Thermochimica Acta, 90 (1985) 313–329
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

FOUR-SEGMENT COMPOSITION MODEL ANALYSES OF BINARY ALKANOL–WATER SYSTEMS

MICHAEL I. DAVIS

Department of Chemistry, University of Texas at El Paso, El Paso, TX 79968 (U.S.A.)

(Received 13 March 1985)

ABSTRACT

Excess molar thermodynamic properties of the five completely miscible alkanol–water systems have been analyzed using the four-segment composition model. The results of these analyses have been interpreted in terms of significant aqueous structural enhancement at alkanol mole fractions (X_A) > 0.1 and of a laminar microheterogeneous pattern of molecular aggregation in the composition segment $1/3 < X_A < 2/3$.

INTRODUCTION

Interest in the physical properties of binary alkanol–water mixtures, and their composition dependence, can be traced back to the late nineteenth century. An appreciation of the breadth of that interest may be gleaned from the review by Franks and Ives [1]. Much of the research that has been carried out during the past thirty years has been directed towards the establishment of plausible models for the structural and dynamic characteristics of the patterns of molecular aggregation, which exist within such mixtures, and the nature of their sensitivities to changes in molar composition.

The four-segment composition model was devised for the purpose of analyzing and interpreting excess molar property data of binary hydro-organic systems. Its evolution and the derivation of its model equations have been described in earlier articles [2,3]. Applications have been reported for various excess thermodynamic properties of the acetonitrile (ACN)–water and tetrahydrofuran (THF)–water systems [3,4].

The underlying assumption of the four-segment model is that binary hydro-organic systems may be treated as though their total composition ranges contain four discrete segments, in each of which the molar properties exhibit no greater than cubic dependence upon mole fraction. The results of the analyses that were carried out on the ACN–water and THF–water data demonstrated that the four model equations of the Appendix constitute an effective curve-fitting tool. Furthermore, supporting evidence was furnished for the contention that each of the seven model parameters may be associ-

0040-6031/85/$03.30

ated with some aspect of the varying patterns of molecular aggregation, that exist within the hydro-organic mixtures, and that the signs and magnitudes of their values serve as clues in the deductive formulation of structural models.

It was a logical extension of the earlier work to implement the four-segment model as an analytical tool for the thermodynamic data that has been accumulated for the five totally miscible alkanol–water systems. Of particular interest was the extent to which the results of such analyses might appear to support some of the ideas which have been promoted in the recent literature.

SOURCES OF DATA

All of the data sets that were employed in this work were taken from the literature. Every effort was made to find the best available data but it is possible that some more suitable sources were inadvertantly overlooked.

Excess molar volumes for the systems methanol (MeOH)–water, ethanol (EtOH)–water and 1-propanol (1-PrOH)–water were taken from ref. 5. For each system, values are reported at 15, 20, 25, 30 and 35°C. Interpolated values of $\Delta\bar{V}$, at each temperature and at an interval of $\Delta X = 0.025$, were obtained using a cubic splines procedure, which introduces a modest level of smoothing. Excess molar expansivities, $\Delta(\partial\bar{V}/\partial T)_{\mathrm{p}}$, at 25°C, were calculated on the assumption that $\Delta\bar{V}$ has a quadratic temperature dependence. The same computation also furnished temperature-smoothed estimates of $\Delta\bar{V}$ at 25°C.

For the same three systems, excess molar isobaric heat capacities and isoentropic compressibilities, at 25°C, were taken from refs. 6 and 7, respectively. Combining the data of refs. 5–7 led to values of the excess molar isothermal compressivities, $\Delta(-\partial\bar{V}/\partial p)_{\mathrm{T}}$, using the relationship given in eqn. (1), which is based upon theoretical arguments that are presented in ref. 8.

$$-(\partial\bar{V}/\partial p)_{\mathrm{T}} = -(\partial\bar{V}/\partial p)_{\mathrm{S}} + TC_{\mathrm{p}}^{-1}(\partial\bar{V}/\partial T)^{2} \tag{1}$$

The excess molar enthalpy (heat of mixing) data used for MeOH–water were a combination of the values given in refs. 9 and 10; those for EtOH–water were taken from ref. 11 and for 1-PrOH–water from refs. 12 and 13. The data of ref. 12 were temperature interpolated to give values at 25°C; those of ref. 13 were corrected from 30 to 25°C using the heat capacity data of ref. 6.

In order to obtain an adequate number of data points for $X_{\mathrm{A}} > 0.3$, excess molar volumes of the 2-PrOH–water system were taken from four different sources [14–17]. Excess molar expansivities were calculated from the data of ref. 17. The excess molar enthalpies were taken from ref. 10. To supplement the excess isobaric heat capacity data of ref. 14 at higher X_A values, several points were taken from a graphical presentation of the unpublished data of Grolier et al. [18]. Such compressibility data as could be located proved to be too sparse in the composition range $X_A > 0.3$ to warrant the use of the four-segment model.

Excess molar volumes, expansivities and isobaric heat capacities for the *t*-BuOH–water system were taken from ref. 19. Excess molar enthalpies were taken from ref. 20. No suitable compressibility data could be located. *t*-BuOH melts at 25.5°C. The authors of ref. 19 report properties of the supercooled liquid at 25°C. The sample used in ref. 20 was reported to melt in the range 24–25°C, and possess 99.7% purity.

