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Excess molar enthalpies of 2-methoxy ethanol+water and 2-ethoxy ethanol+water at 25°C

Michael I. Davis[a,*], M. Concepcion Molina[a], Gérard Douhéret[b]

[a] Department of Chemistry, University of Texas at El Paso, , El Paso TX 79968-0513, USA
[b] UPRESA , CNRS no. 6003, Thermodynamiques des Solutions et Polyméres, Université Blaise Pascal (Clermont–Ferrand), F-63177 Aubiére, France

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Abstract

Excess molar enthalpies have been measured for the systems 2- methoxyethanol+water and 2-ethoxyethanol+water at 25°C. The results are compared with other earlier reports in the literature. Analyses have been carried out using two versions of the four-segment model. The results are compared with those obtained for the excess enthalpies of other related systems. © 1998 Elsevier Science B.V.

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1. Introduction

Some years ago, we published the results of our measurements of the heats of mixing (excess molar enthalpies) of 2-butoxyethanol+water [1]. It was found that the excess molar enthalpies of that system exhibited the same substantial shift in composition dependence, in the vicinity of $x(\mathrm{BuEtOH})=0.02$, as had been reported for several other thermodynamic properties [2].

While decreasing the length of the alkyl chain should inevitably diminish the extent of any labile simulation of micelle formation by the amphiphile, it was felt to be of interest to see if the heats of mixing of these two systems provided any evidence of pseudo-micellar clustering, however modest.

The densities of 2-methoxyethanol+water had been reported on at least three occasions [3–5]. Isobaric molar heat capacities, for that system, were reported by Roux [6]. Values of excess molar isentropic compressibilities, derived from ultrasonic speed measurements, have also been reported [7]. Density values for 2-ethoxyethanol+water are published [4,8] as are molar isobaric heat capacities [9] and excess molar isentropic compressibilities [7].

The earlier heat of mixing data that we have found for these systems [10,11] is generally too sparse to warrant detailed analysis. It is appropriate to observe, however, that the general shapes of the published plots of excess molar enthalpy versus mole fraction are quite similar to our own (see Figs. 1 and 2).

2. Experimental

Spectroscopic grade samples of both of the 2-alkoxyethanols were purchased from Aldrich. They were used from freshly opened containers without

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*Corresponding author. Tel.: +915 7475701 fax: +915 7475748.

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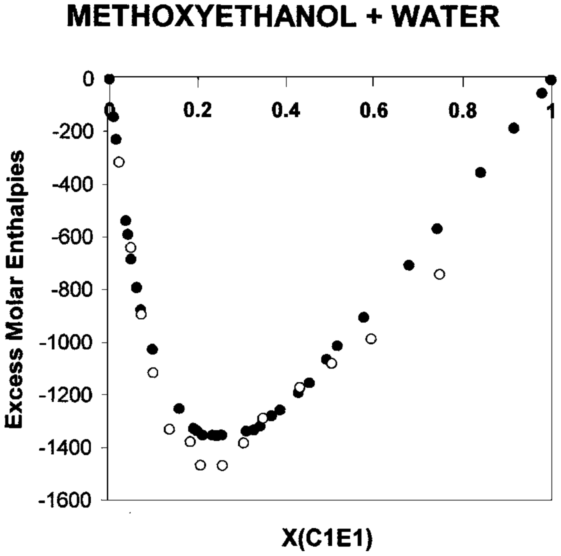

Fig. 1. Excess molar enthalpies of 2-methoxyethanol+water at 25°C. Units=J mol^{-1} Solid circles – this work. Hollow circles – Ref. [10].

further purification. Care was taken to protect the samples from contamination by atmospheric moisture. The water was distilled and deionized.

The heats of mixing measurements were performed using a Parr Solution calorimeter (Model 1451) [12]. The operating procedures that we adopted are described in an earlier publication [1]. The molar heat capacities, which were essential for our interpretation of the calorimetric output, were taken from the literature [6,9].

