Model Systems for Hydrophobic Interactions: Volumes and Heat Capacities of *n*-Alkoxyethanols in Water

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The densities and heat capacities of the first four members of the 2-n-alkoxyethanols were measured in water over the whole mole fraction range with a flow densimeter and a flow microcalorimeter. The methoxy and n-propoxy homologs were studied at 25°C, ethoxyethanol at 10, 25, and 40C, and n-butoxyethanol at 4, 10, 25, 40, and 55°C. While methoxyethanol behaves as a fairly typical polar nonelectrolyte in water, n-butoxyethanol shows trends in the concentration dependence which resemble micellization; some pseudo-microphase transition occurs at about 0.02 mole fraction, and this transition concentration decreases with increasing temperature. There is no simple relationship between this phenomenon and the existence of a lower critical solution temperature at 49°C since the sharpness of the thermodynamic changes is maximum at the lowest temperature and at 55°C the apparent molal quantities on both sides of the two-phase region appear to fall on the same continuous curve. In the region prior to the pseudo-microphase separation the apparent and partial molal heat capacities decrease regularly but beyond approximately 0.01 mole fraction increase sharply to a maximum, suggesting some type of pre-association. The apparent molal heat capacity of water in the binary solutions is larger than the molar heat capacity of water over the whole mole fraction range. The present data seem to be consistent with a clathrate model for hydrophobic hydration and interactions with these systems.

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1. INTRODUCTION

The alkoxyethanols, commercially known as cellosolves, are used extensively as solvents and solubilizing agents in many industries with interests ranging from pharmaceutical to plastic products. These compounds resemble alcohols in many respects, but the introduction of an ether oxygen in the aliphatic chain increases significantly their solubility in water; the homologs up to butyl are completely miscible with water at room temperature. Still, their practical applications have not stimulated much interest for the study of their mixtures with water. The properties of the pure liquids are reasonably well known, but there are relatively few thermodynamic studies of their aqueous solutions, especially in the water-rich region.

Our interest for these aqueous solutions arose from our earlier studies on the heat capacity of aqueous mixtures. We observed that the apparent molal heat capacity of many organic liquids in water decreases in a monotonic way to the molar value as the mole fraction was increased from zero to unity.[1,2] On the other hand, some liquids such as tert-butanol,[3] piperidine,[1] and triethylamine[2] have a very characteristic heat capacity; the apparent and partial molal heat capacities go through a maximum and then decrease sharply in the water-rich region, suggesting some association process similar to micellization[4]. We thought that there might be a relation between this association and the tendency of these solutes to unmix at high temperatures. The alkoxyethanols all have such a tendency and, in the case of n-butoxyethanol, the lower critical solution temperature is 49°C. We therefore undertook a systematic investigation of the heat capacities of the homologous series $ROCH_2CH_2OH$ for R varying from methyl to n-butyl over the whole mole fraction range and with many as a function of temperature. Precise densities are required to calculate the apparent molal heat capacities. Therefore densities were also determined and expansibilities derived from their temperature dependence.

2. EXPERIMENTAL

The origins of the n-alkoxyethanols (RE) are as follows:

2-Methoxyethanol (ME):	Aldrich Chemicals (spectrophotometric gold label grade)
2-Ethoxyethanol (EE):	Fisher (Purified)
2-Propoxyethanol (PE):	ICN Pharmaceutical
2-Butoxyethanol (BE):	Baker Chemicals

Whenever necessary the alkoxyethanols were redistilled and kept over 4 Å molecular sieves. Their purity was estimated as better than 99% by vapor-phase chromatography on 10% SE30 or 10% 20 M Carbowax columns. All

solutions were prepared by weight with deionized (Continental Deionizer Water System) distilled water.

Differences in densities $d - d_0$ and relative changes in heat capacities per unit volume $(\sigma - \sigma_0)/\sigma_0$ were measured with a commercial version (SODEV, Sherbrooke, Quebec) of a flow digital densimeter[5] and a flow microcalorimeter.[6,7] At 25°C the detection limits are 3×10^{-6} g-cm^{-3} and 7×10^{-5} J-°K^{-1}-cm^{-3}. The general procedure and uncertainties at other temperatures have been given elsewhere.[5,7] For heat capacity measurements the flow rate was kept at 0.45 cm^3-min^{-1}, the basic power of the heating element at approximately 21.5 mW, and the increase in temperature during the heat capacity measurement at 0.7°K. The absolute temperature of the measurements was measured to ± 0.01°K with a Hewlett-Packard Quartz thermometer.

3. RESULTS

The apparent molal volumes ϕ_V and heat capacities ϕ_C of the RE in water were calculated from the experimental data with the usual relations

$$\phi_V = M/d - 1000(d - d_0)/mdd_0 \tag{1}$$

and

$$\phi_C = Mc_p + 1000(c_p - c_{p0})/m \tag{2}$$

where M is the solute molecular weight, m the molality, and c_p the specific heat capacity. The density d_0 and specific heat capacity c_{p0} of pure water were taken as those of Kell[8] and Stimson.[9] The difference in specific heat capacity was calculated from the relative change in heat capacity per unit volume with the relation

$$c_p - c_{p0} = c_{p0}\left(\frac{\sigma - \sigma_0}{\sigma_0} + 1\right)\frac{d_0}{d} - c_{p0} \tag{3}$$

where $\sigma_0 = c_{p0}d_0$.

