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Note

Prediction of the temperature dependence of excess volumes in dilute solutions of 1-alkanol in *n*-alkane

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Abstract

A model consisting of the association and Flory's equation of state contributions (Treszczanowicz and Benson, 1985) is used to predict the temperature dependence of the excess volume $A_p^E = (\partial V^E/\partial T)_p$ in diluted regions of alkanols. The model predicts a complex shape for the A_p^E dependence for dilute alkanol solutions as a result of the balance between the association and free volume contributions.

Keywords: Alkane; Alkanol; Binary system; Excess molar volume

In our preceding paper, good qualitative predictions of the temperature dependence of the excess volume $A_p^E = (\partial V^E/\partial T)_p$ (excess isobaric thermal expansion) for 1-alkanol + alkane mixtures were presented [1]. However, the complex shape of the A_p^E curves in the diluted alkanol region was not discussed there. Therefore, this note completes that study.

In the applied theory [2,3], A_p^E is expressed as a sum [1] of the contributions arising from the association and from Flory's equation of state. The functional similarity of the association contribution to the excess heat capacity $C_p^{E,as}$ and the temperature dependence of the excess volume $A_p^{E,as}$ led us [1] to the conclusion that

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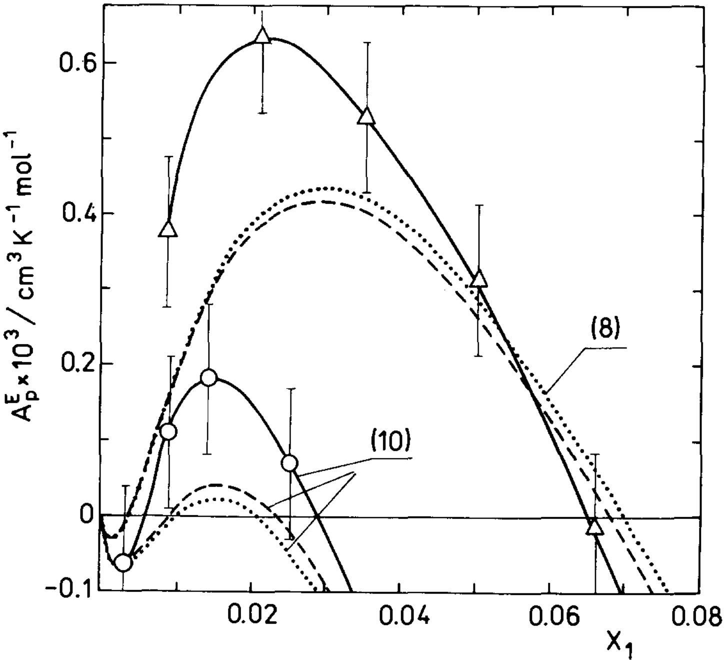

Fig. 1. Excess of the quantity $A_p^E = (\partial V^E/\partial T)_p$ at 298.15 K vs. mole fraction of alkanol x_1 for binary dilute 1-octanol and 1-decanol mixtures in n-hexane. The curves are labelled with the number of carbon atoms in the alkanol. Solid lines are drawn through points estimated from V^E data [10], dashed lines are calculated with X_{12} estimated from equimolar V^E data, dotted lines are obtained from correlation (Eq. (7) in Ref. [1]).

the minimum appearing in the high dilution region on the $C_p^{E,as}$ curve [4–6] (see Refs. [7–9]) will be visible for A_p^E but larger and deeper.

The predicted A_p^E curves presented in Fig. 1 for the diluted binary mixtures of 1-octanol and 1-decanol in n-hexane are in good qualitative agreement with the experimental data [10]. The calculations were performed with Flory's interaction parameters X_{12} correlated in the whole range of mixtures [2] as well as with those estimated directly from the excess volume at equimolar concentration: 10.330 J cm^{-3} mol^{-1} for 1-decanol and 9.936 J cm^{-3} mol^{-1} for the 1-octanol system. The remaining parameters are the same as previously given [1–3]. The experimental error determined by Heintz et al. [10] for the excess volume is $dV^E = \mp 0.003$ cm^3 mol^{-1} and it leads to $dA_p^E = \pm 0.0001$ cm^3 K^{-1} mol^{-1} for A_p^E.

The minimum of the association contribution for A_p^E is too narrow and shallow to be presented in Fig. 1 (the range of the negative A_p^E values represented by the association contribution does not exceed $x_1 = 0.0005$ and the minimum is not deeper than $A_p^E \times 10^3 = -0.002$ cm^3 K^{-1} mol^{-1} at $T = 25$°C for the considered model). Therefore, it seems that the negative association effect at high dilution is insignificant, and that the large, deep minimum is a result of the predominance of the free volume contribution.

