A FOUR SEGMENT COMPOSITION MODEL FOR NON-ELECTROLYTE AQUEOUS MIXTURES

MICHAEL I. DAVIS

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

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ABSTRACT

A model for analysing excess properties of mixtures of water and polar organic liquids, which embodies the assumption that the total composition ranges of such mixtures possess four distinct segments, is described and the results given for analyses of various properties of the ACN–water and THF–water systems. Some tentative conclusions are drawn from the results about patterns of molecular aggregation within these mixtures.

INTRODUCTION

An analytic model, based upon the assumption that mixtures of water and polar organic liquids possess three distinct composition segments, has been devised and demonstrated to be a reasonably effective curve-fitting tool for certain excess properties of the acetonitrile(ACN)–water and dimethylsulfoxide(DMSO)–water systems [1–3]. It is suggested that each of the five parameters of that model can be associated with a particular type of molecular aggregation.

In the course of testing this model, several features have emerged. Some data sets, which are too sparse to allow for the level of flexibility of the full model, are fairly well reproduced using a simpler three-parameter version [2,3]. In some cases, the three-parameter version serves as well as the five in fitting data sets of unusually high point density and precision [2]. At the other extreme are data sets for which the three-segment model is too inflexible to serve as a satisfactory curve-fitting tool.

This article contains the derivation and implementation of a four-segment model which proves to be a significantly better curve-fitting tool and appears to be more informative than the three. It also contains some minor modifications to the parameterization of the three-segment model.

MODIFIED THREE-SEGMENT MODEL EQUATIONS

The following equations are equivalent to those given in ref. 1 but are of a more convenient form

for the water-rich segment $(0 < X_A < X_I)$

$$\Delta \overline{V} = B X_A (1 - X_A) + \Delta \overline{V}_A^0 X_A + \Delta \overline{V}_w^0 \left[(1 - X_A) - (X_I - X_A)^3 / X_I^3 \right]$$
$$+ D_w X_A (X_I - X_A)^2 / X_I^3 \tag{1}$$

for the microheterogeneous segment $(X_I < X_A < X_{II})$

$$\Delta \overline{V} = B X_A (1 - X_A) + \Delta \overline{V}_A^0 X_A + \Delta \overline{V}_w^0 (1 - X_A) \tag{2}$$

for the organic-rich segment $(X_{II} < X_A < 1)$

$$\Delta \overline{V} = B X_A (1 - X_A) + \Delta \overline{V}_A^0 \left[X_A - (X_A - X_{II})^3 / (1 - X_A)^3 \right] + \Delta \overline{V}_w^0 (1 - X_A)$$
$$+ D_A (1 - X_A)(X_A - X_{II})^2 / (1 - X_{II})^3 \tag{3}$$

The equations express the composition dependence of the excess molar volumes but serve equally well for any excess molar property. X_A is the mole fraction of the organic component. X_I and X_{II} are the X_A values at the two segment junctions. $\Delta \overline{V}_w^0$ and $\Delta \overline{V}_A^0$ are constants of integration of the Gibbs–Duhem equation within the microheterogeneous segment. As such they represent excess molar properties of hypothetical standard states of water and the organic component, respectively. B is a Margoules constant for the microheterogeneous segment. D_w and D_A are related to the Margoules constants C_w and C_A of the water-rich and organic-rich segments, respectively.

$$D_w = - \left[\tfrac{1}{2} C_w X_A^3 + \Delta \overline{V}_w^0 \right] \tag{4}$$

$$D_A = - \left[\tfrac{1}{2} C_A (1 - X_A)^3 + \Delta \overline{V}_A^0 \right] \tag{5}$$

Both $\Delta \overline{V}$ and $d\Delta \overline{V}/dX_A$ are required to be single valued at both X_I and X_{II}. The Margoules constant, C, of the microheterogeneous segment is assumed to be zero. If the additional constraints that $d^2 \Delta \overline{V}/dX_A^2$ shall be single valued at X_I or X_{II} are introduced then D_w or D_A vanish.

The options of omitting D_w or D_A or both from the set of analytic variables permit the use of four different versions of the three-segment model.

THE FOUR-SEGMENT MODEL

In those instances where the three-segment model has proved to be less than satisfactory as a curve-fitting tool, the deficiencies seem to be restricted to the water-rich end of the composition scale.

In his discussion of the proton magnetic resonance spectra of acetonitrile–water mixtures, Easteal suggested that this system might be regarded as possessing as many as five distinct segments, two of which correspond to the composition range spanned by the single water-rich segment of the three-segment model [4]. It seemed to be appropriate to devise and test a four-segment model, with the water-rich segment of the existing model being split into two parts.

