ELSEVIER

Excess chemical potential and partial molar enthalpy of 2-*iso*-butoxyethanol in aqueous solution at 20 °C

Candy M.W. Cheung [a], Kitty P.Y. Chan [a], Yoshikata Koga [a,b,∗]

[a] *Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, BC, Canada V6T 1Z1*
[b] *Department of Diversity Sciences, Graduate School of Science and Technology,*
1-33 Yayoi, Inage-ku, Chiba 263-8522, Japan

Abstract

Vapour pressures were determined at 20 °C for aqueous 2-*iso*-butoxyethanol (iBE). Partial pressures and hence, the excess chemical potentials of iBE were calculated by the Boissonnas method. Excess partial molar enthalpies were measured, and the excess partial molar entropies of iBE were then calculated at 20 °C. These data and their mole fraction dependence indicated that there are three mixing schemes operative, in the same way as in aqueous 2-*n*-butoxyethanol (nBE) studied extensively by us. The details of each mixing schemes are identical, but the locus of the transition between mixing schemes I and II occurs at a smaller mole fraction than for aqueous nBE. This suggests that iBE is a stronger hydrophobic solute than nBE, which is consistent with the common understanding.
© 2002 Elsevier Science B.V. All rights reserved.

Keywords: 2-*iso*-Butoxyethanol–H_2O; Excess partial molar enthalpy and entropy; Enthalpic interaction functions; Three mixing schemes identical with 2-*n*-butoxyethanol–H_2O; A stronger hydrophobicity than 2-*n*-butoxyethanol

1. Introduction

2-*iso*-Butoxyethanol (iBE)–H_2O system is known to have the lower critical solution temperature (LCST) at 25.6 °C and at the mole fraction of iBE, x_{iBE}, of 0.052 [1]. Thus, it is a challenge to determine thermodynamic quantities at around room temperatures, due perhaps to a critical slowing down. There have been a number of measurements of thermodynamic quantities at about room temperature [1–3]. We note the data are generally more scattered than normal. In particular, the heat capacity data show some myste-

rious deviations in the range $0.2 < x_{iBE} < 0.6$ [2], which is well outside the phase separation range [1].

In this work, we add the chemical potential and the partial molar enthalpy data at 20 °C, 5 °C below the LCST. We make an attempt at learning the mixing schemes operating in this system and comparing them with those in 2-*n*-butoxyethanol (nBE)–H_2O we have studied extensively [4–7].

2. Experimental

Purified iBE was donated by Professors Murakami and Tamura and was used for vapour pressure measurements. The purification procedure is detailed in [2]. For the excess partial molar enthalpy determination, we used iBE as supplied (Tokyo Kasei, 98%).

∗ Corresponding author. Tel.: +1-604-822-3491;
fax: +1-604-822-2847.
E-mail address: koga@chem.ubc.ca (Y. Koga).

H_2O was triply distilled; last twice in Pyrex glass still immediately before use.

Excess partial molar enthalpies of iBE, H_{iBE}^E, were determined by a home-made titration calorimeter of a similar design to an LKB Bromma 8700 calorimeter [8]. The uncertainty was larger than normal, $\pm 0.1\,kJ\,mol^{-1}$ for the range $x_{iBE} < 0.02$, where H_{iBE}^E values change rapidly, but for $x_{iBE} > 0.02$ the uncertainty was $\pm 0.05\,kJ\,mol^{-1}$ as normal. Vapour pressures were measured at $20.174\,°C$ by a static method, and partial pressures were calculated numerically by the method of Boissonnas [4,9].

3. Results and discussion

Table 1 lists the vapour pressure, p, corrected for $20\,°C$ by the Gibbs–Konovalov relation [4,9]. The uncertainty is estimated as ± 0.008 Torr. An azeotrope is evident in the water-rich region, at about $x_{iBE} = 0.05$; the total pressure, p, reaches the maximum. The Boissonnas method was, therefore, applied starting at both ends from $x_{iBE} = 1$ to 0.068, and from $x_{iBE} = 0$

to 0.041. As pointed out earlier [4,9], the Boissonnas method does not work at an azeotrope. It is a numerical iteration method starting off by assuming that the major component obeys the Rault's law for the first data point in the most dilute solute composition. This assumption was shown wrong in the range of mole fraction of solute larger than 10^{-5} [10,11]. However, the Boissonnas method has its own built-in self-correcting feature and after several data points the partial pressure data become correct [10,11]. This implies for the present case, however, that the partial pressure data are not reliable in the range $x_{iBE} < 0.07$, which is still in the self-correction region starting from $x_{iBE} = 0$. Hence, the excess chemical potential data, Eq. (1), are not reliable also in this range.

