-14.4 ± 0.9	898 ± 79
q_{Pmic}	-0.037 ± 0.002	-1.46 ± 0.22
a_{Pmic}	-5.98 ± 0.08	41.0 ± 6.9
b_{Pmic}	28.9 ± 0.6	126 ± 51
q_W	-0.401 ± 0.001	2.94 ± 0.06
q_A	-0.094 ± 0.002	2.22 ± 0.20
b_L	-1.60 ± 0.01	8.00 ± 0.86
a_A	-2.95 ± 0.02	29.2 ± 2.0

DISCUSSION

The primary objectives of this work were to test the utility of the proposed model equations as a means of analysing the excess molar volume data for the 1-propanol + water system and to provide a basis for comparing the excess molar properties of different amphiphile + water systems. The quality of fit and the internal consistency of the optimised parameter values for the five sets of data encourage the belief that those objectives have been reasonably well accomplished.

Most of the insight into the significance of the optimised parameter values will come from examination of the manner in which they vary as a result of making systematic changes in the molecular structures of the amphiphilic species. There are, however, a number of comments that may be made about the contents of Table 1.

The monomeric solute

a_{mono}

Transfer of 1-propanol molecules from a 1-propanol to a totally aqueous environment results in a substantial decrease in volume. The molar volume of pure 1-propanol is 75.14 $\mathrm{cm^3\ mol^{-1}}$ [2] and its apparent molar volume at infinite dilution is 70.44 $\mathrm{cm^3\ mol^{-1}}$. From ref. 2, the molar isobaric expansivity of 1-propanol is 75.4 $\mathrm{mm^3\ K^{-1}\ mol^{-1}}$, while the apparent molar excess quantity at infinite dilution is 34.6 $\mathrm{mm^3\ K^{-1}\ mol^{-1}}$.

a_{mono} is a composite of several components, including the effects of the solutes present upon the self aggregation of the water molecules of the hydration cosphere. That its value for $(\delta V^{\mathrm{E}}/\delta T)_P$ is so large and negative might be due largely to the breakdown of ice-like aggregation in the vicinity of the alkyl group with increasing temperature.

b_{mono}

The interactions between monomeric solute molecules are thought to be dominated by the effects of cosphere overlap, as opposed to direct contact. The larger part of the cospheres of the 1-propanol monomers is presumed to be made up of the water molecules that are involved in hydrophobic hydration. The negative sign of b_{mono} for V^{E} is consistent with the breakdown of ice-like aggregation. Its positive sign for $(\delta V^{\mathrm{E}}/\delta T)_P$ is consistent with diminishing ice-like aggregation with increasing temperature.

Pseudomicellar aggregation

q_{Pmic}

This quantity appears as an excess molar property of water in some type of hypothetical standard state. That standard state might be envisaged as representing water molecules which are not directly involved in stabilizing the pseudomicellar aggregates but occupy interstitial sites. No satisfactory explanation for its values can be offered at this time.

a_{Pmic}

a_{Pmic} is the apparent molar excess property of 1-propanol in pseudomicellar aggregation. That its value, for V^{E}, is more negative than is a_{mono} is consistent with a lack of hydrophobic hydration in this type of aggregation. That its value is positive for $(\delta V^{\mathrm{E}}/\delta T)_P$ might be due to a general decrease in structural order with increasing temperature.

b_{Pmic}

This parameter reflects in some fashion the effects of solute–solute interaction. Its magnitude might be rationalised in several ways, including aggregate growth.

Pseudolamellar aggregation

q_{W}

q_{W} is the excess molar property of a further hypothetical standard state of water. Apparently, in that state, water adopts a more compact mode of packing than does the pure liquid. Such behavior is consistent with a decrease in the fraction of the molecules that occupy ice-like sites. Since the uncommonly low expansivity of water is attributed to the conversion of water from ice-like to more compact structures, as a result of temperature increases, the substantial positive q_{W} value for $(\delta V^{\mathrm{E}}/\delta T)_P$ seems to be reasonable.

q_{A}

q_{A} is the excess molar property of the amphiphile in its hypothetical standard state. Its negative value for V^{E} is possibly due to more efficient packing promoted by contact with water.

b_{L}

b_{L} is characteristic of the formation of the interface between the two pseudolaminar components. The significance of its values can best be assessed by comparing a wide variety of properties and systems.

