Thermochimica Acta, 131 (1988) 153–170
Elsevier Science Publishers B V , Amsterdam – Printed in The Netherlands

EXCESS MOLAR VOLUMES AND ENTHALPIES OF THE 2-BUTOXYETHANOL + WATER SYSTEM AT 25 °C

MICHAEL I DAVIS and M CONCEPCION MOLINA
Department of Chemistry, University of Texas at El Paso, El Paso, TX 79968 (U S A)

GERARD DOUHERET
Laboratoire de Thermodynamique et Cinétique Chimique, U A C N R S 434, Université Blaise Pascal, F-63170, Aubière (France)

(Received 1 December 1987)

ABSTRACT

Excess molar volumes and excess molar enthalpies have been measured for the 2-butoxyetanol + water system at 25 ° C, across the total composition range The data have been used as a vehicle for modifying the parameterization of the four-segment model equations and for examining the effects of various constraints upon the flexibility of the model The results of the analyses are consistent with the formation of pseudomicellar aggregates

INTRODUCTION

Attention has been drawn to the similarity between the composition dependence of the macroscopic properties of the 2-butoxyethanol + water system and that of non-ionic surfactant + water systems which are known to form micellar aggregates [1] It is argued that the similarity exists because the amphiphilic butoxyethanol molecules form metastable aggregates of a micelle-like nature in an aqueous environment Most of the more detailed studies of the composition dependence of the thermodynamic properties of this system have dealt almost exclusively with mixtures in which the mole fraction of the organic component is relatively small We are interested in trying to interpret the macroscopic data for binary hydro-organic systems across the entire composition range This has involved measuring a number of properties at quite small concentration intervals

In this article we wish to report the results of densimetric and solution calorimetric measurements that were carried out in the El Paso laboratory High quality density data for this system have been reported by Roux [2] Since we required a substantially higher point density at higher mole fractions, we saw fit to make additional measurements in both the Aubière and El Paso laboratories The Aubière data have been reported elsewhere [3]

0040-6031/88/$03.50

Three sets of excess enthalpy data for this system were found in the literature [4–6] These data are too sparse and lacking in mutual consistency for the types of analyses that we wished to perform

EXPERIMENTAL

Samples of Aldrich spectrophotometric grade (99 + %) 2-butoxyethanol were used without further purification Aqueous mixtures were prepared using distilled and deionized water

Volumetric

Densities were determined using a Sodev Model 03-D high precision flow densimeter [7] The temperature was maintained at 25 00 ± 0 02° C using a Sodev Model CT-L programmable circulating thermostat

The mixtures were prepared by weight. The mole fractions are considered to be reliable to $\pm 1 \times 10^{-4}$ The reproducibility of the densities is of the order of 2×10^{-5} g cm^{-3} The value obtained for the density of 2-butoxyethanol of 0 89647 g cm^{-3} compares quite favorably with the values of 0 89678 [2] and 0 89649 [3]

Calorimetric

Heats of mixing were determined using a Parr solution calorimeter [8] The mixing process involves releasing one component, from a 20 ml sample cell, into an insulated reaction vessel that contains roughly 100 ml of the second component. The quantities of the two components were determined by weight. The temperature of the contents of the reaction vessel was monitored by means of a calibrated thermistor and recorded using a Hewlett-Packard 3467A logging multimeter The heat capacity of the calorimeter was determined by the procedure recommended by the manufacturer Thermograms were analyzed graphically, by the method described in ref 8, to obtaine values for the effective temperature of the mixing process, T_m, and the temperature increment ΔT

Heat capacities of the mixtures were obtained by interpolation of the data of Roux [9] The same data were used to correct the $\Delta \overline{H}$ values from T_m to 25° C

Due to the disparity in the volumes of the sample cell and the reaction vessel, it was impossible to span the entire composition range by mixing pure components. The data set therefore includes excess enthalpy values derived from the measurement of the heats of mixing of one pure component (in the sample cell) with mixtures of predetermined excess enthalpy

TABLE 1

Excess molar volumes of the 2-butoxyethanol + water system at 25 ° C

X(BuOEtOH)	$\Delta\bar{V}$	X(BuOEtOH)	$\Delta\bar{V}$	X(BuOEtOH)	$\Delta\bar{V}$
0 00377	−0 0350	0 1635	−0 5605	0 7168	−0 4970
0 00567	−0 0533	0 2196	−0 6479	0 7200	−0 4957
0 00617	−0 0584	0 2261	−0 6572	0 7575	−0 4275
0 00768	−0 0735	0 2511	−0 6848	0 7893	−0 3772
0 00901	−0 0866	0 2704	−0 7010	0 7947	−0 3729
0 01235	−0 1196	0 3121	−0 7264	0 8160	−0 3404
0 01323	−0 1266	0 3558	−0 7494	0 8400	−0 2995
0 01852	−0 1696	0 3914	−0 7566	0 8455	−0 2967
0 02644	−0 2056	0 4222	−0 7527	0 8459	−0 2856
0 03187	−0 2291	0 4663	−0 7409	0 8563	−0 2696
0 03940	−0 2535	0 4998	−0 7202	0 8652	−0 2488
0 04253	−0 2612	0 5311	−0 6998	0 8907	−0 2170
0 04443	−0 2711	0 5510	−0 6854	0 9006	−0 1935
0 05071	−0 2907	0 5829	−0 6461	0 9209	−0 1500
0 0922	−0 4060	0 6121	−0 6280	0 9373	−0 1224
0 1079	−0 4468	0 6559	−0 5760	0 9696	−0 0655
0 1487	−0 5313	0 6768	−0 5518	1	0

