ELSEVIER

Thermochimica Acta 375 (2001) 115–123

thermochimica acta

www.elsevier.com/locate/tca

Prediction of temperature dependence of the excess volume: $(\partial V^E/\partial T)_p$ and $(\partial^2 V^E/\partial T^2)_p$ for 1-alkanol + an alkane binary systems in terms of an associated mixture model

Andrzej J. Treszczanowicz*, Teresa Treszczanowicz

Department of Applied Thermodynamics, Institute of Physical Chemistry, Polish Academy of Sciences,
44/52 Kasprzaka, 01-224 Warszawa, Poland

Received 27 November 2000; received in revised form 27 March 2001; accepted 27 March 2001

Abstract

The predictive ability of the model proposed by Treszczanowicz and Benson [Fluid Phase Equilib. 23 (1985) 117] is tested for temperature dependence of the excess volume: excess molar isobaric thermal expansion defined as $A_p^E = (\partial V^E/\partial T)_p$ and $(\partial^2 V^E/\partial T^2)_p$ for binary systems formed by an 1-alkanol (from C_2 to C_{12}) and an alkane (from C_4 to C_{14}) for all available literature data. The model equations for these properties are expressed as sums of the three contributions: self-association described by athermal associated mixture model and free volume and non-specific interactions described by Flory equation of state. The model correctly predicts A_p^E and sign of temperature derivative $(\partial^2 V^E/\partial T^2)_p$ for regarded class of mixtures. Moreover, the model predicts complex shape of the A_p^E curve and its temperature changes for diluted 1-decanol in *n*-hexane solutions. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Excess molar isobaric thermal expansion; Excess volume; 1-Alkanol; Alkane; Association; Prediction

---

1. Introduction

The present study is an extension of the series of papers about interpretation and prediction of the excess volume V^E [1,2] and excess molar isobaric thermal expansion $A_p^E = (\partial V^E/\partial T)_p$ [3–5] for binary systems formed by 1-alkanols with alkanes applying the model described by Treszczanowicz and Benson [1,2]. The model correctly predicts V^E and A_p^E as concentration function using only one set of parameters for the whole class of 1-alkanol + an alkane mixtures. Moreover, model predicts double minimum on A_p^E curve [4], occurrence common intersection point for series of isotherms of the excess volume and indicates on possibility occurrence such a point for series of isotherms of the excess molar isobaric thermal expansion [5]. The aim of the paper is to test the model for A_p^E and A_p^E temperature dependence for all available literature data for regarded class of mixtures. The discussion obeys mixtures formed by homologous 1-alkanols from C_2 to C_{12} and alkanes from C_4 to C_{14} including branched alkanes.

2. Theory

The model relations for excess thermodynamic properties are expressed as sums of self-association

---

[*] Corresponding author.
E-mail address: atresz@ichf.edu.pl (A.J. Treszczanowicz).

