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AN ANALYTIC MODEL FOR THE EXCESS PROPERTIES OF BINARY LIQUID MIXTURES

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ABSTRACT

A model has been devised to analyse excess property data for binary liquid mixtures. The model embodies the concept of the segmentation of the total composition range into three distinct regions. Results are given for the analyses of $\Delta\bar{V}$, $\Delta\bar{H}$ and $\Delta\eta$ for the acetonitrile–water and dimethylsulfoxide–water systems.

INTRODUCTION

Acetonitrile [CH_3CN] and dimethylsulfoxide [$(CH_3)_2SO$] belong to a class of polar organic liquids which are miscible with water in all proportions. There is an extensive literature describing investigations of the ways in which the physical properties of the binary aqueous systems vary with their molar composition.

Several authors, commenting on studies of the acetonitrile–water system, have subscribed to the view that the total range of composition consists of three fairly distinct segments [1,2]. Striking support for the theory of tripartite segmentation of the composition range is provided by plots of excess viscosity against mole fraction [3] (see Fig. 3).

A plausible rationale for the existence of three composition segments is based upon the notion that the molecules of each of the components might occupy one or other of two distinct types of site. One type of site is that which is characteristic of the pure liquid. The other is characteristic of a pattern of molecular aggregation which has been termed microheterogeneous [4].

At the extremes of the composition range, the substance of greater mole fraction may be termed the solvent; the other is the solute. Some or all of the solvent molecules in the immediate vicinity of a solute molecule occupy "heterogeneous" sites. The remaining solvent molecules occupy pure liquid sites. All of the solute molecules occupy heterogeneous sites. As the concentration of the solute is increased so the fraction of solvent molecules that occupy pure liquid sites decreases. There exists some maximum concentration of solute above which none of the solvent molecules are in pure liquid sites.

It is suggested that in the middle or heterogeneous composition segment, all of the molecules of both species occupy heterogeneous sites. In the water-rich segment there is a distribution of water molecules among heterogeneous and pure liquid sites. In the organic rich segment, the roles of solute and solvent are reversed.

Whatever kinds of molecular clusters exist in these mixtures, they are assumed to be highly labile and the relative locations and orientations of their compositions poorly defined.

While the concept of composition segmentation has been accepted, at least in some quarters, there do not appear to be any published accounts of analytic models which explicitly incorporate it. This article contains a description of the derivation, the algebraic form and the application of a scheme for analysing the excess physical properties of binary liquid systems for which a tripartite segmented composition may be assumed. The analytic model is described in terms of an analysis of a data set consisting of excess molar volumes ($\Delta\overline{V}$). It is assumed to be applicable to other excess properties.

THE ANALYTIC MODEL

The appropriate form of the Gibbs–Duhem equation for the variation of excess molar volumes with molar composition is [5]

$$(1 - x_A)\, \mathrm{d}\Delta\overline{V}_W + x_A\, \mathrm{d}\Delta\overline{V}_A = 0 \tag{1}$$

where $\Delta\overline{V}_W$ and $\Delta\overline{V}_A$ are the respective partial molar excess volumes of water and the organic component; with x_A being the mole fraction of the organic component.

The Margoules equations may be derived by rearranging eqn. (1) and introducing some specific constraints.

$$\frac{1}{x_A}\, \mathrm{d}\Delta\overline{V}_W = -\frac{1}{(1 - x_A)}\, \mathrm{d}\Delta\overline{V}_A = (2B + 3Cx_A)\, \mathrm{d}x_A \tag{2}$$

If eqn. (2) is assumed to be valid within the restricted composition segment $x_\alpha \leq x_A \leq x_\beta$, its solutions are of the form

$$\Delta\overline{V}_W = Bx_A^2 + Cx_A^3 + \Delta\overline{V}_W^0(\alpha\beta) \tag{3}$$

$$\Delta\overline{V}_A = (B + \tfrac{3}{2}C)(1 - x_A)^2 - C(1 - x_A)^3 + \Delta\overline{V}_A^0(\alpha\beta) \tag{4}$$

where $\Delta\overline{V}_W^0(\alpha\beta)$ and $\Delta\overline{V}_A^0(\alpha\beta)$ are constants of integration which are taken to correspond to excess molar properties of hypothetical standard states of water and the organic component, respectively.

It follows that, within the composition segment $x_\alpha \le x_A \le x_\beta$

$$\Delta\bar{V} = (1 - x_A)\,\Delta\bar{V}_W + x_A\,\Delta\bar{V}_A$$

$$= B x_A(1 - x_A) + \frac{C}{2} x_A(1 - x_A^2) + \Delta\bar{V}_W^0(\alpha\beta)(1 - x_A) + \Delta\bar{V}_A^0(\alpha\beta)\,x_A \quad (5)$$

It is assumed that eqns. (3–5) are valid for each of the three composition segments of the binary liquid systems with which we are concerned. It is further assumed that each segment has characteristic values of the four parameters B, C, $\Delta\bar{V}_A^0$ and $\Delta\bar{V}_W^0$.