Units cm^3 mol^{-1}

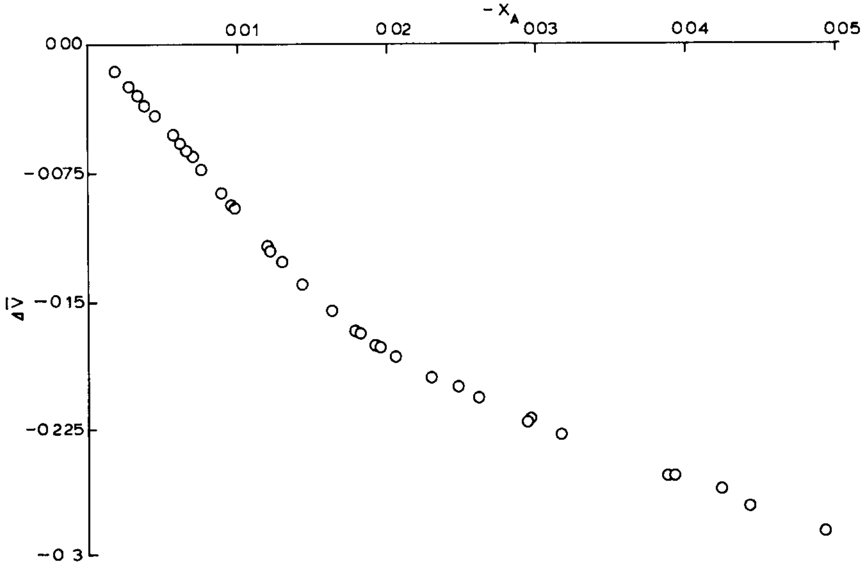

Fig 1 Excess molar volumes of the 2-butoxyethanol–water system at 25 ° C from this work and refs 2 and 3 for the composition range $0 < X$(BuOEtOH) $< 0\ 05$ (units cm^3 mol^{-1})

RESULTS

Values of the excess molar volumes for the 2-butoxyethanol + water system at 25 °C are presented in Table 1 These values are generally

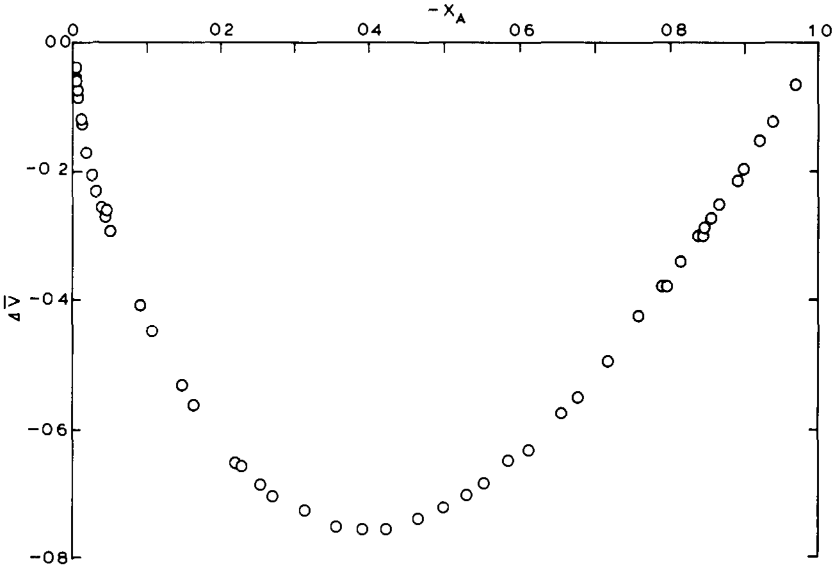

Fig 2 Excess molar volumes of the 2-butoxyethanol + water system at 25 °C El Paso data for the entire composition range (units $cm^3\ mol^{-1}$)

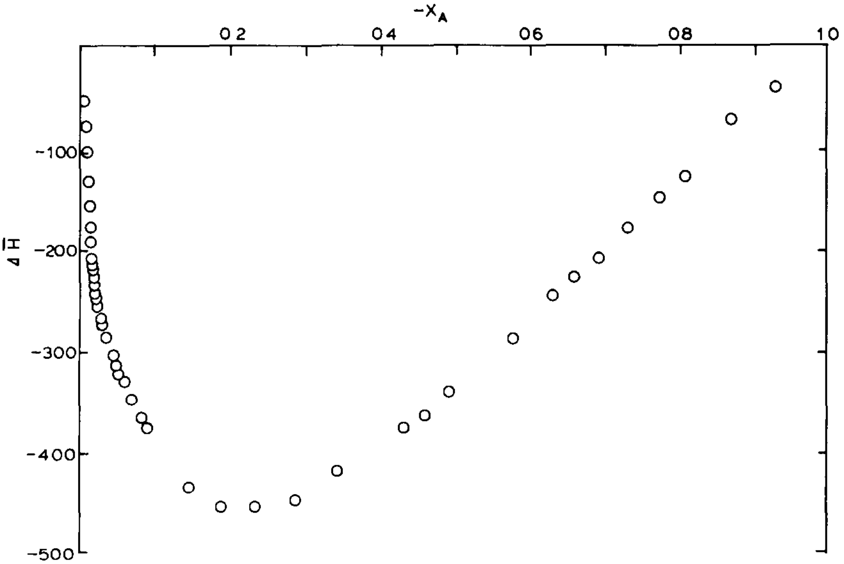

Fig 3 Excess molar enthalpies of the 2-butoxyethanol + water system at 25 °C for the entire composition range (units $J\ mol^{-1}$)