Organic rich mixtures

a_{A}

a_{A} is the apparent molar excess property of water at infinite dilution in 1-propanol. It is envisioned that the water molecules, as monomeric solute species, preferentially occupy sites close to the hydroxyl groups of the

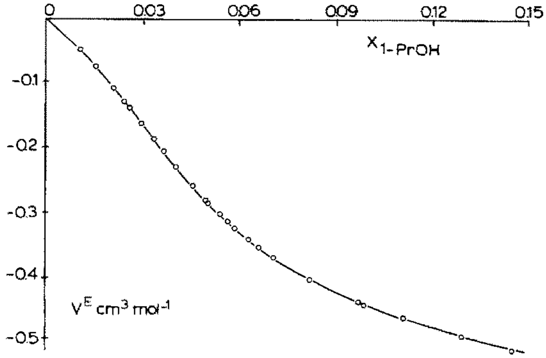

Fig. 4. Fit of the four-segment model to the excess molar volumes of 1-propanol + water at 25 ° C over the composition range $0 < X_{(1\text{-PrOH})} < 0.15$.

solvent. The negative value for V^E suggests that the presence of the water encourages structural order.

CONCLUDING REMARKS

A new version of the four-segment composition model has been employed in the analysis of the excess molar volumes of the 1-propanol + water system, as reported by Benson and Kiyohara [2], at 15, 20, 25, 30 and 35 ° C.

The plots of the 25 ° C data, together with the model version, that are given in Figs. 4 and 5 reveal a gratifying quality of fit. This reflects favorably upon the quality of the data as well as the utility of the model. The combined results of the five different data sets have led to reasonably well defined estimates of the model parameters for the expansivities $(\delta V^E/\delta T)_P$. The excess molar expansivities calculated from the parameters of Table 1 are shown graphically in Fig. 6.

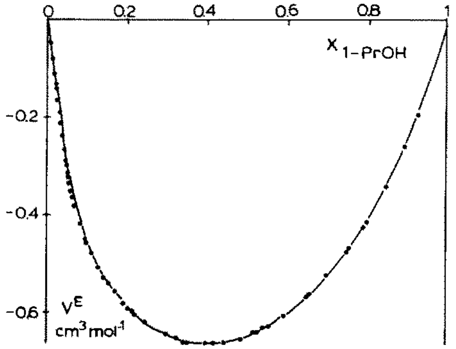

Fig. 5. Fit of the four-segment model to the excess molar volumes of 1-propanol + water at 25 ° C over the total composition range.

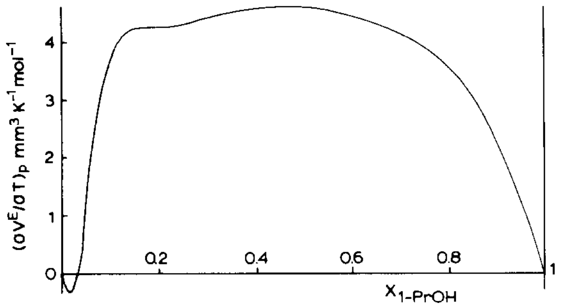

Fig. 6. $(\delta V/\delta T)_p$ for 1-propanol + water at 25 ° C over the total composition range.

Some tentative explanations have been given for the signs and magnitudes of the contents of Table 1. Parallel analyses of this and other excess molar properties of other simple amphiphile + water systems are in progress.

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REFERENCES

1 G. Douheret, A. Pal and M.I. Davis, J. Chem. Soc., Faraday Trans. 1, in press.
2 G.C. Benson and O. Kiyohara, J. Solution Chem., 9 (1980) 791.
3 C. Dethlefsen, P.G. Sorensen and A. Hvidt, J. Solution Chem., 13 (1984) 91.
4 M.I. Davis, Thermochim. Acta, 89 (1985) 325.
5 M.I. Davis, M.C. Molina and G. Douheret, Thermochim. Acta, 131 (1988) 153.
6 M.I. Davis and M. Serratos, unpublished data.
7 P.-G. Nilsson, H. Wennerstrom and B. Lindmann, J. Phys. Chem., 87 (1983) 1377.
8 M.I. Davis, Thermochim. Acta, 63 (1983) 67.