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SEGMENTED COMPOSITION MODEL ANALYSES OF COMPRESSIBILITY DATA FOR SOME NON-ELECTROLYTE AQUEOUS SYSTEMS

MICHAEL I. DAVIS

Chemistry Department, University of Texas at El Paso, El Paso, TX 77968 (U.S.A.)

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ABSTRACT

Excess molar adiabatic and isothermal compressions, for the acetonitrile–water and tetrahydrofuran–water systems, have been determined from data that was taken from the literature. These properties have been analysed, using a segmented composition model, with a view to obtaining information about the nature of the patterns of molecular aggregation within the various composition regions of these two systems. The results tend to support the hypothesis of the existence of laminar microheterogeneous aggregates and are generally consistent with those of earlier analyses of volumetric and thermal data.

INTRODUCTION

The derivation and evolution of a segmented composition model, for analysing the extensive physical properties of non-electrolyte aqueous mixtures, has been described in a number of earlier articles [1–4]. In the most recent article, the results were reported for the analyses of both thermal and volumetric data for the acetonitrile (ACN)–water and tetrahydrofuran (THF)–water systems [4].

It is apparent that the equations, which make up the four-segment model, constitute an effective curve-fitting tool for the excess molar property data of those systems. It also seems to be fair to claim that the optimised parameter values furnish clues as to the nature of the patterns of molecular aggregation within the mixtures. The study of the ACN–water and THF–water systems has been extended to incorporate analyses of quantities which may be derived from the ultrasonic velocity data, that has been reported by Benson and his collaborators at the National Research Council of Canada [5,6].

It is generally accepted that ultrasonic velocities are related to the molar adiabatic (isoentropic) compressions

$$-(\partial\bar{V}/\partial p)_S = \bar{V}/(\rho u^2)^{-1} \tag{1}$$

where $\bar{V}$ is the molar volume, ρ is the density, and u is the ultrasonic velocity.

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Given values for the molar volumes, $\bar{V}$, the molar expansivities, $(\partial\bar{V}/\partial T)_P$ and the molar isobaric heat capacities, $\bar{C}_P$, one may evaluate the isochoric heat capacities, $\bar{C}_V$, and the isothermal compressions, $(\partial\bar{V}/\partial p)_T$.

$$\bar{C}_V = \bar{C}_P\left[1 + \frac{T(\partial\bar{V}/\partial T)_P^2}{\bar{C}_P(\partial\bar{V}/\partial p)_T}\right] \tag{2}$$

$$-(\partial\bar{V}/\partial p)_T = -(\partial\bar{V}/\partial p)_S + T(\partial\bar{V}/\partial T)_P^2/\bar{C}_P \tag{3}$$

One may, further, evaluate the internal pressure function, $(\partial U/\partial V)_T$, from

$$(\partial U/\partial V)_T = (\bar{C}_P - \bar{C}_V)/(\partial\bar{V}/\partial\bar{T})_P - p \tag{4}$$

where p is the prevailing atmospheric pressure.

Both $\bar{C}_V$ and $(\partial\bar{V}/\partial p)_T$ are extensive properties from which the corresponding excess molar properties of the binary mixtures are easily derived. The internal pressure function is an intensive property of the mixtures, from which one may derive an estimate of the internal work associated with the volume change, $\Delta\bar{V}$.

$$\Delta\bar{U} = (\partial U/\partial V)_T\Delta\bar{V} \tag{5}$$

This quantity $\Delta\bar{U}$ is strictly a property of the mixtures. One might regard the mixing process as consisting of two hypothetical stages. The first stage involves reorganisation of the molecules under conditions of constant volume. $\Delta\bar{U}$ is associated with the second stage in which the mixed system changes its volume.

DATA REDUCTION

Volumetric data for the ACN–water and THF–water systems were taken from refs. 7 and 8, respectively. Interpolated values of the excess molar volumes, at intervals of 0.025 in mole fraction, were obtained using a five-point local cubic fit procedure, for each of the temperatures 15, 20, 25, 30 and 35 °C. Excess molar expansions were then determined at each composition, for 25 °C, using a quadratic function of T, and thereafter converted to total molar thermal expansions.

