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ANALYSES OF EXCESS MOLAR VOLUMES OF THE ACETONITRILE–WATER SYSTEM USING SEGMENTED COMPOSITION MODELS

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ABSTRACT

A segmented composition model has been used to analyse a number of sets of values of the excess molar volumes of the acetonitrile–water system, covering fairly wide ranges of temperature and pressure. The assumption of the existence of reasonably discrete composition segments for a binary mixture introduces hypothetical standard states of its components The properties of those hypothetical states have been explored and some conclusions made about the possible patterns of molecular aggregation

INTRODUCTION

A procedure has been devloped for analysing the excess physical properties of binary liquid systems which, like the acetonitrile–water system, might reasonably be treated as if possessing three distinct composition segments [1]. The results of analyses, reported in ref. 1, demonstrate that this three-segment model is a viable curve-fitting tool for the excess properties of the acetonitrile–water system. A further feature of the model is the likelihood that its parameters are each associated with some feature of the patterns of molecular aggregation of the system.

One of the analyses, reported in ref. 1, is of excess molar volumes of acetonitrile–water mixtures at 25°C and ambient pressure. As a logical extension of that work, analyses have been performed of excess molar volume data that have been reported for various combinations of temperature and pressure.

Analyses have been carried out upon data sets of widely varying precision and point density in an effort to appraise the sensitivity of the results to the quality of data. It was found that, in the context of the excess molar volume data for this specific system, it is generally reasonable and frequently desirable to use a simplified version of the model described in ref. 1. Efforts have been made to reconcile the results of these analyses with some prevailing ideas concerning structural patterns in binary systems.

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THE THREE-SEGMENT MODEL

In the context of this model, the excess molar volumes of a binary liquid system are defined when values are assigned to the two segment junctions X_A (the mole fraction of acetonitrile) $= X_I$ and X_{II} and to each of the five parameters $\Delta\bar{V}^0_W$, $\Delta\bar{V}^0_A$, B, C_W and C_A. The respective model equations for the three segments are:

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

$$\Delta\bar{V} = BX_A(1 - X_A) + \Delta\bar{V}^0_W X_A \frac{\{(1 - X_A) - (1 - X_I)^2\}}{X_I^2} + \Delta\bar{V}^0_A X_A - \tfrac{1}{2} C_W X_A (X_I - X_A)^2 \tag{1}$$

for the central (microheterogeneous) segment $(X_I \leqslant X_A \leqslant X_{II})$

$$\Delta\bar{V} = BX_A(1 - X_A) + \Delta\bar{V}^0_W (1 - X_A) + \Delta\bar{V}^0_A X_A \tag{2}$$

for the acetonitrile-rich segment $(X_{II} \leqslant X_A \leqslant 1)$

$$\Delta\bar{V} = BX_A(1 - X_A) + \Delta\bar{V}^0_W (1 - X_A) + \Delta\bar{V}^0_A (1 - X_A) \frac{(X_A - X_{II}^2)}{(1 - X_{II})^2} - \tfrac{1}{2} C_A (1 - X_A)(X_A - X_{II})^2 \tag{3}$$

The derivation of these equations is given in ref. 1. For a specific combination of X_I and X_{II} values, the five parameters are optimised by a straightforward least-squares procedure. The optimum combination of X_I and X_{II} is determined by mapping the standard deviation $\sigma(\Delta\bar{V})$ as a function of X_I and X_{II}.

The parameters $\Delta\bar{V}^0_W$ and $\Delta\bar{V}^0_A$ are constants of integration of the Gibbs–Duhem equation over the composition range of the central segment. As such, they arise as excess molar properties of hypothetical standard states of water and acetonitrile, respectively. They may be regarded as measures of the effects of self-aggregation of the two components within that segment. It is appropriate to note that Naberukhin and Rogov [2] have used the term "microheterogeneous" to describe the central segment. It is their contention that there is a tendency for each of the components to form globules or microphases.

B, C_W and C_A are analogs of the Margoules parameters. B is taken to represent the effect, upon the molar volume, of the interactions between unlike pairs of molecules within the microheterogeneous segment. C_W and C_A are related to the effects of interactions between the mixed aggregates, characteristic of the central segment, and aggregates which are characteristic of the pure liquids.

The derivation of eqns. (1)–(3) includes the assumptions that both $\Delta\bar{V}$ and $d\Delta\bar{V}/dX_A$ are single valued at each of the segment junctions; that is equivalent to assuming that both partial molar volumes are single valued at

$X_A = X_I$ and $X_A = X_{II}$. There is, however, no requirement that the partial molar volume derivatives $d\bar{V}_W/dX_A$ and $d\bar{V}_A/dX_A$ need to be single valued at the segment junctions. If such constraints are added to the model, one obtains the relationships

$$\Delta\bar{V}_W^0 = -\tfrac{1}{2}C_W X_I^3 \tag{4}$$

$$\Delta\bar{V}_A^0 = -\tfrac{1}{2}C_A(1 - X_{II})^3 \tag{5}$$

Consequently, the number of model parameters is reduced from five to three and eqns. (1)–(3) become:

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

$$\Delta\bar{V} = BX_A(1 - X_A) + \Delta\bar{V}_W^0\left[(1 - X_A) - (X_I - X_A)^3/X_I^3\right] + \Delta\bar{V}_A^0 X_A \tag{6}$$

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

$$\Delta\bar{V} = BX_A(1 - X_A) + \Delta\bar{V}_W^0(1 - X_A) + \Delta\bar{V}_A^0 X_A \tag{7}$$

TABLE 1

Results of analyses of excess molar volumes of acetonitrile–water mixtures (25°C, 1 atm) using the five-parameter model