3. Results

The values obtained for the excess molar enthalpies of the two systems are set out in Tables 1 and 2. Plots of the two data sets, together with previously published data sets, are shown in Figs. 1 and 2.

Analyses were performed upon both data sets using the four-segment model. That model and its constituent equations have been presented several times in our previous publications [13]. The four-segment model is

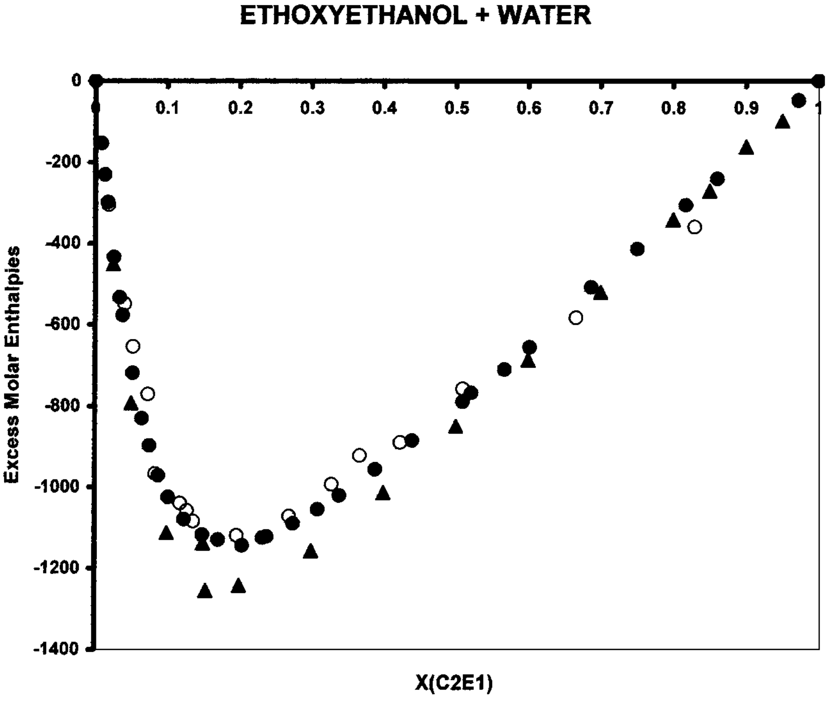

Fig. 2. Excess molar enthalpies of 2-ethoxyethanol+water at 25°C. Units=J mol^{-1} Solid circles –this work. Hollow circles – Ref. [10]. Triangles – Ref. [11].

Table 1
Excess molar enthalpies – 2-methoxyethanol+water

Units J mol^{-1}

X(C1E1)	H^E	X(C1E1)	H^E
0	0	0.3154	−1337.00
0.0095	−144.45	0.3329	−1332.03
0.0155	−230.51	0.3463	−1317.59
0.0390	−539.79	0.3724	−1278.20
0.0440	−591.63	0.3915	−1256.57
0.0520	−685.29	0.4327	−1190.67
0.0647	−792.49	0.4578	−1153.26
0.0744	−876.04	0.4961	−1063.42
0.1018	−1026.51	0.5209	−1012.30
0.1631	−1251.85	0.5804	−902.86
0.1958	−1327.28	0.6817	−705.24
0.2036	−1335.48	0.7455	−567.45
0.2169	−1352.73	0.8422	−353.38
0.2390	−1352.97	0.9170	−184.62
0.2492	−1355.19	0.9799	−50.24
0.2597	−1351.48	1	0