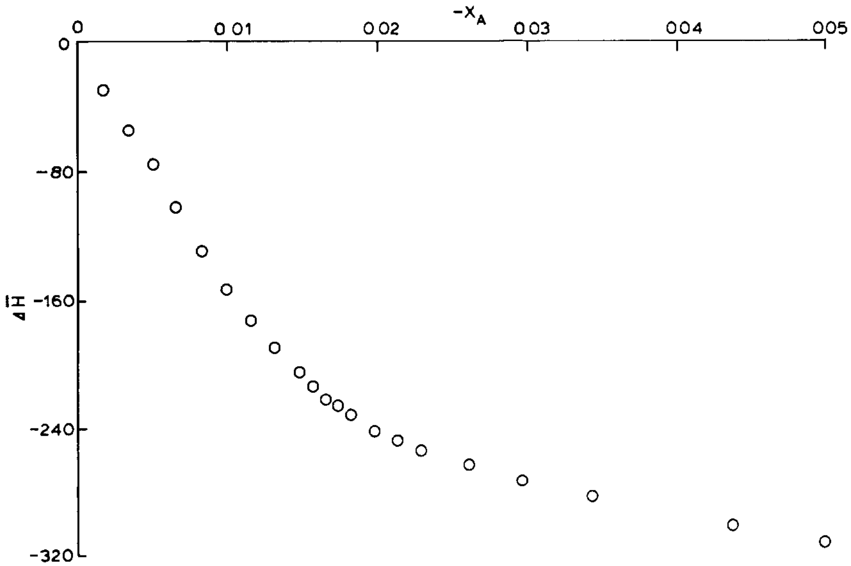

Fig. 4. Excess molar enthalpies of the 2-butoxyethanol + water system at 25 °C for the composition range $0 < X(\text{BuEtOH}) < 0.05$ (units J mol^{-1}).

consistent with those obtained from the data of refs. 2 and 3. The level of mutual consistency is particularly gratifying at low organic mole fractions, as is evident from Fig. 1, which shows a plot of the combined data sets in the range $0 < X_A < 0.05$. The El Paso data are shown across the entire composition range in Fig. 2, revealing a reasonable level of internal consistency.

Values of the excess molar enthalpies for this system at 25 °C are given in Table 3. There is a fairly good level of internal consistency across the entire composition range, as is evident from Fig. 3. Of special note is the pronounced shift in slope of the data around $X_A = 0.025$ which is clearly discernible from Fig. 4 and which mimics a similar trait of the excess molar volumes that appears in Fig. 1.

DATA ANALYSIS

The data were analyzed in the general framework of the four-segment model. The origin and evolution of that model have been described in a number of earlier articles [10–12].

The model is based upon the assumption that one may treat binary hydro-organic systems as though their total composition ranges are partitioned into four reasonably discrete segments. Within each segment, the molar (or excess molar) properties appear to exhibit relatively simple characteristic functional dependence upon mole fractional composition that is, in some manner, determined by the variations in the patterns of molecular aggregation

It was assumed to be appropriate to assign cubic dependence upon mole fraction to each of the segments with the exception of that which spans the range $X_2 < X_A < X_3$, where quadratic dependence seemed to be warranted The condition that $\Delta\bar{Q}$ should be single-valued at each of the three segment junctions is obviously a necessary constraint

In the basic seven-parameter version, the model is further constrained by the condition that $\mathrm{d}\Delta\bar{Q}/\mathrm{d}X_A$ should be single-valued at each segment junction In ref 12 some consideration was given to the effects of relaxing this latter set of constraints It was felt that the data for this particular binary system might be suitable for pursuing a more detailed study of the effects of varying the level of flexibility of the model In addition, we have given some thought to modifying the parameter base

The water-rich segment spans the composition range $0 < X_A < X_1$ In this particular system, one might wish to refer to it as "premicellar" One may write for this segment

$$\Delta\bar{Q}_{(W)} = a_W X_A + b_W X_A^2 + c_W X_A^3 \tag{1}$$

This may be regarded as a form of McMillan–Mayer equation [13]

The parameter a_W is the apparent (and partial) excess molar property of the solute at infinite aqueous dilution b_W is a solute–solute pair interaction parameter which is generally interpreted as being dominated by the effects of the overlap of the solute's aqueous cospheres In some fashion, c_W is a measure of the effects of hydrophobic aggregation

The segment junction X_1 is some kind of analog of a critical micelle concentration The level of direct contact between the hydrophobic butyl groups and water has been reduced to an extremely low level The solvated organic aggregates do not, however, appear to constitute a separable phase

For want of a better expression, the term "secondary" has been applied to the segment which spans the composition range $X_1 < X_A < X_2$ Conceivably it would be appropriate to refer to it as the "pseudomicellar" segment. For this segment, we write

$$\Delta\bar{Q} = (s) = q_S + a_S X_A + b_S X_A^2 + c_S X_A^3 \tag{2}$$

Analogs of q_S and a_S appear in the equations of the pseudophase [14] and mass action [15] models for this composition range