THE ANALYSES

It has been pointed out in a recent article that there are a number of ways in which the results of a four-segment model analysis might be perverted by a combination of flaws in the data and weaknesses in the model [21]. As a consequence, the standard deviations for the model parameters, as estimated from conventional error analyses, are likely to be unduly flattering. More reliable estimates of the confidence limits for the parameters are obtained from a consideration of their respective spreads when their values are estimated using a variety of different strategies. Where possible, all of the different strategies which are described in ref. 21 were employed in the analyses of each of the data sets.

It is appropriate that the same combination of X_A values for the three segment junctions (X_I, X_{II} and X_{III}) should be used for all of the data sets for a specific system. Accordingly, preliminary analyses were carried out to find the most appropriate combination for each system. Since the quality of fit tends to be only modestly sensitive to changes in the segment junction values, the choices were limited to simple fractions.

The combination of $X_{II} = 0.333$ and $X_{III} = 0.667$, which had been found to be optimal for both the ACN–water and THF–water systems [2,3], was also found to be suitable for all five of the alkanol–water systems.

Optimal values of X_I were found to differ from one system to another. The values adopted were 0.125 for both MeOH–water and EtOH–water, 0.111 for 2-PrOH–water and 0.083 for 1-PrOH–water and *t*-BuOH–water.

RESULTS AND DISCUSSION

For each of the data curves, the four-segment model equations were capable of providing a smooth replica which passed through the points in a

TABLE 1

Standard deviations, $\sigma(\Delta\bar{Q})$, for four-segment model curve-fitting of excess molar property data of alkanol–water systems

	$\Delta\bar{V}$ (mm^3)	$\Delta(\partial\bar{V}/\partial T)_p$ ($mm^3\ K^{-1}$)	$-\Delta(\partial\bar{V}/\partial p)_T$ ($mm^3\ MPa^{-1}$)	$\Delta\bar{H}$ (J)	$\Delta\bar{C}_p$ ($J\ K^{-1}$)
MeOH	0.91	0.016	0.013	9.6	0.045
EtOH	1.30	0.033	0.026	3.6	0.088
1-PrOH	1.92	0.090	0.026	8.8	0.081
2-PrOH	6.40	0.331	–	3.2	0.141
t-BuOH	6.81	0.862	–	9.8	0.213

satisfactory manner. The standard deviations, $\sigma(\Delta\bar{Q})$, for each data set are shown in Table 1.

The nature of the four-segment model is such that it is appropriate to present and discuss the results obtained for each individual segment separately. Since the three parameters which characterize the microheterogeneous segment, $X_{II} < X_A < X_{III}$, tend to dominate the overall data profiles and appear in all four of the model equations, they are dealt with first.

The microheterogeneous segment

The term "microheterogeneous", as applied to roughly equimolar mixtures of water and polar organic liquids, appears to have originated with Naberukhin and Rogov [22], who suggested that a two-layered pattern of aggregation exists. It was their contention that the two microphases consist of aggregates containing different stoichiometric ratios of the two components.

Other authors have subscribed to the view that equimolar mixtures contain two microphases, but have different suggestions to offer as to their respective compositions. Larkin expressed the opinion that in the EtOH–water system one of the microphases is purely aqueous while the other contains a random mixture of the two components [23]. Desnoyers has suggested that the organic molecules might tend to adopt a more structured scheme of aggregation, some type of labile micellular analog, which might be thought to constitute a predominantly organic microphase [14,24].

Parameters of the type $\Delta\bar{Q}_w^0$

The parameter $\Delta\bar{Q}_w^0$ appears in the derivation of the segmented composition model equations [2] in a manner which identifies it to be an excess molar property of a hypothetical standard state of water that pertains to mixtures with compositions that fall within the range of the microheterogeneous segment. As such, its values may be considered to be measures of the effects that arise from the differences between the patterns of aqueous self

TABLE 2

Values of parameters of the type $\Delta\bar{Q}_w^0$ for alkanol–water systems (estimated confidence limits in parentheses)

	$\Delta\bar{V}$ (cm^3)	$\Delta(\partial\bar{V}/\partial T)_p$ ($mm^3\ K^{-1}$)	$-\Delta(\partial\bar{V}/\partial p)_T$ ($mm^3\ MPa^{-1}$)	$\Delta\bar{H}$ (kJ)	$\Delta\bar{C}_p$ ($J\ K^{-1}$)
MeOH	−0.01	0.0	0.1	−0.87	8.7
	(0.01)	(0.2)	(0.2)	(0.07)	(0.3)
EtOH	−0.56	4.5	−3.5	−1.03	16.0
	(0.02)	(0.3)	(0.2)	(0.03)	(0.5)
1-PrOH	−0.41	3.2	−2.8	−0.72	11.5
	(0.02)	(0.6)	(0.3)	(0.03)	(0.7)
2-PrOH	−0.57	10.0	–	−1.15	19.1
	(0.20)	(4.4)		(0.05)	(0.8)
t-BuOH	−0.73	9.8	–	−1.21	18.6
	(0.05)	(2.2)		(0.15)	(0.5)

aggregation in the mixtures and those of the pure liquid. The values that were obtained for these parameters are given in Table 2.

That all five values of the parameter $\Delta\bar{H}_w^0$ are quite large and negative is considered to be indicative of the existence of metastable aqueous aggregates, in the roughly equimolar mixtures, and thus supportive of the concept of an aqueous microphase or pseudophase. While the thermal characteristics of the aqueous microphases of the five systems appear to be fairly similar, there is a striking difference between the volumetric characteristics in the MeOH–water system from those in the other four.