Ref.	n	B	$\Delta\bar{V}_W^0$	$\Delta\bar{V}_A^0$	$-\frac{1}{2}C_W X_I^3$	$-\frac{1}{2}C_A(1 - X_{II})^3$	$\sigma(\Delta\bar{V})$
	$X_I = 0.25$, $X_{II} = 0.70$						
3	12	−2.301	−0.274	0.377	−0.230	−0.117	0.0181
4	6	−1.597	−0.367	0.155	0.465	0.169	0.0013
5	24	−1.492	−0.416	0.154	−0.337	0.094	0.0048
6	8	−1.582	−0.418	0.148	−0.372	0.010	0.0015
7	9	−3.589	−0.008	0.586	−1.150	−1.323	0.0605
8	(19)	−1.975	−0.294	0.254	−0.274	−0.015	(0.0021)
9	10	−3.162	−0.080	0.625	0.874	−0.591	0.0196
10	27	−1.507	−0.411	0.138	−0.378	0.162	0.0023
11	10	−1.622	−0.390	0.173	−0.391	0.095	0.0047
12	88	−1.537	−0.402	0.150	−0.382	0.137	0.0027
13	8	−1.571	−0.401	0.161	−0.360	0.189	0.0031
4, 6		−1.455	−0.439	0.127	−0.360	0.136	0.0140
5, 11		−1.516	−0.409	0.154	−0.357	0.104	0.0053
10, 13		−1.529	−0.407	0.145	−0.372	0.172	0.0031
5, 10, 11, 12, 13		−1.520	−0.406	0.148	−0.375	0.139	0.0037
σ*		0.019	0.004	0.005	0.009	0.009	
	$X_I = 0.257$, $X_{II} = 0.695$						
5, 10, 11, 12, 13		−1.517	−0.407	0.147	−0.406	0.147	0.0037
	$X_I = 0.254$, $X_{II} = 0.688$						
12		−1.540	−0.402	0.151	−0.401	0.152	0.0027

n = Number of data points

σ* = Standard errors of parameters (fixed X_I, X_{II})

Units = cm^3

for the acetonitrile-rich segment ($X_{II} \leqslant X_A \leqslant 1$)

$$\Delta\bar{V} = BX_A(1 - X_A) + \Delta\bar{V}_W^0(1 - X_A) + \Delta\bar{V}_A^0\left[X_A - (X_A - X_{II})^3/(1 - X_{II})^3\right] \quad (8)$$

EXCESS MOLAR VOLUMES AT 25°C AND 1 ATM

Eleven sets of values of either densities or excess molar volumes of acetonitrile–water mixtures were taken from the literature [3–13]. Each of the data sets was analysed using the five-parameter version of the three-segment model. The results are set out in Table 1. The optimum combinations of X_I and X_{II} for the larger data sets were all close to $X_I = 0.25$, $X_{II} = 0.70$. Unless stated otherwise, all the results reported in this work correspond to that combination.

The results appear to speak for themselves The data of refs. 3, 7 and 9 are less internally consistent that the other sets and yield significantly different parameter sets. The density tabulation of ref 8 consists not of primary data but of values of a fitting function. Consequently its analysis is more properly judged on the consistency of its parameter values with the other sets than on the standard deviation $\sigma(\Delta V)$.

The other seven data sets were obtained using three different techniques. The data of refs. 4 and 6 were combined to form a representative set of pycnometric values. Similarly, a combined dilatometric set was formed from the data of refs. 5 and 11. The data of refs. 10, 12, and 13 were obtained using vibrating tube densimeters. The data of refs. 10 and 13 were combined into one set, leaving the very large set of ref. 12 to serve as a standard. There is a striking similarity between the parameter sets derived for the three combined data sets. Although the pycnometric data are less precise than the others, it is apparent that the information they provide is fairly useful. It should be acknowledged that some of the less precise data sets were obtained in conjunction with viscosity determinations, where the precision requirements are quite modest

The data of refs. 5, 10, 11, 12 and 13 were combined to form one large set. As can be seen in Table 1, analyses of this large set and of the data of ref. 12 alone give essentially the same results.

It is noted that the conditions expressed by eqns. (4) and (5) are satisfied by the two largest data sets, when the segment junctions are optimised and very nearly so when the combination $X_I = 0.25$, $X_{II} = 0.70$ is imposed. This finding prompted a further series of analyses using the three-parameter model as defined by eqns. (6)–(8) The results of these analyses are given in Table 2.

The differences between the results of the two sets of analyses border on

TABLE 2

Results of analyses of excess molar volumes of acetonitrile–water mixtures (25°C, 1 atm) using the three-parameter model

Ref	B	$\Delta\bar{V}^0_{\mathrm{W}}$	$\Delta\bar{V}^0_{\mathrm{A}}$	$\sigma(\Delta\bar{V})$
	$X_{\mathrm{I}} = 0.25$, $X_{\mathrm{II}} = 0.70$			
3	−1.966	−0.297	0.249	0.0216
4	−1.877	−0.270	0.190	0.0056
5	−1.526	−0.399	0.151	0.0055
6	−1.516	−0.420	0.118	0.0053
7	−1.099	−0.499	−0.069	0.0793
8	−1.792	−0.313	0.189	0.0084
9	−3.190	0.070	0.463	0.0605
10	−1.555	−0.400	0.148	0.0023
11	−1.568	−0.396	0.154	0.0047
12	−1.540	−0.398	0.148	0.0028
13	−1.627	−0.387	0.173	0.0029
4, 6	−1.509	−0.423	0.135	0.0128
5, 11	−1.529	−0.400	0.149	0.0056
10, 13	−1.580	−0.395	0.156	0.0032
5, 10, 11, 12, 13	−1.539	−0.399	0.149	0.0038
σ^*	(0.008)	(0.002)	(0.002)	
	$X_{\mathrm{I}} = 0.257$, $X_{\mathrm{II}} = 0.695$			
5, 10, 11, 12, 13	−1.517	−0.407	0.147	0.0037
	$X_{\mathrm{I}} = 0.254$, $X_{\mathrm{II}} = 0.688$			
12	−1.540	−0.401	0.152	0.0026

being insignificant. It should be noted that there are some systematic differences between the data of ref. 12 and the best three-parameter curve, although they are too small to show up on a normal sized graph. Those differences are not substantially diminished by going to the five-parameter model.