Structural considerations

The term microheterogeneous, as applied to the central composition segment, appears to have been coined by Naberukhin and Rogov [5]. It fits their contention that, in roughly equimolar mixtures of water and polar organic liquids, the molecules of the two components tend to adopt new patterns of self-aggregation. The composite structure is envisioned to be one of layered microphases. The parameters $\Delta \overline{V}_w^0$ and $\Delta \overline{V}_A^0$ are regarded as excess properties of these microphases.

At the interface between the two microphases, it is assumed that the organic molecules tend to be oriented with their polar groups in contact with the aqueous microphase. Parameters of the type B are taken to represent the effects of the potential interactions at this interface. It is implied that contact between pairs of microphase organic molecules tends to be dominated by that between their respective hydrocarbon moieties.

There are obviously limits to the range of molar compositions in which all of the molecules of both species can be accomodated into this microheterogeneous scheme.

In the organic-rich segment, it is assumed that the excess organic molecules will tend to adopt the self-aggregative patterns of the pure liquid. The effects of the interactions between pure liquid aggregates and microheterogeneous aggregates are considered to be represented by parameters of the type D_A.

Apart from the renumbering of the segment junction mole fractions, the model equations for the microheterogeneous and organic-rich segments are the same for both the three- and four-segment models.

In the three-segment model, the water molecules are treated as though they are either involved in the microheterogeneous aggregates or in clustering patterns which are typical of the pure liquid. The fact that the model fails to provide satisfactory replicas for the water-rich segments of some of the data sets that have been looked at suggests that some allowance needs to be made for a further type of aqueous self-aggregation.

For $X_A < X_{II}$, there are more water molecules than can be accomodated in the microheterogeneous scheme of aggregation. It is suggested that there exists some type of secondary aqueous microphase, with an excess molar volume $\Delta \overline{V}_S^0$.

In the composition segment $X_I < X_A < X_{II}$ all of the water molecules exist in one or other of the two microphase environments. For $X_A < X_I$, some of the water molecules are to be found in environments that are more typical of the pure liquid.

The name "water-rich" has been retained for the composition segment $0 < X_A < X_I$. For want of a more graphic term, the name "secondary" has been applied to the segment $X_I < X_A < X_{II}$.

Derivation of the model equations

The derivation of the model equations closely parallels that of the three-segment model [1]. Each of the four segments is initially characterized by the Margoules constants B and C and by quantities of the type $\Delta\overline{V}_w^0$ and $\Delta\overline{V}_A^0$. $\Delta\overline{V}_w^0$ is clearly zero for the water-rich segment as is $\Delta\overline{V}_A^0$ for the organic-rich segment. It is thought to be appropriate to set C, for the microheterogeneous segment, equal to zero. The number of parameters is reduced from 13 to seven by imposing the conditions that $\Delta\overline{V}$ and $d\Delta\overline{V}/dX_A$ shall be single valued at X_I, X_{II} and at X_{III}.

The resulting equations are

for the water-rich segment $(0 < X_A < X_I)$

$$\Delta\overline{V} = BX_A(1 - X_A) + \Delta\overline{V}_A^0 X_A + \Delta\overline{V}_w^0\left[(1 - X_A) - (X_{II} - X_A)^3/X_{II}^3\right]$$
$$+ \Delta\overline{V}_S^0\left[(X_{II} - X_A)^3/X_{II}^3 - (X_I - X_A)^3/X_I^3\right]$$
$$+ D_w X_A(X_I - X_A)^2/X_I^3 + D_S X_A(X_{II} - X_A)^2/X_{II}^3 \tag{6}$$

for the secondary aqueous segment $(X_I < X_A < X_{II})$

$$\Delta\overline{V} = BX_A(1 - X_A) + \Delta\overline{V}_A^0 X_A + \Delta\overline{V}_w^0\left[(1 - X_A) - (X_{II} - X_A)^3/X_{II}^3\right]$$
$$+ \Delta\overline{V}_S^0(X_{II} - X_A)^3/X_{II}^3 + D_S X_A(X_{II} - X_A)^2/X_{II}^3 \tag{7}$$

for the microheterogeneous segment $(X_{II} < X_A < X_{III})$

$$\Delta\overline{V} = BX_A(1 - X_A) + \Delta\overline{V}_A^0 X_A + \Delta\overline{V}_w^0(1 - X_A) \tag{8}$$

for the organic-rich segment $(X_{III} < X_A < 1)$

$$\Delta\overline{V} = BX_A(1 - X_A) + \Delta\overline{V}_A^0\left[X_A - (X_A - X_{III})^3/X_{III}^3\right] + \Delta\overline{V}_w^0(1 - X_A)$$
$$+ D_A(1 - X_A)(X_A - X_{III})^2/(1 - X_{III})^3 \tag{9}$$

The parameters B, $\Delta\overline{V}_w^0$, $\Delta\overline{V}_A^0$ and D_A are interpreted in the same manner as they were in the three-segment model.