The experimental data Δd and $\Delta \sigma / \sigma_0$ and the derived ϕ_V and ϕ_C are given elsewhere.[4] These functions were measured over the whole mole fraction range at 25°C for the four alkoxyethanols (ME, EE, PE, and BE), at 10 and 40°C for EE and at 4, 10, 40, and 55°C for BE. The system BE-water unmixes at a lower critical solution temperature of 49°C for a critical mole fraction of 0.05_2.[10-14] Therefore, at 55°C, measurements were made on both sides of the two-phase region. Since changes in ϕ_V and ϕ_C are much more important in the water-rich region, a large number of data points were

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[4] A complete set of tabular data is available at a nominal charge, from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A OS2.

determined for molalities lower than 2 moles-kg^{-1}. At low molalities ϕ_V and ϕ_C vary linearly with m and can be fitted to an equation of the type

$$\phi_Y = \phi_Y^{\ominus} + A_Y m \qquad (4)$$

where the subscript Y stands for V or C. From a least-squares analysis it is possible to derive the standard apparent or partial molal quantity $\phi_Y^{\ominus} = \overline{Y}^{\ominus}$ and the limiting slope A_Y. The values of $\overline{V}^{\ominus}$, $\overline{C}_p^{\ominus}$, A_V, and A_C and the range of m used for the analysis are given in Table I for the different RE and temperatures. The molar volumes V° and heat capacities C_p° of the pure RE are also given in Table I.

As mentioned earlier, there exist few thermodynamic data on these systems in the literature, and consequently a check for the accuracy is difficult to make. We have not found any values for $\overline{V}^{\ominus}$. Onken[15] has measured the densities of pure BE at 20, 30, 40, 60, and 80°C; V° derived from these densities (131.20, 132.44, 133.70, 136.74, and 139.24 cm^3-mole^{-1} respectively) fall within 0.1 cm^3-mole^{-1}, on the curve derived from the V° given in Table I. The value of V° given by Chakhovskoy et al.[16] at 20°C (130.93 cm^3-mole^{-1}) is also in good agreement with Onken's value and the present interpolated one. Scatchard and Wilson[17] measured the densities of the BE–H$_2$O system at 27°C at high mole fractions, and the derived V° (132.08 cm^3-mole^{-1}) is again in good agreement with our interpolated value (132.05 cm^3-mole^{-1}). Chu and Thompson[18] also measured the densities of some RE–H$_2$O mixtures at 25°C but not in the water-rich region. The derived V° for ME (79.24), EE (97.40), and BE (131.80) are all in good agreement with the values in Table I with the possible exception of EE where the difference is 0.25 cm^3-mole^{-1}. With the exception of EE where there is a systematic difference, their ϕ_V also agree with the present data within 0.1 cm^3-mole^{-1}. McKinley and Nibarger[19] also measured the densities of EE–H$_2$O mixtures at 25°C but did not give the experimental data, making any comparison difficult.[5]

Kusano et al.[20] measured C_p° and $\overline{C}_p^{\ominus}$ of RE at 25°C. With both functions the agreement with Table I is within 1%. For C_p° their values (174.9, 210.8, 241.6, and 273.1 $\pm$ 0.2 J-°K^{-1}-mole^{-1} respectively) are probably more precise than ours since in our procedure σ of RE was measured relative to pure water, and under the best conditions $\Delta\sigma$ can be measured to 0.5%. On the other hand, our $C_p^{\ominus}$ are probably more accurate since Kusano et al. derived their $\overline{C}_p^{\ominus}$ from C_p° and the temperature dependence of the standard enthalpies of solution. Their values are respectively 290 $\pm$ 4, 387 $\pm$ 5, 468 $\pm$ 5, and 556 $\pm$ 7 J-°K^{-1}-mole^{-1}. Onken[15] determined C_p° of BE from 25 to 100°C. His values at 25, 40, and 55°C (273.3, 280.6, and 287.0 J-°K^{-1}-

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[5] Note added in proof: Harada et al. (see ref. 37) have recently studied the volumes and compressibilities of ethylene glycol derivatives in water, and their $V^{\ominus}$ are, in general, in excellent agreement with ours.

Table I. Volumes and Heat Capacities of 2-*n*-Alkoxyethanols in Water

2-*n*-Alkoxy-ethanol	T, °C	$V^{\ominus}$, cm^3-mole^{-1}	A_V, cm^3-mole^{-2}-kg	m_{max}, moles-kg^{-1}	$V°$, cm^3-mole^{-1}	$\bar{C}_P^{\ominus}$, J-°K^{-1}-mole^{-1}	A_C, J-°K^{-1}-mole^{-2}-kg	m_{max}, moles-kg^{-1}	$C_{P}^{°}$, J-°K^{-1}-mole^{-1}
ME	25	75.11	-0.47_0	0.8	79.25	286.7	-8.7	4	176.4
EE	10	90.18	-1.3_8	0.6	95.78	384.1	-19	1.6	205.2
	25	90.97	-0.8_6	0.6	97.15	383.5	-11.7	3.4	210.3
	40	92.02	-0.5_9	0.6	98.64	383.8	-8.7	2	217.2
PE	25	107.10	-1.3_3	0.4	114.58	470.9	-10.9	0.5	244.3
BE	4	120.70	-2.7_1	0.5	129.28	557.7	-19.4	0.5	261.2
	10	121.33	-2.4_7	0.4	129.98	556.0	-7.1	0.5	263.3
	25	122.91	-1.5_3	0.4	131.78	555.6	-5.6	0.4	270.6
	40	124.54	-0.4_1	0.45	133.71	550.2	-6.1	0.6	281.5
	55	126.37	$+0.7_4$	0.6	135.70	550.2	-26.5	0.6	290.1