Molar isoentropic compressions were calculated from the data of refs. 5 and 6. Values of those quantities were then obtained, by interpolation, at the 0.025 mole fraction interval. Isobaric heat capacities were taken from refs. 5 (ACN–water) and 6 (THF–water).

Isothermal compressions, isochoric heat capacities and internal pressures were calculated using eqns. (2–4).

The excess molar isochoric heat capacities, determined by this procedure, appear to be similar to those depicted graphically in refs. 5 and 6. The molar excess expansivities are generally consistent with the graphs of coefficients of thermal expansion that are given in refs. 7 and 8. It is noteworthy that the excess isoentropic and isothermal compressibility coefficients shown in refs. 5 and 6 are virtually identical. Care must be exercised in the definition of the excess molar compressibilities. It is suggested that it is preferable to avoid trying to deal with excess intensive properties, such as coefficients of expansion and compression, and that excess extensive properties are better defined and generally more meaningful.

ANALYSES

The analytical procedure is based upon the assumption that it is reasonable to treat binary systems of this type as though they possess four distinct composition segments, with boundaries at X_A (mole fraction of the organic component) $= X_I$, X_{II} and X_{III}.

The segment $X_{II} < X_A < X_{III}$ is termed microheterogeneous, in view of the contention that, in roughly equimolar mixtures, the individual component molecules tend to self-aggregate in laminar microphases. For $X_A > X_{III}$, the number of organic molecules present exceeds that which can be accommodated in the microheterogeneous aggregates, giving rise to an organic-rich segment. It is suggested that the excess organic molecules tend to self-aggregate in the mode favored by the pure liquid.

For $X_A < X_{II}$, there is an excess of water molecules. It has been found to be expedient to treat this composition range as though consisting of two separate segments. In the segment $X_I < X_A < X_{II}$, the excess water molecules are assumed to adopt a second type of microphase aggregation. This is referred to as the secondary segment. For $X_A < X_I$, termed the water-rich segment, some fraction of the water molecules are assumed to adopt pure liquid patterns of aggregation.

For these analyses, the values of the segment junction compositions were fixed. The set $X_I = 0.111$, $X_{II} = 0.333$ and $X_{III} = 0.667$ was adopted for the ACN–water system, having been found to be optimal in the work reported previously [4]. The values $X_I = 0.083$, $X_{II} = 0.333$ and $X_{III} = 0.667$ were used for the THF–water system. This value of X_I, represents a marginal curve-fitting improvement over that reported in ref. 4.

There are seven parameters in the full four-segment model. Parameters of the types B, $\Delta\bar{Q}_W^0$ and $\Delta\bar{Q}_A^0$ are descriptive of the microheterogeneous segment. $\Delta\bar{Q}_W^0$ and $\Delta\bar{Q}_A^0$ are excess molar properties of hypothetical standard states of the two components, which are referred to as the aqueous and organic microphases, respectively. B is treated as being a property of the interface between the two types of microphase. D_A only appears in the equation for the organic-rich segment and is taken to represent the effect of interactions between microheterogeneous and pure organic aggregates. $\Delta\bar{Q}_S^0$

is an excess molar property of the secondary aqueous microphase. D_S is taken to represent the effects of interactions between the secondary microphase and heterogeneous aggregates. D_W arises only in the equation for the water-rich segment. It is regarded as representing the effects of interactions between microheterogeneous and pure water aggregates.

The set of four analytical equations is set out in Appendix A.

RESULTS AND DISCUSSION

The results of the analyses are given in Tables 1 and 2. For the sake of convenience, results of analyses reported in ref. 4 have also been included.