With three composition segments, there are two segment junctions at mole fractions $x_A = x_I$ and x_{II}. The individual segments will be identified by the symbols ω (water-rich), h(heterogeneous) and a (organic rich). Thus, for example, B(h) is a parameter associated with the segment $x_I \le x_A \le x_{II}$.

The size of the parameter set, required to define $\Delta\bar{V}$ across the entire composition range, is reduced by the introduction of a number of constraints. Some of these constraints, as listed, are mandatory; others constitute additional model assumptions.

1. The quantities $\Delta\bar{V}_W^0(\omega)$ and $\Delta\bar{V}_A^0(\mathrm{a})$ must both be zero since $\Delta\bar{V}$ is by definition zero at both $x_A = 0$ and $x_A = 1$.

2. $\Delta\bar{V}$ must be single valued at both of the segment junctions x_I and x_{II}.

3. It is assumed that it is appropriate to require that $\mathrm{d}\Delta\bar{V}/\mathrm{d}x_A$ is also single valued at x_I and x_{II}.

4. Continuous function analyses were performed upon a variety of data sets, using the procedure of Redlich and Kister [6]. From these analyses it was possible to generate functions of the type $\mathrm{d}\Delta\bar{V}/\mathrm{d}x_A$. Plots of $\mathrm{d}\Delta\bar{V}/\mathrm{d}x_A$ against x_A tend to support the general proposition of tripartite segmentation. Furthermore, in the middle segment, $\mathrm{d}\Delta\bar{V}/\mathrm{d}x_A$ appears to vary in an approximately linear fashion with x_A. This suggests that, in the middle segment $\Delta\bar{V}$ might be adequately represented by a quadratic function of x_A. This, in turn, suggests that the parameter C(h) might be ignored. Thus the condition $C(\mathrm{h}) = 0$ was incorporated into the analytic model.

For the segment $x_I \le x_A \le x_{II}$

$$\Delta\bar{V}(\mathrm{h}) = B(\mathrm{h})\,x_A(1 - x_A) + \Delta\bar{V}_W^0(\mathrm{h})(1 - x_A) + \Delta\bar{V}_A^0(\mathrm{h})\,x_A \quad (6)$$

The conditions that $\Delta\bar{V}_W(\omega) = \Delta\bar{V}_W(\mathrm{h})$ and $\Delta\bar{V}_A(\omega) = \Delta\bar{V}_A(\mathrm{h})$ at $x_A = x_I$ lead to the equations

$$B(\omega) = B(\mathrm{h}) + \frac{\Delta\bar{V}_W^0(\mathrm{h})}{x_I^2} - C(\omega)\,x_I \quad (7)$$

$$\Delta\bar{V}_A^0(\omega) = \Delta\bar{V}_A^0(\mathrm{h}) - \Delta\bar{V}_W^0(\mathrm{h})\frac{(1 - x_I)^2}{x_I^2} - \frac{C(\omega)(1 - x_I)^2}{2} \quad (8)$$

Making the appropriate substitutions in eqns. (3) and (4) leads to

$$\Delta\bar{V}_{\mathrm{W}}(\omega) = B(\mathrm{h})\, x_{\mathrm{A}}^2 + \Delta\bar{V}_{\mathrm{W}}^0(\mathrm{h}) \frac{x_{\mathrm{A}}^2}{x_{\mathrm{I}}^2} + C(\omega)\, x_{\mathrm{A}}^2 (x_{\mathrm{A}} - x_{\mathrm{I}}) \tag{9}$$

$$\Delta\bar{V}_{\mathrm{A}}(\omega) = B(\mathrm{h})(1 - x_{\mathrm{A}})^2 + \Delta\bar{V}_{\mathrm{A}}^0(\mathrm{h}) + \Delta\bar{V}_{\mathrm{W}}(\mathrm{h}) \left\{ \frac{(1 - x_{\mathrm{A}})^2 - (1 - x_{\mathrm{I}})^2}{x_{\mathrm{I}}^2} \right\}$$
$$+ C(\omega) \left\{ x_{\mathrm{A}}(x_{\mathrm{I}} - x_{\mathrm{A}})(1 - x_{\mathrm{A}}) - \frac{(x_{\mathrm{I}} - x_{\mathrm{A}})^2}{2} \right\} \tag{10}$$

and thus

$$\Delta\bar{V}(\omega) = B(\mathrm{h})\, x_{\mathrm{A}}(1 - x_{\mathrm{A}}) + \Delta\bar{V}_{\mathrm{A}}^0(\mathrm{h})\, x_{\mathrm{A}}$$
$$+ \Delta V_{\mathrm{W}}^0(\mathrm{h})\, x_{\mathrm{A}} \left\{ \frac{(1 - x_{\mathrm{A}}) - (1 - x_{\mathrm{I}})^2}{x_{\mathrm{I}}^2} \right\} - \frac{C(\omega)\, x_{\mathrm{A}}(x_{\mathrm{I}} - x_{\mathrm{A}})^2}{2} \tag{11}$$