mole^{-1} respectively) agree within 1% with C_p° of Table I. He also measured heat capacities of BE–H$_2$O mixtures at high mole fractions, and the agreement between his derived ϕ_C and the present data is very satisfactory.

Recently Picker et al.[21] have developed a flow dilatometer for precise expansibility measurements. The apparent molal expansibilities ϕ_E of BE derived from these direct measurements are equal, within the experimental uncertainty, to those calculated from the temperature dependence of ϕ_V at various temperatures.

Whenever a comparison with literature data was possible the agreement was within the uncertainty of both sets of data. We are therefore confident that the accuracy of the present data over the whole mole fraction range at various temperatures is comparable with the precision of the measurements given in Table I.

4. DISCUSSION

In general, thermodynamic properties of binary liquid mixtures are discussed in terms of molar excess functions. Besides a pronounced asymmetry these curves for RE–H$_2$O mixtures (not shown) do not have any anomalous behavior. However, as was discussed by de Visser et al.[3], these functions do not reflect properly the characteristic interactions taking place in organic–water mixtures. On the other hand, apparent or partial molal quantities show spectacular changes in the water-rich region, indicating that important structural changes are taking place especially with long-chain homologs and at low temperatures. It is therefore in terms of these functions that the present results will be discussed.

4.1. Temperature Dependence of Standard Quantities and Limiting Slopes

The temperature dependence of $\bar{V}^{\circ}$, V°, $\bar{C}_p^{\circ}$, and C_p° is shown for EE in Fig. 1a and for BE in Fig 1b. The function $\bar{C}_p^{\circ}$ of EE is nearly independent of temperature while that of BE decreases slightly. A more meaningful procedure for investigating solute–solvent interactions is to examine $\bar{C}_p^{\circ} - C_p^\circ$. This function decreases with temperature with both solutes, and the decrease is largest with the higher homolog. This is believed to be typical of hydrophobic solutes. Hydrophobic hydration causes a positive contribution to heat capacities[22] and, if this type of hydration is related to the extent of structure in liquid water, it is expected that this positive hydration contribution should decrease with increasing temperature. However, we would expect the decrease in $\bar{C}_p^{\circ} - C_p^\circ$ with temperature to be somewhat larger than is observed.
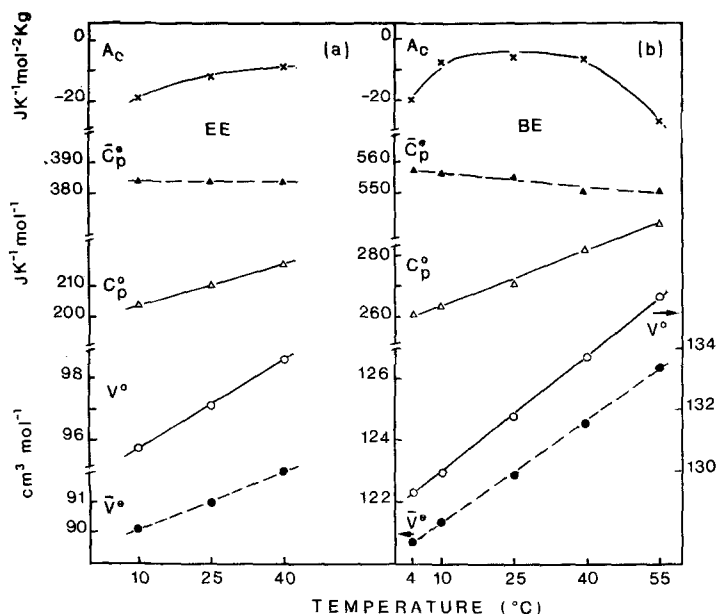
Fig. 1. Temperature dependence of the parameters $\bar{V}^{\oplus}$, V°, $\bar{C}_{p}^{\oplus}$, C_{p}°, and A_{c} for 2-ethoxy-ethanol and 2-n-butoxyethanol in water.

The volumes $\bar{V}^{\oplus}$ are smaller than V° at all temperatures. This is again characteristic of hydrophobic hydration[22]; hydrophobic hydration occurs with an economy of space, the solute occupying on a time average some of the natural void space present in liquid water.

From the temperature dependence of $\bar{V}^{\oplus}$ and V° the corresponding standard partial molal and molar expansibilities (e.g., $\bar{E}^{\oplus} = d\bar{V}^{\oplus}/dT$) can be derived (Table II). Both $\bar{E}^{\oplus}$ and E° are positive, but $\bar{E}^{\oplus} - E^{\circ}$ is negative.