The excess chemical potential of iBE, μ_{iBE}^E, was calculated as,

$$\mu_{iBE}^E = RT \ln \left\{ \frac{p_{iBE}}{(x_{iBE}\, p_{iBE}^0)} \right\} \tag{1}$$

where p_{iBE}^0 is the vapour pressure of pure iBE. The gas phase virial correction is negligibly small in

Table 1
Vapour pressures of 2-*iso*-butoxyethanol–H_2O at $20\,°C$

| x_{iBE}	p^a (Torr)	$p_{iBE}{}^a$ (Torr)	$p_W{}^a$ (Torr)	x_{iBE} (Torr)	p (Torr)	p_{iBE} (Torr)	p_W (Torr)
0	17.543	0	17.543	0.01389	17.587	0.287	17.300
0.03350	17.641	0.640	17.001	0.04920	17.648	0.745	16.904
0.06873	17.657	Azeotrope?	Azeotrope?	0.08450	17.636	1.007	16.629
0.09988	17.631	1.013	16.618	0.1144	17.600	1.043	16.557
0.1327	17.547	1.083	16.464	0.1499	17.510	1.105	16.405
0.1669	17.498	1.111	16.386	0.1833	17.480	1.119	16.361
0.1999	17.446	1.132	16.314	0.2170	17.413	1.144	16.269
0.2337	17.387	1.151	16.236	0.2502	17.360	1.159	16.202
0.2659	17.327	1.167	16.160	0.2826	17.259	1.183	16.076
0.3025	17.198	1.195	16.003	0.3221	17.113	1.211	15.902
0.3411	17.005	1.231	15.774	0.3575	16.887	1.250	15.636
0.3628	16.838	1.259	15.580	0.3735	16.804	1.264	15.540
0.3846	16.693	1.281	15.412	0.3902	16.688	1.282	15.406
0.4059	16.557	1.300	15.257	0.4095	16.507	1.307	15.199
0.4215	16.400	1.322	15.078	0.4362	16.272	1.339	14.933
0.4368	16.288	1.337	14.951	0.4665	16.000	1.372	14.628
0.5027	15.589	1.417	14.172	0.5307	15.282	1.448	13.834
0.5611	14.923	1.482	13.441	0.5926	14.568	1.513	13.055
0.6266	13.943	1.563	12.380	0.6671	13.213	1.618	11.595
0.7097	12.375	1.675	10.700	0.7578	11.277	1.744	9.534
0.8042	10.187	1.804	8.383	0.8542	8.542	1.887	6.655
0.9051	6.811	1.964	4.847	0.9485	5.337	2.014	3.322
1	2.214	2.214	0				

[a] Uncertainty: ± 0.008 Torr.
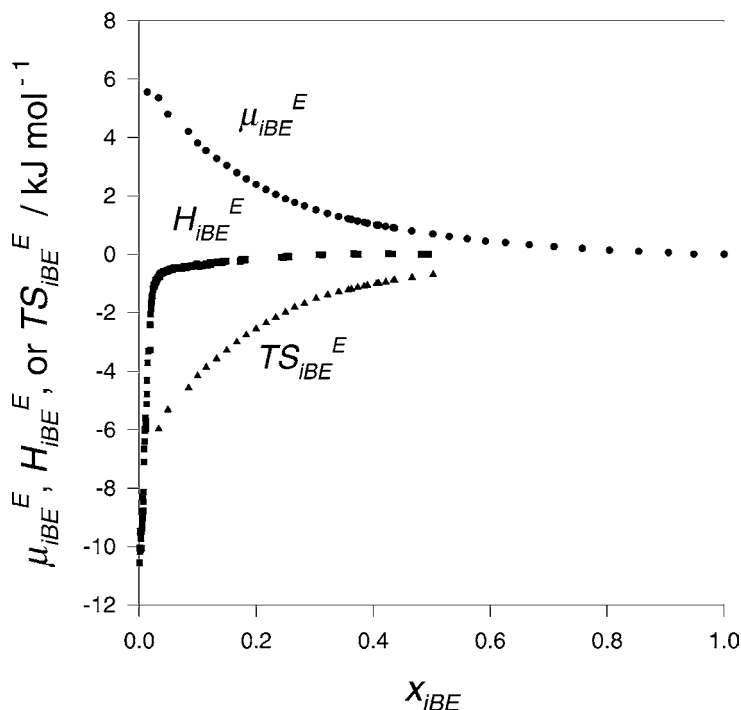
Fig. 1. Excess chemical potential, μ_{iBE}^E, excess partial molar enthalpy, H_{iBE}^E, and entropy times temperature, TS_{iBE}^E, of iBE at 20 °C.

comparison with the liquid phase non-ideality, and hence was ignored in Eq. (1). The μ_{iBE}^E data are plotted in Fig. 1. The uncertainty is estimated as $\pm 0.01\,\text{kJ mol}^{-1}$.

