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Excess thermodynamic properties of mixtures of 2-butoxyethanol and water at 25°C

Aase Hvidt [a],* and Yoshikata Koga [b]

[a] *Department of Chemistry, H.C. Ørsted Institute, 5, Universitetsparken, DK-2100 Copenhagen Ø (Denmark)*
[b] *Department of Chemistry, The University of British Columbia, Vancouver, B.C. V6T 1Z1 (Canada)*

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Abstract

Available measurements of thermodynamic properties (enthalpy, Gibbs free energy and volume) of mixtures of water with 2-butoxyethanol at 25°C are discussed, with emphasis on the concentration dependence of the excess functions, and on the role played by water. The data support the view that in the water-rich concentration range the nonpolar groups of the alcohol molecules introduce labile, highly cooperative, energy-low structures in water. At lower water concentrations, exposure of nonpolar groups to water appears to be minimized by formation of micellar-like alcohol structures.

INTRODUCTION

Extensive measurements are available of thermodynamic properties of mixtures of (W) with 2-butoxyethanol (BE). The enthalpy [1,2], Gibbs free energy [3], volume [2,4,5] and heat capacity [4], at 25°C, are measured over the whole mole fraction range of the components. A pronounced concentration dependence of the properties has been taken as indication that "pseudo-micro-phase transitions" [6,7]), or "transitions in the mixing scheme" [1,8] occur with changes in composition and/or temperature of the mixtures. Some interpretations of the experimental data attach importance to the elucidation of interactions between BE molecules in aqueous solution [1,2,6], and the standard (or reference) state of BE is, therefore, chosen to be "infinite dilution in aqueous solution".

The aim of the present paper is to call attention to the part played by water in the thermodynamics of BE–W mixtures. At 25°C BE, as well as W, is liquid in the pure state, so aqueous solutions of BE can be treated as

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* Corresponding author.

liquid mixtures, with the pure liquid state considered to be the standard state of both components.

The partial contributions of BE and W to the integral excess enthalpy of BE–W mixtures are calculated from available experimental data, and discussed with reference to a tendency of BE molecules to associate to micellar-like structures, when exposed to water, and a tendency of water to form low-energy, ordered structures, when exposed to nonpolar groups of solute molecules.

VARIOUS REPRESENTATIONS OF THERMODYNAMIC DATA ON BE–W MIXTURES AT 25°C

Figure 1 shows available measurements of molar excess function G^E_m, H^E_m and TS^E_m of BE–W mixtures at 25°C, as functions of the mole fraction, x, of BE.

It is significant that the enthalpy of mixing BE and W is negative for all concentrations of the components. The BE molecule ($CH_3CH_2CH_2CH_2OCH_2CH_2OH$) has a rather high content of nonpolar groups. Interactions of these groups with other (polar or nonpolar) molecular groups are due to van der Waals forces, and the attraction is weaker than the mutual attraction of water molecules in the liquid state [9, 10]. Nevertheless, the enthalpy of BE–W mixtures is found to be lower

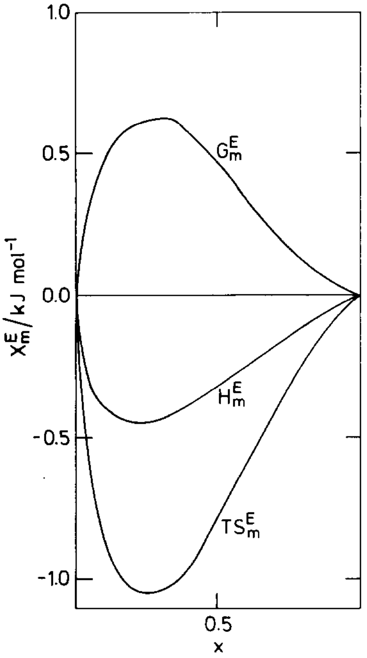

Fig. 1. Excess thermodynamic functions of mixtures of 2-butoxyethanol and water at 25°C: H^E_m [1], G^E_m [1, 3], and $TS^E_m = H^E_m - G^E_m$. x is the mole fraction of the alcohol.

than the enthalpy of pure water (see Fig. 1); this observation indicates that interactions, in the mixtures, of water molecules with one another, or with polar groups of the BE molecules are important for the thermodynamic behaviour of the mixtures. These interactions are established with a considerable loss of entropy (see Fig. 1).