Table II. Expansibilities of 2-n-Alkoxyethanol in Water[a]

	Ethoxyethanol			Butoxyethanol	
T	$\bar{E}^{\oplus}$	E°		$\bar{E}^{\oplus}$	E°
7	0.105	0.117			
17.5	0.105	0.120		0.0527	0.0913
32.5	0.109	0.129		0.0700	0.0993
47.5	0.122	0.133			

[a] All units in cm-$^{\circ}$K^{-1}-mole^{-1}.

This sign is the expected one for hydrophobic solutes.[3] There is more free space in a pure organic liquid than in the vicinity of a hydrophobic solute in water since $\bar{V}^{\oplus} - V^{\circ} < 0$. Consequently we would expect the expansibility of the pure RE to be larger than $\bar{E}^{\oplus}$. There might be an additional positive contribution to $\bar{E}^{\oplus}$ arising from a modification of the hydrophobic cosphere as the temperature is increased,[23] but the cavity effect gives the sign to $\bar{E}^{\oplus} - E^{\circ}$.

Some information can also be drawn from the limiting slopes A_C and A_V. The parameter A_C of *tert*-butanol was negative at low temperatures and leveled off to a positive value at high temperatures.[3] With EE the trend is similar but A_C never becomes positive (Fig. 1a). With BE, A_C goes through a flat maximum (Fig. 1b) between 25 and 40°C and, as with EE, remains negative. This suggests that the interactions influencing these concentration dependences are complex and, unless data can be obtained at very low concentrations where we can determine unambiguously the pair-interaction parameter, it is not easy to interpret this slope. On the other hand, the parameter A_V is negative, except for BE at 55°C, and becomes more negative the longer the alkyl chain and the lower the temperature. This is the usual behavior observed with hydrophobic solutes.

4.2. Concentration Dependence of Thermodynamic Functions

The concentration (mole fractions or molalities) dependence of the apparent molal functions ϕ_C, ϕ_V, and ϕ_E $(=d\phi_V/dT)$ are summarized in Figs. 2 to 6. In Fig. 2 $\phi_C - \phi_C^{\oplus}$ and $\phi_V - \phi_V^{\oplus}$ are given for the four homologs as a function of mole fraction at 25°C. The water-rich region is shown for $\phi_C - \phi_C^{\oplus}$ in Fig. 3. The temperature dependence of ϕ_C and ϕ_V is shown for EE and BE in Figs. 4 and 5. Finally the mole fraction dependence of ϕ_E is given in Fig. 6 at 25°C for EE and BE.

The behavior of ϕ_V is typical of most organic solutes in water. It goes through a minimum and levels off to V° which is larger than $\bar{V}^{\oplus}$. The minimum occurs at a lower concentration and is sharper the more hydrophobic the solute, and the depth of the minimum decreases with increasing chain length (except with ME) and increasing temperature.

The concentration dependence of ϕ_C is much more specific to chain length and to temperature. The two lower homologs ME and EE are typical of a class of solutes including dimethyl sulfoxide,[24] dioxane,[25] acetone,[24] dimethylformamide,[26] and ethers and esters[27] where ϕ_C decreases in a regular way to C_P°; ϕ_C of ME is approximately linear in volume fraction (not shown). However, with PE, the decrease in ϕ_C is sharper and a shoulder appears, and with BE a minimum followed by a maximum in ϕ_C is seen. The changes in the water-rich region are shown more clearly in Fig. 3. With
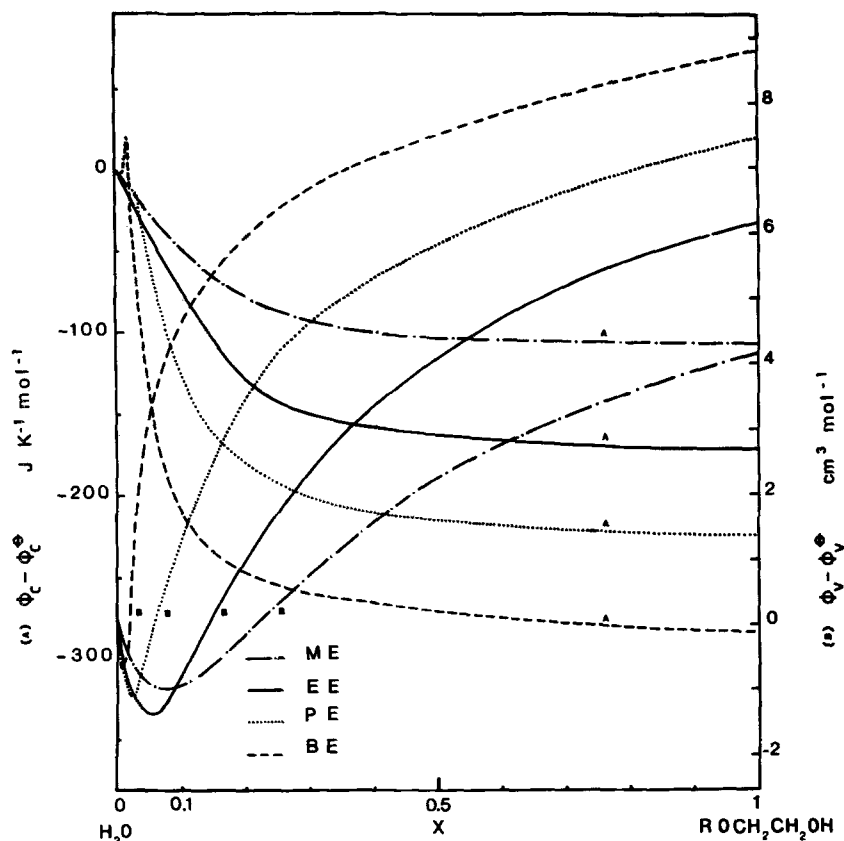
Fig. 2. Excess apparent molal heat capacities and volumes of 2-n-alkoxyethanols in water at 25°C.