The excess partial molar enthalpies of iBE, H_{iBE}^E, are plotted in Fig. 1, and the details are shown in Fig. 2. The excess partial molar entropies of iBE, S_{iBE}^E were calculated as,

$$TS_{iBE}^E = H_{iBE}^E - \mu_{iBE}^E \tag{2}$$

and are plotted also in Fig. 1.

The detailed x_{iBE}-dependence of H_{iBE}^E (Fig. 2), suggests that there are three composition regions in each of which the thermodynamic behaviour is clearly different from those of other regions. We thus, conclude that there are three different mixing schemes operative just as the case for aqueous nBE that we have studied extensively [4–7].

In order to see the change in mixing schemes more closely, we calculate what we call the iBE–iBE interaction in terms of enthalpy, $H_{iBE-iBE}^E$,

as [5,6]:

$$H_{iBE-iBE}^E \equiv N\left(\frac{\partial H_{iBE}^E}{\partial n_{iBE}}\right) = (1 - x_{iBE})\left(\frac{\partial H_{iBE}^E}{\partial x_{iBE}}\right)$$

$$\approx (1 - x_{iBE})\left(\frac{\delta H_{iBE}^E}{\delta x_{iBE}}\right) \tag{3}$$

where N is the total amount of solution. The physical meaning of the enthalpic interaction function, $H_{iBE-iBE}^E$ has been discussed at some length earlier [5,6]. Briefly, since the excess partial molar enthalpy of iBE, H_{iBE}^E, is the actual enthalpic situation of iBE in the system, the n_{iBE}-derivative of H_{iBE}^E, $H_{iBE-iBE}^E$, signifies the effect of incoming iBE on the enthalpic situation of the existing iBE. In the last approximate expression of Eq. (3), δx_{iBE} is the interval of x_{iBE} at which the values of H_{iBE}^E were read off the smooth curve drawn through all the data points of H_{iBE}^E (Fig. 2), and δH_{iBE}^E is the increment. The appropriate interval, δx_{iBE} is determined as follows: for the purpose of mathematical rigor, the smaller the value
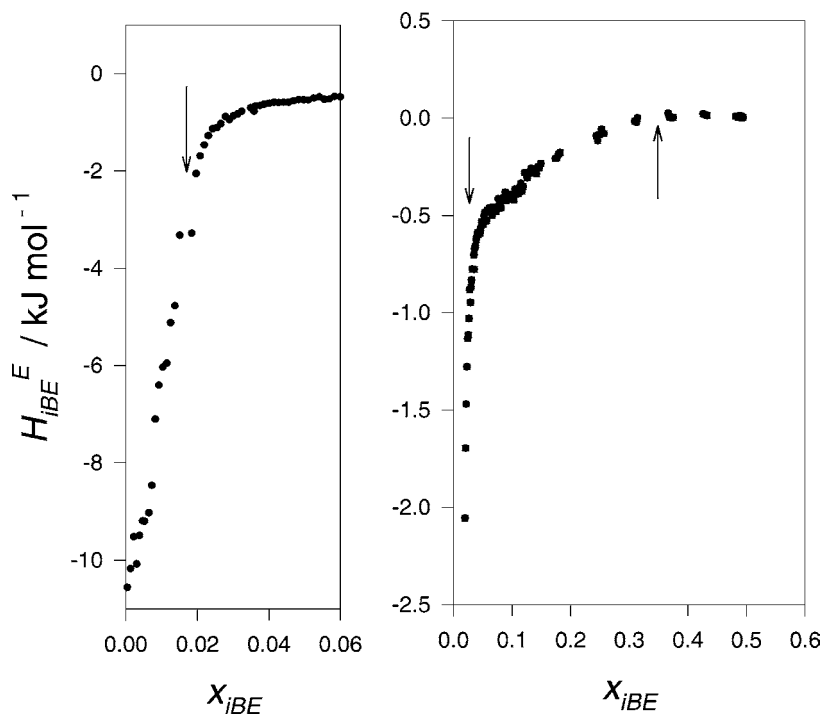
Fig. 2. The details of excess partial molar enthalpy of iBE, H_{iBE}^{E}, at 25 °C. The arrows indicate the loci of changes in thermodynamic behaviour.

of δx_{iBE} the better. A small value of δx_{iBE}, however, brings about a small value of δH_{iBE}^{E} and hence its relative uncertainty is large. A large value of δx_{iBE}, on the other hand, tends to result in smearing the detail of a sharp curvature in H_{iBE}^{E} versus x_{iBE}. A systematic trial leads to an appropriate δx_{iBE} value. The detail has been discussed earlier [12]. In the present case, $\delta x_{iBE} = 0.002$ for $x_{iBE} < 0.03$, $\delta x_{iBE} = 0.01$ for $0.03 < x_{iBE} < 0.1$, and $\delta x_{iBE} = 0.04$ for $x_{iBE} > 0.1$.