$\Delta\overline{V}_S^0$ is the most important of the three new parameters. It is the excess molar volume of the hypothetical standard state of the secondary aqueous segment. As such, it is interpreted as a property of a secondary aqueous microphase.

The parameters D_w and D_S are defined by the equations

$$D_S = -\left[\tfrac{1}{2} C_S X_{II}^3 + \Delta \overline{V}_w^0\right] \tag{10}$$

$$D_w = -\left[\tfrac{1}{2}(C_w - C_S) X_I^3 + \Delta \overline{V}_s^0\right] \tag{11}$$

where C_w and C_S are Margoules constants for the water-rich and secondary aqueous segments, respectively.

D_w, D_S and D_A can be set equal to zero by adding the constraints that $d^2 \Delta \overline{V}/d X_A^2$ shall be single valued at X_I, X_{II} and X_{III}, respectively. With the options of omitting any or all of those three parameters, there are eight possible versions of the four-segment model.

ANALYSES

Analyses have been carried out for three types of excess molar property data for both the acetonitrile(ACN)–water and the tetrahydro-furan(THF)–water systems. The effectiveness of the three-segment model as a curve-fitting tool for the excess properties of the ACN–water system has already been demonstrated [1–3]. It was of interest to find out if there is any significant improvement in the quality of fit using the four-segment model.

The three-segment model was found to be less than satisfactory for use with the excess properties of the THF–water system. It was hoped that the four-segment model would prove to be more acceptable.

DATA SETS

All of the data sets used in this work were taken from the literature. To warrant the level of flexibility of the four-segment model, data sets should contain at least 30 points which are fairly evenly distributed across the entire composition range.

Acetonitrile–water

Excess molar volumes have been reported by Handa and Benson at 5 degree intervals over the temperature range 15–35°C [6]. Benson et al. reported excess molar heat capacities at 25°C [7].

Heats of mixing at 5, 25 and 45°C have been reported by Morcom and Smith [8]. The individual data sets are really too sparse for four-segment analyses, if the segment junction composition values are to be treated as analytic variables. A composite data set for 25°C was constructed on the basis of the assumption that the heat capacities of ref. 7 are insensitive to variations in temperature.

Tetrahydrofuran–water

Excess molar volumes were taken from two articles, both coming from the same laboratory [9,10]. Reference 9 also contains heats of mixing data. The same research group have also reported values for the excess molar heat capacities at 25°C [11].

STRATEGY

In the first round of analyses, the molar compositions of the segment junctions were treated as analytic variables. All four versions of the three-segment model and all eight of the four were tried.

For any specific combination of values for the segment junctions, the optimum set of physical parameters can be determined by a straightforward linear least-squares procedure. Optimization of the segment junctions is more complicated because of the discontinuities in $\Delta \overline{V}$. It was accomplished by a procedure in which the standard deviations of $\Delta \overline{V}$ are mapped as a function of X_I, X_{II} and X_{III}. The possibility exists for multiple minima and appropriate checks need to be made.

There is some variation among the optimum segment junctions found for the various data sets of the two systems. An effort was made, for each system, to find a compromise set of segment junctions.

A final set of analyses was carried out using the compromise segment junction combinations.

RESULTS

Variable segment junctions

Acetonitrile–water
Volumetric data, Table 1. Neither D_w nor D_A help to improve the quality of fit for the three-segment model over that of the simple three-parameter version. The optimised segment junctions are all fairly close to the combination of $X_I = 0.25$ and $X_{II} = 0.70$ that was used in the analyses reported in ref. 2.

Neither D_S nor D_A affect the quality of fit for the four-segment model analyses. It was found that there are two sets of optimum solutions; one with the parameter D_w included in the variable set, the other with it excluded.
Thermal Data, Table 2. Both D_w and D_A play significant roles in producing the optimal three-segment model for the excess molar heat capacities. Only D_w appears to be significant for the heats of mixing.