TEMPERATURE DEPENDENCE OF THE EXCESS MOLAR VOLUMES

Refs. 5, 8, 9, 11 and 12 each contain either density or excess molar volume values for acetonitrile–water mixtures at ambient pressure and temperatures other than 25°C. Two other data sets were found for 20°C [14,15]. Each of the data sets was analysed, using both versions of the three-segment model. The results of those analyses are set out in Tables 3 and 4.

From the standpoint of internal consistency, as judged from the standard deviations $\sigma(\Delta\bar{V})$, the data of refs. 9, 14 and 15 are of lower quality than the others. It is also apparent that the data of ref. 12 is of exceptionally high caliber.

TABLE 3

Results of analyses of excess molar volumes of acetonitrile–water mixtures in the temperature range 5–75°C, using the five-parameter model ($X_I = 0.25$, $X_{II} = 0.70$)

Ref.	n	T(°C)	B	$\Delta\bar{V}_W^0$	$\Delta\bar{V}_A^0$	$-\frac{1}{2}C_W X_I^3$	$-\frac{1}{2}C_A(1-X_{II})^3$	σ
8	(19)	5	−1.520	−0.484	0 139	−0 577	0.122	(0.0088)
5	12	6	−1 265	−0 500	0.097	−0.454	0 083	0.0061
8	(19)	15	−1 498	−0.490	0 156	−0 343	0 119	(0 0037)
12	91	15	−1 446	−0 440	0 124	−0 442	0.127	0.0028
14	9	20	−4.413	−0 152	0 950	−0 940	−1 216	0.0470
15	13	20	−2.893	−0 294	0.513	−0 320	0 224	0 0309
12	83	20	−1.533	−0.414	0.142	−0 411	0 143	0 0023
5, 10, 11, 12, 13	157	25	−1.520	−0.406	0.148	−0.375	0 139	0 0037
12	88	25	−1 537	−0.402	0.150	−0.382	0 137	0.0027
12	89	30	−1 618	−0.385	0 176	−0.369	0 113	0 0025
8	(19)	35	−1.627	−0 412	0 174	−0 219	0.144	(0.0023)
9	10	35	−2.956	−0 098	0 529	0.809	−0 213	0.0287
12	58	35	−1.655	−0 377	0 189	−0 341	0 121	0 0032
9	10	45	−2.755	−0 135	0.446	0.712	0.040	0.0403
11	10	50	−1 943	−0.323	0.272	−0 316	−0 203	0.0080
9	10	55	−2 350	−0 205	0.318	0.775	0.442	0.0555
11	9	75	−2 107	−0 315	0 343	−0 235	0 146	0 0082

TABLE 4

Results of analyses of excess molar volumes of acetonitrile–water mixtures in the temperature range 5–75°C, using the three-parameter model ($X_I = 0.25$, $X_{II} = 0.70$)

Ref.	T(°C)	B	$\Delta\bar{V}_W^0$	$\Delta\bar{V}_A^0$	σ
8	5	−1.447	−0 504	0 126	(0 0087)
5	6	−1.294	−0.490	0 099	0 0057
8	15	−1 568	−0.463	0 160	(0.0061)
12	15	−1.447	−0 440	0 125	0 0028
14	20	−2 026	−0.541	0 279	0 0668
15	20	−2 691	−0 318	0.441	0 0285
12	20	−1.537	−0 413	0 143	0.0023
5, 10, 11, 12, 13	25	−1.539	−0 399	0 149	0 0038
12	25	−1 540	−0 398	0 148	0 0028
12	30	−1 577	−0.387	0 158	0 0031
8	35	−1.732	−0 376	0 184	(0 0066)
9	35	−3.240	+0 072	0 469	0 0524
12	35	−1 620	−0.375	0 171	0 0040
9	45	−3.199	+0.043	0 456	0 0513
11	50	−1 624	−0 358	0 158	0.0159
9	55	−3.233	+0 043	0.463	0 0595
11	75	−2 015	−0 316	0.301	0 0103

TABLE 5

Temperature dependence of the three-segment model parameters for the excess molar volumes of the acetonitrile–water system ($X_I = 0.25$, $X_{II} = 0.70$)

FIVE-PARAMETER VERSION

Parameter	Range of T(°C)	fcn(T°C)	$\sigma(B)$
B	5–75	$-1.305-0.0108T$	0.0717
	15–35	$-1.306-0.0101T$	0.0182
$\Delta\bar{V}_W^0$	5–75	$-0.524+5.37\times10^{-3}T-3.38\times10^{-5}T^2$	0.0197
	15–35	$-0.532+7.53\times10^{-3}T-8.86\times10^{-5}T^2$	0.0025
$-\frac{1}{2}C_W X_I^3$	5–75	$-0.547+8.90\times10^{-3}T-6.56\times10^{-5}T^2$	0.0536
	15–35	$-0.547+8.02\times10^{-3}T-6.29\times10^{-5}T^2$	0.0044
$\Delta\bar{V}_A^0$	5–75	$0.083+3.31\times10^{-3}T$	0.0197
	15–35	$0.074+3.28\times10^{-3}T$	0.0037
$-\frac{1}{2}C_A(1-X_{II})^3$	5–75	$0.113+0.52\times10^{-3}T$	0.0155
	15–35	$0.149-0.84\times10^{-3}T$	0.0101