Table 2
Excess molar enthalpies – 2-ethoxyethanol+water

Units J mol^{-1}

X(C2E1)	H^E	X(C2E1)	H^E
0	0	0.2387	−1122.05
0.0086	−152.23	0.2750	−1089.67
0.0131	−230.32	0.3090	−1055.15
0.0174	−298.97	0.3391	−1020.70
0.0259	−433.88	0.3888	−956.22
0.0343	−533.72	0.4397	−885.68
0.0383	−577.09	0.5098	−789.41
0.0525	−718.28	0.5215	−767.57
0.0650	−830.53	0.5675	−709.52
0.0758	−897.95	0.6022	−656.03
0.0879	−971.72	0.6869	−509.08
0.1020	−1024.59	0.7508	−413.78
0.1239	−1079.31	0.8172	−305.96
0.1494	−1117.33	0.8609	−240.65
0.1713	−1130.00	0.9720	−47.06
0.2044	−1143.83	1	0
0.2326	−1125.50		

constructed in such a way as to permit separate analyses of different regions of the total composition range. Of particular interest to us were the results of analyzing the data for the water-rich segments. In addition, we have implemented a version of the Mass-Action model similar to that described by Roux and Desnoyers [14,15].

Both of these analytic schemes provide estimates of the molar enthalpy of solution of the amphiphiles at infinite dilution.

The values obtained, in kJ mol^{-1}, are given below. The mass action results are in parentheses:

$$C_1E_1 = -15.5(-14.6)\ C_2E_1 = -19.0(-17.9)$$
$$C_4E_1 = -16.8(-16.6)$$

These may be compared with the values that we have calculated for the primary alkanols [16–18]:

$$C_1E_0 = -7.1(-7.1)\ C_2E_0 = -10.3(-10.0)$$
$$C_3E_0 = -10.1(-9.9)$$

There are also literature values for the infinite dilution enthalpies of solution of other 1-alkanols [19] that demonstrate that the solution process becomes progressively less exothermic as the alkyl chain is extended beyond two carbons, in that series, as well as for the alkoxyethanols.

$$C_4E_0 = -9.3\ C_5E_0 = -7.7\ C_6E_0 = -6.5$$

The mass action model furnishes values for enthalpy change that results when monomeric amphiphiles form clusters. Taken together with the molar Gibbs free energies of cluster formation, which are related to the equilibrium constant and are thus also parameters of the mass action model, the enthalpies provide estimates of entropy changes.

	C_1E_1	C_2E_1	C_4E_1	
ΔH	6.75	10.65	15.49	kJ mol^{-1}
ΔG	−5.80	−5.87	−7.29	kJ mol^{-1}
ΔS	42.1	55.4	76.4	J K^{-1} mol^{-1}

These results indicate that the formation of clusters, in an aqueous environment is an endothermic process. That the process occurs at all is evidently the result of substantial entropy increase. In a recent article [20], we have attributed the nature of the changes due to cluster formation of a variety of thermodynamic properties to the destruction, of the ice-like aggregation of individual solvent water molecules that results from direct contact with their hydrophobic alkyl groups.

Fig. 3 shows partial excess molar enthalpies of water in the water-rich segments of the three mixtures.