EE the shape of the concentration dependence of ϕ_C does not depend very much on temperature (Fig. 4). On the other hand, temperature has a marked effect on BE in the water-rich region (Fig. 5). The maximum in ϕ_C is largest at low temperatures and vanishes completely at high temperatures. The changes are much more spectacular if $\bar{C}_p$ (obtained from a plot of $\Delta(\phi_C m)/\Delta m$ versus mean molality) are plotted instead of ϕ_C. It was shown elsewhere[28] that the concentration dependence of $\bar{C}_p$ of BE at 4°C approaches a first-order transition at about 0.025 mole fraction. Beyond 0.1 mole fraction $\bar{C}_p$ shows little concentration dependence and has a value close to C_p°. Parallel studies in our laboratory on ionic surfactants in water show very similar trends for the concentration dependence of ϕ_C and $\bar{C}_p$; there is a sharp increase in $\bar{C}_p$ just before the critical micelle concentration, especially with sodium decanoate, followed by a very large decrease during micellization, a
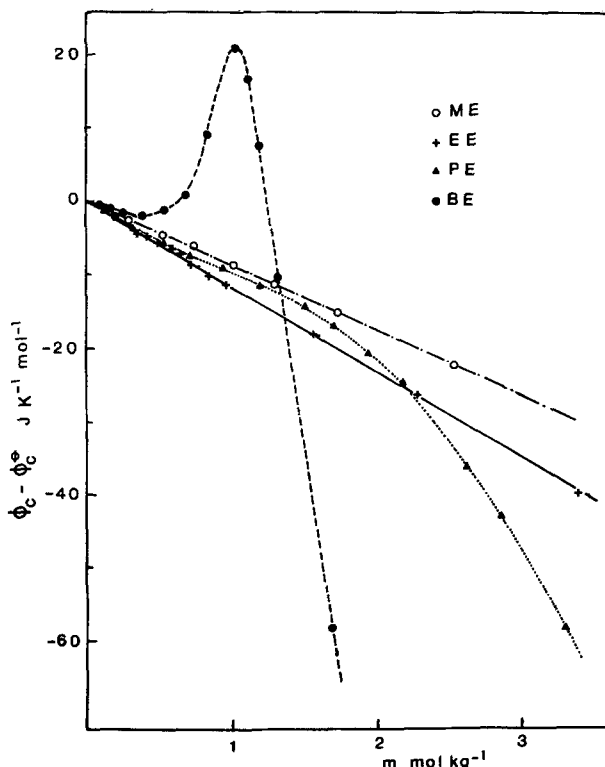
Fig. 3. Excess apparent molal heat capacities of 2-*n*-alkoxyethanols in the water rich-region at 25°C.

shallow minimum, and a constant $\bar{C}_p$ in the postmicellar region. The constancy and magnitude of $\bar{C}_p$ in the postmicellar region[4] is consistent with models suggesting that the state of the hydrophobic chains in the interior of a micelle is similar to that of a pure organic liquid. Also, heat capacity data tell us that at high concentrations the hydrophobic part of BE is seeing only other hydrophobic groups and not water. It therefore seems that BE exists as microphases or aggregates beyond the transition region. This effect persists up to high temperatures although the maximum in ϕ_C or in $\bar{C}_p$ during aggregation is also less sharp at high temperatures.

Similar trends were also observed with *tert*-butanol,[3] triethylamine,[2] piperidine,[25] and diethylmethylamine.[29]

The concentration dependence of ϕ_E is not as specific as ϕ_C, as seen in Fig. 6. With both EE and BE, ϕ_E increases to a maximum and then levels off to the value of E°. The changes are of course much sharper with BE. The same general behavior was observed with *tert*-butanol[3] and with surfactants.
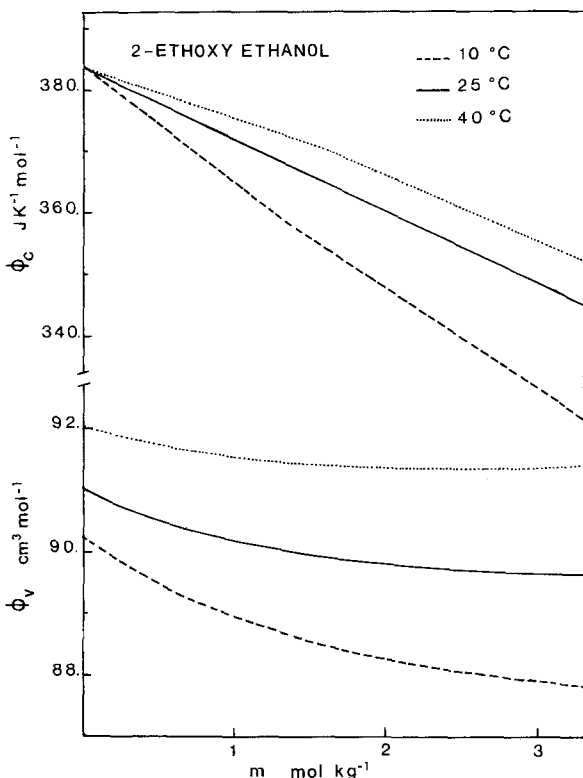
Fig. 4. Apparent molal heat capacities and volumes of 2-ethoxyethanol in the water-rich region at various temperatures.