PII: S0040-6031(01)00528-7

Nomenclature

A_p^{E}	excess molar isobaric thermal expansion $(=(\partial V^{\mathrm{E}}/\partial T)_p)$
c	constant
C_p^{E}	excess molar isobaric heat capacity
$K^{(\varphi)}$	association constant for homologous alkanol
$n_{\mathrm{C}}^{(1)}$	number of carbon atoms of the alkanol
P_i^*	characteristic pressure of the pure component i
R	gas constant ($=8.31451\ \mathrm{J\ mol^{-1}\ K^{-1}}$)
r_i	number of segments distinguished on molecule of component i
t	Celsius temperature
T	absolute temperature
T^*	characteristic temperature of the mixture
T_i^*	characteristic temperature of the pure component i
$\tilde{v}$	reduced volume of the mixture
$\tilde{v}_i$	reduced volume pure liquid i
V_{m}^*	characteristic volume of the mixture $(=V_1^* x_1 + V_2^* x_2)$
$V_{\mathrm{m}}^{\mathrm{id}}$	molar volume an ideal mixture $(=V_1^0 x_1 + V_2^0 x_2)$
V_i^*	characteristic volume of the pure component i
V_i^0	molar volume of the pure component i
V^{E}	excess molar volume
x_i	molar fractions of the ith component
X_{12}	interchange interaction Flory parameter given by Eq. (4)
X_{A}^0	the average degree of self-association in pure alkanol i
X_{A}	the average degree of self-association of an alkanol in mixture
Greek letters	
$\alpha_{\mathrm{OH}}^{(1)}$	van der Waals volume fraction of hydroxyl group in alkanol molecule
$\alpha_{p,i}$	isobaric thermal expansion coefficient of pure component i $(=(\partial V_i^0/\partial T)_p/V_i^0)$
β_{21}	$\beta_{T,2}/\beta_{T,1}$
$\beta_{T,i}$	isentropic compressibility coefficient of pure component i
Δh	standard enthalpy for H-bond formation
Δs	standard entropy for H-bond formation
Δv	standard volume for H-bond formation
φ_i	segment fractions of the ith component $(=r_i x_i/(r_1 x_1 + r_2 x_2))$
θ_2	site fraction of the component
$\kappa_{\mathrm{S}}^{\mathrm{E}}$	excess isentropic compressibility coefficient $(=\kappa_{\mathrm{S}} - \kappa_{\mathrm{S}}^{\mathrm{id}})$
κ_{S}	isentropic compressibility coefficient of real mixture
$\kappa_{\mathrm{S}}^{\mathrm{id}}$	isentropic compressibility coefficient an ideal mixture $(=\frac{(\partial V_{\mathrm{m}}^{\mathrm{id}}/\partial P)_{\mathrm{S}}/}{V_{\mathrm{m}}^{\mathrm{id}}})$

and equation of state contribution. The self-association contribution is described by athermal associated mixture model of the Mecke and Kempter type. The free volume and non-specific interaction contributions are described the by Flory [1,2] equation of state. Relations for excess volume V^{E} [1,2], excess molar isobaric thermal expansion (cf. [3–5]) $A_p^{\mathrm{E}} = (\partial V^{\mathrm{E}}/\partial T)_p$ are as follows:

$$V^{\mathrm{E}} = \underset{\text{EOS contribution}}{V_{\mathrm{m}}^*[\tilde{v} - (\tilde{v}_1^0 x_1 + \tilde{v}_2^0 x_2)]} + \underset{\text{association contribution}}{\Delta v\, x_1 \left(\frac{1}{X_{\mathrm{A}}^0} - \frac{1}{X_{\mathrm{A}}}\right)} \tag{1}$$

$$A_p^{\mathrm{E}} = \underset{\text{EOS contribution}}{V_{\mathrm{m}}^* \left[\left(\frac{\partial \tilde{v}}{\partial T}\right)_p - (\alpha_{p,1}\tilde{v}_1\varphi_1 - \alpha_{p,2}\tilde{v}_2\varphi_2)\right]} + \underset{\text{association contribution}}{\frac{\Delta h\,\Delta v}{RT^2} x_1 \left(\varphi_{\mathrm{A}}^0 - \frac{\varphi_{\mathrm{A}}}{\varphi_1} - \frac{1}{X_{\mathrm{A}}^0} + \frac{1}{X_{\mathrm{A}}}\right)} \tag{2}$$

where x_1, $x_2 = 1 - x_1$ and φ_1, $\varphi_2 = 1 - \varphi_1$ are mole and segment fractions of the nominal (stoichiometric) components, $\varphi_{\mathrm{A}}^0, \varphi_{\mathrm{A}}$, and $X_{\mathrm{A}}^0, X_{\mathrm{A}}$ are segment fractions of an alkanol monomer and average degree of association in pure alkanol and mixture. The $\tilde{v}, \tilde{v}_i$ are reduced volumes of the mixture and pure component i and $\alpha_{p,i}$ is coefficient of isobaric thermal expansion of the pure component i. The self-association constant of an alkanol

$$K^{(\varphi)} = \frac{\exp[(1 - \Delta h/RT) + (\Delta s/R)]}{r_1} \tag{3}$$

depends on alkanol number of segments $r_1 = V_1^*/V_{\mathrm{CH_4}}^{\mathrm{vdW}}$, where V_1^* is the characteristic volume of alkanol and $V_{\mathrm{CH_4}}^{\mathrm{vdW}} = 17.12\ \mathrm{cm^3\ mol^{-1}}$ the van der Waals volume of methane used as volume unit. Association

