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Temperature dependence of excess volume of 1-alkanol + n-alkane binary systems in terms of an association model with a Flory contribution term

Andrzej J. Treszczanowicz * and Teresa Treszczanowicz *
Institute of Physical Chemistry, Polish Academy of Sciences, 44/52 Kasprzaka Str., 01-224 Warsaw, Poland

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Abstract

The model of associated mixtures proposed recently (A.T. Treszczanowicz and G.C. Benson, Fluid Phase Equilibria, 23 (1985) 117), for the excess volume is used to predict its temperature derivative $A_p^E = (\partial V^E/\partial T)_p$ for 1-alkanol + alkane mixtures. The model parameters estimated for excess volume are adopted. The model predicts the A_p^E values fairly well. The shape and size of A_p^E are discussed as a result of mutual compensation effects of association, non-specific interactions and free volume contributions.

INTRODUCTION

Our recently proposed model [1] describes the excess volume for 1-alkanol + n-alkane mixtures fairly well and predicts V^E of 1-alkanol + branched alkane mixtures [3]. A similar attempt was presented by Heintz and co-workers for excess volume of the same class of mixtures [24, 25] but was not tested for temperature dependence of excess volume.

The aim of this paper is to apply our model to predict the temperature derivative of the excess volume. The temperature derivative of the excess volume at constant pressure is given by

$$A_p^E = (\partial V^E/\partial T)_p$$
$$= (\partial V_m/\partial T)_p - [(\partial V_1/\partial T)_p x_1 + (\partial V_2/\partial T)_p x_2] \quad (1)$$

and is directly related to isobaric thermal expansion coefficient $\alpha_{p,m}$

$$A_p^E = \alpha_{p,m} V_m - (\alpha_{p,1} V_1 x_1 + \alpha_{p,2} V_2 x_2) \quad (2)$$

where $V_m = V_1 x_1 + V_2 x_2$ is the molar volume of the mixture; V_1, V_2, $\alpha_{p,1}$, $\alpha_{p,2}$ and x_1, x_2 are, respectively, the molar volumes, isobaric thermal expansion coefficients, and mole fractions of the pure components 1 and 2.

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* Corresponding authors.

TABLE 1

Physical properties of some components: molar volume V, coefficients of isobaric thermal expansion α_p and isothermal compressibility β_T at $t = 25°C$ and characteristic parameters: volume V^*, pressure P^* and temperature T^*

Component i	$V/cm^3\ mol^{-1}$	$10^3\alpha_p/K^{-1}$	$10^6\beta_T/atm^{-1}$	$V^*/cm^3\ mol^{-1}$	$P^*/J\ cm^{-3}$	T^*/K
1-Nonanol [a]	174.97	0.818	76.0	144.704	475.4	5876.6
n-Nonane [b]	179.70	1.092	119.1	141.910	444.1	4989.0
n-Undecane [b]	212.24	0.994	104.0	170.271	448.6	5248.4
n-Dodecane [c]	228.55	0.960	100.1	184.397	445.2	5351.0
n-Tetradecane [b]	261.33	0.885	88.9	213.571	450.4	5607.6

[a] V and α_p from density [20], β_T interpolated from values for the other 1-alkanols [1]. [b] V and α_p from density [21], β_T obtained from the thermal pressure coefficient estimated by method of Manzini and Crescenzi [22]. [c] Taken from one of our previous papers [23].

A_p^E is a molar function and directly expresses the excess volume changes in temperature and seems to be more convenient for our purposes. Our treatment of the excess molar volumes of associated mixtures [1, 2] assumes two contributions: the physical contribution described by the Flory equation of state theory and the chemical one described by an athermal associated model with continuous association of the Mecke–Kempter type. Therefore, the temperature derivative of V^E, i.e. the excess molar quantity A_p^E is also expressed as the sum of these contributions

$$A_p^E = A_p^{E,(F)} + A_p^{E,as} \tag{3}$$

The association term $A_p^{E,as}$ is obtained by differentiation of the chemical contribution to V^E with respect to temperature using $(\partial/\partial T)_p = (\Delta h_H/RT^2)K^{(\phi)}(\partial/\partial K^{(\phi)})_p$

$$A_p^{E,as} = \left(\frac{\partial V^E}{\partial T}\right)_p^{as} = \frac{\Delta h_H \Delta v_H}{RT^2}x_1\left[\frac{1}{1+K^{(\phi)}} - \frac{\ln(1+K^{(\phi)})}{K^{(\phi)}} - \frac{1}{1+K^{(\phi)}\phi_1} + \frac{\ln(1+K^{(\phi)}\phi_1)}{K^{(\phi)}\phi_1}\right] \tag{4}$$