Equations which are analogous to (9)–(11) can be derived for the organic-rich segment

$$\Delta\bar{V}(\mathrm{a}) = B(\mathrm{h})\, x_{\mathrm{A}}(1 - x_{\mathrm{A}}) + \Delta\bar{V}_{\mathrm{W}}^0(\mathrm{h})(1 - x_{\mathrm{A}})$$
$$+ \Delta V_{\mathrm{A}}^0(\mathrm{h})(1 - x_{\mathrm{A}}) \left\{ \frac{(x_{\mathrm{A}} - x_{\mathrm{II}}^2)}{(1 - x_{\mathrm{II}})^2} \right\} - C(\mathrm{a}) \frac{(1 - x_{\mathrm{A}})(x_{\mathrm{A}} - x_{\mathrm{II}})^2}{2} \tag{12}$$

To define the excess molar volumes $\Delta\bar{V}$, across the entire composition range, it is necessary to specify the values of the composition junctions x_{I} and x_{II} and of the five parameters $B(\mathrm{h})$, $\Delta\bar{V}_{\mathrm{W}}^0(\mathrm{h})$, $\Delta\bar{V}_{\mathrm{A}}^0(\mathrm{h})$, $C(\omega)$ and $C(\mathrm{a})$.

It is a relatively simple matter to devise a computer program to find the optimum values of the five parameters for a specific combination of x_{I} and x_{II}.

Since $\Delta\bar{V}$ is a discontinuous function of x_{A}, it was deemed to be safest to optimise the combination of x_{I} and x_{II} values by mapping the standard deviation, $\sigma(\Delta\bar{V})$, as a function of those two variables and thereby locating the minimum value of $\sigma(\Delta\bar{V})$. The map not only provided the optimised model but furnished a basis for assessing the sensitivity of the quality of fit to the choice of x_{I} and x_{II} values.

THE DATA SETS

In this study, only the systems acetonitrile–water and dimethylsulfoxide–water were considered. For both of those systems, excess molar volumes, excess enthalpies and excess viscosities were analysed. Virtually all of the data that was used in these analyses was extracted from the literature. All of the data corresponds to a temperature of 25°C.

Excess molar volumes

Excess molar volumes for the acetonitrile–water system were derived from tabulated information in refs. 7 and 8. Those of the dimethylsulfoxide–water system were taken from refs. 7 and 9. Internal consistency checks were carried out upon both composite data sets and in both cases a few of the individual data points were rejected.

Excess molar enthalpies

The molar heats of mixing data for acetonitrile–water and dimethylsulfoxide–water were taken from refs. 10 and 11, respectively. A few additional points, for each of the data sets, were obtained by the author using a Parr 1451 solution calorimeter.

Excess viscosities

While excess molar volumes and enthalpies are unambiguously defined, the term excess viscosity is open to several different interpretations, depending upon how one chooses to define the ideal viscosity of a binary system. For the purpose of these analyses, the definition adopted was [12]

$$\Delta\eta = \eta(\text{exp}) - \eta(\text{ideal})$$

$$\ln[\eta(\text{ideal})] = (1 - x_A)\ln(\eta_W^0) + x_A \ln(\eta_A^0) \qquad (13)$$

Viscosity values for the acetonitrile–water system were taken from the tabulation of Moreau and Douhéret [3]. Attention should be drawn to the fact that these values do not constitute a primary data set but were obtained by fitting smooth curves to the original data of Mato and Hernandez [13] at several different temperatures and interpolating to give experimental values at desired mole fractions and 25°C. As a consequence, the analysis, in this instance, is of an algebraic summary of a primary data set.

The viscosity values for the dimethylsulfoxide—water system were taken from ref. 9.

RESULTS

The results of the various analyses are presented in Table 1. The quality of the curve-fitting can be judged from Figs. 1–3.

For each of the six data sets, two sets of the parameter values are given. In each case, the first set corresponds to the optimum combination of the segment junctions x_I an x_{II}. The second sets correspond to a combination of x_I and x_{II} that was judged to be consistent with all three data sets for that specific system.

TABLE I

Results of analyses

	Acetonitrile–water system						
	$\Delta\bar{V}$ (ml)		$\Delta\bar{H}$ (kcal)			$\Delta\eta$ (cP)	
x_I	0.25	0.17	0.13 [a]	0.14 [a]	0.17	0.23	0.17
x_{II}	0.67	0.66	0.54	0.625	0.66	0.71	0.66
B	−1.45	−1.61	+0.70	+0.66	+0.64	+0.12	+0.15
$\Delta\bar{V}_W^0$	−0.41	−0.37	−0.04	−0.03	−0.03	+0.15	+0.17
$\Delta\bar{V}_A^0$	+0.12	+0.16	+0.16	+0.18	−0.19	−0.20	−0.23
$C(\omega)$	+49.8	+9.0	+78.4	+73.2	+54.2	−92.8	−158.2
$C(a)$	−13.2	−10.0	−6.4	−7.0	−6.4	−58.4	−38.0
σ	0.0028	0.0033	0.0007	0.0008	0.0011	0.0052	0.0097

[a] Double minimum.