$H_{iBE-iBE}^{E}$ thus calculated is shown in Fig. 3. The uncertainty is estimated as $\pm 0.1\,\text{kJ}\,\text{mol}^{-1}$. Its x_{iBE}-dependence is almost identical to the case of aqueous nBE [4–7]. Fig. 4 shows the excess partial molar volume of iBE, V_{iBE}^{E}, calculated from the excess molar volume data at 25 °C [3]. Reflecting the fact that the LCST is at 25.6 °C at $x_{iBE} = 0.052$, the data scatter much in the region, $0.03 < x_{iBE} < 0.07$. Aside from the scatter, Fig. 4 is almost identical again to the equivalent plots of the excess partial molar volume of nBE at 25 °C [13]. We conclude, therefore, by analogy to the case of nBE–H$_2$O [4–7,13], that

the three mixing schemes operative in iBE–H$_2$O are qualitatively the same as those in nBE–H$_2$O.

Thus, mixing scheme I operative in the most water-rich region is that in which iBE enhances the hydrogen bond network of H$_2$O in its immediate vicinity ("an iceberg formation") and at the same time reduces the hydrogen bond probability of bulk H$_2$O away from solutes. As the solute composition increases, the hydrogen bond probability of bulk H$_2$O decreases to the hydrogen bond percolation threshold, and the hydrogen bond network is no longer connected throughout the entire system. Thus, the characteristics of liquid H$_2$O is lost. The system changes to mixing scheme II. The transition from mixing scheme I to II occurs in a narrow composition range, from point X at $x_{iBE} = 0.012$ to point Y at $x_{iBE} = 0.026$ at 20 °C, with the nominal midpoint M at $x_{iBE} = 0.019$, as shown in Fig. 3. For nBE–H$_2$O, we have no boundary data at 20 °C. Point X, however, could be interpolated, which yields $x_{nBE} = 0.019$, which should be compared with $x_{iBE} = 0.012$ for point X of iBE–H$_2$O. (Note that
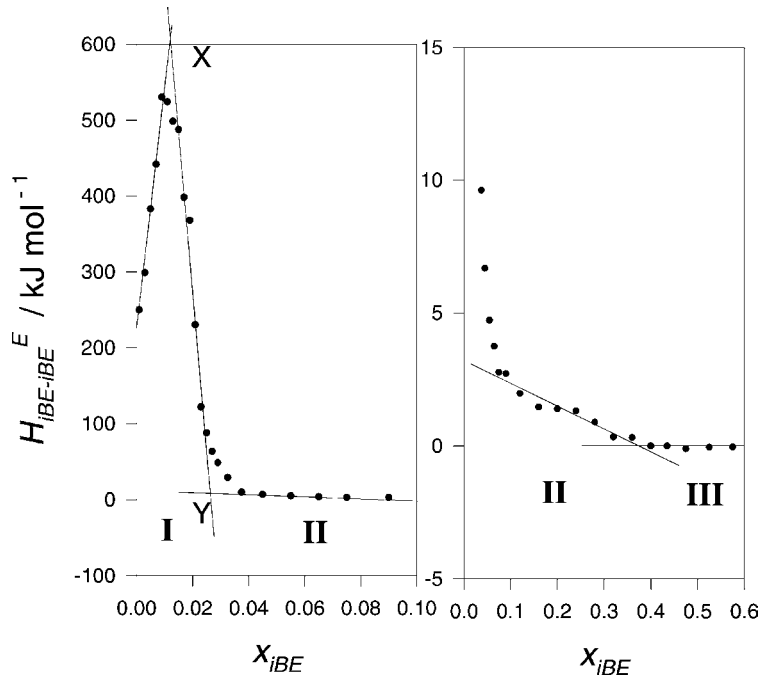
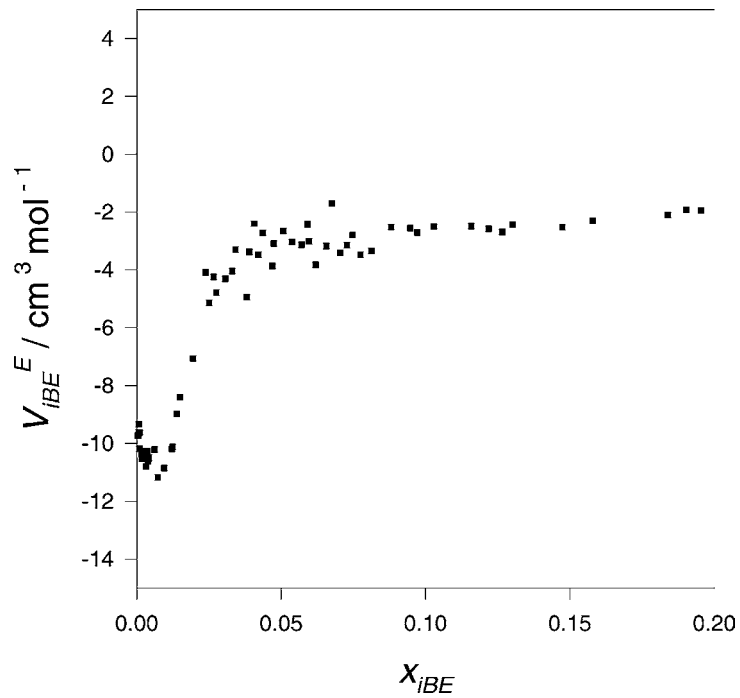Fig. 3. Enthalpic interaction function between iBE and iBE. See text for detail.