Direct measurements of the partial molar excess enthalpy of both W and BE are reported in ref. 1, but the values of $H_m^E(W)$ are less accurate than the values of $H_m^E(BE)$. In the following $H_m^E(W)$ is calculated from values of $H_m^E(BE)$, using the Gibbs–Duhem relation

$$\frac{\Delta H_m^E(W)}{\Delta x} = -\frac{x}{1-x}\frac{\Delta H_m^E(BE)}{\Delta x} \tag{1}$$

Calculated values of $H_m^E(W)$, together with the directly measured values of $H_m^E(BE)$ [1], are shown in Fig. 2, as functions of x.

The inflection point for $x = 0.018$, where $dH_m^E(BE)/dx \approx 1000\ \text{kJ mol}^{-1}$, and $dH_m^E(W)/dx \approx -20\ \text{kJ mol}^{-1}$, is in accordance with the maximum in a plot of $(1-x)\,dH_m^E(BE)/dx$ shown in ref. 1.

The molar integral excess enthalpy of the mixtures H_m^E, and the partial contributions from BE and W ($xH_m^E(BE)$ and $(1-x)H_m^E(W)$, respectively) are illustrated in Fig. 3. It may be noted that for $x > 0.02$ the larger contribution to the integral excess enthalpy is due to the excess enthalpy of water.

Figures 4 and 5 show the apparent molar excess enthalpy of BE, $H_m^{E,app}(BE) = H_m^E/x$, and the apparent molar volume of BE, $V_m^{app}(BE) = [V_m - (1-x)V_m^*(W)]/x$, both as a function of x. The apparent molar volume of BE is determined by measurements of the density of the mixtures, as described in ref. 5.

DISCUSSION OF THERMODYNAMIC DATA ON BE–W MIXTURES AT 25°C

A characteristic feature of BE–W mixtures is the negative excess enthalpy of BE at infinite dilution ($-16.5\ \text{kJ mol}^{-1}$, see Fig. 2), and the strong concentration dependence of the enthalpy in the most water-rich concentration range. Positive values of $dH_m(BE)/dx$ have been taken as an indication that BE–BE interaction in the mixture is repulsive in terms of enthalpy [1].

$H_m^E(BE)$ and $H_m^E(W)$ are, however, interdependent; as illustrated in Fig. 2 they are both negative, and increasing (towards zero) with increasing concentration. Figure 3 shows that over most of the mole fraction range the contribution of water to the excess enthalpy of the mixtures is even larger than that of the alcohol.

Thermodynamic data on dilute aqueous solutions of BE have been discussed on the basis of a virial expansion in the solute concentration [2, 6]; the virial coefficients are taken as measure of contributions due to