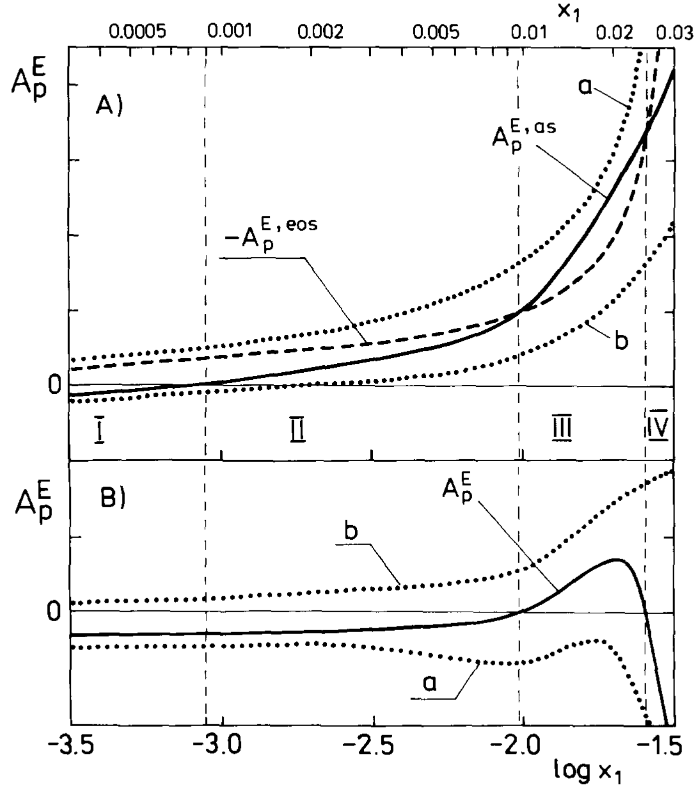

Fig. 2. Compensation effects (schematic) between contributions to A_p^E for diluted solutions vs. the logarithm of the mole fraction of alkanol $\lg(x_1)$ for a "W-shaped" system (regions numbered with roman numerals are discussed in the text).

(A) Comparison of the contributions: solid line represents $A_p^{E,as}$ and dashed line $-A_p^{E,eos}$ contributions. The dotted, supplementary curves represent $A_p^{E,eos}$ for a system with (a) more and (b) less negative values.

(B) The total quantity $A_p^E = A_p^{E,as} + A_p^{E,eos}$. The dotted curves represent A_p^E for a system with (a) more and (b) less negative $A_p^{E,eos}$ values.

The appearance of a local maximum in the dilute alkanol range presented in Fig. 1, at $x_1 \approx 0.015$ for 1-decanol and $x_1 \approx 0.020$ for 1-octanol, can be explained as being the result of the predominance of the positive association effect over the negative equation of state contribution. Fig. 2 shows a schematic representation of the balance of these contributions against the logarithm of the alkanol mole fractions in dilute alkanol solutions (from $x_1 = 0.0003$ to 0.03). For clarity, the discussed range of concentration is divided into four regions.

I. For the high dilution region where association and equation of state contribution are negative, $A_p^{E,as} < 0$ and $A_p^{E,eos} < 0$.

II. Where the association contribution is positive but lower than $-A_p^{E,eos}$, i.e. $-A_p^{E,eos} > A_p^{E,as} > 0$, and negative A_p^E values are observed.

III. Where the positive association contribution is higher than $-A_p^{\mathrm{E,eos}}$, i.e. $A_p^{\mathrm{E,as}} > -A_p^{\mathrm{E,eos}} > 0$, and a positive local A_p^{E} maximum is observed.

IV. Where the positive association contribution is lower than $-A_p^{\mathrm{E,eos}}$, i.e. $-A_p^{\mathrm{E,eos}} > A_p^{\mathrm{E,as}} > 0$, which in this case leads to negative A_p^{E} values. This region extends up to pure alkanol.

For a system with a larger free volume contribution than that presented above (formed by shorter alkanes or a longer alkanol), region III disappears (see upper dotted curve (a) in Fig. 2(A)) and negative A_p^{E} values are observed in the whole concentration range. The local maximum can be observed even in the negative A_p^{E} range (see lower dotted curve (a) in Fig. 2(B) in addition to excess of isentropic compressibility for alkanol + alkane mixtures [11,12]).

For a system with a lower free volume contribution (formed by shorter alkanols and longer alkanes) (see lower dotted curve (b) in Fig. 2(A)), region III enlarges up to $x_1 = 1$ (see upper dotted curve (b) in Fig. 2(B) and the series of A_p^{E} curves presented in Ref. [1] for hexanol, butanol and propanol systems).

It is interesting that the simple model can also predict such a complex shape of the A_p^{E} curve for dilute alkanol solutions. These would be an interesting area for experimental research.

References

[1] A.J. Treszczanowicz and T. Treszczanowicz, Thermochim. Acta, 237 (1994) 277.
[2] A.J. Treszczanowicz and G.C. Benson, Fluid Phase Equilib., 23 (1985) 117.
[3] A.J. Treszczanowicz, Bull. Acad. Polon. Sci. Chim., 40 (1992) 221.
[4] W.M. Recko, Bull. Acad. Polon. Sci. Chim., 18 (1970) 297.
[5] M.K. Woycicka and B. Kalinowska, Bull. Acad. Polon. Sci.: Chim., 23 (1975) 759.
[6] M. Costas and D. Patterson, J. Chem. Soc. Faraday Trans. 1, 89 (1985) 172.
[7] A.J. Treszczanowicz, Bull. Acad. Polon. Sci.: Chim., 18 (1970) 159.
[8] A.J. Treszczanowicz, Bull. Acad. Polon. Sci.: Chim., 18 (1970) 729.
[9] A.J. Treszczanowicz, Bull. Acad. Polon. Sci.: Chim., 18 (1970) 197.
[10] A. Heintz, B. Schmittecker, D. Wagner and R.N. Lichtenthaler, Ber. Bunsenges. Phys. Chem., 31 (1986) 487.
[11] O. Kiyohara and G.C. Benson, J. Chem. Thermodyn., 11 (1979) 861.
[12] Y.P. Handa, C.J. Halpin and G.C. Benson, J. Chem. Thermodyn., 13 (1981) 875.