Temperature derivatives at 25°C (cm^3 T^{-1} mole^{-1})

	5–75°C	15–35°C
dB/dT	-0.0108	-0.0101
$d\Delta\bar{V}_W^0/dT$	3.68×10^{-3}	3.10×10^{-3}
$d\Delta\bar{V}_A^0/dT$	3.31×10^{-3}	3.28×10^{-3}
$-\frac{1}{2}X_I^3 dC_W/dT$	5.62×10^{-3}	4.88×10^{-3}
$-\frac{1}{2}(1-X_{II})^3 dC_A/dT$	0.52×10^{-3}	-0.84×10^{-3}

THREE-PARAMETER VERSION

Parameter	Range of T(°C)	fcn (T°C)	$\sigma(B)$
B	5–75	$-1.349-8.18\times10^{-3}T$	0.0711
	15–35	$-1.352-7.70\times10^{-3}T$	0.0190
$\Delta\bar{V}_W^0$	5–75	$-0.523+5.23\times10^{-3}T-3.96\times10^{-5}T^2$	0.0103
	15–35	$-0.537+7.98\times10^{-3}T-9.71\times10^{-5}T^2$	0.0024
$\Delta\bar{V}_A^0$	5–75	$0.097+2.27\times10^{-3}T$	0.0222
	15–35	$0.096+2.14\times10^{-3}T$	0.0029

Temperature derivatives at 25°C

	5–75	15–35
dB/dT	-0.00818	-0.00770
$d\Delta\bar{V}_W^0/dT$	0.00325	0.00313
$d\Delta\bar{V}_A^0/dT$	0.00227	0.00214

The temperature dependence of each of the model parameters was investigated. Two series of analyses were performed. One series involved the combined data of refs. 5, 8, 11 and 12 and spans the temperature range 5–75°C; the other series used only the data of ref. 12 which spans only the range 15–35°C.

With the exception of $\Delta\bar{V}_W^0$ and $-\frac{1}{2}C_W X_I^3$, the parameters were found to vary in an approximately linear fashion with temperature. The results of these analyses are given in Table 5.

It is judged that the use of the five-parameter model, in preference to the three-parameter model, is only warranted for data sets of the high point density and level of precision that is exemplified by those of ref. 12. Even in those cases, the distinction between the results of the two versions of the analytic process must be approached with considerable caution insofar as physical interpretation is concerned.

From the values of the temperature derivatives of the model parameters, which are reported for 25°C in Table 5, it is possible to calculate the molar expansivities $d\bar{V}/dT$ and the coefficients of thermal expansion α in the form of functions of X_A. Plots of the excess coefficients of thermal expansion and of the partial molar excess expansivities against X_A, based upon the results given in Table 5 are very similar to those shown in ref. 12.

The parameters $\Delta\bar{V}_W^0$ and $\Delta\bar{V}_A^0$ arise in the derivation of the model

TABLE 6

Results of analyses of the temperature dependence of hypothetical standard states of acetonitrile and water in their mixtures

	$\bar{V}^0$(0°C)	A_1	A_2	A_3
WATER				
5–75°C				
$\bar{V}^0$ (Normal)	18.013	−0.023	+1 054	−0 258
$\bar{V}^0$ (Hypothetical)	17.490	+0 538	+0.669	−0 266
15–35°C				
$\bar{V}^0$ (Normal)	18.006	+0.044	+0.829	
$\bar{V}^0$ (Hypothetical)	17.468	+0 866	−0 200	
ACETONITRILE				
5–75°C				
$\bar{V}^0$ (Normal)	51.081	7 285	−1 088	2.187
$\bar{V}^0$ (Hypothetical)	51.179	7.480	−0 920	2 017
15–35°C				
$\bar{V}^0$ (Normal)	51.141	6.550	1 400	
$\bar{V}^0$ (Hypothetical)	51 237	6.762	1 400	

Volume units = cm^3.

Fitting equation

$$\bar{V}^0 = \bar{V}^0(0°C) + A_1(T/100) + A_2(T/100)^2 + A_3(T/100)^3$$

equations in a manner which identifies them as excess properties of hypothetical standard states. The temperature dependence of the two pure liquid molar volumes are known [9,12,16,17]. Consequently it is possible to calculate the molar volumes of the two hypothetical standard states and to compare their respective temperature dependences with those of the pure (normal) liquids.

The results of fitting polynomial functions of T(°C) to the molar volumes of both the normal and hypothetical states of the two component liquids are set out in Table 6. It is noted that there is an appreciable difference between the temperature sensitivities of the molar volumes of the two states of water but not for those of acetonitrile.

PRESSURE DEPENDENCE OF THE EXCESS MOLAR VOLUMES

Refs. 11 and 13 contain tabulations of excess molar volumes of acetonitrile–water mixtures at 25°C and pressures up to 250 MPa. These data sets are relatively sparse and only the results of the three-parameter analyses are considered. The results of those analyses are given in Table 7.