The volumetric properties of pure liquid water set it apart from all other liquids. In recent years, a plausible rationale for the structural and dynamic character of water has emerged from the results of both molecular dynamics and Monte Carlo computer simulations [25,26]. The picture is one of a vast macromolecular network of hydrogen bonds in which, at any given time, virtually all of the molecules participate. Individual molecules may be located in any one of a wide variety of local structural patterns, which are in a constant state of flux. It is therefore possible to think in terms of some large number of distinguishable structural sites, each with a characteristic energy and volume. The relative populations of such sites would be expected to conform to a Boltzmann distribution.

Ice-like structural sites are generally regarded as possessing the lowest energy and the greatest volume. An increase in temperature, in addition to increasing the volumes of each type of structural site, leads to a net transfer of molecules from ice-like sites to the more compact alternatives. This constitutes a rationale for the existence of a temperature of maximum density and for the exceptionally small expansivity of water at 25°C.

An increase in pressure, in addition to decreasing the volumes of the individual structural sites, results in a net transfer of molecules from ice-like to the more compact sites. Hydrogen bonding results in water having a relatively low compressibility. However, at low temperatures, its value is thought to be enhanced by the results of the structural changes. This explains why the compressibility of water decreases up to 63°C, after which it follows the more normal pattern of increasing with increasing temperature.

That the $\Delta\bar{V}_{\mathrm{w}}^{0}$ values for the aqueous microphases, of all but the MeOH–water system, are quite large and negative suggests that there is a substantial depletion of the population of ice-like sites. Similar conclusions might be reached from the notable increases in the molar expansivities over the pure liquid value of 4.65 $\mathrm{mm^3\ K^{-1}\ mol^{-1}}$ and the decreases in the excess molar compressivity from the value of 8.18 $\mathrm{mm^3\ MPa^{-1}\ mol^{-1}}$ [27]. The volumetric properties of the aqueous microphases of the four larger alkanol–water systems are very similar to those of both the ACN–water and THF–water systems [3,4]. By contrast, the volumetric characteristics of water, in roughly equimolar mixtures of MeOH and water, appear to be indistinguishable from those of the pure liquid.

All five of the alkanol–water systems have $\Delta\bar{H}_{\mathrm{w}}^{0}$ values which are quite large and negative. One plausible explanation for this phenomenon is that the efficiency of hydrogen bonding, in the aggregates that make up the aqueous microphase, is greater than that in the pure liquid. The idea that there are enhanced attractions between water molecules in hydro-organic systems has been promoted by Hertz and co-workers on the basis of their studies of hydrodynamic properties [28,29]. It may be argued that such enhanced attractions are responsible for the pronounced viscosity maxima at $X_{\mathrm{A}} \simeq 0.2$, in alkanol–water and other hydro-organic systems [1]. Four-segment model analysis of the excess molar entropy data for EtOH–water of ref. 11 suggests that the aqueous microphase is of significantly lower entropy than is the pure liquid.

The $\Delta\bar{C}_{\mathrm{pw}}^{0}$ values for all of the alkanol–water systems are quite large and positive. Evidently, such structural enhancement as exists in the aqueous microphases of those systems is relatively fragile, in the sense that it tends to dissipate fairly rapidly with increasing temperature.

The combination of values obtained for the parameters of the type $\Delta\bar{Q}_{\mathrm{w}}^{0}$ give an internally consistent impression that, in roughly equimolar alkanol–water mixtures, metastable aqueous aggregates are formed. In the MeOH–water system, these aggregates would appear to retain the geometric characteristics of those of the pure liquid, while there is extensive structural modification in the other four systems.

It is interesting to note that the $|\Delta\bar{Q}_{\mathrm{w}}^{0}|$ values for 1-PrOH–water are consistently smaller than those of EtOH–water, while those for both 2-PrOH–water and *t*-BuOH–water are all larger.

Parameters of the type $\Delta\bar{Q}_{A}^{0}$

Values of parameters of the type $\Delta\bar{Q}_{\mathrm{A}}^{0}$ are regarded as being measures of the effects of differences between the patterns of alkanol self aggregation in

TABLE 3

Parameters of the type $\Delta\overline{Q}_{\mathrm{A}}^{0}$ for alkanol–water systems

	$\Delta\overline{V}$ (cm^3)	$\Delta(\partial\overline{V}/\partial T)_{\mathrm{p}}$ (mm^3 K^{-1})	$-\Delta(\partial\overline{V}/\partial p)_{\mathrm{T}}$ (mm^3 MPa^{-1})	$\Delta\overline{H}$ (kJ)	$\Delta\overline{C}_{\mathrm{p}}$ (J K^{-})
MeOH	0.04	−3.5	−2.7	−0.18	−0.1
	(0.01)	(0.2)	(0.4)	(0.07)	(0.3)
EtOH	−0.09	0.5	−2.4	−0.18	2.4
	(0.02)	(0.2)	(0.2)	(0.03)	(0.7)
1-PrOH	−0.10	2.9	−0.6	0.01	2.4
	(0.03)	(0.2)	(0.2)	(0.05)	(0.8)
2-PrOH	0.08	9.6	–	0.21	5.1
	(0.10)	(3.0)		(0.03)	(1.3)
t-BuOH	0.28	10.4	–	0.47	−3.0
	(0.11)	(2.0)		(0.14)	(2.0)

roughly equimolar mixtures and in the respective pure liquids. In the case of *t*-BuOH, one is actually dealing with a supercooled liquid.