	Dimethylsulfoxide–water system					
	$\Delta\bar{V}$ (ml)		$\Delta\bar{H}$ (kcal)		$\Delta\bar{\eta}$ (cP)	
x_I	0.28	0.31	0.22	0.31	0.34	0.31
x_{II}	0.495	0.49	0.45	0.49	0.49	0.49
B	−5.97	−5.45	−2.41	−2.22	+14.9	+19.0
$\Delta\bar{V}_W^0$	+0.01	−0.10	−0.43	−0.48	+1.3	+0.5
$\Delta\bar{V}_A^0$	+1.10	+0.95	+0.39	+9.35	−4.7	−5.9
$C(\omega)$	55.8	−43.4	−9.8	−5.8	+170.3	+197.2
$C(a)$	−3.0	−3.6	−1.2	−2.4	−1.3	−4.5
σ	0.0038	0.0050	0.0059	0.0063	0.0065	0.0125

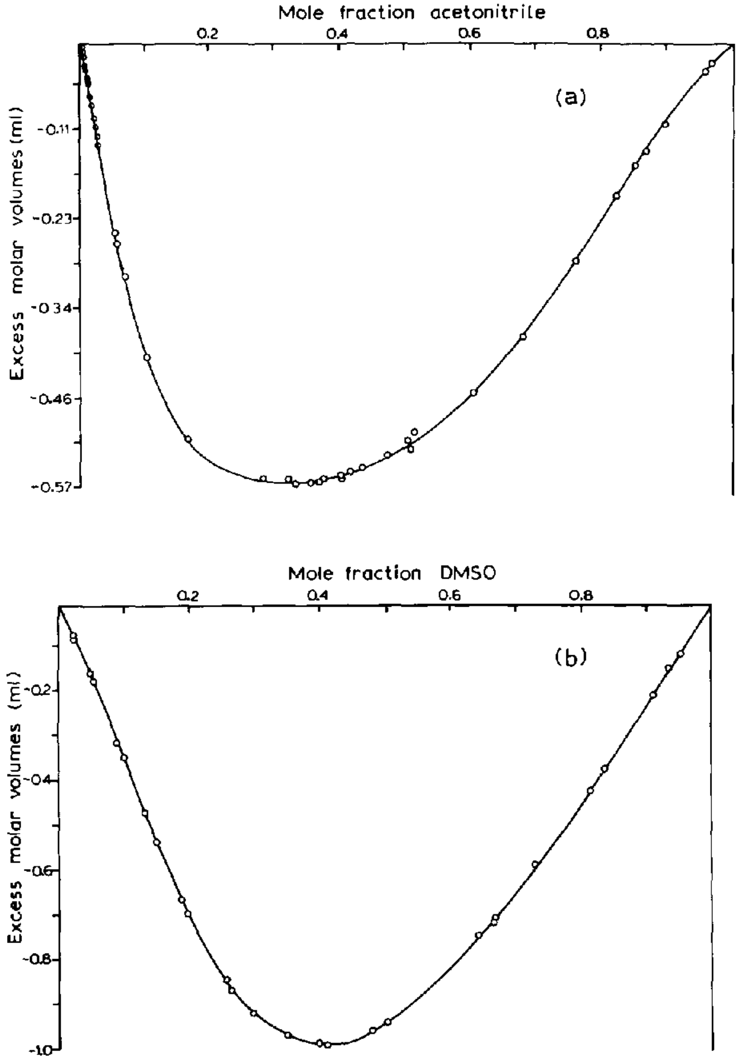

Fig. 1. Excess molar volumes. (a) Acetonitrile–water system; (b) dimethylsulfoxide–water system.

In order to estimate the sensitivity of the quality of fit to variations in the combination x_{I} and x_{II}, use was made of a test described by Hamilton [14]. This involves the calculation of the R factor ratio, which in this context is defined by

$$R(x_{\mathrm{I}}, x_{\mathrm{II}}) = \frac{\sigma(\Delta\bar{V})(x_{\mathrm{I}}, x_{\mathrm{II}})}{\sigma(\Delta\bar{V})_{\mathrm{optimum}}} \tag{14}$$

The combination x_{I}, x_{II} is rejected at the significance level α, if $R(x_{\mathrm{I}}$,