Increasing the mole fraction of a surfactant beyond its critical micelle concentration is believed to result in increase in size and modification in shape of the micellar aggregates [16] The parameters b_S and c_S are presumably measures of the effects of that phenomenon

At some point in the increase of the mole fraction of the organic component, there must cease to be sufficient water present to envelope totally the pseudomicellar aggregates One feasible outcome of that situation is that the scheme of aggregation adopts a laminar form which is exemplified by lamellar phase lyotropic liquid crystals and lipid bilayers

The segment which spans the composition range $X_2 < X_A < X_3$ has been termed "microheterogeneous " Across this segment, the composition dependence of the excess molar properties appears to be particularly simple, and we find it to be appropriate to write

$$\Delta\bar{Q}_M = q_W X_W + q_A X_A + b_M X_A X_W \tag{3}$$

When X_A excedes X_3, this pattern of aggregation appears to give way to that which characterizes the organic-rich segment For this segment we write

$$\Delta\bar{Q}_A = a_A X_W + b_A X_W^2 + c_A X_W^3 \tag{4}$$

It is thought that this segment is characterized by some kind of reverse micellar aggregation scheme, with the aqueous aggregates increasing in size and changing shape with increasing water mole fraction until the laminar scheme becomes dominant

Between them these four equations contain no less than 13 parameters That number is reduced to ten by the requirement that $\Delta\bar{Q}$ be single-valued at each of the three segment junctions The three constraints are

$$\begin{aligned} c_S = {} & -q_S X_2^{-3} - a_S X_2^{-2} - b_S X_2^{-1} + q_W (1 - X_2) X_2^{-3} \\ & + q_A X_2^{-2} + b_M (1 - X_2) X_2^{-2} \end{aligned} \tag{5}$$

$$c_W = -a_W X_1^{-2} - b_W X_2^{-1} + q_S X_1^{-3} + a_S X_1^{-2} + b_S X_1^{-1} + c_S \tag{6}$$

$$\begin{aligned} c_W = {} & -a_A (1 - X_3)^{-2} - b_A (1 - X_3)^{-1} + q_W (1 - X_3)^{-2} \\ & + q_A X_3 (1 - X_3)^{-3} + b_M X_3 (1 - X_3)^{-2} \end{aligned} \tag{7}$$

We are still confronted with a substantial number of parameters to be optimized Many data sets exist with a sufficient points density and level of internal consistency to support a model of this flexibility but that does not eliminate the desirability of identifying justifiable simplifications We have considered the merits of two different approaches to reducing the complex nature of the model that is represented by eqns 1–7

One approach involves reducing one or more of the three cubic eqns (1), (2) and (4) to quadratic form. The other consideration is of the effects of requiring that $\mathrm{d}\Delta\bar{Q}/\mathrm{d}X_A$ should be single-valued at one or more of the three segment junctions

It is quite obvious that reducing the equation for the water-rich segment to quadratic form would lead to a very significant reduction in the quality of fit The reduction of eqns (2) and (4) to quadratic form requires that eqns (5) and (7) be replaced by analogous expressions for b_S and b_A As is evident from the results set out in Table 2, this eight-parameter model gives a quality of fit vastly inferior to that of the ten-parameter model of eqns

TABLE 2

Standard deviations for different sets of four-segment model equations applied to excess molar volumes and excess molar enthalpy data of the 2-butoxyethanol + water system

Model-10 defined by eqns (1)–(7)
Model-9 quadratic equation for secondary segment only
Model-8 quadratic equations for secondary and organic rich segments
Segment junctions at X(BuOEtOH) = 0 025, 0 25 and 0 5

	Model-10	Model-9	Model-8
XSVC	3 03	3 25	4 32
XSVEP	3 41	3 49	4 45
XSHEP	2 86	3 22	3 61
SSVC	1 78	2 15	3 51
SSVEP	2 64	2 79	3 89
SSHEP	2 17	2 69	3 17

Units excess molar volumes, $mm^3\ mol^{-1}$, excess molar enthalpies, $J\ mol^{-1}$

(1)–(7) Restoring the organic segment equation to its cubic form produced a nine-parameter model which the results given in Table 2 show to be better than the eight-parameter version but still significantly worse than the ten-parameter model

Far better results were obtained from model equations derived from those of the ten-parameter model by the imposition of the conditions that $d\Delta\bar{Q}/dX_A$ should be single-valued at the segment junctions Those constraints led to the equations

$$b_S = -3q_S X_2^{-2} - 2a_S X_2^{-1} + q_W(3 - 2X_2)X_2^{-2} + 2q_A X_2^{-1} + b_m(2 - X_2)X_2^{-1} \tag{8}$$

$$b_W = -2a_W X_1^{-1} + 3q_S X_1^{-2} + 2a_S X_1^{-1} + b_S \tag{9}$$

$$b_A = -2a_A(1 - X_3)^{-1} + 2q_W(1 - X_3)^{-1} + q_A(1 + 2X_3)(1 - X_3)^{-1} + b_M(1 + X_3)(1 - X_3)^{-1} \tag{10}$$

These constraints may be imposed collectively or singly When all three constraints are simultaneously imposed there is generally a non-trivial deterioration of the quality of fit accompanied by some fairly substantial changes in some of the parameters We felt that it was desirable to explore the effects of these constraints separately in terms of the overall quality of fit, the r m s deviations of the fitted curves within the individual segments and the sensitivity of the optimized parameter values

In addition to the various constrained analyses, we analysed the individual segments of the data sets separately This provides a means of evaluating the quality of the data and the validity of eqns (1)–(4)