In the four-segment analyses, D_A is again a significant parameter for the

TABLE 1

Segmented composition model analyses of excess molar volumes of acetonitrile–water mixtures

Temp. (°C) = 15	20	25	30	35
No. of points = 91	83	88	89	58
σ [6] (mm^3) = 3.1	2.5	2.3	1.6	1.2
3-Segment analyses				
X_I	0.250	0.251	0.254	0.251	0.254
X_{II}	0.703	0.701	0.688	0.644	0.643
B (cm^3)	−1.444	−1.531	−1.541	−1.655	−1.700
$\Delta\overline{V}_w^0$	−0.441	−0.414	−0.401	−0.379	−0.370
$\Delta\overline{V}_A^0$	0.124	0.142	0.152	0.187	0.203
σ (mm^3)	2.75	2.25	2.61	2.32	2.60
4-Segment analyses				
Type *A*				
X_I	0.222	0.218	0.215	0.211	0.213
X_{II}	0.413	0.396	0.463	0.465	0.460
X_{III}	0.730	0.728	0.739	0.699	0.708
B (cm^3)	−1.339	−1.420	−1.317	−1.389	−1.377
$\Delta\overline{V}_w^0$	−0.474	−0.448	−0.472	−0.459	−0.464
$\Delta\overline{V}_A^0$	0.107	0.123	0.115	0.139	0.143
$\Delta\overline{V}_S^0$	−0.325	−0.284	−0.275	−0.253	−0.220
σ (mm^3)	2.37	1.73	1.57	1.19	1.04
Type *B*				
X_I	0.110	0.106	0.123	0.116	– [a]
X_{II}	0.317	0.312	0.351	0.349	–
X_{III}	0.722	0.719	0.724	0.684	–
B (cm^3)	−1.376	−1.460	−1.396	−1.488	–
$\Delta\overline{V}_w^0$	−0.461	−0.435	−0.443	−0.425	–
$\Delta\overline{V}_A^0$	0.112	0.129	0.126	0.154	–
$\Delta\overline{V}_S^0$	−0.133	−0.110	−0.142	−0.124	–
D_w	0.177	0.148	0.145	0.128	–
σ (mm^3)	1.96	1.13	1.43	1.20	–

[a] No solutions of this type.

heat capacities but not for the heats of mixing. The role played by D_w in the three-segment analyses appears to have been taken over by $\Delta\overline{C}_S^0$ and $\Delta\overline{H}_S^0$ and by D_S.

Tetrahydrofuran–water
Volumetric data, Table 3. The three-segment model is not an effective curve-fitting tool for this data. Apart from the 35°C set, the optimised segment junction values do not correspond to the conceptual aspects of the model.

The four-segment model is a significantly better curve-fitting tool and its optimised segment junction values appear to be reasonable.

TABLE 2

Segmented composition model analyses of excess thermal data for acetonitrile–water mixtures (25°C)

	$\Delta \bar{C}_p$ (J mol^{-1} °C^{-1})	$\Delta \bar{H}$ (J mol^{-1})
No. of points =	39	42
σ(lit) =	0.04	not calc.
3 - Segment analyses		
X_I	0.191	0.128
X_{II}	0.725	0.621
B	29.89	2854
$\Delta \bar{C}_w^0$	0.91	−148
$\Delta \bar{C}_A^0$	0.75	751
D_w	9.88	−219
D_A	−7.41	a
σ	0.071	7.26
4 - Segment analyses		
X_I	0.113	0.104
X_{II}	0.286	0.391
X_{III}	0.751	0.638
B	32.78	3159
$\Delta \bar{C}_w^0$	0.22	−231
$\Delta \bar{C}_A^0$	0.09	687
$\Delta \bar{C}_S^0$	3.49	−207
D_w	a	a
D_S	3.43	252
D_A	−5.98	a
σ	0.040	7.08

[a] Parameter not included in optimal data set.

Thermal data, Table 4. The three-segment model fails to do justice to the heats of mixing data but is quite effective for the excess heat capacities. There is a substantial improvement in the quality of fit for ΔH on switching to the four-segment model. There appear to be two choices for an optimised four-segment model for the heat capacity data.

Representative segment junction combinations

Various combinations of simple fractional values for the segment junction compositions were tested to find representative sets for each of the two systems. It transpired that for the three-segment model the combination of $X = 0.20$ and $X = 0.667$ is the most suitable for both systems. For the four-segment models, the best X_I values for the two systems are different with the best X_{II} and X_{III} combination being the same. That these representative segment junction combinations give reasonable fitted curves for all

TABLE 3

Segmented composition model analyses of excess molar volumes of tetrahydrofuran–water mixtures

	Temp. (°C) = 15	20	25 [9]	25 [10]	30	35
	No. of points = 33	32	58	40	33	32
3 - Segment models						
5-Parameter X_I 0.080	0.081	0.072	0.075	0.078	0.184	
X_{II} 0.191	0.191	0.174	0.175	0.170	0.680	
σ 4.67	4.36	4.20	5.41	5.62	5.38	
3-Parameter X_I 0.341	0.330	0.320	0.317	0.294	0.282	
X_{II} 0.750	0.719	0.665	0.726	0.683	0.680	
σ 11.74	9.63	7.40	7.35	6.79	5.70	
4 - Segment models						
X_I	0.089	0.090	0.086	0.085	0.083	0.092
X_{II}	0.350	0.361	0.318	0.326	0.312	0.323
X_{III}	0.735	0.729	0.640	0.719	0.682	0.691
B	−2.125	−2.132	−2.503	−2.277	−2.384	−2.393
$\Delta\bar{V}_w^0$	−0.664	−0.633	−0.538	−0.562	−0.509	−0.487
$\Delta\bar{V}_A^0$	0.118	0.121	0.210	0.145	0.172	0.178
$\Delta\bar{V}_S^0$	−0.065	−0.083	−0.047	−0.056	−0.058	−0.088
D_w	0.328	0.321	0.234	0.245	0.224	0.236
σ	2.60	2.35	2.74	2.93	2.14	2.27