If the sharp decrease in ϕ_C corresponds to some pseudophase transition, then a phase diagram of these internal structures in the BE–H$_2$O system can be drawn as shown in Fig. 7. The microphase transition was taken at the concentration at which $\bar{C}_p$ goes through a maximum. The region where a maximum in ϕ_C exists is also shown in Fig. 7. The lines were not drawn beyond 55°C since no data points were measured at higher temperatures and the sharpness of the transition decreases with increasing temperature.

There is no direct relation between the existence of a lower critical solution temperature and the existence of microphases in the solution. The transitions are larger at low temperature than near the phase separation. Parallel studies[27] on other systems that have a tendency to unmix also indicate that these systems do not necessarily show pseudotransitions. Also, at 55°C, ϕ_C and ϕ_V were measured on both sides of the two-phase region, and it would be possible to draw a smooth line between the values in the water-
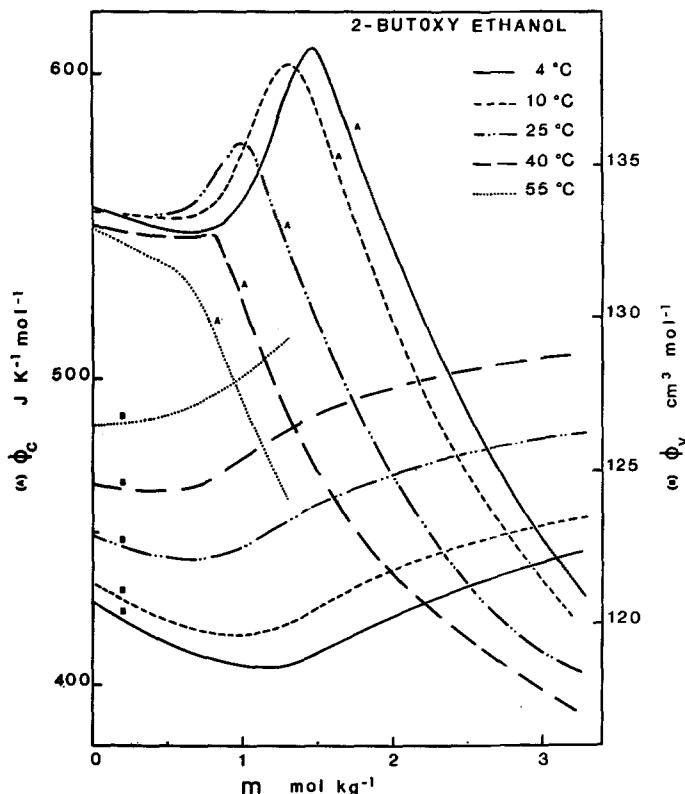
Fig. 5. Apparent molal heat capacities and volumes of 2-n-butoxyethanol in the water-rich region at various temperatures.

rich region and in the BE-rich region (not shown), indicating that nothing anomalous is occurring in these regions, at least with this system.

The presence of a region where microphases or aggregates of hydrophobic solutes exist could explain why substances like alcohols usually need to be added to stabilize microemulsions.[30] Work is presently under way in our laboratory to investigate such a relationship.

4.3. Apparent Molal Quantities of Water in the Mixtures

It was noted recently[3,26] that the apparent molal heat capacity of water in *tert*-butanol and dimethylformamide was of the same magnitude or larger than C_p° of pure water. On the other hand, ϕ_V(water) decreased in a regular way from 18 cm^3-mole^{-1} in pure water to values between 15 and 16 cm^3-mole^{-1}, as we would expect for water molecules in an unstructured
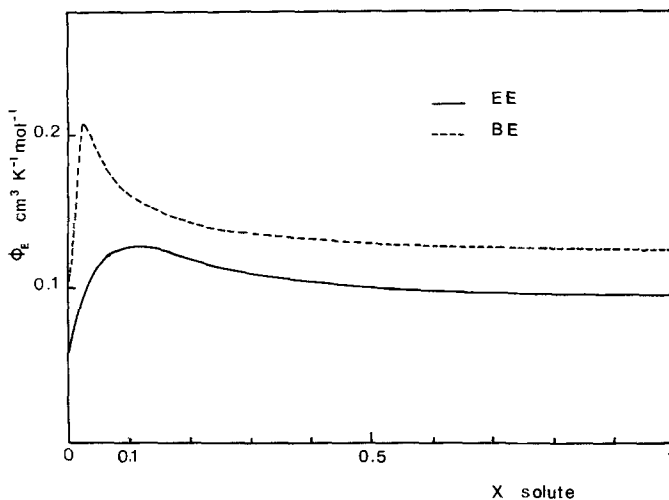
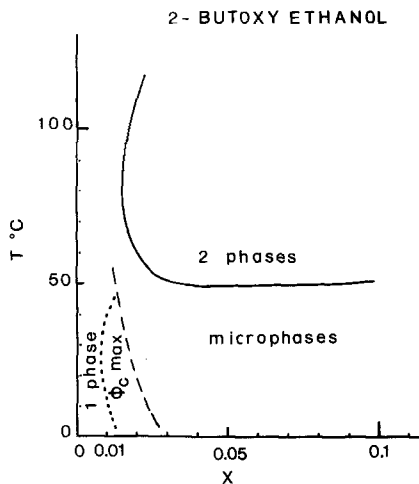**Fig. 6.** Apparent molal expansibilities of 2-ethoxyethanol and 2-n-butoxyethanol in water at 25°C.