Such structural character as exists in the pure alkanols is attributed to hydrogen bonding between pairs of hydroxyl groups. Since each alkanol molecule possesses only one oxygen-bound hydrogen atom, aggregation is limited to the formation of chains and rings. Since each oxygen has two lone pairs of electrons, the possibility exists for the alkanol molecules to form hydrogen bonds to water without sacrificing those to their own kind. This is a somewhat different situation to that which exists in mixtures of water with aprotic polar organic liquids. For both ACN–water and THF–water, the rather large and positive values of $\Delta\overline{H}_{\mathrm{A}}^{0}$ were taken to indicate that there is a significant reduction of organic dipole–dipole attraction, brought about by polar group contact with water [3].

Values obtained for parameters of the type $\Delta\overline{Q}_{\mathrm{A}}^{0}$ are given in Table 3.

The $\Delta\overline{H}_{\mathrm{A}}^{0}$ values are all significantly lower than those for both ACN–water (0.79 kJ mol^{-1}) and THF–water (0.76 kJ mol^{-1}) [3]. The values for MeOH–water and EtOH–water might be interpreted as being indicative of enhanced alkanol–alkanol hydrogen bonding. In the same vein, there is no measureable effect in the 1-PrOH–water system, but an apparent reduction in the inter-alkanol hydrogen bonding efficiencies in both 2-PrOH–water and *t*-BuOH–water.

For the sequence EtOH–water, 2-PrOH–water and *t*-BuOH–water, both the $\Delta\overline{V}_{\mathrm{A}}^{0}$ and $\Delta\overline{H}_{\mathrm{A}}^{0}$ values show fairly substantial increases, while there are no such obvious trends for the sequence MeOH–water, EtOH–water and 1-PrOH–water. Of interest, but not readily explained, is the distinction between the respective $\Delta\overline{C}_{\mathrm{pA}}^{0}$ values of the 2-PrOH–water and *t*-BuOH–water systems. The *t*-BuOH–water result may be associated with the difficulties inherent in assigning a value to the molar heat capacity of the pure supercooled liquid.

It seems to be reasonable to assume that, in equimolar mixtures of alkanols and water, the alkanol molecules would tend to exhibit a preference for those orientations which result in their hydroxyl groups being in contact with the metastable aqueous aggregates.

When trying to envisage the patterns of molecular aggregation which might exist in monophase hydro-organic systems, it seems to be appropriate to look for analogs of such stable patterns as have been identified in surfactant–water systems and microemulsions. Thus, at modest alkanol mole fractions, one might consider the existence of labile aggregates of a micellular nature; and at modest water mole fractions labile analogs of inverse micelles. In certain surfactant–water systems, there exists, at compositions which lie between micellular and inverse micellular regions, a lamellar phase lyotropic liquid crystal region [30]. In an earlier paper, a labile analog of that aggregative scheme was proposed for the microheterogeneous segment of the ACN–water system [31]. The organic microphase is envisioned as bearing a structural resemblance to a phospholipid bilayer. The aqueous microphase is not thought to be more than one or two molecular layers in thickness. It is suggested that this constitutes a reasonable approach to discussing molecular aggregation in the alkanol–water systems, with the exception of MeOH–water.

Parameters of the type B

The hypothesis that, in roughly equimolar alkanol–water mixtures, a crude and labile pattern of laminar aqueous and organic microphases exists, implies the existence of some kind of alkanol–water interface. Since the parameters $\Delta\overline{Q}_{\mathrm{w}}^{0}$ and $\Delta\overline{Q}_{\mathrm{A}}^{0}$ have been assigned to represent the effects of self aggregation of water and the alkanol, respectively, the parameters of type B are left to account for the direct effects of the interactions between the two types of molecules.

The values that were obtained for the parameters of type B are given in Table 4.

There are several striking features to these results. It is only in the case of MeOH–water that $B(\Delta\overline{H})$ is negative. Here, seemingly, the alkanol–water hydrogen bonding is especially efficient. While it is evident that there is no enthalpic advantage to forming the alkanol–water interface, the positive values of $B(\Delta\overline{H})$ for the other four alkanol–water systems are not necessarily so large as to discount the existence of fairly strong attractions. Extrapolation of the $B(\Delta\overline{H})$ values for the *n*-alkanol–water systems beyond 1-PrOH leads to values which might be regarded as being too high to be compatible with miscibility. That is to say that, while there is no requirement that the formation of the interface has to be exothermic, there is a point at which the natural entropic advantage of mixing is outweighed.

TABLE 4

Parameters of the type B for alkanol–water systems

	$\Delta\bar{V}$ (cm^3)	$\Delta(\partial\bar{V}/\partial T)_p$ (mm^3 K^{-1})	$-\Delta(\partial\bar{V}/\partial p)_T$ (mm^3 MPa^{-1})	$\Delta\bar{H}$ (kJ)	$\Delta\bar{C}_p$ (J K^{-1})
MeOH	−4.08	1.0	−39.0	−1.06	1.0
	(0.03)	(0.5)	(1.0)	(0.25)	(1.0)
EtOH	−2.99	2.1	−27.7	0.78	3.8
	(0.06)	(1.0)	(1.0)	(0.05)	(1.5)
1-PrOH	−1.56	6.0	−16.8	2.03	21.8
	(0.10)	(3.0)	(1.0)	(0.16)	(3.0)
2-PrOH	−2.87	−25.8	–	1.99	−3.7
	(0.90)	(15.0)		(0.10)	(3.0)
t-BuOH	−2.41	−44.5	–	1.68	−15.3
	(0.35)	(16.0)		(0.20)	(2.0)

All of the $B(\Delta\bar{V})$ values are significant and negative. That appears to be true of all hydro-organic systems. There is obviously a packing consideration here which leads to combinations of negative $B(\Delta\bar{V})$ and positive $B(\Delta\bar{H})$ values. At the same time, there is a rough correlation between the two sets of values.