of the data sets can be verified by comparing the contents of Tables 5 and 6 with those of Tables 1–4.

Fixed segment junctions

Acetonitrile–water

Three-segment models, Table 5a. Analyses of the three individual heats of mixing data sets of ref. 8 were carried out, in addition to the sets previously analysed. The standard deviations for the various data sets are roughly one third higher than those of the optimal fits. There does not appear to be any facet of the results of these analyses which contradicts conclusions reached in the earlier articles [1–3].

Four-segment models, Table 5b. There is a general pattern of improvement in the quality of fit, going from the three- to the four-segment model. There are only modest changes in the magnitudes of the values of the three major parameters B, $\Delta\bar{V}_w^0$ and $\Delta\bar{V}_A^0$.

It was found out that the parameter D_S could be omitted without impairing the quality of fit. It will be noted that the compromise segment junction values are close to those of the optimal solutions of type B of Table 1.

TABLE 4

Segmented composition model analyses of excess molar thermal properties of tetrahydrofuran–water mixtures (25°C)

	$\Delta\bar{C}$ (J mol^{-1} °C^{-1})		$\Delta\bar{H}$ (J mol^{-1})
No. of points =	39		38
σ(lit.; mm^3) =	0.14		0.66
3-Segment models			
X_I	0.203		0.188
X_{II}	0.725		0.589
B	11.41		-993
$\Delta\bar{C}_w^0$	12.36		-920
$\Delta\bar{C}_A^0$	4.01		967
D_w	0.06		a
D_A	-10.85		a
σ	0.149		12.90
4-Segment models			
X_I	0.178	0.074	0.150
X_{II}	0.598	0.261	0.563
X_{III}	0.933	0.709	0.710
B	56.04	8.11	1178
$\Delta\bar{C}_w^0$	-6.62	13.06	-1541
$\Delta\bar{C}_A^0$	-1.08	4.83	533
$\Delta\bar{C}_S^0$	9.53	3.42	-673
D_w	a	-5.70	a
D_S	28.89	a	a
D_A	a	-12.01	a
σ	0.115	0.117	3.30

a Parameter not part of optimum set.

The standard deviation $\sigma(\Delta\bar{C}_p)$ is found to be quite sensitive to the choice of X_{III}. It is worth noting that the optimum X_{III} value for the excess molar heat capacity data of de Visser et al. [12] is 0.657.

Tetrahydrofuran–water

Three-segment models, Table 6a. Several additional sets of heats of mixing data were analysed at this stage [13,14].

It is interesting to note that while the three-segment model is a poor curve-fitting tool for the volumetric data, insofar as it gave nonsensical segment junction values and standard deviations which are substantially higher than those obtained with the four-segment model, the values obtained for B, $\Delta\bar{V}_w^0$ and $\Delta\bar{V}_A^0$ are quite similar for the two models.

Four-segment models, Table 6b. There are some modest differences between the parameter sets obtained for the two 25°C $\Delta\bar{V}$ data sets. The differences

TABLE 5

Fixed junction analyses of excess molar properties of acetonitrile–water mixtures

3-*Segment analyses* ($X_I = 0.200$, $X_{II} = 0.667$)

$\Delta \bar{V}$ Temp. (°C) =	15	20	25	30	35
B (cm^3)	−1.497	−1.595	−1.629	−1.709	−1.764
$\Delta \bar{V}_w^0$	−0.427	−0.399	−0.380	−0.364	−0.354
$\Delta \bar{V}_A^0$	0.135	0.155	0.171	0.197	0.216
D_w	0.248	0.230	0.217	0.203	0.207
D_A	0.021	0.021	−0.006	−0.051	−0.061
σ (mm^3)	3.19	2.83	3.33	2.95	3.46

	$\Delta \bar{C}_p$	$\Delta \bar{H}$ 5°C	$\Delta \bar{H}$ 25°C	$\Delta \bar{H}_{comb.}$	$\Delta \bar{H}$ 45°C
B	28.80	2147	2581	2725	3442
$\Delta \bar{C}_w^0$	0.94	−120	−93	−111	−115
$\Delta \bar{C}_A^0$	1.32	757	797	771	760
D_w	9.96	−708	−578	−518	−282
D_A	−8.17	−215	−326	−319	−430
σ	0.093	7.28	6.41	9.74	8.90