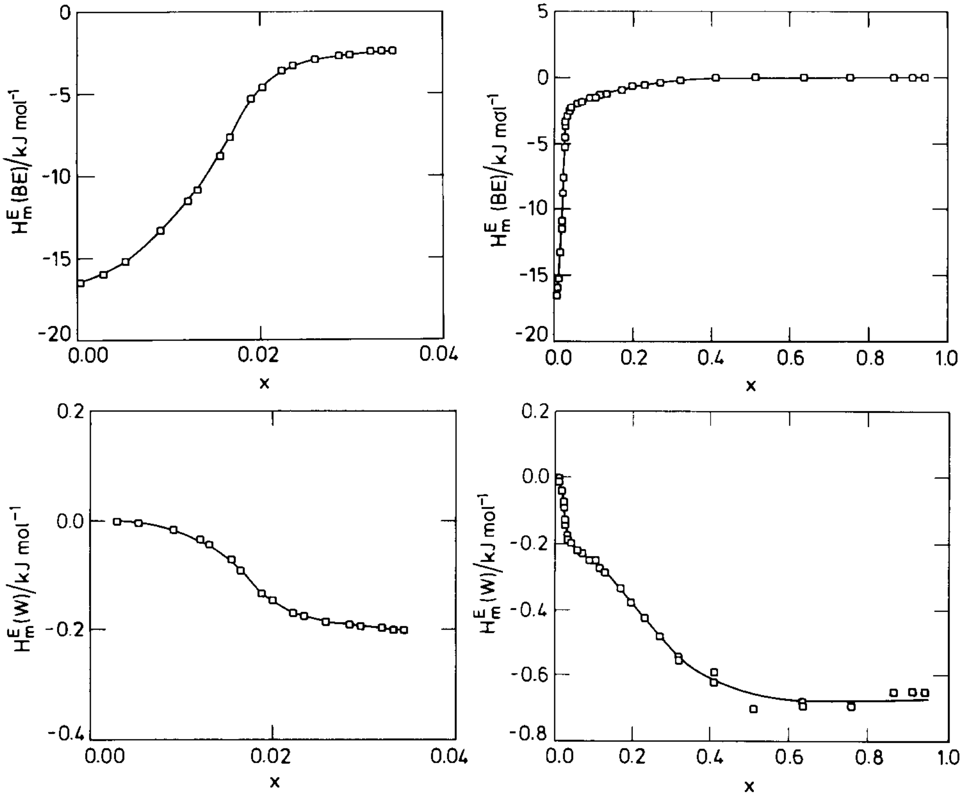

Fig. 2. Partial molar excess enthalpy of 2-butoxyethanol (H_m^E(BE)) and water (H_m^E(W)) in binary mixtures, at 25°C, with the mole fraction x of the alcohol. H_m^E(BE) is from ref. 1, and H_m^E(W) is calculated according to eqn. (1).

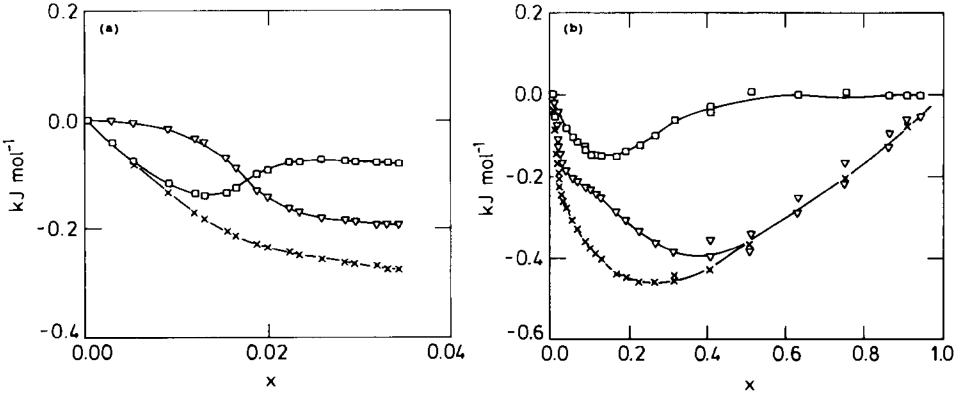

Fig. 3. Partial contributions of 2-butoxyethanol (xH_m^E(BE), □), and of water ($(1-x)H_m^E$(W), ▽) to the molar enthalpy (H_m^E, ×) of 2-butoxyethanol–water mixtures at 25°C. x is the mole fraction of the alcohol.