Six data sets were analyzed XSVEP contains the El Paso values of the excess molar volumes that are given in Table 1 XSVC is a combination of

TABLE 3

Excess molar enthalpies of the 2-butoxyethanol + water system at 25 ° C

X(BuOEtOH)	$\Delta\bar{H}$	X(BuOEtOH)	$\Delta\bar{H}$	X(BuOEtOH)	$\Delta\bar{H}$
0	0	0 0216	-248 3	0 2875	-446 3
0 0017	-27 2	0 0231	-253 5	0 3410	-420 1
0 0034	-53 5	0 0264	-264 3	0 4327	-376 3
0 0051	-76 8	0 0299	-273 1	0 4615	-362 9
0 0067	-101 8	0 0346	-284 0	0 4930	-340 5
0 0085	-130 3	0 0440	-302 7	0 5782	-287 0
0 0102	-154 8	0 0500	-312 9	0 6330	-244 2
0 0118	-174 0	0 0510	-322 2	0 6612	-266 5
0 0133	-190 5	0 0586	-329 1	0 6948	-206 1
0 0150	-205 9	0 0685	-347 4	0 7313	-178 3
0 0159	-213 4	0 0799	-365 9	0 7737	-147 1
0 0167	-221 1	0 0870	-373 6	0 8085	-127 5
0 0175	-225 8	0 1455	-435 8	0 8709	-71 2
0 0184	-232 9	0 1881	-452 9	0 9310	-41 3
0 0200	-242 0	0 2318	-451 7	1	0

Units J mol^{-1}

the El Paso data with that of refs 2 and 3, with a few points deleted on the grounds that they appeared to be inconsistent with the rest XSHEP contains the El Paso values of the excess enthalpies that are given in Table 3 A

TABLE 4(a)

Results of four-segment model analyses of the excess molar volumes and enthalpies of the 2-butoxyethanol + water system at 25 ° C

Model-13 No constraints

Model-10 $\Delta\bar{Q}$ single-valued at all three segment junctions

Model-9 $\mathrm{d}\Delta\bar{Q}/\mathrm{d}X_A$ single-valued at X_3

Model-8 $\mathrm{d}\Delta\bar{Q}/\mathrm{d}X_A$ single-valued at X_2 and X_3

Model-7 $\mathrm{d}\Delta\bar{Q}/\mathrm{d}X_A$ single-valued at all three segment junctions

$X_1 = 0\ 025$, $X_2 = 0\ 25$, $X_3 = 0\ 5$

	Model				
	13	10	9	8	7
Overall standard deviations					
XSVC	2 98	3 03	3 02	3 17	3 16
XSVEP	3 48	3 41	3 38	3 40	3 38
XSHEP	2 55	2 86	2 84	2 87	3 01
SSVC	1 65	1 78	1 79	2 04	2 02
SSVEP	2 65	2 67	2 64	2 68	2 67
SSHEP	1 60	2 17	2 16	2 26	2 28

Units excess molar volumes, $\text{mm}^3\ \text{mol}^{-1}$, excess molar enthalpies, J mol^{-1}

TABLE 4(b)

Mean deviations (mm^3 mol^{-1} or J mol^{-1}) and parameter values (cm^3 mol^{-1} or KJ mol^{-1}) for the individual segments

	Model				
	13	10	9	8	7
Organic-rich segment					
Mean deviations					
XSVC	4.45	4.45	4.47	4.53	4.53
XSVEP	4.30	4.31	4.31	4.32	4.32
XSHEP	3.37	3.40	3.44	3.47	3.46
SSVC	2.41	2.42	2.43	2.49	2.49
SSVEP	3.32	3.32	3.33	3.34	3.34
SSHEP	1.88	2.01	2.08	2.14	2.13
a_A					
XSVC	−1.96	−1.96	−1.97	−1.98	−1.98
XSVEP	−1.98	−1.98	−1.99	−1.99	−1.99
SSVC	−1.97	−1.96	−1.97	−1.98	−1.98
SSVEP	−1.98	−1.98	−1.99	−1.99	−1.99
XSHEP	−0.52	−0.53	−0.54	−0.55	−0.55
SSHEP	−0.51	−0.53	−0.54	−0.55	−0.55
b_A					
XSVC	0.38	0.39	0.45	0.52	0.52
XSVEP	0.51	0.52	0.56	0.59	0.59
SSVC	0.42	0.42	0.47	0.54	0.54
SSVEP	0.51	0.53	0.56	0.59	0.59
XSHEP	−0.80	−0.70	−0.62	−0.57	−0.58
SSHEP	−0.86	−0.84	−0.63	−0.57	−0.58
c_A					
XSVC	1.32	1.29	1.19	1.09	1.09
XSVEP	1.13	1.12	1.05	1.01	1.01
SSVC	1.25	1.26	1.17	1.07	1.07
SSVEP	1.14	1.11	1.05	1.01	1.00
XSHEP	1.04	0.84	0.71	0.63	0.65
SSHEP	1.14	0.84	0.74	0.65	0.66
Microheterogenous segment					
mean deviations					
XSVC	1.64	1.84	2.02	2.18	2.17
XSVEP	1.71	1.78	1.86	1.84	1.84
XSHEP	1.66	2.42	2.26	3.06	2.89
SSVC	1.32	1.55	1.81	2.12	2.13
SSVEP	1.41	1.49	1.55	1.53	1.55
SSHEP	0.47	1.33	1.11	2.28	2.18