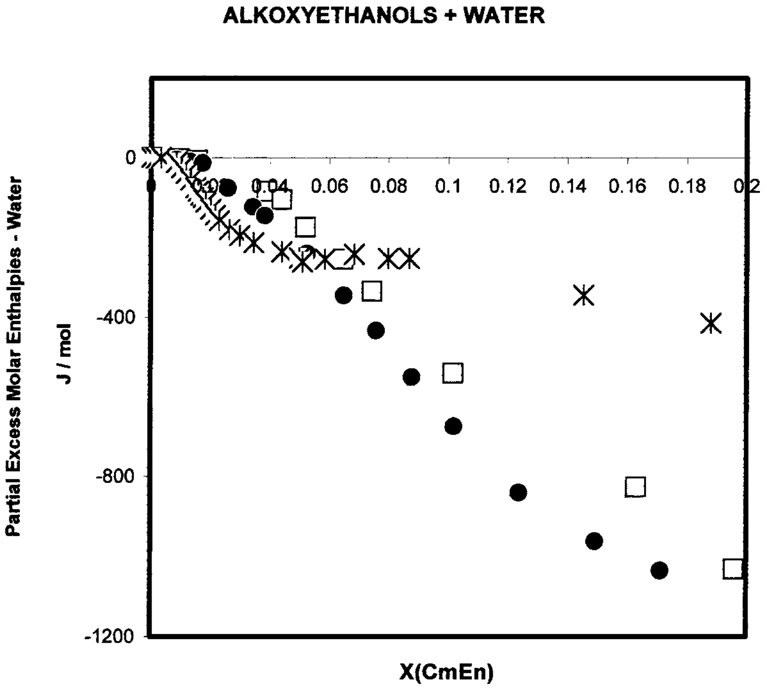

Fig. 3. Partial excess molar enthalpies of water in water rich mixtures with 2-alkoxyethanols. Units=J mol^{-1} Symbols □ – C_1E_1+ water; ● – C_2E_1+ water; * – C_4E_1+ water.

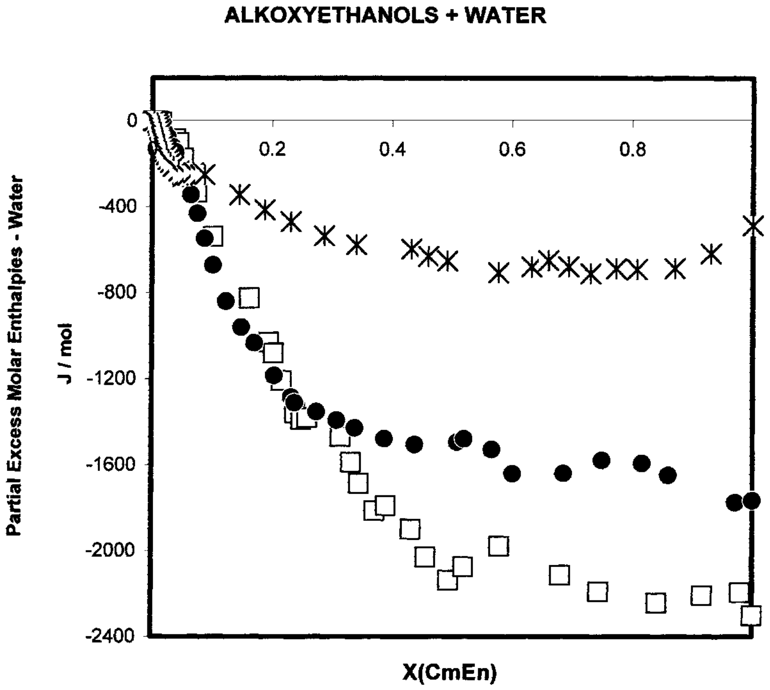

Fig. 4. Partial excess molar enthalpies of water in 2-alkoxyethanol+water systems across the entire composition range. Units=J mol^{-1} Symbols □ – C_1E_1+water; ● – C_2E_1+water; * – C_4E_1+water.

In all three systems, the partial molar excess enthalpies are small and negative at extreme dilutions. This has been attributed to enthalpic effects of diminishing the interactions between pairs of monomeric solute amphiphiles and rebuilding the ice-like cages [21]. Fig. 3 shows very clearly the sharp change in the composition dependence of the enthalpies of mixing of C_4E_1 with water at $X(C_4E_1)=0.015$. There are similar, but less pronounced changes for the C_2E_1+water and C_1E_1+water systems at higher amphiphile mole fractions.

One further item of interest is the molar enthalpy of a solution of water at infinite dilution in the amphiphilic solvent. The results of our analyses are:

$$C_1E_1 = -2.32\ C_2E_1 = -1.73 \text{ and}$$
$$C_4E_1 = -0.55\text{kJmol}^{-1}$$

Bearing in mind that over 40 kJ mole^{-1} has to be expended to separate the water molecules before immersing them in the solvent, it is evident that the solvation of individual water molecules is highly exothermic. It would appear that there is a net increase in the number of hydrogen bonds.

Fig. 4 shows the partial excess molar enthalpies of water at higher mole fractions of the amphiphiles. It is seen that those values remain very nearly constant from equimolar mixtures up to pure amphiphiles. It is not unlikely that the water molecules find their way into the polar regions of a bilayered arrangement of the alkoxyethanols.

Acknowledgements

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