One intriguing aspect of these results is the switch in signs of both $B[\Delta(\partial\bar{V}/\partial T]_p]$ and $B(\Delta\bar{C}_p)$ on going from the *n*-alkanol to the branched alkanol–water systems. There is no obvious explanation for this phenomenon. It is clearly a feature of the data profiles that more ambitious models of structural aggregation might be required to rationalize.

Parameters of the type D_A

The microheterogeneous segment spans the composition range $1/3 < X_A < 2/3$. It is suggested that as X_A is increased across that range the molecular aggregates vary in nature from crudely micellular to an inverse micellular form. Whatever the geometric details of the scheme of aggregation, it would seem that, when $X_A > 2/3$, it cannot accomodate all of the organic molecules. The excess might then be assumed to tend to aggregate in the manner which is characteristic of the pure alkanol.

Parameters of the type D_A are regarded as being crude measures of the effects of the interactions between labile inverse micellular aggregates and clusters of the pure alkanol. Such effects would include exchange of alkanol molecules between the two types of aggregate and the dispersion of the aqueous clusters that form the cores of the inverse micellular analogs.

The values that were obtained for parameters of the type D_A are given in Table 5.

In general, these parameter values indicate relatively small effects. For the 2-PrOH–water and *t*-BuOH–water systems, the data in the alkanol-rich

TABLE 5

Parameters of the type D_A for alkanol–water systems

	$\Delta\bar{V}$ (cm^3)	$\Delta(\partial\bar{V}/\partial T)_p$ (mm^3 K^{-1})	$-\Delta(\partial\bar{V}/\partial p)_T$ (mm^3 MPa^{-1})	$\Delta\bar{H}$ (kJ)	$\Delta\bar{C}_p$ (J K^{-1})
MeOH	−0.03	1.8	2.1	0.11	−1.3
	(0.02)	(0.2)	(0.3)	(0.06)	(0.6)
EtOH	0.02	0.2	1.4	−0.04	−2.3
	(0.02)	(0.2)	(0.3)	(0.06)	(1.0)
1-PrOH	−0.07	0.9	−0.1	−0.04	0.5
	(0.02)	(0.9)	(0.3)	(0.07)	(1.0)
2-PrOH	−0.06	−7.5	–	−0.31	−6.3
	(0.50)	(4.0)		(0.06)	(2.0)
t-BuOH	−0.22	−8.2	–	−0.20	10.8
	(0.15)	(4.0)		(0.10)	(5.0)

segment tend to be too sparse, and the uncertainties too large, to warrant any physical significance being assigned to the D_A values. Thus, it is felt that the four-segment analyses of the alkanol–water systems fail to reveal any dramatic structural changes in the alkanol-rich segment. This might be interpreted as an indication that the tendency for the water molecules to cluster is maintained up to quite high alkanol mole fractions.

Parameters of the types $\Delta\bar{Q}_s^0$ *and* D_s

The composition segment $X_I < X_A < X_{II}$ is referred to as the secondary segment.

Desnoyers has drawn attention to the fact that some alkanol–water systems exhibit patterns of composition-dependence of their physical properties, at relatively low alkanol mole fractions, which resemble those of surfactant–water systems below their critical micelle concentrations [24]. It is concluded that it is reasonable to imagine that the alkanol–water systems undergo a pseudo-phase transition at some composition which is analogous to the CMC and that the alkanols tend to cluster together to form labile micellular aggregates.

In a recent study of the excess apparent molar volumes of 1-PrOH in its aqueous mixtures, Hvidt and co-workers concluded that hydrophobic hydration (the effects upon aqueous aggregation of contact between water and hydrocarbon molecular moieties) is limited to the composition range $X_A < 0.1$ [32].

Accepting these arguments as being reasonable, it would be appropriate to regard the secondary segment as one in which the pattern of molecular aggregation is one of a labile micellular nature.

Parameters of the type $\Delta\bar{Q}_s^0$ are excess molar properties of water in a hypothetical standard state that pertains to mixtures whose compositions fall

TABLE 6

Parameters for alkanol–water systems

	$\Delta\overline{V}$ (cm^3)	$\Delta(\partial\overline{V}/\partial T)_p$ (mm^3 K^{-1})	$-\Delta(\partial\overline{V}/\partial P)_T$ (mm^3 MPa^{-1})	$\Delta\overline{H}$ (kJ)	$\Delta\overline{C}_p$ (J K^{-1})
Parameters of the type $\Delta\overline{Q}^0_s$					
MeOH	0.08	−1.6	0.3	−0.06	1.7
	(0.02)	(0.7)	(0.2)	(0.05)	(0.6)
EtOH	0.19	−7.0	−1.1	−0.12	4.9
	(0.03)	(0.7)	(0.3)	(0.05)	(1.0)
1-PrOH	−0.20	1.2	−1.8	−0.51	12.4
	(0.03)	(1.1)	(0.4)	(0.05)	(1.0)
2-PrOH	−0.29	−5.7	–	−0.73	18.4
	(0.10)	(5.0)		(0.05)	(2.0)
t-BuOH	−0.42	3.2	–	−0.76	21.2
	(0.10)	(3.5)		(0.10)	(4.0)
Parameters of the type D_s					
MeOH	0.19	−4.1	−0.6	0.18	−0.5
	(0.05)	(2.0)	(0.5)	(0.10)	(1.5)
EtOH	−0.04	3.7	−1.6	−0.80	10.9
	(0.06)	(2.0)	(1.0)	(0.16)	(2.5)
1-PrOH	−0.12	6.6	−1.4	0.13	4.5
	(0.09)	(5.0)	(1.3)	(0.13)	(2.0)
2-PrOH	0.10	12.5	–	0.08	−0.4
	(0.15)	(5.0)		(0.14)	(5.0)
t-BuOH	0.31	−11.5	–	0.20	−2.7
	(0.20)	(15.0)		(0.25)	(10.0)