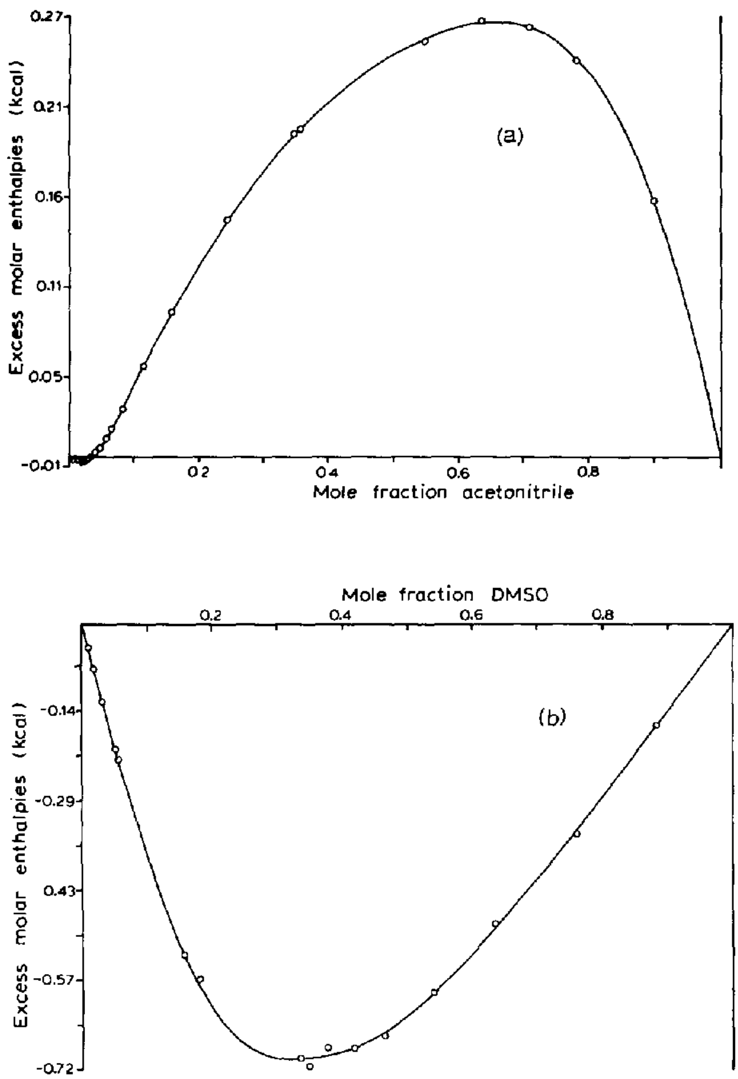

Fig. 2. Molar heats of mixing. (a) Acetonitrile–water system; (b) dimethylsulfoxide–water system.

$x_{II}) > R_{n-p,p,\alpha}$, where $R_{n-p,p,\alpha}$ is a tabulated quantity that depends upon the number of observations, n, the number of model parameters, p, and the specific significance level. For each data set, there is a range of combinations of x_I and x_{II} pairs which cannot be rejected at the 5% significance level. For a specific binary system, it is hoped that there will be a range of x_I, x_{II} pairs which cannot be dismissed at the 5% significance level for any of the data sets. This has proved to be the case for both of the systems being analysed in this work.

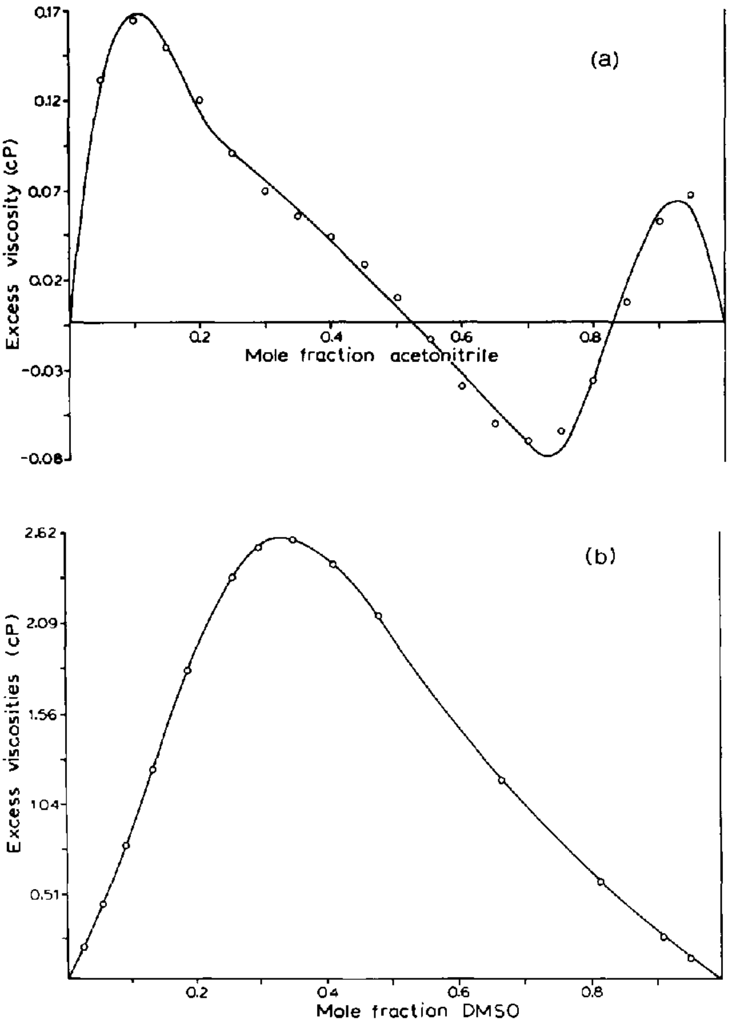

Fig. 3. Excess viscosities. (a) Acetonitrile–water system; (b), dimethylsulfoxide–water system.