The microheterogeneous segment

The results indicate that, in both systems, microphase water has a higher expansivity and a lower compressibility than the pure liquid. The effects are more pronounced in the THF–water system than in the ACN–water system. The molar heat capacities of microphase water in the ACN–water system are virtually the same as those of the pure liquid, while those for THF–water are quite significantly higher. It is noted that the internal pressure, $(\partial U/\partial V)_T = 687$ J cm^{-3}, of the microphase water in the THF–water system is substantially higher than that of the pure liquid (169 J cm^{-3}) while that of the ACN–water system is virtually the same (156 J cm^{-3}). These results, together with those given in the earlier papers, suggest that, in these systems, the water molecules tend to adopt a substantially more compact and generally lower enthalpy pattern of self-aggregation. The only system, that has been studied so far, which has failed to exhibit a significant negative

TABLE 1

Results of analyses of excess molar properties of acetonitrile–water mixtures ($T = 25\,°$C; $X_I = 0.111$; $X_{II} = 0.333$; $X_{III} = 0.667$)

	$(\partial\bar{V}/\partial T)_P$ (mm^3 K^{-1})	$-(\partial\bar{V}/\partial p)_S$ (mm^3 MPa^{-1})	$-(\partial\bar{V}/\partial p)_T$ (mm^3 MPa^{-1})	$\Delta\bar{C}_V$ (J K^{-1})	$\Delta\bar{U}$ (J)	$\Delta\bar{V}$ (cm^3)	$\Delta\bar{C}_P$ (J K^{-1})	$\Delta\bar{H}$ (J)
B	−8.43	−16.45	−19.41	23.8	−620	1.41	29.2	2760
$\Delta\bar{Q}^0_W$	2.38	−2.63	−2.12	−0.5	−199	−0.44	0.3	−140
$\Delta\bar{Q}^0_A$	3.25	−0.27	−0.02	−0.8	75	0.13	1.3	760
$\Delta\bar{Q}^0_S$	1.11	−0.58	−0.68	4.7	6	−0.12	4.1	−220
D_S	4.33	−1.18	−1.10	−5.3	−24	0.00	−0.3	70
D_W	−2.66	0.11	0.03	0.9	122	0.14	−1.0	−20
D_A	−3.92	0.42	1.08	−4.4	1	0.07	−8.1	−250
σ	0.049	0.0104	0.0236	0.102	0.265	0.0016	0.078	4.1

TABLE 2

Results of analyses of excess molar properties of tetrahydrofuran–water mixtures ($T = 25\,^\circ$C; $X_I = 0.083$; $X_{II} = 0.333$; $X_{III} = 0.667$)

	$(\partial\bar{V}/\partial T)_P$ (mm^3 K^{-1})	$-(\partial\bar{V}/\partial p)_S$ (mm^3 MPa^{-1})	$-(\partial\bar{V}/\partial p)_T$ (mm^3 MPa^{-1})	$\Delta\bar{C}_V$ (J K^{-1})	$\Delta\bar{U}$ (J)	$\Delta\bar{V}$ (cm^3)	$\Delta\bar{C}_P$ (J K^{-1})	$\Delta\bar{H}$ (J)
B	−10.50	−19.87	−21.50	2.9	−776	−2.31	2.6	−10
$\Delta\bar{Q}_W^0$	8.13	−4.60	−3.13	5.8	−332	−0.56	14.1	−1130
$\Delta\bar{Q}_A^0$	2.40	−0.08	−0.21	4.1	76	0.16	6.5	720
$\Delta\bar{Q}_S^0$	−1.38	−1.00	−1.32	7.7	108	−0.06	4.8	−420
D_S	−4.09	−2.39	−3.48	4.6	−163	−0.03	2.2	0
D_W	−3.66	1.15	1.43	−6.3	69	0.26	−7.1	420
D_A	−0.54	0.21	1.94	−10.4	13	0.02	−13.3	−50
σ	0.104	0.0129	0.0288	0.078	0.679	0.0027	0.137	7.5

excess molar volume for its aqueous microphase is the methanol–water system [9].

The organic microphases, of these two systems, are slightly less dense and of significantly higher enthalpy than the corresponding pure liquids. Their expansivities are fractionally higher than, and their compressibilities are almost identical to, those of the pure liquids. The two ACN heat capacities are virtually unchanged, but there is a fairly substantial increase in those of THF. It is suggested that, in these microphases, the organic components tend to be aligned with their respective polar groups oriented towards the aqueous mirophase, thereby sacrificing some part of the self-aggregative cohesion between pairs of polar groups.