The two data sets appear to be mutually consistent; with the dilatometric data of ref. 11 showing slightly better internal consistency than does the densimetric data of ref. 13. The optimised parameter values vary in a

TABLE 7

Results of analyses of excess molar volumes of acetonitrile–water mixtures at elevated pressures ($T = 25°C$, $X_{I} = 0.25$, $X_{II} = 0.70$)

Ref	P(MPa)	B	$\Delta\bar{V}^0_W$	$\Delta\bar{V}^0_A$	$\sigma(\Delta\bar{V})$
	0.1	−1.539	−0.399	0.149	
11	10	−1.385	−0.370	0.145	0.0020
11	50	−0.956	−0.293	0.138	0.0028
13		−0.899	−0.299	0.120	0.0088
11+13		−0.933	−0.296	0.134	0.0060
11	100	−0.633	−0.225	0.114	0.0046
13		−0.610	−0.221	0.112	0.0091
11+13		−0.627	−0.223	0.113	0.0070
11	150	−0.465	−0.172	0.099	0.0057
13		−0.443	−0.167	0.102	0.0102
11+13		−0.461	−0.169	0.101	0.0083
11	200	−0.312	−0.136	0.076	0.0061
13		−0.330	−0.127	0.095	0.0100
11+13		−0.326	−0.131	0.085	0.0089
11	250	−0.265	−0.102	0.078	0.0058
13		−0.355	−0.087	0.107	0.0090
11+13		−0.306	−0.095	0.092	0.0076

Volume units = cm^3

TABLE 8

Pressure dependence of the parameters of the three segment model for the excess molar volumes of the acetonitrile–water system at 25°C

Polynomial fit

B	$= -1.527 + 1.378(P/100)$	$-0.568(P/100)^2$	$+0.088(P/100)^3$
$\Delta\bar{V}_W^0$	$= -0.397 + 0.243$	-0.082	$+0.013$
$\Delta\bar{V}_A^0$	$= 0.151 - 0.042$	$+0.004$	

Units volume = cm^3, pressure = MPa

Tait equation parameters [eqn (9)]

	B_0 [a]	α	$\beta(10^8\ \mathrm{Pa})$
B	-1.540	1.201	1.072
$\Delta\bar{V}_W^0$	-0.399	1.244	1.631
$\Delta\bar{V}_A^0$	$+0.149$	-24.87	-119.6

Pressure derivatives at $P = 0.1$ MPa (cm^3 $\times 10^{-5}$/Pa)

	From polynomial fit	From Tait equation
$(\delta B/\delta p)T$	1.378×10^{-3}	1.287×10^{-3}
$(\delta\Delta\bar{V}_W^0/\delta p)T$	0.243×10^{-3}	0.246×10^{-3}
$(\delta\Delta\bar{V}_A^0/\delta p)T$	-0.042×10^{-3}	-0.031×10^{-3}

[a] Values adopted for the parameters at zero pressure

reasonably smooth fashion with increasing pressure. The polynomial pressure dependences of the three parameters were estimated and are given in Table 8. The pressure dependences of the parameters may also be expressed in terms of an analog of the Tait equation

$$\frac{B_0 - B}{B_0 p} = \frac{\alpha}{\beta + p} \tag{9}$$

where B_0 is the value of the parameter at zero pressure.

If the B_0 values are fixed, it is a simple matter to optimise α and β. The pressure derivatives of the model parameters, at 0.1 MPa (1 atm) and 25°C, were estimated from both the polynomial and Tait equation analyses. The two sets of values are quite similar, as shown in Table 8.

From the values derived for $\Delta\bar{V}_W^0$ and $\Delta\bar{V}_A^0$, together with the molar volumes of the pure liquids [13,16,17], it was possible to determine the sensitivities of the molar volumes of the hypothetical (microphase) states of the components to applied pressure. The results of those analyses are given in Table 9. As with the sensitivities to temperature variations, there is little difference between the normal and hypothetical states of acetonitrile. Larger differences are found between the pressure sensitivities of the molar volumes of the two states of water.

TABLE 9

Results of analyses of the pressure dependence of hypothetical standard states of water and acetonitrile in their mixtures at 25°C

WATER

$\bar{V}^0$ (Normal) $= 18.070 - 0.819(P/100) + 0.114(P/100)^2 - 0.011(P/100)^3$
$\bar{V}^0$ (Hypothetical $= 17.671 - 0.574 \quad + 0.030 \quad - 0.003$

Tait equation parameters

	$\bar{V}^0$(0Pa)	α	β
$\bar{V}^0$ (Normal)	18.070	0.310	6.83×10^8 Pa
$\bar{V}^0$ (Hypothetical)	17.671	0.405	12.30

ACETONITRILE

$\bar{V}^0$ (Normal) $= 52.858 - 5.347(P/100) + 1.524(P/100)^2 - 0.211(P/100)^3$
$\bar{V}^0$ (Hypothetical) $= 53.011 - 5.396(P/100) + 1.533(P/100)^2 - 0.212(P/100)^3$

Tait equation parameters

	$\bar{V}^0$ (0Pa)	α	β
$\bar{V}^0$ (Normal)	= 52.870	0.106	0.388×10^8 Pa
$\bar{V}^0$ (Hypothetical)	= 53.019	0.107	0.385

Units: volumes = cm^3, pressures = MPa

TABLE 10

Results of analyses of excess molar volumes of acetonitrile–water mixtures at elevated pressures ($T = 50$ and 75°C, $X_{\mathrm{I}} = 0.25$, $X_{\mathrm{II}} = 0.70$)

P (MPa)	B	$\Delta\bar{V}^0_{\mathrm{W}}$	$\Delta\bar{V}^0_{\mathrm{A}}$	σ
$T = 50$°C				
0.1	−1.624	−0.358	0.248	0.0159
10	−1.461	−0.331	0.193	0.0131
50	−0.854	−0.267	0.175	0.0113
100	−0.451	−0.213	0.129	0.0094
150	−0.274	−0.170	0.116	0.0090
200	−0.155	−0.139	0.096	0.0054
250	−0.096	−0.112	0.090	0.0047
$T = 75$°C				
0.1	−2.015	−0.316	0.301	0.0103
10	−1.572	−0.307	0.277	0.0107
50	−0.709	−0.252	0.217	0.0105
100	−0.308	−0.198	0.177	0.0081
150	−0.101	−0.161	0.146	0.0076
200	0.014	−0.136	0.115	0.0064
250	0.063	−0.111	0.101	0.0052

Gotze and Schneider [11] provide tables of excess molar volumes in the pressure range 0.1–250 MPa at both 50 and 75°C. Each of the data sets was analysed using the three-parameter model. The results of those analyses are given in Table 10.