Fig. 7. Phase diagram of 2-n-butoxy-ethanol–water system.

medium. The trends of ϕ_V(water) are also quite regular in the various RE (not shown); for example, in BE, $\phi_V^{\ominus}$(water) has a value of 15.5 cm^3-mole^{-1}. In all RE ϕ_C(water) is again abnormally high over the whole range of mole fractions, as seen from Fig. 8. Not only does ϕ_C(water) remain larger than C_p° of pure water but $\overline{C}_p^{\ominus}$(water) increases with temperature and reaches the very high value of 98 J-°K^{-1}-mole^{-1} for BE at 40°C. De Visser *et al.*[31] have undertaken a systematic investigation of the properties of water in
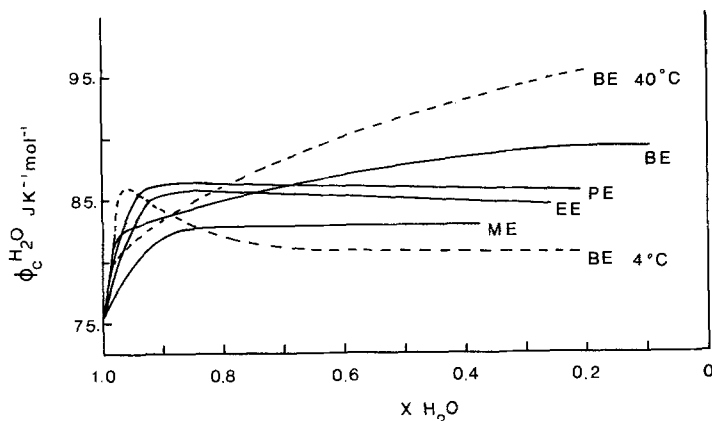
Fig. 8. Apparent molal heat capacity of water in 2-alkoxyethanol–water mixtures.

nonaqueous solvents and they find that $\bar{V}^{\ominus}$(water) varies in a systematic way with the molar volume of the solvent, but they find no such relationship with $\bar{C}_p^{\ominus}$(water). Therefore the meaning of these high heat capacities is still an open question and we should be careful in attributing high values of heat capacities necessarily to structure. We can well imagine, in the nonaqueous end of BE–H$_2$O mixtures, that water could be highly structured, but it is more difficult to suggest this for simpler liquids like dimethylformamide.

4.4. Clathrate Model

A model to be valid should explain all the properties of the system. Unfortunately, with RE, few systematic investigations have been made, especially in the water-rich region. We therefore have to rely on other similar systems where plenty of data are available. The *tert*-butanol–water mixtures fall in this category. The concentration dependence of ϕ_C, ϕ_E, and ϕ_V of BE is very similar to that of *tert*-butanol[3] at low temperatures, but the various transitions are sharper with BE. We would therefore expect that models which are valid for alcohols will apply also to RE.

A large quantity of data are available for alcohol–water mixtures.[22] In particular, Blandamer *et al.*[32] have examined the ultrasonic absorption of *tert*-butanol–water mixtures and found that at least two relaxation frequencies were required to account for the overall relaxation curve. They suggested that the results could be interpreted with a clathrate hydrate model. As the concentration increases, two or more solutes may share a clathrate; eventually, at higher concentrations, the clathrates are destroyed completely and bare alcohol molecules exist. Fanning and Kruus[33] observed that the ultrasonic absorption of 2-isobutoxyethanol was similar to that of alcohols

and amines and suggested that the large absorption could be related to a phenomenon that resembles phase separation. Recently Tamura et al.[34] reexamined the ultrasonic absorption of tert-butanol in water and made quantitative predictions of the relaxation absorption with a clathrate model similar to that of Blandamer.

Muller[35] measured the fluorine chemical shift of 6,6,6-trifluoro-1-hexanol in various organic-aqueous mixed solvents and found that to interpret tert-butanol–water mixtures strong association between alcohol mixtures similar to micellization has to be assumed.

Finally, Iwasaki and Fujiyama[36] have refined the clathrate model for tert-butanol–water mixtures. They reduced the Rayleigh intensities of their light-scattering spectra to concentration fluctuations and found that three regions had to be assumed. At low concentrations ($X < 1/22$) single-solute clathrate hydrates exist with an average structure $(H_2O)_{21} \cdot TBA$. As the concentration increases, solvent-shared association complexes similar to solid clathrates begin to form and reach the maximum stability at $X = 0.16$ with the average structure $(H_2O)_{105}(TBA)_5$. At higher concentration unhydrated TBA molecules exist. These two critical concentrations correspond approximately to the maximum in ϕ_C and the region where ϕ_C begins to level off.