4-*Segment analyses* ($X_I = 0.111$, $X_{II} = 0.333$, $X_{III} = 0.667$)

$\Delta \bar{V}$ Temp. (°C) =	15	20	25	30	35
B	−1.356	−1.440	−1.411	−1.500	−1.519
$\Delta \bar{V}_w^0$	−0.456	−0.439	−0.438	−0.422	−0.418
$\Delta \bar{V}_A^0$	0.107	0.123	0.127	0.156	0.166
$\Delta \bar{V}_S^0$	−0.140	−0.123	−0.118	−0.115	−0.108
D_w	0.184	0.158	0.139	0.126	0.110
D_S	−0.028	−0.034	0.003	0.023	0.042
D_A	0.072	0.076	0.069	0.018	0.023
σ	2.01	1.21	1.58	1.23	1.36

	$\Delta \bar{C}_p$	$\Delta \bar{H}$ 5°C	$\Delta \bar{H}$ 25°C	$\Delta \bar{H}_{comb.}$	$\Delta \bar{H}$ 45°C
B	29.17	2132	2761	3095	3870
$\Delta \bar{C}_w^0$	0.31	−106	−136	−206	−225
$\Delta \bar{C}_A^0$	1.26	754	758	694	671
$\Delta \bar{C}_S^0$	4.14	−202	−217	−229	−140
D_w	−0.97	−114	−20	−16	−72
D_S	−0.29	−203	71	240	262
D_A	−8.10	−203	−251	−176	−268
σ	0.78	3.96	4.12	7.42	4.77

between the two data sets, which were obtained in the same laboratory using different measurement techniques, are shown graphically in ref. 10. The authors of ref. 10 express the opinion that the data of ref. 9 are the more accurate.

TABLE 6

Fixed junction analyses of excess molar properties of tetrahydrofuran–water mixtures

3-Segment analyses ($X_I = 0.200$, $X_{II} = 0.667$)

$\Delta \bar{V}$ Temp. (°C) =	15	20	25 [10]	25 [9]	30	35
B	−2.443	−2.507	−2.542	−2.789	−2.536	−2.566
$\Delta \bar{V}_w^0$	−0.578	−0.530	−0.495	−0.465	−0.458	−0.441
$\Delta \bar{V}_A^0$	0.181	0.196	0.202	0.270	0.202	0.215
D_w	0.746	0.618	0.538	0.486	0.449	0.383
D_A	−0.038	−0.071	−0.040	−0.159	−0.031	−0.033
σ	9.73	8.86	7.25	7.24	6.45	5.53

	$\Delta \bar{H}$ 25°C [9]	$\Delta \bar{H}$ 25°C [13]	$\Delta \bar{H}$ 25°C [14]	$\Delta \bar{H}$ 10°C [14]	$\Delta \bar{C}_p$
B	−678	+111	−947	−997	7.99
$\Delta \bar{H}_w^0$	−960	−1081	−894	−1079	12.76
$\Delta \bar{H}_A^0$	857	615	899	806	5.29
D_w	−70	403	−352	−345	−1.32
D_A	−311	169	−303	−147	−11.05
σ	14.46	18.47	16.45	19.99	0.171

4-Segment analyses ($X_I = 0.091$, $X_{II} = 0.333$, $X_{III} = 0.667$)

$\Delta \bar{V}$ Temp. (°C) =	15	20	25 [10]	25 [9]	30	35
B	−2.163	−2.184	−2.281	−2.442	−2.349	−2.403
$\Delta \bar{V}_w^0$	−0.654	−0.619	−0.562	−0.552	−0.520	−0.485
$\Delta \bar{V}_A^0$	0.125	0.131	0.146	0.195	0.166	0.181
$\Delta \bar{V}_S^0$	−0.067	−0.083	−0.072	−0.066	−0.085	−0.087
D_w	0.330	0.318	0.265	0.259	0.258	0.235
D_S	0.068	0.097	−0.007	−0.013	−0.012	−0.043
D_A	0.061	0.049	0.064	−0.016	0.031	0.031
σ	2.87	2.55	3.14	2.81	2.33	2.39

	$\Delta \bar{H}$ 25°C [9]	$\Delta \bar{H}$ 25°C [13]	$\Delta \bar{H}$ 25°C [14]	$\Delta \bar{H}$ 10°C [14]	$\Delta \bar{C}_p$
B	26	1097	106	−46	2.20
$\Delta \bar{H}_w^0$	−1141	−1357	−1158	−1305	14.18
$\Delta \bar{H}_A^0$	711	421	686	602	6.55
$\Delta \bar{H}_S^0$	−449	−340	−460	−474	5.27
D_w	382	270	342	265	−6.67
D_S	78	272	169	−108	1.36
D_A	−40	518	61	224	−13.45
σ	7.00	8.22	8.31	8.34	0.318

There are somewhat larger differences among the parameter sets derived for the three 25°C $\Delta \bar{H}$ data sets. While the data of refs. 9 and 14 are mutually consistent, there are some systematic differences between them and the data of ref. 13. Those differences are shown graphically in ref. 13.