TABLE 4(b) (continued)

	Model				
	13	10	9	8	7
q_W					
XSVC	−0 23	−0 25	−0 26	−0 23	−0 23
XSVEP	−0 23	−0 24	−0 25	−0 24	−0 24
SSVC	−0 23	−0 25	−0 26	−0 23	−0 23
SSVEP	−0 23	−0 24	−0 25	−0 23	−0 23
XSHEP	−0 53	−0 47	−0 49	−0 47	−0 47
SSHEP	−0 52	−0 48	−0 50	−0 47	−0 47
q_A					
XSVC	0 43	0 41	0 36	0 41	0 41
XSVEP	0 43	0 41	0 39	0 41	0 41
SSVC	0 44	0 40	0 36	0 42	0 42
SSVEP	0 43	0 42	0 39	0 41	0 42
XSHEP	0 06	0 21	0 14	0 17	0 16
SSHEP	0 07	0 18	0 13	0 17	0 16
b_M					
XSVC	−3 27	−3 21	−3 09	−3 26	−3 26
XSVEP	−3 24	−3 23	−3 17	−3 24	−3 24
SSVC	−3 30	−3 19	−3 09	−3 27	−3 27
SSVEP	−3 27	−3 24	−3 17	−3 25	−3 25
XSHEP	−0 42	−0 83	−0 65	−0 76	−0 74
SSHEP	−0 44	−0 74	−0 61	−0 75	−0 73
Secondary segment					
Mean deviations					
XSVC	1 72	2 01	1 97	2 47	2 46
XSVEP	1 39	1 72	1 69	2 04	2 04
XSHEP	1 83	2 29	2 40	2 15	2 15
SSVC	0 68	1 17	1 12	1 78	1 78
SSVEP	0 60	1 11	1 07	1 49	1 53
SSHEP	0 99	1 59	1 68	1 41	1 19
q_S					
XSVC	−0 11	−0 11	−0 11	−0 12	−0 12
XSVEP	−0 11	−0 11	−0 11	−0 12	−0 12
SSVC	−0 11	−0 11	−0 11	−0 12	−0 12
SSVEP	−0 11	−0 11	−0 11	−0 12	−0 11
XSHEP	−0 20	−0 19	−0 19	−0 20	−0 20
SSHEP	−0 20	−0 19	−0 19	−0 20	−0 20

(continued)

TABLE 4(b) (continued)

	Model				
	13	10	9	8	7
a_S					
XSVC	−4 26	−3 97	−3 98	−3 74	−3 96
XSVEP	−4 31	−3 92	−3 93	−3 75	−3 97
SSVC	−4 23	−3 96	−3 97	−3 74	−3 97
SSVEP	−4 05	−3 90	−3 91	−3 74	−3 78
XSHEP	−3 08	−2 91	−2 93	−2 81	−3 06
SSHEP	−3 10	−2 92	−2 93	−2 79	−3 11
b_S					
XSVC	10 03	9 04	9 17	6 76	6 72
XSVEP	10 15	8 28	8 37	6 69	6 61
SSVC	9 68	8 98	9 09	6 76	6 77
SSVEP	9 76	8 16	8 24	6 66	6 92
XSHEP	8 06	10 24	10 49	9 20	8 18
SSHEP	8 44	10 41	10 60	9 05	8 54
c_S					
XSVC	−12 7	−9 4	−9 8	−3 4	−3 3
XSVEP	−12 3	−7 1	−7 4	−3 1	−2 9
SSVC	−11 8	−9 3	−9 6	−3 4	−3 4
SSVEP	−11 4	−6 8	−7 1	−3 0	−3 5
XSHEP	−5 1	−11 0	−11 8	−8 2	−6 2
SSHEP	−6 5	−11 6	−12 2	−7 9	−6 9
Water-rich segment					
Mean deviations					
XSVC	0 64	0 95	0 94	1 18	1 20
XSVEP	0 27	0 36	0 36	0 40	0 36
XSHEP	1 49	2 07	2 06	2 14	2 69
SSVC	0 63	1 02	1 01	1 25	1 01
SSVEP	0 19	1 18	1 17	1 23	1 36
SSHEP	1 38	2 21	2 20	2 31	2 55
a_W					
XSVC	−8 70	−8 89	−8 88	−8 96	−8 98
XSVEP	−8 65	−8 82	−8 81	−8 85	−8 96
SSVC	−8 72	−8 93	−8 93	−9 00	−8 99
SSVEP	−8 58	−9 35	−9 35	−9 38	−9 06
XSHEP	−16 01	−16 61	−16 60	−16 64	−17 32
SSHEP	−16 21	−16 92	−16 91	−16 97	−17 31
b_W					
XSVC	−174 9	−143 5	−144 1	−130 9	−127 6
XSVEP	−184 6	−153 5	−153 8	−146 7	−130 5
SSVC	−172 8	−137 3	−137 8	−125 1	−125 1
SSVEP	−220 2	−75 0	−75 3	−68 6	−117 0

TABLE 4(b) (continued)