Table 1

Physical properties of component liquids: molar volume V_i, coefficients of isobaric thermal expansion $\alpha_{p,i}$, isothermal compressibility $\beta_{T,i}$ at 298.15 K and characteristic parameters: volume V_i^*, pressure P_i^* and temperature T_i^*

Component i	V_i (cm^3/mol)	α_p ($\times 10^3$ K^{-1})	β_T (TPa^{-1})	V_i^* (cm^3/mol)	P_i^* (J/cm^3)	T_i^* (K)
1-Alkanols						
Ethanol	58.678	1.093	1162.2	46.332	449.7	4987.5
Propanol	75.161	0.995	1015.2	60.289	454.1	5245.6
Butanol	91.984	0.932	942.4	74.566	448.7	5442.0
Pentanol	108.681	0.893	882.2	88.694	453.1	5577.9
Hexanol	125.316	0.870	839.4	102.682	460.3	5663.9
Heptanol	141.90	0.850	800.0	116.68	468.5	5742.5
Octanol	158.474	0.827	775.7	130.848	466.2	5837.8
Nonanol	174.97	0.818	750.1	144.704	475.4	5876.6
Decanol	191.503	0.812	738.0	158.549	478.6	5903.0
Dodecanol	224.290	0.800	712.6	186.100	486.2	5956.9
Alkanes						
n-Butane	101.45	2.021	2974.3	71.19	411.5	3814.9
n-Pentane	116.137	1.610	2132.5	85.353	416.7	4158.1
n-Hexane	131.597	1.387	1703.9	99.543	424.2	4436.1
n-Heptane	147.448	1.256	1460.6	113.601	431.9	4648.1
n-Octane	163.504	1.164	1302.4	127.698	436.8	4827.0
Iso-octane	166.098	1.197	1542.1	129.083	383.2	4759.5
n-Nonane	179.696	1.092	1175.4	141.910	444.1	4989.0
n-Decane	195.945	1.051	1109.6	155.750	447.0	5091.4
n-Undecane	212.24	0.994	1026.4	170.271	448.6	5248.4
n-Dodecane	228.550	0.960	987.7	184.397	445.2	5351.0
n-Tetradecane	261.33	0.885	877.4	213.571	450.4	5607.6

parameters: standard enthalpy $\Delta h = -24.4$ kJ mol^{-1}, entropy $\Delta s = -33$ J K^{-1} mol^{-1} and volume $\Delta v = -10$ cm^3 mol^{-1} [1,2] are the same for regarded homologous 1-alkanols [1,2]. The interaction parameter in the Flory equation of state contributions, X_{12} (see Appendix A), depends on the length of component molecules in the whole regarded class of mixtures according to the formula

$$X_{12} = 10^3 (V_1^*)^{1/3} (V_2^*)^{-3/2} [101.35(\alpha_{\mathrm{OH}}^{(1)}) + 1.254] \tag{4}$$

where

$$\alpha_{\mathrm{OH}}^{(1)} = \frac{V_{\mathrm{OH}}^{\mathrm{vdW}}}{V_{\mathrm{OH}}^{\mathrm{vdW}} + V_{\mathrm{CH_3}}^{\mathrm{vdW}} + (n_{\mathrm{C}}^{(1)} - 1) V_{\mathrm{CH_2}}^{\mathrm{vdW}}} \tag{5}$$

is volume fraction of the hydroxyl group and $n_{\mathrm{C}}^{(1)}$ the number of C-atoms in alkanol molecule, and $V_{\mathrm{OH}}^{\mathrm{vdW}} = 8.04$, $V_{\mathrm{CH_3}}^{\mathrm{vdW}} = 13.21$ and $V_{\mathrm{CH_2}}^{\mathrm{vdW}} = 10.21$ cm^3/mol are van der Waals volume, respectively, for OH, CH$_3$ and CH$_2$ group. The model parameters were estimated using excess enthalpy H^E and excess molar isobaric heat capacity C_p^E for the one chosen system and excess volume V^E for series systems formed by 1-alkanols from C_2 to C_{12} and alkanes from C_5 to C_{16} [1,2].

It should be noted the functional identity of the chemical contributions to C_p^E and to A_p^E (see Eq. (A.3) in Appendix A). Therefore, detailed discussion of the chemical contribution to C_p^E as a function of the concentration, self-association constant and molecular size ratio, which was presented by Treszczanowicz and Kehiaian [6,7] is valuable also in the case of chemical contribution to A_p^E.