Parameters of the general type B are regarded as being measures of the effect of the interactions, across the interface between the two microphases, upon the various physical properties of these systems. In both systems there is a significant contraction which becomes more marked with increasing temperature. It is noted that there is a significant decrease both in the isothermal and isoentropic compressions. The interface in the THF–water system has relatively little effect upon either the enthalpy or the heat capacities, while in the ACN–water system both the enthalpy and the two heat capacities show marked increases. From an analysis of the somewhat sparse vapor pressure data of Vierk [10], it is apparent that the interface introduces a large negative contribution to the excess entropy of the system.

The organic-rich segment

It is suggested that at and above $X_A = X_{III}$, the microheterogeneous molecular aggregates tend to assume some kind of inverted micellular form. Thus, in the organic-rich segment, it is envisaged that there are two types of aggregate; the microheterogeneous, and those characteristic of the pure organic component. In this context, it seems to be reasonable to regard the aggregates of the pure organic liquids as relatively small clusters with the polar groups tending to be directed towards the center and the hydrocarbon portions tending to form an outer shell. The parameters of the type D_A are thought to be indicators of the effects of the interactions between the two types of aggregates. Among the effects of these interactions must be the dispersion of the aqueous microphase. Studies of the diffusion coefficient data of Easteal [11] indicate that water molecules in the ACN–water system tend to be less mobile in the organic-rich segment than in the microheterogeneous, suggesting that the aqueous microphase resists dispersion up to quite high mole fractions of the organic component. There is a modest volume increase, associated with the interaction and enhanced compressibility. For both systems, the heat capacities are substantially diminished by the interaction. In some way the interaction between the two aggregates diminishes the natural loss of thermal stability that results from an increasing temperature.

The secondary segment

It is thought that at mole fractions of $< X_{II}$, the microheterogeneous aggregates tend to adopt a micellular form; that is to say that they have an aqueous outer layer. It is suggested that additional water molecules then form a second outer layer. The physical characteristics of this second layer appear to be similar to those of the aqueous microphase, but the magnitudes of their deviations from the properties of the pure liquid are generally smaller.

The water-rich segment

The parameters of the type D_W are assumed to represent the effects of the interactions between microheterogeneous aggregates (with the secondary layer) and aggregates of pure water. The effects are, in general, of the opposite sign to those of aqueous microphase formation. The interactions appear to increase the molar volumes and the compressivity, while they diminish the expansivity and the heat capacities.

CONCLUSIONS

Ultrasonic velocity data, when combined with isobaric heat capacities and volumetric data, widen the range of thermodynamic properties that can be studied for these non-electrolyte aqueous systems.

While it cannot be claimed that this additional information has provided any dramatically new evidence concerning the patterns of molecular aggregation which exist within these systems, it does appear to support the ideas that have been proposed in preceding articles [4].

The concept of the formation of microheterogeneous aggregates, proposed by Naberukhin and Rogov [12] for roughly equimolar mixtures, seems to provide a reasonable explanation for the accumulated data. Both ACN and THF appear to induce the water molecules to adopt a pattern of self-aggregation which is markedly different from that of pure water. The quantitative effects of mixing with THF are consistently greater than with ACN. This aqueous microphase is considerably more compact than pure water and significantly less compressible. On the other hand, it has a much higher thermal expansivity. It is suggested that the exceptionally low expansivity of pure water can be explained in terms of the temperature increase leading to a shift from ice-like to more compact polyhedral patterns of aggregation [13]. If, as proposed, the aqueous microphase in these mixtures is relatively devoid of ice-like aggregation, a more normal level of expansivity could be expected. The aqueous microphase in the THF–water system has a significantly lower enthalpy and higher heat capacities than does pure water. The same trends, but of far lesser magnitude, are found for the ACN–water system. These trends are assumed to reflect higher hydrogen-bonding efficiency in the microphase. In the THF–water system, there is a substantial difference between the isobaric and isochoric heat capacities, which is usually the case for liquids but is not so for pure water.