DISCUSSION

Curve fitting

The four-segment model is a significantly better curve-fitting tool than the three. Its use is, however, only warranted for large high-precision data sets, particularly if the segment junction values are to be included among the data analytic variables. In this context, it is appropriate to note that the size of a data set can be misleading. For quite valid reasons, many investigators have made most of their measurements on water-rich mixtures, with relatively sparse information about the other composition regions.

It is probable that the model could be further improved in the extreme water-rich range. It is doubtful whether the model gives an accurate account of the systems close to infinite dilution.

The quality of fit appears to be good enough to warrant serious consideration of the implications of the various sets of model parameter values.

INTERPRETATION OF THE RESULTS

The principal aqueous microphase

It is suggested that, in the vicinity of the polar groups of the organic molecules, the water molecules tend to adopt a pattern of self-aggregation which is different from that of the pure liquid. The quantities $\Delta \bar{V}_w^0$, $\Delta \bar{H}_w^0$ and $\Delta \bar{C}_w^0$ are treated as excess molar properties of this aqueous microphase.

The analyses indicate that, in both systems, the aqueous microphase is significantly more compact than is pure water. The effect appears to be more pronounced in the THF–water system than in the ACN–water system. For both systems, the magnitude of the contraction decreases quite significantly with increasing temperature. Earlier studies of the ACN–water system [2] indicate that the microphase water exhibits a more normal pattern of thermal expansion than does pure water.

$\Delta \bar{H}_w^0$ is moderately negative (-100 J) for the ACN–water system and quite significantly so (-1000 J) for THF–water. $\Delta \bar{C}_w^0$ is almost negligible for ACN–water but quite large and positive for THF–water. It is suggested that the microphase is more highly structured in THF–water. Such a suggestion might well account for the exceptionally high viscosity of water-rich mixtures ($\eta = 1.75$ cp for $X_A = 0.13$) [15].

The organic microphase

It is suggested that those organic molecules, which are in direct contact with the aqueous microphase, tend to form a layered microphase with the

polar groups inclined towards the water molecules. In such a situation, contact between pairs of organic molecules would tend to be restricted to that of their hydrocarbon groups.

$\Delta \overline{V}_A^0$ and $\Delta \overline{H}_A^0$ are both positive for both systems, which is consistent with diminished intermolecular attraction. The magnitudes of both parameters are nearly the same for both systems. $\Delta \overline{C}_A^0$ is somewhat larger for the THF–water system than the ACN–water system, which suggests that the organic microphase is more highly structured in the former system.

The microphase interface

Parameters of type B are regarded as being measures of the effects, upon the various physical properties, of the interactions existing across the interface between the aqueous and organic microphases.

$B(\Delta \overline{V})$ is quite large and negative for both systems. The value for THF–water is roughly half as large again as that for ACN–water but still substantially less than that for DMSO–water [1]. The volume decrease must be due to more efficient packing, since $B(\Delta \overline{H})$ is quite large and positive for ACN–water and quite small for THF–water.

There is a substantial difference between the values of $B(\Delta \overline{C})$ for ACN–water (large and positive) and THF–water (very small). The result for ACN–water suggests a low entropy interface. This is consistent with the existence of an upper critical solution temperature of $-1.05 \pm 0.15°C$ at $X = 0.38 \pm 0.02$ [16].

The organic-rich segment

It is suggested that in the organic-rich segment, the microheterogeneous aggregates tend to adopt an inverted micellular form. Parameters of the type D_A are taken to represent the effects of the interactions between such aggregates and those of the pure organic component.

$D_A(\Delta \overline{V})$ is virtually negligible for both systems, possibly because in the pure liquids the molecules tend to form small clusters with their polar groups innermost and their hydrocarbon moieties forming an outer shell similar to that of an inverted micelle.

$D_A(\Delta \overline{H})$ is apparently negative for the ACN–water system, but poorly defined for THF–water. $D_A(\Delta \overline{C}_p)$ is quite large and negative for both systems. This might be an artifact of the model equations, but it may indicate that at lower temperatures mixing of the two types of molecular aggregates leads to some kind of enhanced freedom of motion which diminishes as the temperature increases.