within the secondary segment. One possible rationale for the differences between the parameters $\Delta\overline{Q}^0_w$ and $\Delta\overline{Q}^0_s$ is that, whereas in the microheterogeneous segment all of the water molecules are envisaged as being interfacial (in contact with the hydroxyl groups of the alkanol molecules), some fraction of those in the secondary segment occupy more remote interstitial sites. In this context, parameters of the type $\Delta\overline{Q}^0_s$ would be characteristic of the effects of self aggregation of the water molecules that occupy interstitial sites. In that case, parameters of the type D_s might be regarded as crude measures of the effects of expanding the aqueous microphase as the alkanol mole fraction falls from X_{II} to X_I.

The values that were obtained for the parameters of the types $\Delta\overline{Q}^0_s$ and D_s are given in Table 6.

The two parameters are quite strongly correlated. As a consequence, it is wiser to consider their combined effects than to try to interpret their individual contributions.

For the MeOH–water system, the contribution made by these two components to $\Delta\overline{H}$ is insignificant, while there is a modest positive contribution to $\Delta\overline{V}$. For the other four systems, $\Delta\overline{H}^0_s$ and $D_s(\Delta\overline{H})$ combine to give quite substantially negative contributions. For these systems, it would appear that the interstitial water, like the interfacial water of the microheterogeneous segment, possesses enhanced hydrogen-bonding efficiency. There is a modest positive contribution to $\Delta\bar{V}$ in the EtOH–water system, but negative contributions for 1-PrOH–water, 2-PrOH–water and *t*-BuOH–water.

For all five systems, there are positive contributions to $\Delta\bar{C}_p$. There is no obvious pattern to the combined contributions of the two types of parameters to $\Delta(\partial\bar{V}/\partial T)_p$.

The results of the four-segment analyses, of all but the MeOH–water system, seem to be consistent with the existence, within the secondary segment, of micelle-like aggregates of the alkanol molecules within the confines of a continuous metastable aqueous microphase.

Parameters of the type D_w

As the mole fraction of the alkanol decreases, from the segment junction value of X_I, several structural changes might be anticipated. The physical significance of the segment junction at $X_A = X_I$ might be described in two somewhat different ways. It may be that this represents the greatest proportion of water molecules that can be accommodated in the aqueous microphase that envelopes the pseudo-micellular aggregates and that additional water molecules will tend to form aggregates more like those of the pure liquid. This would imply that the micelle-like aggregates persist down to quite low mole fractions of alkanol.

The alternative is to regard the segment junction X_I as an analog of the critical micelle concentration and to anticipate that the addition of more water will lead to the dispersion of the micelle-like aggregates and the appearance of evidence for hydrophobic hydration. This would seem to be more in line with the ideas expressed in refs. 24 and 32.

The question arises as to whether or not the stabilization, which appears to characterize the aqueous microphase, is the result of the collaborative effects of the alkanol molecules that make up a labile micellular aggregate or arise from the interactions between water molecules and hydroxyl groups, regardless of the alkanol molecule's structural environment. Parameters of the type D_w might then be regarded as being not only measures of the effects of hydrophobic hydration but possibly of the destruction of the aqueous microphase as the water content of the mixtures is increased.

The values that were obtained for parameters of the type D_w are given in Table 7.

The D_w values for the MeOH–water system are all too small to be regarded as having any physical significance. Those for EtOH–water are by no means all trivial but indicate the existence of smaller effects than those of the three larger alkanol–water systems.

TABLE 7

Parameters of the type D_w for alkanol–water systems

	$\Delta\bar{V}$ (cm^3)	$\Delta(\partial\bar{V}/\partial T)_p$ (mm^3 K^{-1})	$-\Delta(\partial\bar{V}/\partial p)_T$ (mm^3 KPa^{-1})	$\Delta\bar{H}$ (kJ)	$\Delta\bar{C}_p$ (J K^{-1})
MeOH	−0.02	0.4	0.1	0.06	−2.3
	(0.01)	(0.5)	(0.3)	(0.10)	(0.7)
EtOH	0.16	0.9	2.5	0.15	−10.2
	(0.04)	(0.5)	(0.3)	(0.05)	(1.0)
1-PrOH	0.49	−10.8	2.1	0.59	−21.8
	(0.10)	(2.0)	(0.5)	(0.10)	(3.0)
2-PrOH	0.85	−10.5	–	0.65	−31.7
	(0.10)	(5.0)		(0.05)	(5.0)
t-BuOH	0.86	−19.5	–	0.45	−40.9
	(0.10)	(10.0)		(0.10)	(7.0)

It is suggested that the D_w values for the three larger alkanol–water systems are consistent with a significant level of hydrophobic hydration. While their signs are those which one would anticipate as a result of dispersion of the aqueous microphase, their magnitudes appear to be too large to be ascribed to that cause alone. This is especially noticeable in the cases of contributions to the excess molar expansivities. Hydrophobic hydration is generally regarded as leading to an enhancement of the population of ice-like sites and, thus, to an increase in molar volume [32]. The $D_w(\Delta\bar{V})$ values are consistent with that notion. Since, however, the $D_w(\Delta\bar{H})$ values are positive, the conclusion that is drawn from the four-segment analyses must be that there is no evidence of the formation of stable clathrate-like aggregates.