All relations for properties which appear in the paper and which are necessary to understand the paper are given in Appendix A. Properties of pure components and calculated characteristic parameters were collected in the Table 1.

3. Results and discussion

The experimental excess volume data measured at three or more temperatures [8–24] were used to estimate $A_p^{\mathrm{E}} = (\partial V^{\mathrm{E}}/\partial T)_p$ and the temperature derivative $(\partial^2 V^{\mathrm{E}}/\partial T^2)_p$ at 298.15 K. These properties were calculated (at the same concentration) using the relation

$$V^{\mathrm{E}} = V_{25}^{\mathrm{E}} + A_{p,25}^{\mathrm{E}}(T - 298.15) + \tfrac{1}{2}c(T - 298.15)^2 \tag{6}$$

where V_{25}^{E} is excess volume, $A_{p,25}^{\mathrm{E}}$ the excess molar isobaric thermal expansion and c the temperature second derivative of the excess volume $c = (\partial^2 V^{\mathrm{E}}/\partial T^2)_p$ at $T = 298.15$ K. The A_p^{E} and $(\partial^2 V^{\mathrm{E}}/\partial T^2)_p$ data estimated at equimolar concentration are compared with the model predictions in the Table 2. The experimental error A_p^{E} estimated using best V^{E} data rather not exceed $\pm 0.4 \times 10^{-3}$ cm^3 K^{-1} mol^{-1} in the middle of the temperature range [5], what leads to the value $\pm 0.8 \times 10^{-4}$ cm^3 K^{-2} mol^{-1} for the second derivative. The derivative $(\partial^2 V^{\mathrm{E}}/\partial T^2)_p$ was calculated numerically and given in the Table 2.

Interesting regularities for A_p^{E} and $(\partial^2 V^{\mathrm{E}}/\partial T^2)_p$ observed for investigated mixtures are given in

Table 2

Comparison of experimental data and model predictions for $A_p^{\mathrm{E}} = (\partial V^{\mathrm{E}}/\partial T)_p$ and $(\partial^2 V^{\mathrm{E}}/\partial T^2)_p$ at equimolar concentration for 1-alkanol + alkane mixtures at 298.15 K and 0.1 MPa, size ratio parameter $r_{21} = V_2^*/V_1^*$, ratio of compressibility coefficients $\beta_{21} = \beta_{T,2}/\beta_{T,1}$ calculated from data reported in Table 1 and Flory interaction parameter X_{12} calculated from Eq. (4)