The secondary aqueous microphase

The parameters $\Delta \overline{V}_S^0$, $\Delta \overline{H}_S^0$ and $\Delta \overline{C}_S^0$ are taken to represent the excess molar properties of a secondary aqueous microphase. This microphase is

formed from water molecules, too numerous to be accomodated in the microheterogeneous aggregates but in direct contact with them. It is the introduction of this type of parameter which distinguishes the four-segment model from the three.

The $\Delta \overline{V}_S^0$ values for both systems are negative but considerably smaller than the corresponding $\Delta \overline{V}_w^0$ values.

The $\Delta \overline{H}_S^0$ values for the two systems are much closer than are the corresponding $\Delta \overline{H}_w^0$ values. There is a comparable situation with the $\Delta \overline{C}_S^0$ values.

There are two possible explanations for the origin of this second aqueous microphase. Either it is formed from water molecules which are in contact with the hydrocarbon groups of the organic molecules or the microheterogeneous aggregates tend to assume a micellular form and the new microphase constitutes an enveloping layer.

That there is a noticeable improvement in the quality of fit in going from the three- to the four-segment model would seem to support the concept of a secondary microphase. If that microphase was induced by contact between its component water molecules and the hydrocarbon groups of the organic molecules, one would expect the parameter $D_s(\Delta \overline{H})$ to be quite large and positive. What is found is that, for most of the data sets, that parameter could be omitted without making much difference to the quality of fit. When included, the values are of mixed sign.

Clearly, the results are not conclusive. They suggest that this secondary aqueous microphase is more likely to be an outer layer to a micellular microheterogeneous aggregate than a microlayer in contact with hydrocarbon groups.

The water-rich segment

At the composition $X_A = X_1$, all of the water molecules are either constituents of microheterogeneous aggregates or of the secondary microphase. As the mole fraction of the organic component decreases, so an increasing proportion of the water molecules will be situated in pure liquid environments. As infinite dilution is approached the microheterogeneous aggregates will tend to disperse with the organic molecules becoming isolated solute species.

Parameters of the type D_w represent the effects upon the physical properties of the interactions between pure water and the mixed aggregates. If the tentative conclusions reached about the structural characteristics of the secondary segment are correct, then it is only in the water-rich segment that one would expect to find any appreciable effects from the interactions between water and hydrocarbon groups.

$D_w(\Delta \overline{V})$ is a non-trivial positive quantity for both systems, larger for THF–water than for ACN–water. The parameters $D_w(\Delta \overline{H})$ and $D_w(\Delta \overline{C}_p)$

are both quite small for the ACN–water system. $D_w(\Delta\overline{H})$ is quite substantial and positive for the THF–water system. $D_w(\Delta\overline{C}_p)$ is quite large and negative for the same system.

One possible explanation for the THF–water results is that the additional water tends to destabilise the microheterogeneous aggregates, the effect being more pronounced at lower temperatures.

CONCLUSIONS

It has been demonstrated that a model, which embodies the assumption that the ACN–water and THF–water systems each have four distinct composition segments, is a superior curve-fitting tool to the model previously described in which only three segments were assumed. Plots of the data-sets used in this work can be found in earlier articles [6–11]. The fitted curves of this work all pass neatly through the data points.

The results of the various analyses support, but do not conclusively prove, the existence of a structural pattern of layered microphases across the composition range 0.333–0.667. The aqueous microphase appears to be more compact and of lower enthalpy than pure water. The organic microphases are less compact and of higher enthalpy than the corresponding pure liquids. The results suggest that the microphases are more structurally ordered in the THF–water system than in the ACN–water system.

It is suggested that the microheterogeneous aggregates tend to have a micellular character at the water-rich end of the composition range and an inverted micellular character at the organic-rich end.

If that concept is correct then the organic-rich segment is a mixture of microheterogeneous and pure organic molecular aggregates.

The assumption made, in the formulation of the three-segment model, was that there is a single water-rich segment in which microheterogenous aggregates coexist with pure water aggregates. Experience would seem to indicate that this assumption is overly simplistic. It is suggested that those water molecules which are in direct contact with the microheterogeneous aggregates form a distinct secondary microphase.

The model that seems to be emerging from these studies is one in which direct contact between water molecules and the hydrocarbon groups of the organic molecules is kept to a bare minimum.

It should be stressed again that the interpretation of bulk properties of liquid mixtures is inevitably a highly speculative business. The models described in this and earlier articles [1–3] have sought to quantify the general ideas of composition segmentation and microphase formation which have been voiced in the literature for some time. Whether or not the tentative conclusions that have been drawn hitherto will prove to have any great merit does not affect the contention that this is a viable approach to the study of this particular class of systems.

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