It would appear that the structural characteristics of the water-rich segments of MeOH–water and EtOH–water are different from those of the three larger alkanol–water systems and probably from each other.

CONCLUSIONS

The four-segment model proved to be an effective curve-fitting tool for all of the data sets for which results are reported.

The various values that were obtained for parameters of the type $\Delta\bar{Q}_w^0$ are consistent with the formation, in roughly equimolar mixtures, of metastable aqueous aggregates. These aggregates appear to be sufficiently well characterized to warrant the use of the terms pseudo-phase or microphase. Their volumetric properties, with the striking exception of the MeOH–water system, are similar to those found earlier in the ACN–water and THF–water systems [3]. The thermal characteristics of all five alkanol–water systems resemble those of THF–water. Preliminary investigations of other types of binary hydro-organic systems reveal that, with very few exceptions, the values for $\Delta\overline{V}_w^0$ and $\Delta\overline{H}_w^0$ are significant and negative [33]. Thus, it is felt that the concept of enhanced aqueous aggregation in these systems, articulated by Hertz and co-workers [28,29], is supported by the results of four-segment model analyses.

Given the existence of metastable aqueous aggregates, in roughly equimolar mixtures of water and polar organic liquids, it seems to be reasonable to accept, as a plausible corollary, that, by tending to orient themselves with their polar groups in contact with water, the organic molecules form a labile, crudely structured microphase. The assumed existence of two microphases invokes the concept of some kind of interface.

For the *n*-alkanol–water systems, it would seem that the formation of the organic microphase is accomplished without any significant lessening of interalkanol hydrogen bonding. Such is not, however, the case for the two branched alkanol–water systems. Only in the case of MeOH–water does there appear to be any enthalpic advantage to the formation of an interface. Here, it may be that the aqueous aggregates are globular rather than laminar.

While the results of the analyses furnish no direct evidence as to the geometric aspects of the patterns of molecular aggregation, considerations of stoichiometric factors and structural patterns known to exist in surfactant–water systems lead to the tentative suggestion that a laminar arrangement exists in roughly equimolar mixtures. At the organic-rich end of the microheterogeneous segment, the mixed aggregates are thought to have assumed some kind of inverse micellular form. At the water-rich end, crude, possibly disk-shaped, micellular aggregates are envisaged.

In the organic-rich segment, the results of the analyses seem to be consistent with the suggestion that the aqueous clusters persist up to quite high alkanol mole fractions.

Several different patterns of behavior are observed in the secondary segments. Here, it is thought that the pattern of molecular aggregation is pseudo-micellular. The water molecules are considered to be distributed among interfacial and interstitial sites. In the 1-PrOH–water, 2-PrOH–water and *t*-BuOH–water systems, the volumetric and thermal characteristics of the two kinds of aqueous sites are not markedly different. While the thermal data for EtOH–water might be interpreted in terms of some kind of stabilization of the interstitial sites, the volumetric data suggest a scheme of aggregation which is more like that of the pure liquid than of the interfacial sites. The data for the MeOH–water system are such that one is inclined to conclude that there is no secondary segment and that it is inappropriate to try to describe it in the same terms as the other four alkanol–water systems.

The results obtained for the water-rich segments of the 1-PrOH–water, 2-PrOH–water and *t*-BuOH–water systems are markedly different from those for MeOH–water and EtOH–water. For the three larger alkanols, there are some quite dramatic changes in physical properties, which can be likened to those occurring in surfactant–water systems [24]. Here, it would seem that hydrophobic hydration may be regarded as being an important effect, but one which is limited to the lower range of alkanol mole fractions. Hydrophilic hydration also makes a contribution to the physical properties in this segment, but that effect persists up to quite substantial alkanol mole fractions [32].

The pattern of changes in physical properties in the water-rich segment of the EtOH–water system is similar to, but of substantially smaller magnitude than that of the larger alkanol–water systems. It would appear that there is not the same level of hydrophobic hydration; nor is there the same degree of aqueous structural modification that is associated with hydrophilic hydration. There is no evidence for hydrophobic hydration in the MeOH–water system, presumably because larger hydrocarbon groups are required to produce such effects.

Whether or not the conclusions that have been drawn from the results of the four-segment analyses about the patterns of molecular aggregation that exist within these alkanol–water mixtures will prove to be realistic remains to be seen. The results can, however, be claimed to possess a certain measure of internal consistency and to fit in with some of the ideas that other authors have expressed, on the basis of different methods of appraising the same types of data. It does not seem to be unwarranted to suggest that the four-segment model approach to summarizing the physical property data of hydro-organic systems furnishes a useful basis for formulating and discussing structural models.

More systems need to be analyzed by this approach, and the analytic scheme needs to be extended to non-thermodynamic properties. Efforts are being made in both ventures. Most of the attempts to furnish quantitative interpretations of the excess molar properties of binary hydro-organic systems have been restricted to the water-rich mixtures in the general context of the McMillan–Mayer approach [34]. An effort is currently being made to reconcile the vast body of information which that approach has yielded with the results of four-segment model analyses.