System (1 + 2)	r_{21}	β_{21}	X_{12} (J cm^3)	A_p^{E} ($\times 10^3$ cm^3 K^{-1} mol^{-1})		$(\partial^2 V^{\mathrm{E}}/\partial T^2)_p$ ($\times 10^3$ cm^3 K^{-1} mol^{-1})		References
				Experimental	Predicted	Experimental	Predicted	
2 + *n*-4	1.54	2.56	45.898	−0.8[a]	−0.48	−0.09[a]	−0.091	[8]
2 + *n*-6	2.15	1.47	27.755	5.0, 5.6	5.53	0.08, 0.04	0.066	[9,10]
2 + *n*-7	2.45	1.26	22.771	5.5	5.96	−0.16	0.076	[11]
2 + *iso*-8	2.79	1.33	18.798	6.2	5.92	0.15	0.079	[12]
3 + *n*-4	1.18	2.93	32.236	−4.8[a]	−7.8	−0.15[a]	−0.212	[13]
3 + *n*-6	1.65	1.68	19.496	3.3, 3.7	2.19	0.11, 0.21	0.018	[14,10]
3 + *n*-7	1.88	1.44	15.994	4.8c	4.20	0.05[c]	0.051	[15]
3 + *n*-9	2.35	1.16	11.454	6.8	5.35	0.16	0.071	[16]
3 + *n*-11	2.82	1.01	8.715	7.0	5.84	0.13	0.079	[17,18]
3 + *n*-12	3.05	0.97	7.733	6.4	6.02	0.17	0.082	[17,18]
4 + *n*-4	0.95	3.16	25.507	−8.2[a]	−12.25	−0.24[a]	−0.283	[19]
4 + *n*-6	1.33	1.81	15.427	1.6	0.85	0.07	−0.001	[14]
4 + *n*-7	1.52	1.55	12.653	2.8	2.79	0.28	0.031	[20]
4 + *n*-10	2.09	1.18	7.882	4.2[b]	5.08	0.21[b]	0.067	[21]
5 + *n*-6	1.12	1.93	13.131	−6.6	−0.93	0.03	0.026	[22]
5 + *n*-7	1.28	1.66	10.770	2.3[d]	1.46	0.03[d]	0.013	[15]
5 + *n*-8	1.44	1.48	9.037	1.6	2.89	0.10	0.035	[23]
5 + *n*-10	1.76	1.26	6.709	6.4	4.47	−0.19	0.058	[22]
6 + *n*-6	0.97	2.03	11.731	−2.2	−2.44	−0.01	−0.045	[14]
6 + *n*-9	1.38	1.40	6.892	3.1	3.22	0.01	0.040	[16]
7 + *n*-7	0.97	1.83	8.891	0.2[e]	−0.88	-0.00_3[e]	−0.017	[15]
8 + *n*-6	0.76	2.20	10.256	−5.4	−4.96	−0.08	−0.078	[14]
8 + *n*-9	1.08	1.52	6.025	−0.2	1.87	0.09	0.022	[16]
9 + *n*-10	1.08	1.48	5.037	2.0	2.09	−0.03	0.026	[24]
9 + *n*-14	1.48	1.17	3.137	2.7	5.02	0.09	0.061	[24]
10 + *n*-6	0.63	2.31	9.592	−8.3	−6.81	−0.98	−0.099	[14]
10 + *n*-9	0.90	1.59	5.635	0.7	0.76	0.04	0.008	[16]
12 + *n*-6	0.53	2.39	9.299	–	−8.20	–	−0.116	–

[a] At $p = 5$ MPa.

[b] V^{E} at various p.

[c] At $x_1 = 0.52263$.

[d] At $x_1 = 0.49259$.

[e] At $x_1 = 0.4859$.

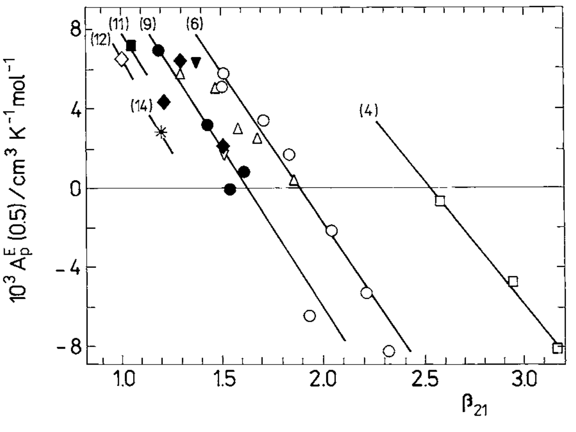

Fig. 1. The excess molar isobaric thermal expansion $A_p^{\mathrm{E}} = (\partial V^{\mathrm{E}}/\partial T)_p$ for equimolar mixtures of 1-alkanol with *n*-alkane at 298.15 K vs. ratio of isothermal compressibility coefficients of an alkane and alkanol $\beta_{21} = \beta_{T,2}/\beta_{T,1}$. Points denote data for mixtures formed by: (□) *n*-butane; (○) *n*-hexane; (△) *n*-heptane; (▽) *n*-octane; (▼) *iso*-octane; (●) *n*-nonane; (◆) *n*-decane; (■) *n*-undecane; (◇) dodecane and (∗) *n*-tetradecane. Lines are labeled with alkane C atoms.