Studies of other thermodynamic functions (free energies, enthalpies, and compressibilities), viscosity, and NMR and ESR spectra of RE in water should give a severe test of the clathrate model. Already enthalpy measurements presently underway appear consistent with this model.

ACKNOWLEDGMENT

REFERENCES

1. J. E. Desnoyers, O. Kiyohara, and G. Perron, *Adv. Chem. Ser.* **155**, 274 (1976).
2. C. de Visser, G. Perron, and J. E. Desnoyers, *J. Am. Chem. Soc.* **18**, 5894, (1977).
3. C. de Visser, G. Perron, and J. E. Desnoyers, *Can. J. Chem.* **55**, 586 (1977).
4. G. M. Musbally, G. Perron, and J. E. Desnoyers, *J. Colloid Interface Sci.* **48**, 494 (1974).
5. P. Picker, E. Tremblay, and C. Jolicoeur, *J. Solution Chem.* **3**, 377 (1974).
6. P. Picker, P. A. Leduc, P. R. Philip, and J. E. Desnoyers, *J. Chem. Thermodyn.* **3**, 631 (1971).
7. J. E. Desnoyers, C. de Visser, G. Perron, and P. Picker, *J. Solution Chem.* **5**, 605 (1976).

8. G. S. Kell, *J. Chem. Eng. Data* **12**, 66 (1967).
9. H. F. Stimson, *Am. J. Phys.* **23**, 614 (1955).
10. L. Cox and L. H. Cretcher, *J. Am. Chem. Soc.* **48**, 451 (1926).
11. G. Poppe, *Bull. Soc. Chim. Belg.* **44**, 640 (1935).
12. N. Chakhovskoy, *Bull. Soc. Chim. Belg.* **65**, 476 (1956).
13. G. Schneider and O. Wilhelm, *Z. Phys. Chem. (Frankfurt)* **80**, 219 (1959).
14. C. M. Ellis, *J. Chem. Educ.* **44**, 405 (1967).
15. Von. Y. Onken, *Z. Elektrochem.* **63**, 321 (1959).
16. N. Chakhovskoy, R. H. Martin, and R. Van Wechel, *Bull. Soc. Chim. Belg.* **65**, 453 (1956).
17. G. Scatchard and G. M. Wilson, *J. Am. Chem. Soc.* **86**, 133 (1964).
18. K. Y. Chu and A. R. Thompson, *J. Chem. Eng. Data.* **5**, 147 (1960).
19. L. McKinley and A. Nibarger, *J. Am. Chem. Soc.* **61**, 373 (1939).
20. K. Kusano, J. Suurkuusk, and I. Wadsö, *J. Chem. Thermodyn.* **5**, 757 (1973).
21. P. Picker, J. L. Fortier, M. A. Simard, and C. Jolicoeur, in preparation.
22. F. Franks and D. S. Reid, in *Water, A Comprehensive Treatise,* F. Franks, ed., Vol. 2, Plenum Press, New York, (1973), Chap. 5.
23. G. Perron, N. Desrosiers, and J. E. Desnoyers, *Can. J. Chem.* **54**, 2163 (1976).
24. O. Kiyohara, G. Perron, and J. E. Desnoyers, *Can. J. Chem.* **53**, 3263 (1975).
25. O. Kiyohara, G. Perron, and J. E. Desnoyers, *Can. J. Chem.* **53**, 2591 (1975).
26. C. de Visser, G. Perron, J. E. Desnoyers, W. J. M. Heuvelsland, and G. Somsen, *J. Chem. Eng. Data* **22**, 74 (1977).
27. G. Roux, G. Perron, and J. E. Desnoyers, in preparation.
28. G. Roux, G. Perron, and J. E. Desnoyers, *J. Phys. Chem.* **82**, 966 (1978).
29. G. Roux, G. Perron, and J. E. Desnoyers, unpublished results.
30. *Micellization, Solubilization, and Microemulsions,* K. L. Mittal, ed., Vols. 1 and 2 (Plenum Press; New York, 1977).
31. C. de Visser, W. J. M. Heuvelsland, L. A. Dunn, and G. Somsen, *J. Chem. Soc. Faraday Trans. 1,* **74**, 1159 (1978).
32. M. J. Blandamer, D. E. Clark, N. J. Hidden, and M. C. R. Symons, *Trans. Faraday Soc.* **64**, 2691 (1968).
33. R. J. Fanning and P. Kruus, *Can. J. Chem.* **48**, 2052 (1970).
34. K. Tamura, M. Maekawa, and T. Yasunaga, *J. Phys. Chem.* **81**, 2122 (1977).
35. N. Muller, *J. Magn. Reson.* **28**, 203 (1977).
36. K. Iwasaki and T. Fujiyama, *J. Phys. Chem.* **81**, 1908 (1977).
37. S. Harada, T. Nakajima, T. Komatsu, and T. Nakagama, *J. Solution Chem.* **7**, 463 (1978).