	Model				
	13	10	9	8	7
XSHEP	20 2	114 7	113 5	120 8	213 4
SSHEP	48 6	162 1	161 2	169 9	216 6
c_W					
XSVC	8101	6944	6965	6480	6378
XSVEP	8493	7213	7226	6694	6438
SSVC	8066	6760	6778	6308	6354
SSVEP	10890	4912	4925	4648	6118
XSHEP	8694	5349	5389	5132	2340
SSHEP	7932	3916	3946	3639	2231

cubic splines procedure was employed to produce a modest level of local data smoothing and led to the formation of the data sets SSVEP, SSVC and SSHEP This procedure, which has proved to be both effective and useful for many other data sets was found to be somewhat ill-suited to the low organic mole fractions data of XSVEP The results of these analyses are set out in Table 4

The values cited for the segment junction compositions were selected on the basis of simplex optimization of each of the data sets

There is relatively little difference between the standard deviations of the excess volume data sets from the 13-parameter and ten-parameter sets of model equations More substantial differences exist for the excess molar enthalpy data, reflecting the fact that this is an inherently less precise set of measurements at higher organic mole fractions

The organic-rich segment

The contents of Table 4 appear to convey the information that, as far as the organic rich segment is concerned, neither the quality of fit nor the optimized parameter values are particularly sensitive to the changes in the model constraints The differences between the excess volume parameter values for model-13 (totally unconstrained) and model-10 (constraints of eqns (5)–(7) are negligible compared to the variations for a given model among the four data sets The differences between model-13 and model-10 parameters values for the excess enthalpy data merely reflect modest uncertainties in the data

Model-9 adds the constraint that $\mathrm{d}\Delta\overline{Q}/\mathrm{d}X_A$ should be single-valued at X_3 but at neither of the other segment junctions That constraint would be expected, if inappropriate, to have a major impact upon the parameter values and quality of fit of the organic-rich and microheterogeneous segments and much less upon those for the other two segments Only minor changes are discernible There are further modest changes in the parameter values as one passes to model-8, which adds the further constraint that $\mathrm{d}\Delta\bar{Q}/\mathrm{d}X_A$ should be single-valued at X_2

The microheterogeneous segment

The parameter values for the excess molar volumes in this segment exhibit a fairly high degree of consistency, as can be seen in Table 4(b) There are more substantial differences between the values obtained using model-13 and model-10 for the excess molar enthalpies Requiring that $\mathrm{d}\Delta\bar{Q}/\mathrm{d}X_A$ be single-valued at X_3 alone (model-9) appears to affect the parameter values more than making the same requirement at both X_2 and X_3

The secondary segment

Here the parameters b_S and c_S appear to be highly sensitive to the choice of model, as is the quality of fit The differences between the results of model-13 and those of model-10 must reflect to some extent imperfections in the data sets, but also may result from shortcomings in one or more of the model equations As might be expected, the results of model-9 are virtually identical to those of model-10 What is particularly interesting is the shift in parameter values and quality of fit going from model-9 to model-8 This is in contrast to the relatively small changes in going from model-8 to model-7

The water-rich segment

Here the parameters b_W and c_W are also sensitive to the choice of models The mean deviations of model-13 and model-10 differ by considerable amounts It is clearly worth posing the question whether some alternative choice of model equation for this or the secondary segment might be found to be less sensitive to the application of single-valuedness constraints

General

We have, in the foregoing paragraphs, drawn attention to some of the less positive aspects of these analyses One should not, perhaps, have expected more or even as much from such a naive model The standard deviations for model-10 and model-9 may surely be regarded as indicators of both a satisfactory level of internal consistency for the various data sets and a good curve fitting capability for the model equations What might be regarded as the major parameters of the model equations, those which are the variables of model-7, appear to be reasonably insensitive to model constraints

DISCUSSION

The water-rich segment

The value of a_W for the excess molar volume data is the apparent excess molar volume of the solute at infinite aqueous dilution It leads to a value for the apparent molar volume of 122 92 cm^3, which compares favorably with the value of 122 91 cm^3 quoted in ref 2 This value is also very close to that of 122 90 cm^3 predicted by a group additivity scheme that was recently developed in this laboratory along the lines of ref 17

The value of a_W for the excess molar enthalpy data indicates that the transfer of 2-butoxyethanol molecules from their own pure liquid to a totally aqueous environment is a moderately exothermic process To convert that value into an estimate of the solvation enthalpy, we would need to be in possession of a value of the molar enthalpy of vaporisation of the solute and a reasonable estimate of the enthalpy of formation of the aqueous cavities in which the solute molecules reside

Values of quantities of the type b_W have a tendency to be sensitive to the choice of analytic procedure by which they are determined If they are to be interpreted as measures of the effects of solvent cosphere overlap, as is implied by the Savage–Wood additivity rule [18], they should be identified with the mole fraction derivative of the appropriate apparent molar quantity extrapolated to infinite dilution Most data sets are not sufficiently precise to warrant that kind of analytic scheme

Wood has stated that the values reported for excess volume pair-interaction coefficients do not provide an adequate data base for setting up the same kind of group pair-contribution tables as have been established for molar enthalpies and free energies [19]

In a recent study of the excess molar volumes of amide–water systems, Davis showed that certain trends exist among b_W values even though there was an inadequate data base to identify specific group pair contributions [20]

The value of 114 kJ for b_W of the excess enthalpy data compares favorably with the estimate of 105 kJ obtained from the group pair-interaction parameters of ref 21

The parameters of the type c_W are measures of the effects of hydrophobic aggregation These are clearly substantial effects c_W is not an independent parameter of our analyses