where $K^{(\phi)} = \exp(1 - \Delta h_H/RT + \Delta s_H/R)/r_1$ is the association constant; Δh_H, Δs_H and Δv_H are the standard enthalpy, entropy and volume of H-bond formation, respectively; $r_1 = V_1^*/17.12$ is the number of 1-alkanol segments; x_1, $x_2 = 1 - x_1$ and $\phi_1 = V_1^* x_1/V^*$, $\phi_2 = 1 - \phi_1$ are molar and segment fractions; $V^* = V_1^* x_1 + V_2^* x_2$ and V_i^* are characteristic volumes of the mixture and pure component liquids ($i = 1, 2$).

The Flory equation of state contribution $A_p^{E,(F)}$ is derived by differentiation and is given in the form

$$A_p^{E,(F)} = V^*\left(\frac{3\tilde{v}^{7/3}}{T^*(4 - 3\tilde{v}^{1/2})} - (\alpha_{p,1}\tilde{v}_1\phi_1 + \alpha_{p,2}\tilde{v}_2\phi_2)\right) \tag{5}$$

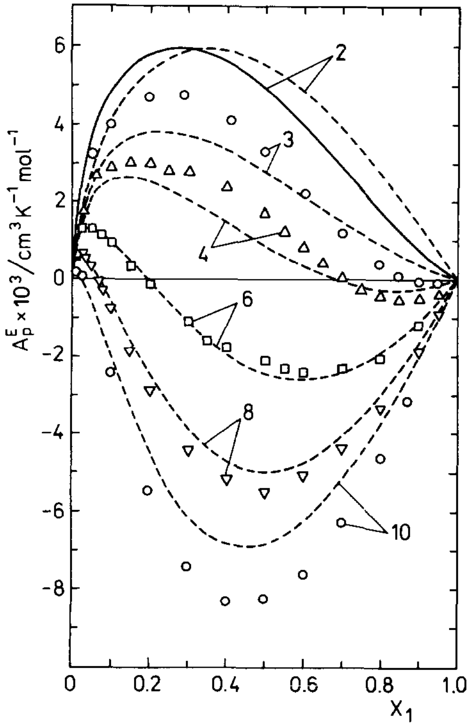

Fig. 1. The excess quantity $A_p^E = (\partial V^E/\partial T)_p$ for series of binary systems formed by 1-alkanol with *n*-hexane at 298.15 K. The dashed line denotes the predicted values, solid line represents the data estimated for systems formed by ethanol [13] and points denote A_p^E values calculated from V^E data [11]. Curves are labelled with number of alkanol C atoms.

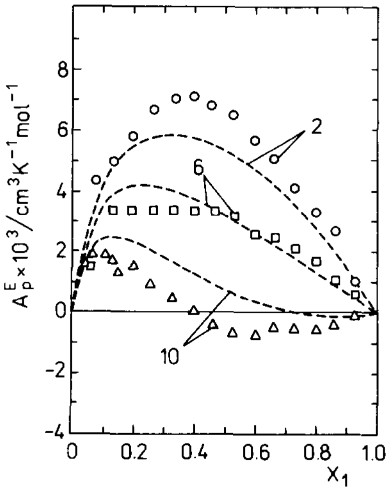

Fig. 2. The excess quantity $A_p^E = (\partial V^E/\partial T)_p$ for series of binary systemd formed by 1-alkanol with *n*-nonane at 298.15 K. The dashed line denotes the predicted values and points denote A_p^E values calculated from V^E data [19]. Curves are labelled with number of alkanol C atoms.

where reduced volumes $\tilde{v}$, $\tilde{v}_i$ of the mixture and pure liquid i are calculated by solving the Flory equation of state [1]. The reduced temperature of mixture is given by the relation

$$\tilde{T} = \left(\sum_{i=1}^{2} \phi_i P_i^* \tilde{T}_i \right) \Bigg/ \left(\sum_{i=1}^{2} \phi_i P_i^* - \phi_i \theta_2 X_{12} \right) \tag{6}$$