The sensitivity of the model parameters to pressure changes at 50 and 75°C was investigated giving the results set out in Table 11.

The molar volumes of normal water at elevated temperatures and pressures [16,17] were combined with the values obtained for $\Delta\bar{V}_W^0$ to give estimates of the molar volumes of the hypothetical state. The results of analyses of those estimates are given in Table 12. There appears to be a lack

TABLE 11

Pressure dependence of the parameters of the three-segment model for the excess molar volumes of acetonitrile–water mixtures at 50 and 75°C ($X_I = 0.25$, $X_{II} = 0.70$)

Polynomial fits

B (50°C)	$= -1.632 + 1.943(P/100)$	$-0.912(P/100)^2$	$+0.153(P/100)^3$
(75°C)	$= -1.939 + 3.124$	-1.749	$+0.329$
$\Delta\bar{V}_W^0$ (50°C)	$= -0.355 + 0.206$	-0.073	$+0.012$
(75°C)	$= -0.319 + 0.157$	-0.042	$+0.005$
$\Delta\bar{V}_A^0$ (50°C)	$= 0.227 - 0.118$	$+0.026$	
(75°C)	$= 0.293 - 0.144$	$+0.027$	

Tait equation parameters

	B_0 (assumed)	α	β
B (50°C)	-1.625	1.384	1.063×10^8 Pa
(75°C)	-2.015	1.224	0.446
$\Delta\bar{V}_W^0$ (50°C)	-0.358	1.077	1.520
(75°C)	-0.316	1.388	2.821
$\Delta\bar{V}_A^0$ (50°C)	$+0.227$	0.983	5.549
(75°C)	$+0.301$	0.982	1.251

Pressure derivatives at P = 0 *(*$cm^3 \times 10^{-5}/Pa$*)*

	50°C		75°C	
	Polynomial	Tait	Polynomial	Tait
$(\delta\beta/\delta P)_T$	1.943×10^{-3}	2.116×10^{-3}	3.124×10^{-3}	5.530×10^{-3}
$(\delta\Delta\bar{V}_W^0/\delta P)_T$	0.206×10^{-3}	0.254×10^{-3}	0.157×10^{-3}	0.155×10^{-3}
$(\delta\Delta\bar{V}_A^0/\delta P)_T$	-0.118×10^{-3}	-0.042×10^{-3}	-0.144×10^{-3}	-0.236×10^{-3}

TABLE 12

Results of analyses of the pressure dependence of the molar volume of a hypothetical state of water in its mixtures with acetonitrile at 50 and 75°C

T = 50°C

Polynomial fits

$\bar{V}_W^0$ (Normal)	$=18.234-0.800(P/100)$	$+0.107(P/100)^2$	$-0.010(P/100)^3$
$\bar{V}_W^0$ (Hypothetical)	$=17.880-0.595$	$+0.034$	$+0.002$

Tait equation parameters

	$\bar{V}_W^0$ (0 atm)	α	β
Normal	18.234	0.308	6.972×10^8 Pa
Hypothetical	17.876	0.410	12.264

T = 75°C

Polynomial fits

$\bar{V}_W^0$ (Normal)	$=18.482-0.832(P/100)$	$+0.113(P/1000^2$	$-0.010(P/100)^3$
$\bar{V}_W^0$ (Hypothetical)	$=18.163-0.675$	$+0.071$	-0.005

Tait equation parameters

	$\bar{V}_W^0$ (0 atm)	α	β
Normal	18.482	0.305	6.740×10^8 Pa
Hypothetical	18.166	0.269	6.863

Pressure derivatives at P = *0* (*cm*^{3} × *10*$^{-5}$*/Pa*)

		25°C	50°C	75°C
$(\delta V/\delta P)_T$ Normal	Polynomial	−0.819	−0.800	−0.832
	Tait	−0.820	−0.806	−0.836
Hypothetical	Polynomial	−0.574	−0.595	−0.675
	Tait	−0.581	−0.598	−0.712

of information about the molar volumes of pure acetonitrile at elevated temperatures and pressures.

DISCUSSION OF RESULTS

Curve fitting

In the course of this work, an alternative, simpler version of the three-segment model, described in ref. 1, has been introduced. From the experience gained in carrying out the analyses reported in this work and those involved in various other investigations, it has been possible to form some general conclusions about the relative merits of the three- and five-parameter versions.

(1) The three-parameter version has proved to be a fairly satisfactory curve-fitting tool for all of the excess volume data sets.

(2) For sparse data sets, the three-parameter version is preferred over the five-parameter version and also over conventional continuous function fits since it is far more resistant to the effects of modest data errors. This point is particularly well illustrated by the results of analyses of viscosity data [18].

(3) The use of the five-parameter version is only warranted for data sets with a uniformly high point density and a reasonably high level of precision, as exemplified by those reported in ref. 12.

(4) The finding that there are small systematic differences between the excess volume data of ref. 12 and the optimised five-parameter model curves suggest that, for the water-rich segment at least, there is room for improvement in the model. Since the differences are very small, the excess molar volume data is not a suitable vehicle for further model elaboration. There are, however, other data accumulations for which the shortcomings of the five-parameter model as a curve-fitting tool are more pronounced and it is hoped that they will furnish the basis for an improved model [19].

(5) The same combination of values for the segment junctions X_{I} and X_{II} was used for all of the analyses. That combination was only adopted as being universally appropriate after it has been found to be very close to being optimal for all of the more substantial data sets.