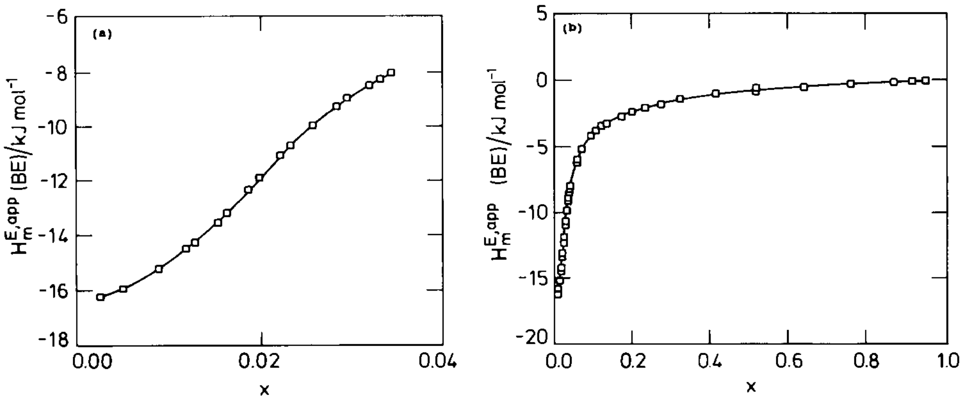

Fig. 4. Apparent molar excess enthalpy of 2-butoxyethanol ($H_m^{E,app}(BE) = H_m^E/x$) in binary aqueous mixtures at 25°C. x is the mole fraction of the alcohol.

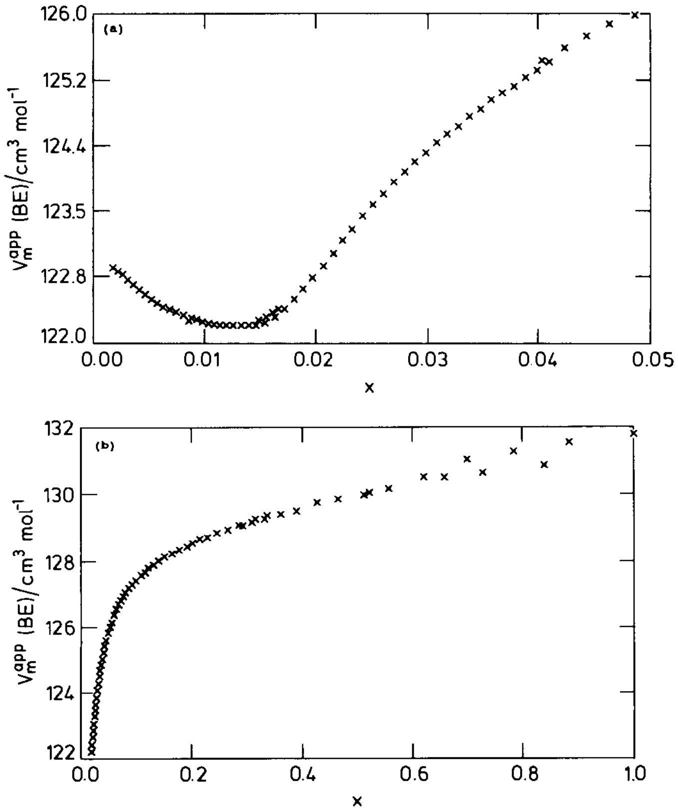

Fig. 5. Apparent molar volume of 2-butoxyethanol, $V_m^{app}(BE)$, in binary aqueous mixtures at 25°C. x is the mole fraction of the alcohol. Part of the data is published in ref. 5.

interactions between solute molecules. The data in Figs. 1–3 may, however, encourage an interpretation which pays importance to solute–solvent interactions.

The data on BE–W mixtures is in accordance with the opinion that nonpolar solute molecules introduce low-energy structures in solvent water; this phenomenon has tentatively been described as labile solute–solvent equilibria of the following type [10]

$$R + nH_2O \rightleftarrows R(H_2O)_n$$

where

$$\Delta H^0 < 0, \Delta S^0 < 0, \Delta V^0 > 0, n \gg 1. \tag{2}$$

R denotes a nonpolar molecule surrounded by bulk water, and $R(H_2O)_n$ denotes this group surrounded by a hydration sphere of n water molecules with a lower energy, a lower entropy, but a larger volume than bulk water.