where X_{12} is the Flory interchange interaction parameter given by eqn. (7); $\tilde{T}_i = T/T_i^*$, T_i^* and P_i^* are the reduced and characteristic temperature and characteristic pressure of the ith component, respectively; $\theta_2 = \phi_2/(\phi_1 r_{21}^{-1/3} + \phi_2)$ is the surface fraction of the component 2; and $r_{21} = V_2^*/V_1^*$ is the size ratio parameter. Characteristic parameters are calculated from the molar volume V_i, isobaric thermal expansion coefficient $\alpha_{p,i}$ and isothermal compressibility coefficient $\beta_{T,i}$ taken from a previous paper [1]. Missing values for some components are listed in Table 1. The model parameters used in this work are $\Delta h_H = -24.4\ \mathrm{kJ\ mol^{-1}}$, $\Delta s_H = -33\ \mathrm{J\ K^{-1}\ mol^{-1}}$, $\Delta v_H = -10\ \mathrm{cm^3\ mol^{-1}}$ [1]. The Flory interchange interaction parameter X_{12} is correlated versus the length of component molecules by

$$X_{12} = 10^3 (V_1^*)^{1/3} (V_2^*)^{-3/2} [101.35(\alpha_{OH})^2 + 1.254] \tag{7}$$

where the fraction of hydroxyl group in alkanol, $\alpha_{OH} = 8.04/[21.71 + 10.23(n_c - 1)]$ is a ratio of van der Waals volume of the OH group and alkanol with n_c carbon atoms. More details of the derivation of the model have been given in a preceding paper [1].

RESULTS AND DISCUSSION

The excess volume data for 1-alkanol + n-hexane systems presented by Heintz et al. [11] and those for 1-alkanol + n-nonane given by Wagner and Heintz [19] were used for calculation of the excess quantity A_p^E. For the above systems the A_p^E data were calculated from direct experimental V^E values at three or more temperatures for each concentration, while those for the ethanol + n-hexane system [13] were calculated from smoothed V^E data [4], using the quadratic temperature equation.

For the 1-alkanol + n-hexane series the model predicts qualitatively the size and shape of the A_p^E curves very well [5] and also their changes from positive in the whole concentration range for short alkanol molecules to negative for long alkanol molecules, as is presented in Fig. 1. Similarly, for the 1-alkanol + n-nonane series a good prediction is evident, which is presented in Fig. 2. Moreover, experimental V^E and A_p^E data for other systems at equimolar concentration are compared in Table 2. It is interesting to note that this model even predicts the small positive region of A_p^E in the dilute region of alkanol and inversion of the A_p^E sign.

In addition, an attempt was made to discuss magnitudes of the contributions to A_p^E due to association, non-specific interactions and free volume as

TABLE 2

Comparison of experimental data and calculated results for the excess volume V^E and excess thermal expansion A_p^E at equimolar concentration for binary mixtures of 1-alkanols with *n*-alkanes using eqns. (3–5)

Name of system	t/°C	$V^E(0.5)$/cm^3 mol^{-1}		$A_p^E(0.5)$/cm^3 K^{-1} mol^{-1}		Ref.
		Expt.[a]	Calc.	Expt.[b]	Calc	
2+6	25	0.409	0.472	0.0050	0.0055	13
	25	0.394		0.0056		14
+7	25	0.476	0.463	0.0036	0.0060	16
	35	0.541[c]	0.526	0.0078[c]	0.0067	18
3+6	25	0.180	0.237	0.0033	0.0028	11
	25	0.164		0.0026		14
+9	25	0.405	0.344	0.0067	0.0054	19
+11	25	0.457	0.341	0.0068	0.0058	15
+12	25	0.464	0.339	0.0064	0.0060	15
4+6	25	0.043	0.087	0.0016	0.0009	11
+7	25	0.184	0.198	0.0052	0.0027	12
+10	25	0.363	0.306	0.0042	0.0051	10
5+6	25	−0.198	−0.101	−0.0066	−0.0009	7
+8	25	0.107	0.170	0.0016	0.0029	8
+10	25	0.291	0.259	0.0064	0.0045	7
6+6	25	−0.224	−0.220	−0.0022	−0.0029	11
+9	25	0.173	0.172	0.0031	0.0032	19
8+6	25	−0.431	−0.424	−0.0054	−0.0050	11
+7	27.5	−0.253[c]	−0.203	−0.0006[c]	−0.0018	17
+9	25	0.036	0.059	−0.0002	0.0019	19
9+10	35	0.080	0.071	0.0017	0.0021	9
+14	35	0.284	0.302	0.0037	0.0056	9
10+6	25	−0.587	−0.610	−0.0083	−0.0068	11
+9	25	−0.076	−0.050	−0.0004	0.0008	19
12+7	35	−0.447[c]	−0.515	−0.0042	−0.0052	17
+9	42.5	−0.187[c]	−0.141	−0.0002[c]	−0.0004	19

[a] Taken from smoothed experimental data [4]. [b] Estimated from temperature relation $V^E = V^E(25) + A_p^E(25)(t - 25) + c(t - 25)^2$ at $x_1 = 0.5$. [c] Average value from data at two temperatures.

well as their influence on the size and shape of A_p^E. These contributions can be obtained as follows: (i) the association contribution $A_p^{E,as}$ is directly calculated from eqn. (4); (ii) the free volume contribution $A_p^{E,fv}$ is estimated by putting $X_{12} = 0$ into eqn. (5); (iii) the non-specific interactions contribution is calculated as a difference between estimated A_p^E (with non-zero X_{12}) and a sum of the free volume and association contributions, i.e. $A_p^{E,nsi} = A_p^E - (A_p^{E,fv} + A_p^{E,as})$.