Structural information

The central composition segment ($X_{\mathrm{I}} \leqslant X_{\mathrm{A}} \leqslant X_{\mathrm{II}}$) has been termed "microheterogeneous" [2]. It is implied that the spatial distribution of the component molecules is not random; there being a tendency towards the formation of small homogeneous aggregates or microphases. One possible arrangement, suggested in ref. 1, is that of inverted micelles with aqueous cores that are ensheathed by acetonitrile molecules which tend to be oriented with their polar groups in contact with the cores.

It is appropriate to note, in this context, that the acetonitrile–water system has an upper critical solution temperature of -1.05 ± 0.15°C at $X_{\mathrm{A}} = 0.38 \pm 0.02$ [5].

The quantities $\Delta\overline{V}_{\mathrm{W}}^{0}$ and $\Delta\overline{V}_{\mathrm{A}}^{0}$ correspond to excess molar volumes of hypothetical standard states. If one accepts the general thesis of the existence of microphases, these two quantities may be presumed to represent information about microphase structure. It was the possibility that a consistent and plausible set of characteristics of the microphases might emerge that prompted the performance of many of the analyses reported in this work.

$\Delta\bar{V}^0_W$

Much has been written about the structure of water both as a pure liquid and in the role of a solvent. Descriptive statements made in a recent review article [20] have been accepted as a basis for the following discussion.

The structure of liquid water is described in terms of the existence of two types of local molecular grouping. In addition to the ice-like (hexagonal) pattern of aggregation, water molecules tend to organise in various other polyhedric geometries. An equilibrium is deemed to exist between hexagonal grouping, on the one hand, and the more compact alternative polyhedric groupings on the other. The equilibrium is shifted towards more abundant polyhedric grouping as either the temperature or the external pressure is increased.

This model appears to account for the existence of the density maximum at 4°C and for the unusually high heat capacity. This structural equilibrium is regarded as being sensitive not only to changes in pressure and temperature, but also to the presence of dissolved species.

The finding that $\Delta\bar{V}^0_{\mathrm{W}}$ is negative is consistent with the idea that the presence of acetonitrile molecules tends to diminish the fraction of the water molecules involved in hexagonal aggregation.

In the pure liquid, the transition from hexagonal to the alternative polyhedric groupings is endothermic. Three-segment model analyses of the heats of mixing at 25°C indicate that, in acetonitrile–water mixtures, the change from normal water to the hypothetical microphase state is modestly exothermic [1]. This is consistent with the statement that the presence of a relatively inert solute increases the net hydrogen bonding of the nearest water molecules [20].

From the results given in Table 6, it is seen that the microphase state has a substantially higher coefficient of thermal expansion than does the normal liquid. Indeed, the microphase state lacks the 4°C density maximum of the normal liquid. It is rationalised that in normal water the natural tendency for a substance to expand on heating is offset by the conversion of hexagonal into more compact hexagonal groupings. That the microphase state should behave more conventionally, in this regard, is consistent with a relative lack of hexagonally grouped molecules.

$\Delta\bar{V}^0_{\mathrm{W}}$ decreases significantly with increasing pressure. In the normal liquid, the elevation of external pressure would be expected to favor the conversion of hexagonal to the more compact polyhedric groupings in the same way that it favors the conversion of ice into liquid water. The results given in Table 12, which describe the microphase state as being less compressible than the normal liquid, are consistent with the former having a substantially greater proportion of molecules in the more compact patterns of aggregation.

One of the noteworthy properties of normal water is that its isothermal compressibility has a minimum value at 46°C. This is borne out by the pattern of $(\delta V/\delta P)_T$ given for normal water in Table 12. While the information about the microphase state at elevated temperatures and pressures is not as precise as one might wish, the indications are that it behaves more like a conventional liquid.

$\Delta\bar{V}_A^0$

Acetonitrile boils at 81.6°C and has a molar heat of vaporisation of 8.17 kcal mole^{-1} [21]. It presumably qualifies for the description of a moderately structured liquid. Such distinctive aggregative patterns as exist are assumed to owe their origin to the attractions between the polar and polarisable CN groups.

It is envisaged that in the transition from the normal liquid to the microphase state, contacts between pairs of polar groups are replaced by polar group contact with the aqueous microphases. Thus the dominant adhesive aspect of pure acetonitrile self-aggregation is reduced. This conjecture is consistent with the determination that both $\Delta\bar{V}_A^0$ and $\Delta\bar{H}_A^0$ are positive [1].

While there are marked differences between the responses of the molar volumes of normal and microphase water to changes in temperature and pressure, those of the two states of acetonitrile are quite similar. From Table 6, it is evident that the microphase state has a slightly higher expansivity than does the pure liquid. From the manner in which $\Delta\bar{V}_A^0$ varies with external pressure (Tables 7 and 10), it is evident that the microphase state is more easily compressed than the pure liquid. Both responses to changes of condition are consistent with weaker intermolecular forces in the microphase state.

B

In some fashion, parameters of the type B represent the effects upon the molar properties of the interactions between unlike pairs of molecules. The values correspond to the mixing of components that are in their hypothetical rather than their normal liquid states.

Any model of the structure of the interface between the two microphases must reconcile the findings that, while $B(\Delta\bar{V})$ is quite large and negative, $B(\Delta\bar{H})$ is significantly positive [1]. A highly idealised representation of the suggested structure of the interface is shown in Fig. 1.

In the context of this model, the quantity $B(\Delta\bar{V})$ is related to $2r_B - (r_A + r_W)$. Even in the microphase state, water molecules are arranged in a relatively open structure. The distance r_A is thought to be typical of the relatively loose packing of hydrocarbons. Evidently the water and acetonitrile molecules can pack together in a manner consistent with a relatively small distance r_B.