DISCUSSION

There are two aspects to any analytic model. One must first address the question of whether or not the model is capable of providing acceptable facsimiles of experimental data. If one is satisfied, on that count, one may then tackle the question of whether the analytic parameters provide useful physical information.

Judging from a visual appraisal of Figs. 1–3 and the magnitudes of the estimated standard deviations, the model seems to be an adequate curve fitting tool. The quality of fit is comparable to that obtained using the more conventional Redlich–Kister procedure [6]. It seems to be fair to claim that the success of the model in its curve-fitting role constitutes a measure of support for the general concept of tripartite segmentation.

Neither the segment junctions x_I and x_{II} nor the analytic parameters are very precisely defined by any of the data sets, but there are features of the results which warrant some discussion.

In order to facilitate discussion of the individual parameter values, graphs have been constructed to show the relative magnitudes of their specific contributions to the model versions of each of the data sets (Figs. 4–6).

It has been deemed to be appropriate to associate each of the five parameters with a particular type of intermolecular interaction. $\Delta\bar{V}_W^0(h)$ and

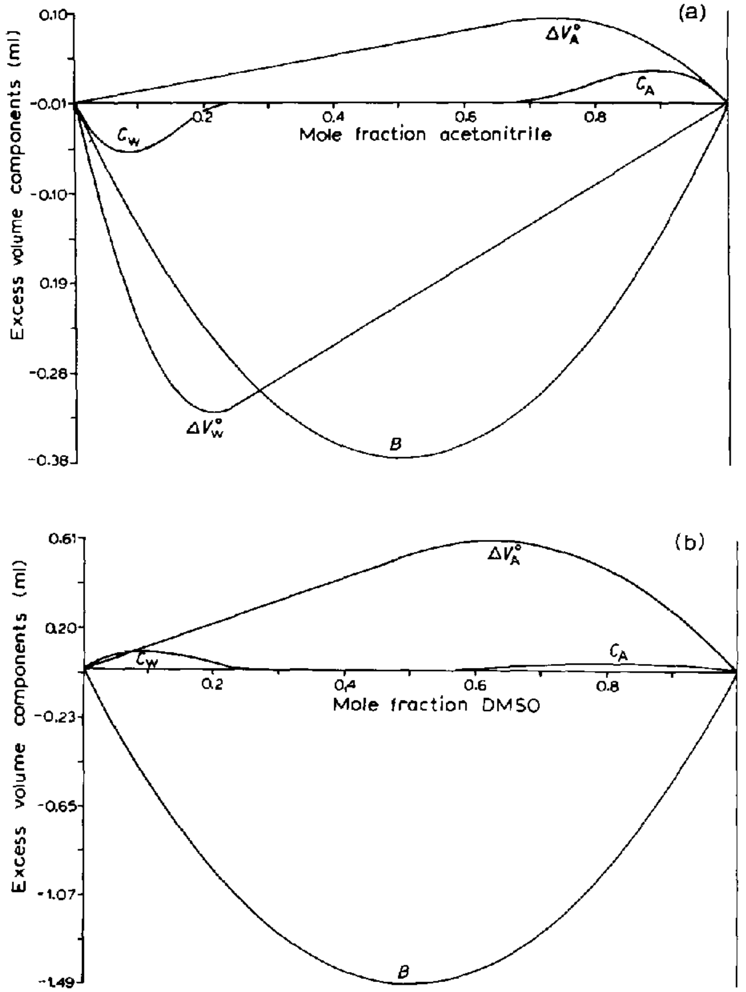

Fig. 4. Components of the excess molar volumes. (a) Acetonitrile–water system; (b) dimethylsulfoxide–water system.

$\Delta\bar{V}_A^0$(h) are taken to represent the effects of self aggregation of water and the organic component, respectively, within the heterogeneous clusters. B(h) is, in some fashion, a measure of the interactions between unlike molecules within the heterogeneous clusters. $C(\omega)$ and C(a) are taken to represent the effects of interactions between molecules in heterogeneous cluster sites, on the one hand, and those of either pure water or pure organic clusters, on the other.