Figure 3 presents separation of these contributions for the 1-hexanol + *n*-hexane system, characterized by positive–negative shape. The effect of

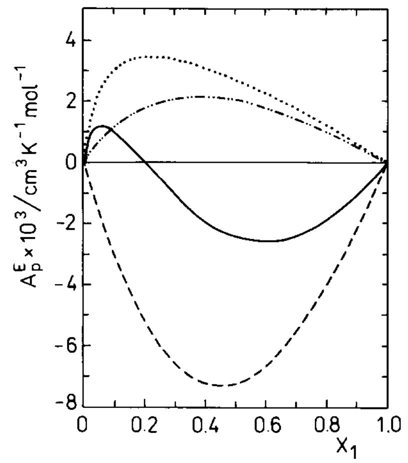

Fig. 3. Contributions to excess quantity $A_p^E = (\partial V^E/\partial T)_p$ for 1-hexanol + n-hexane system vs. 1-hexanol mole fractions x_1 at 25°C. Notation: ——, total A_p^E curve and contributions to: ····, association $A_p^{E,as}$; —···—···—, non-specific interactions $A_p^{E,nsi}$; – – –, free volume $A_p^{E,fv}$.

compensation of negative free volume by the positive contribution arising from association and non-specific interactions is visible. However, the magnitudes of these contributions change markedly with size of the component molecules, e.g. for the series 1-alkanol + n-hexane, as is shown in Fig. 4. For a short alkanol molecule the positive contributions predominate which lead to positive A_p^E values over the whole concentration range. In the case of a long alkanol molecule the reverse effect is observed; the free volume contribution predominates which leads to negative A_p^E values. This discussion is quite similar to that presented recently [2] (see also ref. 1) for excess volume.

It is worth noting that relation (4) for the association contribution $A_p^{E,as}$ is given by the same function of $K^{(\phi)}$ and x_1 as the association contribution to excess heat capacity $C_p^{E,as}$, both differing by the factor $\Delta h_H \Delta v_H$ instead of $(\Delta h_H)^2$ (see ref. 6). This similarity led to the conclusion that the minimum on the C_p^E curve of the 1-alkanol + n-alkane mixtures at a very high dilution region of alkanol [26] (cf. [6]) should also be found for A_p^E but that it should be larger and deeper than that for C_p^E due to the non-negligible negative free volume contribution. Therefore, systems characterized by the positive-negative shape presented in Figs. 1 and 2 may, in fact, be the "W-shape". However, the minimum in the high dilution region seems to be beyond the capabilities of the current measuring technique.

In conclusion we can say that good qualitative agreement is observed between the excess volume V^E and the excess quantity A_p^E. In some cases the A_p^E predictions are much better than experimental data of lower quality (see Table 2) in spite of the rough simplicity of the model.

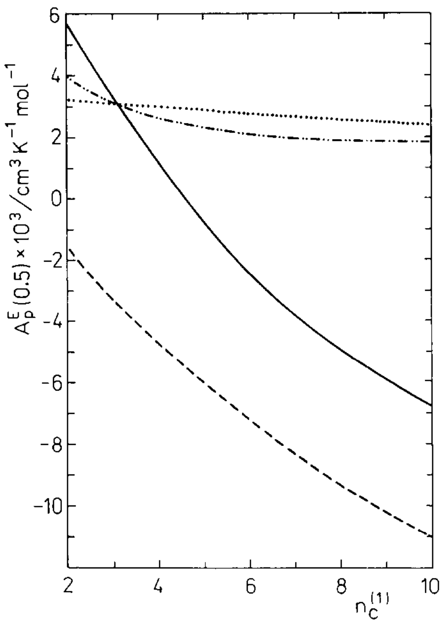

Fig. 4. Contributions to equimolar values of $A_p^E(0.5)$ for (A_i, H) series formed by 1-alkanols with *n*-hexane at 25°C vs. alkanol number of C atoms $n_c^{(1)}$. Notation is the same as in Fig. 3.

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