That the excess molar enthalpy component $B(\Delta\bar{H})$ is positive implies that, although the attractions between the nitrile groups and water molecules are strong enough for the two liquids to be miscible, they are not so strong as

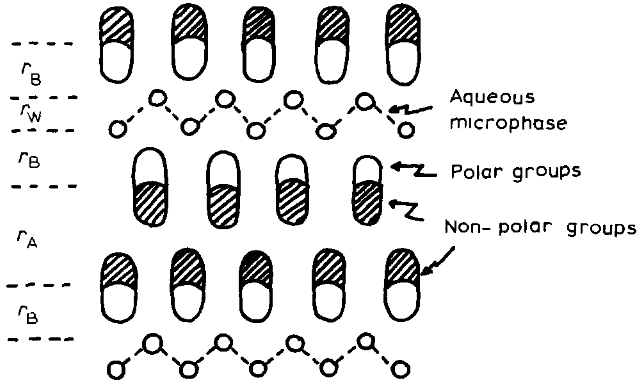

Fig 1 Suggested microphase layering pattern in the acetonitrile–water system

to compensate for the net decrease in the number of hydrogen bonds.

$B(\Delta\bar{V})$ becomes more negative as the temperature increases. The magnitude of the changes in $B(\Delta\bar{V})$ are such as to suggest that while the microphases exhibit fairly significant thermal expansion, there is relatively little change in the dimensions of their interface.

$B(\Delta\bar{V})$ becomes less negative as the external pressure is increased and even changes sign with the combination of high pressure and temperature (Table 10). This suggests that the interfacial dimensions are less sensitive to pressure than are the microphase volumes. In that context it is noted that acetonitrile is considerably more compressible than water.

The water-rich segment

In a detailed analysis of the physical properties of relatively dilute solutions of polar organic solvents in water, one might hope to find evidence of two distinct types of solute–solvent interaction: one involving the polar group, the other the hydrocarbon group or groups.

Since the three-parameter model appears to serve as well as the five-parameter model in reproducing the excess molar volume curves, one deduces that either (a) the volume changes are dominated by one type of interaction, (b) the two interactions have comparable effects, or (c) there is little or no orientational preference of the acetonitrile molecules relative to neighboring water molecules.

It has been found that the five-parameter model is significantly better than the three-parameter model in accounting for the heats of mixing and excess heat capacities in the water-rich region [19]. It is by no means obvious what the significance of the parameter C_W is. Efforts are being made to develop a more explicit model for the water-rich segment. It is suggested that the results of these analyses are inconsistent with the idea that, in the water-rich segment, the acetonitrile molecules occupy cavities in an essentially unperturbed aqueous environment.

The acetonitrile-rich segment

The model proposed for this segment places the solute water molecules on the inside of inverted micellular aggregates. Analyses of the physical properties of dilute solutions of water in acetonitrile might be hoped to furnish evidence of the nature of interactions between these micellular aggregates and aggregates of pure acetonitrile. That the three-parameter version serves as well as the five-parameter version in this segment seems to suggest that, insofar as the volume is concerned, there is little difference between the effects of interactions between the two dissimilar aggregates on the one hand and between pairs of micellular aggregates on the other.

SUMMARY

Analyses have been performed on excess molar volume data for the acetonitrile–water system at various temperatures and pressures. As the name is intended to suggest, the three-segment analytic model incorporates the assumption that the total composition range of this system can be treated as having three distinct segments. In addition to the five-parameter version of this model, which has been described earlier [1], a modified three-parameter version was used.

The combination of the segment junction values of X_A (mole fraction of acetonitrile) equal to 0.25 and 0.70 was found to be close to the optimal combinations for the more extensive and precise of the individual data sets and was adopted as a fixed entity for the entire series of analyses.

Most of the individual data sets are relatively sparse (less than 20 independent measurements to cover the total composition range). In such cases, the three-parameter version is the preferred curve-fitting tool since the additional parameters are apt to give rise to undue sensitivity to even modest individual data errors.

There is little difference between the optimised model excess molar volume curves obtained for the three- and five-parameter analyses of the higher quality data sets. It is noted that for certain other types of data, there is a marked improvement in the quality of fit in going from the three- to the five-parameter model, so the five-parameter version is by no means redundant. It is also noted that there appears to be room for improvement upon the five-parameter model as far as reproducing and interpreting excess properties in the water-rich segment is concerned.

A natural consequence of assuming the existence of discrete composition segments is the appearance of hypothetical standard states of both water and

acetonitrile. Associated with these states are the excess molar volumes $\Delta \bar{V}_W^0$ and $\Delta \bar{V}_A^0$, which are parameters of the analytical models. From the results of the numerous analyses, it was possible to estimate the molar volumes of the hypothetical states and to compare their respective sensitivities to changes in temperature and pressure with those of the normal liquids.

The hypothetical state of water is significantly more compact than the normal liquid and, unlike the latter, exhibits conventional patterns of thermal expansion and isothermal compression. The hypothetical state of acetonitrile is somewhat less compact than the normal liquid.

The effects upon the molar volumes of acetonitrile–water contact within the central composition segment are represented by the parameter *B*. Arguments are presented to demonstrate that the combinations of $\Delta \bar{V}_W^0$, $\Delta \bar{V}_A^0$ and *B* are consistent with, but do not prove, the existence of inverted micellular aggregates within the central segment. This structural model is consistent with the use of the term microphases to describe the aqueous core and organic outer layer of the mixed aggregates.

The lack of distinction between the results of the three- and five-parameter analyses leads to the conclusion that the excess molar volume data yield little in the way of information about the structural characteristics of either the water-rich or acetonitrile-rich segments. It is hoped that some such information will emerge from studies of other properties of the system [19].

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