APPENDIX. THE FOUR-SEGMENT MODEL EQUATIONS

Microheterogeneous segment: $X_{\mathrm{II}} < X_{\mathrm{A}} < X_{\mathrm{III}}$

$$\Delta\bar{Q}(\mathrm{micr}) = BX_{\mathrm{A}}(1 - X_{\mathrm{A}}) + \Delta\bar{Q}^0_{\mathrm{w}}(1 - X_{\mathrm{A}}) + \Delta\bar{Q}^0_{\mathrm{A}}X_{\mathrm{A}}$$

Organic-rich segment: $X_{\mathrm{III}} < X_{\mathrm{A}} < 1$

$$\Delta\bar{Q}(\mathrm{org}) = \Delta\bar{Q}(\mathrm{micr}) - \Delta\bar{Q}^0_{\mathrm{A}}[(X_{\mathrm{A}} - X_{\mathrm{III}})/(1 - X_{\mathrm{III}})]^3$$

$$+ D_A(1 - X_A)(X_A - X_{III})^2/(1 - X_{III})^3$$

Secondary segment: $X_{\mathrm{I}} < X_{\mathrm{A}} < X_{\mathrm{II}}$

$$\Delta\bar{Q}(\mathrm{sec}) = \Delta\bar{Q}(\mathrm{micr}) - \Delta\bar{Q}^0_{\mathrm{w}}[(X_{\mathrm{II}} - X_{\mathrm{A}})/X_{\mathrm{II}}]^3 + \Delta\bar{Q}^0_{\mathrm{s}}[(X_{\mathrm{II}} - X_{\mathrm{A}})/X_{\mathrm{II}}]^3$$

$$+ D_{\mathrm{s}} X_{\mathrm{A}}(X_{\mathrm{II}} - X_{\mathrm{A}})^2/X_{\mathrm{II}}^3$$

Water-rich segment: $0 < X_{\mathrm{A}} < X_{\mathrm{I}}$

$$\Delta\bar{Q}(\mathrm{wat}) = \Delta\bar{Q}(\mathrm{sec}) - \Delta\bar{Q}^0_{\mathrm{s}}[(X_{\mathrm{I}} - X_{\mathrm{A}})/X_{\mathrm{I}}]^3 + D_{\mathrm{w}} X_{\mathrm{A}}(X_{\mathrm{I}} - X_{\mathrm{A}})^2/X_{\mathrm{I}}^3$$

For greater detail see ref. 3.

REFERENCES

1 F. Franks and D.J.G. Ives, Q. Rev., 20 (1966) 1.
2 M.I. Davis, Thermochim. Acta, 71 (1983) 59.
3 M.I. Davis, Thermochim. Acta, 77 (1984) 421.
4 M.I. Davis, Thermochim. Acta, 81 (1984) 157.
5 G.C. Benson and O. Kiyohara, J. Solution Chem., 9 (1980) 791.
6 G.C. Benson, P.J. D'Arcy and O. Kiyohara, J. Solution Chem., 9 (1980) 981.
7 G.C. Benson and O. Kiyohara, J. Solution Chem., 10 (1981) 281.
8 G.C. Benson and O. Kiyohara, J. Chem. Thermodyn., 11 (1979) 1061.
9 L. Benjamin and G.C. Benson, J. Phys. Chem., 67 (1963) 858.
10 R.F. Lama and B.C.-Y. Lu, J. Chem. Eng. Data, 10 (1965) 216.
11 J.A. Larkin and R.C. Pemberton, Natl. Phys. Lab. Rep. Chem., 43 (1976).
12 E. Bose, Z. Phys. Chem., Abt. A, 58 (1907) 585.
13 S.R. Goodwin and D.M.J. Newsham, J. Chem. Thermodyn., 3 (1971) 325.
14 G. Roux, D. Roberts, G. Perron and J.E. Desnoyers, J. Solution Chem., 9 (1980) 629.
15 S.G. Bruun and Aa. Hvidt, Ber. Bunsenges. Phys. Chem., 81 (1977) 936.
16 K-Y. Chu and A.R. Thompson, J. Chem. Eng. Data, 7 (1962) 358.
17 J. D'Ans and E. Lax (Eds.), Taschenbuch fur Physiker und Chemiker, Vol. I, 3rd edn. Springer Verlag, Berlin, 1967, p. 821.
18 J-P.E. Grolier, A. Roux and E. Wilhelm, unpublished results.
19 C. de Visser, G. Perron and J.E. Desnoyers, Can. J. Chem., 55 (1977) 856.
20 H. Arm, Helv. Chim. Acta, 45 (1962) 1803.
21 M.I. Davis, Thermochim. Acta, 89 (1985) 325.
22 Yu.I. Naberukhin and V.A. Rogov, Russ. Chem. Rev., 40 (1971) 207.
23 J.A. Larkin, J. Chem. Thermodyn., 7 (1975) 137.
24 J.E. Desnoyers, Pure Appl. Chem., 54 (1982) 1469.
25 F.H. Stillinger, Science, 209 (1980) 451.
26 W.L. Jorgensen, J. Chem. Phys., 77 (1982) 4156.
27 G.S. Kell, J. Phys. Chem. Ref. Data, 6 (1977) 1109.
28 H.G. Hertz and H. Leiter, Z. Phys. Chem., Neue Folge, 133 (1982) 45.
29 H. Leiter, C. Albayrak and H.G. Hertz, J. Mol. Liq., 27 (1984) 211.

30 S. Friberg, L. Rydhag and T. Doi, Lyotropic Liquid Crystals, Advances in Chemistry 152, American Chemical Society, Washington, DC, 1976, p. 28.
31 M.I. Davis, Thermochim. Acta, 71 (1983) 59.
32 C. Dethlefsen, P.G. Sorensen and Aa. Hvidt, J. Solution Chem., 13 (1984) 191.
33 M.I. Davis, research in progress.
34 W.G. McMillan and J.E. Mayer, J. Chem. Phys., 13 (1945) 276.