$\Delta\bar{V}_A^0(h)$, $\Delta\bar{H}_A^0(h)$ *and* $\Delta\eta_A^0(h)$

For both of the systems that have been studied, there appears to be a

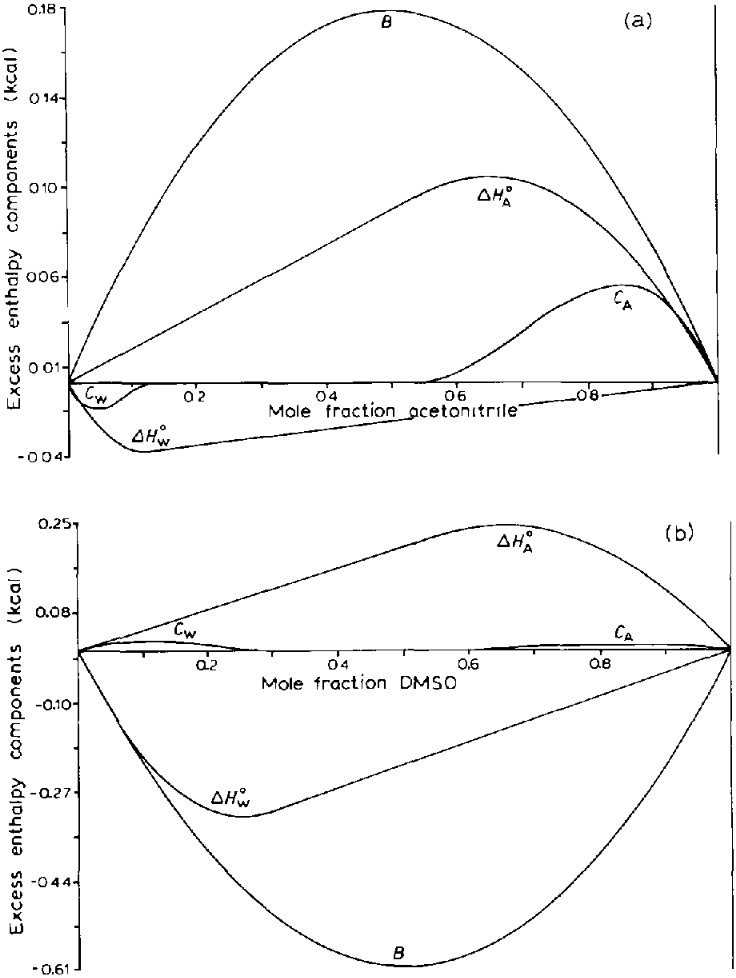

Fig. 5. Components of the excess molar enthalpies. (a) Acetonitrile–water system, (b) dimethylsulfoxide–water system.

consistent set of excess properties for the standard state of the organic component in the heterogeneous clusters.

ΔH_A^0(h) is positive, which suggests a decrease in the mutual attractions of pairs of acetonitrile or dimethylsulfoxide molecules in passing from pure liquid to heterogeneous clusters. The diminished cohesion is also indicated by lowering of the density and viscosity. Dipole–dipole attractions which might be assumed to have some influence upon the self-aggregative characteristics of the pure liquids become less important in the heterogeneous clusters.

$\Delta\overline{V}_W^0(h)$, $\Delta\overline{H}_W^0(h)$ *and* $\Delta\eta_W(h)$

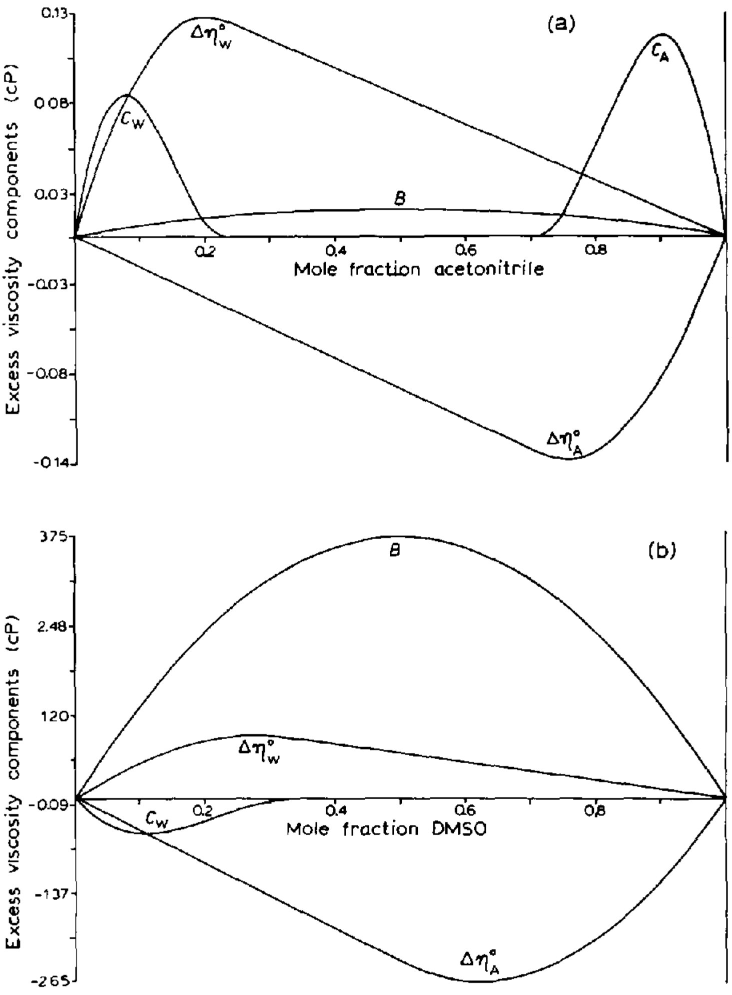

Fig. 6. Components of the excess viscosities, (a) Acetonitrile–water system; (b) dimethylsulfoxide–water system.

We should not expect that physical quantities, that are associated with the self aggregation of water molecules in mixtures or solutions, will be found to conform to any simple pattern. There is a marked difference between the sets of parameters obtained for acetonitrile–water, on the one hand, and dimethylsulfoxide–water, on the other.