The excess properties of the organic microphases of the two systems are quite similar, with the exception of the heat capacities. The increases in the molar volumes, expansivities and enthalpies suggest a weaker pattern of self-aggregation, which would presumably entail a partial destruction of the dipolar attractions of the pure liquids.

The volumetric effects of the interactions across the interface between the two microphases are qualitatively similar in the two systems; the effects being more marked in THF–water than in ACN–water. In ACN–water, formation of the interface involves a substantial enthalpy and heat capacity increase. It is suggested that the attractions between water and ACN molecules are barely strong enough to avoid a complete phase separation and that the high heat capacities reflect a low entropy interface.

While a moderately coherent pattern of behavior seems to be emerging for the microheterogeneous segment, where both the conceptual and algebraic aspects of the model are quite simple, the other three segments are far more difficult to characterize. It is suggested that microheterogeneous aggregates tend to be formed across the entire composition range.

There was no aspect of these analyses which indicated the need for incorporating extra segments into the model. The separation of the composition range $0 < X_A < X_{II}$ into two distinct segments appears to be a necessary feature of the model.

APPENDIX: FOUR-SEGMENT MODEL EQUATIONS

These equations are reproduced from ref. 4 for the reader's convenience. $\overline{Q}$ represents some excess molar property of the binary system at a composition X_A (mole fraction of the organic component).

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

$$\begin{aligned}\Delta\overline{Q} = {} & BX_A(1-X_A) + \Delta\overline{Q}_A^0 X_A + \Delta\overline{Q}_W^0\left[(1-X_A) - (X_{II}-X_A)^3/X_{II}^3\right] \\ & + \Delta\overline{Q}_S^0\left[(X_{II}-X_A)^3/X_{II}^3 - (X_I-X_A)^3/X_I^3\right] \\ & + D_S X_A (X_{II}-X_A)^2/X_{II}^3 + D_W X_A (X_I-X_A)^2/X_I^3 \qquad \text{(A1)}\end{aligned}$$

The secondary segment: $X_I < X_A < X_{II}$

$$\begin{aligned}\Delta\overline{Q} = {} & BX_A(1-X_A) + \Delta\overline{Q}_A^0 X_A + \Delta\overline{Q}_W^0\left[(1-X_A) - (X_{II}-X_A)^3/X_{II}^3\right] \\ & + \Delta\overline{Q}_S^0 (X_{II}-X_A)^3/X_{II}^3 + D_S X_A (X_{II}-X_A)^2/X_{II}^3 \qquad \text{(A2)}\end{aligned}$$

The microheterogeneous segment: $X_{II} < X_A < X_{III}$

$$\Delta\overline{Q} = BX_A(1-X_A) + \Delta\overline{Q}_A^0 X_A + \Delta\overline{Q}_W^0 (1-X_A) \qquad \text{(A3)}$$

The organic-rich segment: $X_{III} < X_A < 1$

$$\begin{aligned}\Delta\overline{Q} = {} & BX_A(1-X_A) + \Delta\overline{Q}_A^0\left[X_A - (X_A-X_{III})^3/(1-X_{III})^3\right] \\ & + \Delta\overline{Q}_W^0 (1-X_A) + D_A(1-X_A)(X_A-X_{III})^2/(1-X_{III})^3 \qquad \text{(A4)}\end{aligned}$$

where:

$\Delta\overline{Q}_W^0$	is the excess molar property of the principal aqueous microphase
$\Delta\overline{Q}_A^0$	is the excess molar property of the organic microphase
B	is a property of the interface between the two principal microphases
$\Delta\overline{Q}_S^0$	is the excess molar property of the secondary aqueous microphase
D_A	is a property of the interaction between microheterogeneous and organic aggregates
D_S	is a property of the interaction between microheterogeneous aggregates and the secondary microphase
D_W	is a property of the interaction between microheterogeneous and pure water aggregates

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