Fig. 4. Excess partial molar volume of iBE, V_{iBE}^E, at 25 °C, calculated using the volume data of [3].

x_{nBE} is the mole fraction of nBE in nBE–H_2O.) It is the general observation that the larger the hydrophobic moiety of solute alcohol, the smaller the value of its mole fraction at the boundary from mixing scheme I to II [14]. Thus, from the loci of point X, iBE seems to be a stronger hydrophobic solute than nBE, which is consistent with the fact that iBE has an extra methyl group.

As evident from Fig. 3, mixing scheme II spans from $x_{iBE} = 0.019$ (midpoint M) to $x_{iBE} = 0.35$. In this region, the positive slopes of H_{iBE}^E and S_{iBE}^E are consistent with an interacting system which exhibits phase separation with an LCST [5,6]. Thus, the solution in this range consists of two kinds of clusters rich in each component. They will grow in size to the macroscopic level at the LCST to induce phase separation. There is no longer the hydrogen bond network connected throughout of the system.

Mixing scheme III, $x_{iBE} > 0.35$, on the other hand, is characterised with zero H_{iBE}^E and almost zero S_{iBE}^E, which suggests that iBE in this range is in the same environment as in its pure state. We suggest as in nBE–H_2O [4–7,13] that iBE forms a cluster of its own kind and H_2O interacts with the surfaces of such clusters as a single molecule.

Acknowledgements

References

[1] G. Perron, F. Quirion, D. Lambert, J. Ledoux, L. Ghaioha, R. Bennes, M. Privat, J.E. Desnoyers, J. Solution Chem. 22 (1993) 107.
[2] H. Doi, K. Tamura, S. Murakami, J. Chem. Thermodyn. 32 (2000) 729.
[3] M.I. Davis, M. Chacon, Thermochim. Acta 190 (1991) 259.
[4] Y. Koga, J. Phys. Chem. 95 (1991) 4119.
[5] Y. Koga, J. Phys. Chem. 100 (1996) 5172.
[6] Y. Koga, J. Crystall. Soc. Jpn. 37 (1995) 172.
[7] W. Siu, Y. Koga, Can. J. Chem. 67 (1989) 671.
[8] Y. Koga, Can. J. Chem. 66 (1988) 1187.
[9] Y. Koga, W.W.Y. Siu, T.Y.H. Wong, J. Phys. Chem. 94 (1990) 7700.
[10] Y. Koga, J. Phys. Chem. 99 (1995) 6231.
[11] P. Westh, C.A. Haynes, Y. Koga, J. Phys. Chem. B 102 (1998) 4982.
[12] M.T. Parsons, P. Westh, J.V. Davies, Ch. Trandum, E.C.H. To, W.M. Chiang, E.G.M. Yee, Y. Koga, J. Solution Chem. 30 (2001) 1007.
[13] Y. Koga, J. Phys. Chem. 96 (1992) 10466.
[14] S.H. Tanaka, H.I. Yoshihara, A.W.-C. Ho, F.W. Lau, P. Westh, Y. Koga, Can. J. Chem. 74 (1996) 713.