In the acetonitrile–water system, there is a fairly substantial decrease in volume and a modest increase in viscosity, but essentially no enthalpy change. By contrast, the enthalpy change for the self aggregation of water in the DMSO–water system is significantly negative. The changes in volume and viscosity represent very small components of the overall changes.

$B^{\bar{V}}(h)$, $B^{\bar{H}}(h)$ *and* $B^{\eta}(h)$

The contributions to the three excess properties of the DMSO–H_2O system from the interactions between unlike molecules are significant and consistent with enhanced cohesion.

In the acetonitrile–water system, there is a fairly substantial contraction, a modest increase in viscosity and quite a large positive enthalpy change.

$C^{\bar{V}}(\omega)$, $C^{\bar{H}}(\omega)$ *and* $C^{\eta}(\omega)$

The interactions between the heterogeneous clusters and pure water clusters lead to relatively small changes in the excess properties. It seems to be this type of interaction which is responsible for the fact that the mixing of acetonitrile and water is exothermic at very low acetonitrile mole fractions, while it is endothermic at all other compositions. The effects upon the volume and viscosity are both small and in the direction consistent with increased cohesion. The corresponding excess property components for the DMSO–water system have signs that are consistent with decreased cohesion.

$C^{\bar{V}}(a)$, $C^{\bar{H}}(a)$ *and* $C^{\eta}(a)$

In the acetonitrile–water system, the interactions between the heterogeneous clusters and pure acetonitrile are slightly endothermic and lead to a modest increase in density. There is, however, a very noticeable if not large increase in viscosity.

The interactions between the heterogeneous clusters and pure dimethylsulfoxide lead to almost negligible changes in the excess properties.

Some general observations

It is suggested that the potential interactions between water and polar organic molecules result in a non-random pattern of aggregation that might be described as a form of clustering. These clusters are presumed to be labile with only very loosely defined structures and without a dominant stoichiometric formula. The molecular ratios of these clusters are assumed to vary over a wide range.

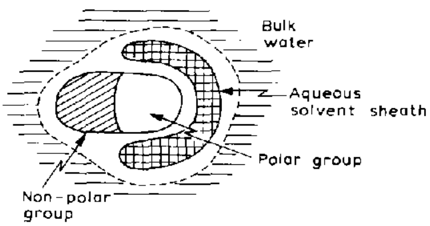

Fig. 7. Monomer cluster in bulk water.

It is assumed that, at the two extremes of molar composition, the clusters are made up of a single solute molecule together with some number of solvent molecules. It is suggested that only the polar group of the organic molecule is capable of disrupting the normal pattern of water clustering. At very low x_A, it is suggested that those water molecules in the immediate vicinity of the polar group form a solvent sheath as shown in Fig. 7. Some measure of the size of the solvent sheath is given by the expression for the partial (or apparent) excess molar volume of the solute at infinite dilution

$$\Delta\bar{V}_{A(x_A=0)} = B^V(\mathrm{h}) + \Delta\bar{V}_A^0(h) + \Delta\bar{V}_W^0(\mathrm{h})\left[\frac{2}{x_I} - 1\right] - \frac{C^V(\omega)}{2}\, x_I^2 \qquad (15)$$

At the other end of the composition range, it is suggested that individual water molecules are surrounded by solvent molecules with their polar groups pointing inwards as in Fig. 8. It is further suggested that these monomeric clusters aggregate through water–water attraction (hydrogen bonding) to form loose-knit, inverted micellular entities as depicted in Fig. 9. This model is consistent with the general pattern of decreased cohesion of the organic components in the heterogeneous segments. It is also consistent with the finding that the excess property contributions from the self aggregation of water are either negligible or suggestive of enhanced cohesion.

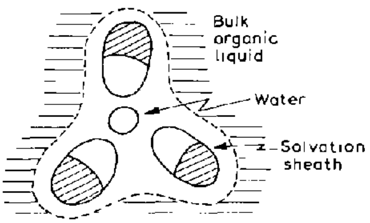

Fig. 8. Monomer cluster in bulk organic component.

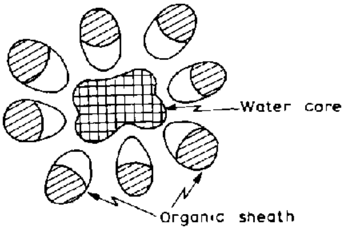

Fig. 9. Aggregated cluster.

SUMMARY

An analytic model has been devised. In addition to the basic premise that, for these binary systems at least, the concept of a tripartite segmentation of the total range of compositions is valid, the model contains a number of constraints upon the Gibbs–Duhem equation.

The model seems to be acceptable in terms of the quality of fit that it provides for the various excess property data sets that have been analysed.

The interpretations offered for the significance of the values derived for the curve-fitting parameters are obviously subject to debate as are the models suggested for the modes of cluster aggregation and indeed the concept of composition segmentation.

The model does seem to offer a promising general approach to problems of interpreting excess property data for this type of system. The extent to which that promise is fulfilled will become evident as a greater variety of both binary systems and excess physical properties are analysed.

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