If p is the extent of the hydration reaction (2), $p = [R(H_2O)_n]([R] + [R(H_2O)_n])$, the contribution to the apparent molar enthalpy of BE, $H_m^{app}(BE)$, and the apparent molar volume, $V_m^{app}(BE)$, (illustrated in Figs. 4 and 5), is $p\Delta H^0$, and $p\Delta V^0$, respectively; p increases with increasing water concentration.

The equilibrium constant of the reaction (2) may be expressed as

$$K = \frac{p}{1-p}[H_2O]^{-n} \tag{3}$$

where $[H_2O]$ is the molar concentration of "free" bulk water.

$$p = \frac{K[H_2O]^n}{1 + K[H_2O]^n} \tag{4}$$

$$\frac{dp}{d\ln[H_2O]} = np(1-p) \qquad (\leqslant n/4) \tag{5}$$

The slope of plots of $H_m^{E,app}(BE)$ vs. x, and of $V_m^{app}(BE)$ vs. x, for $x \rightarrow 0$ (see Figs. 4 and 5) illustrates an important feature of the "hydration" of nonpolar solute molecules in aqueous solution. The slope indicates that the equilibrium (2) is far from completely displaced towards the right hand side even at the highest possible water concentration, 55.5 mol l^{-1}. At infinite dilution p appears to be above one half, but well below unity (see eqn. (5)); thus $K[H_2O]^n$ is only slightly above unity for $[H_2O] = 55.5$ mol l^{-1} (see eqn. (3)), i.e. $K = (55.5 - \varepsilon)(1\ \mathrm{mol}^{-1})^n$, where $\varepsilon \ll 55.5$. The hydration spheres appear as "flickering clusters" of hydrogen bonded water molecules, sometimes denoted "icelike", because $\Delta H\,\Delta V < 0$.

The maximal slope of the plot of $H_m^{E,app}$(BE) vs. x (in Fig. 4) is 400 kJ mol^{-1}, corresponding to $\Delta H^0 = -1600/n$ kJ mol^{-1}. Comparison with estimates of ΔH^0 for methane (-35 kJ mol^{-1}) or ethane (-42 kJ mol^{-1}) [11], suggests that n (the number of water molecules in a hydration sphere) for BE is about 40 times the value of n for the small hydrocarbons.

In the range $0.03 < x < 0.4$, the data in Figs. 1–5 suggest that BE molecules, with increasing concentration, gradually associate to micellar-like structures in which the nonpolar groups are withdrawn from exposure to water. The driving force behind this association of BE molecules is the strong attraction of water molecules for one another, and for the polar groups of the BE molecules, rather than any strong mutual attraction of the nonpolar groups. For $x > 0.4$, mixing of BE and W may be considered as a dissolution of W in BE with a nearly constant dissolution enthalpy of -0.7 kJ mol^{-1}, mainly due to interactions of the water molecules with the polar groups of the BE molecules.

CONCLUSIONS

A recent review article by Desnoyers [7] is entitled, "Why Measure Thermodynamic Properties of Micellar Systems?". One answer to this question, supplementary to the arguments given in the review, might be, "In order to obtain insight into the nature of water as a solvent". The present paper is an attempt to focus interest on characteristic properties of solvent water.

Solvent water is not to be considered as a continuum in which reactions between solute molecules may occur, but rather as an "active" component of an aqueous solution. The experimental data on BE mixtures, discussed in the present paper, is in accordance with the understanding that interactions of water with the amphipatic BE molecules involve a cooperative action of many water molecules per BE molecule. The interaction is characterized by large, compensating energy and entropy contributions to the Gibbs free energy of the mixtures. In the water-rich concentration range abrupt perturbations of the interaction with changes in concentration may justify designations such as "pseudo-microphase transitions" [6, 7] or "transitions in the mixing scheme" [1, 8].

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