The parameters q_S, a_S and b_S describe the characteristics of some kind of pseudomicellar pattern of molecular aggregation q_S assumes the role of an excess molar property of some hypothetical standard state of water a_S is the apparent excess molar property of the solute in the pseudomicellar state and is presumed to contain contributions from the water molecules which are most closely associated, by hydrogen bonding, with the polar head groups If one accepts the proposition that, as the mole fraction of the organic component increases across the secondary segment, the pseudomicellar aggregates are increasing in size and adopting a progressively more laminar form, then b_S would seem to be some kind of measure of the effects of that structural modification Comparing the a_W and a_S values, one observes that the apparent molar volumes and enthalpies of the solute in the pseudomicellar state are of the same sign but much smaller magnitude than in a monomeric state A similar conclusion has been reached from analyses of several non-ionic surfactant + water systems using a mass-action model [15]

The parameters q_W, q_A and b_M are interpreted in terms of some type of laminar pattern of aggregation q_W and q_A are in the form of excess molar properties of hypothetical standard states of the two components and are thus measures of the effects of changes to their respective patterns of self aggregation b_M is thus some measure of the effects of the interactions across the interface of the two pseudophases The q_W values for both the excess molar volumes and enthalpies are quite similar to those reported for alkanol–water systems [22] and for the THF + water system [23]

Positive values of q_A for both excess molar volumes and enthalpies have been obtained for the THF + water system and for the 2-propanol + water and t-butanol + water systems but not ethanol + water and 1-propanol + water To make any logical comparison of the values of this quantity for different binary systems, one would need to have some means of taking into account the various effects of the modes of self-aggregation of the organic components in their respective pure states Conceivably this could be accomplished by determining the properties of those organic species at infinite dilution in a suitable inert solvent

Negative b_M values for excess molar volume data appear to be a characteristic of all mixtures of water with polar organic liquids By contrast, the values obtained from excess enthalpy data of many such systems are found to be positive

The parameters a_A are apparent excess molar properties of water at infinite dilution in the organic solvent For excess molar volumes this quantity appears to be invariably negative There is little information to be found for excess molar enthalpies b_A and c_A are measures of the effects of the growth of the aqueous clusters which are assumed to form the cores of some type of reverse micellar aggregates

SUMMARY

Values have been reported for the excess molar volumes and enthalpies of the 2-butoxyethanol + water system at 25 °C Our analyses show both data sets to possess a good level of internal consistency The excess molar volumes are consistent with those reported in the literature [2,3] The excess molar enthalpy data are reasonably consistent with the relatively few values reported in ref 4 and fall within the rather broad range of values of ref 4–6

The parameter base of the equations for the four-segment model for analyzing excess molar property data for binary hydro-organic systems has been modified in a manner which renders its results more easily compared to those derived from other approaches (13–15) A study has been made of the effects of different constraints upon the four-segment model equations It appears that nine parameters are required to provide a satisfactory algebraic summary of each of the two data sets

While the parameter values appear to be reasonable, and in general conform with the results of other investigations, similar detailed analyses will need to be carried out upon many other data sets of a wider variety of properties of this and other related systems before one can express real confidence in the manner in which they are interpreted

An investigation is currently being carried out to see if some more accurate equation for the water rich region, than a simple cubic function of mole fraction, can be found

ACKNOWLEDGMENTS

This work was supported by the National Institutes of Health in the form of an Academic Research Enhancement Award (M I D) and an institutional Minority Biomedical Research Support grant RR 08012 (M I D and M C M) The project is also supported by the Centre Nationale de Recherche Scientifique (G D)

REFERENCES

1 J E Desnoyers, Pure Appl Chem , 54 (1982) 1469
2 G Roux Int Data Ser B, (1978) 52
3 G Douhéret and A Pal, J Chem Eng Data 33 (1988) 40
4 U Onken, Z Electrochem , 63 (1959) 321
5 G Scatchard and G M Wilson, J Am Chem Soc 86 (1964) 133
6 G Pathak, S S Katti and S B Kulkarni, Indian J Chem 8 (1970) 357
7 P Picker, E Tremblay and C Jolicouer J Solution Chem , 3 (1974) 377
8 Instruction Manual No 454 Parr Instrument Company, Moline, IL 61265, U S A
9 G Roux, Int Data Ser B, (1978) 45
10 M I Davis, Thermochim Acta, 63 (1983) 67
11 M I Davis, Thermochim Acta, 77 (1984) 421
12 M I Davis, Thermochim Acta, 89 (1985) 325
13 W G McMillan and J E Mayer, J Chem Phys , 13 (1945) 276
14 G Douhéret and A Viallard in L Mittal and B Lindman (Eds), Surfactants in Solution, Vol 2 Plenum Press, New York, 1984, p , 857

15 J E Desnoyers, G Perron and A H Roux, in R Zana (Ed) Surfactant Solutions, Marcel Dekker, New York, 1987, p 20

16 C Tanford, Y Nozaki and M F Rohde, J Phys Chem , 81 (1977) 1555

17 C Jolicouer and G Lacroix, Can J Chem , 54 (1976) 624

18 J J Savage and R H Wood, J Solution Chem , 5 (1976) 733

19 I R Tasker, J J Spitzer, S K Suri and R H Wood, J Chem Eng Data, 28 (1983) 266

20 M I Davis, Thermochim Acta, 120 (1987) 299

21 I R Tasker and R H Wood, J Solution Chem , 11 (1982) 481

22 M I Davis, Thermochim Acta, 81 (1984) 157

23 M I Davis, Thermochim Acta, 77 (1984) 421