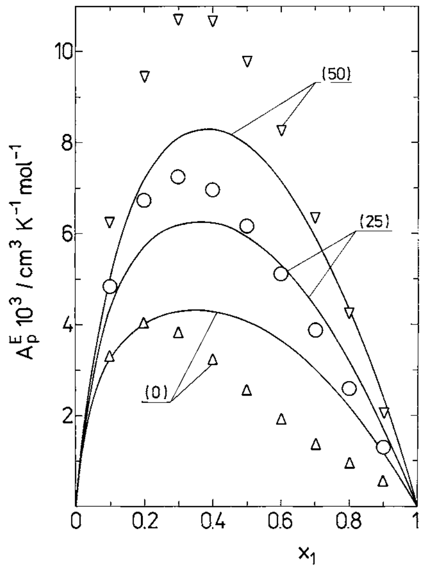

Fig. 2. Series of isotherms (temperature *t* (°C) given in parenthesis) of the excess molar isobaric thermal expansion $A_p^{\mathrm{E}} = (\partial V^{\mathrm{E}}/\partial T)_p$ for ethanol + *iso*-octane system vs. ethanol mole fraction x_1. Points denote A_p^{E} data estimated from V^{E} [11] by Eq. (6): (△) isotherm at 0°C; (○) isotherm at 25°C and (▽) isotherm at 50°C. Solid lines represent model predictions.

Table 2, e.g. in series of binary mixtures formed by an alkane with homologous 1-alkanols. Fig. 1 presents A_p^{E} data at equimolar concentration plotted against the ratio $\beta_{21} = \beta_{T,2}/\beta_{T,1}$ of the isothermal compressibility coefficients of an alkane and 1-alkanol. The ratio reflects in a certain degree on magnitude of the packing effects (free volume and interstitial accommodation) in the mixture. We can see that A_p^{E} data at equimolar concentration for series of mixtures formed by *n*-butane, *n*-hexane and *n*-nonane with homologous 1-alkanols fall on approximately along straight line. The A_p^{E} data for mixtures formed by alkane with number of C-atoms between 6 and 9 are located mostly between line for *n*-hexane and for *n*-nonane. Single experimental points presented in Fig. 1 for mixtures formed by longer alkane molecules are out of the line for *n*-nonane exhibit visible shift depending on the length of alkane molecule. Unfortunately, lack of the excess volume data which allow to estimate A_p^{E} for homologous series of mixtures formed by alkanes with number of C-atoms higher than 9. Moreover, lack of the data for systems formed by branched alkanes [2], except ethanol + *iso*-octane [12] system. It is worth noting that the excess volume at equimolar concentration plotted against the $\beta_{T,2}$ for series formed by given 1-alkanol with homologous *n*-alkanes also fall on along the straight line (see Fig. 4 in [2]).

In Fig. 2 are compared experimental and predicted A_p^{E} data for ethanol + *iso*-octane system as a function of ethanol mole fraction. The model predicts correctly positive A_p^{E} values in the whole concentration range and increase A_p^{E} magnitudes with temperature rise (cf. Table 2). Such behavior is characteristic for systems with low β_{21} ratio, for these systems large, positive sum of association and non-specific interaction contributions predominates over the slight, negative free volume contribution.

In contrary, the 1-decanol + *n*-hexane system presented in Figs. 3 and 4 characterizes predomination of the large, negative free volume contribution nearly over the whole concentration range except the region of diluted alkanol. Considerable asymmetry of the chemical contribution as a function of concentration (see Fig. 5) leads to occurrence positive A_p^{E} values in diluted alkanol region. Similar behavior is observed also for other systems with high β_{21} ratio. These are systems formed by *n*-butane with short molecule alkanols: ethanol [8], 1-propanol [13], 1-butanol

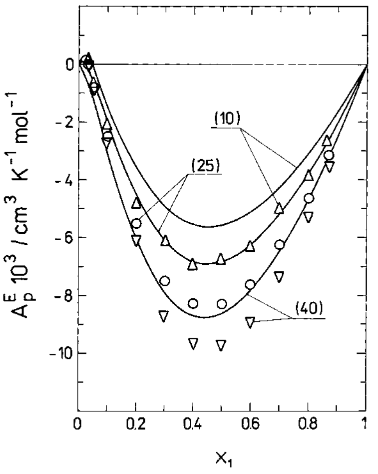

Fig. 3. Series of isotherms (temperature t (°C) given in parenthesis) of the excess molar isobaric thermal expansion $A_p^{\mathrm{E}} = (\partial V^{\mathrm{E}}/\partial T)_p$ for 1-decanol + n-hexane system vs. decanol mole fraction x_1. Points denote A_p^{E} data estimated from V^{E} [14] by Eq. (6): (△) isotherm at 10°C; (○) isotherm at 25°C and (▽) isotherm at 40°C. Solid lines represent model predictions.

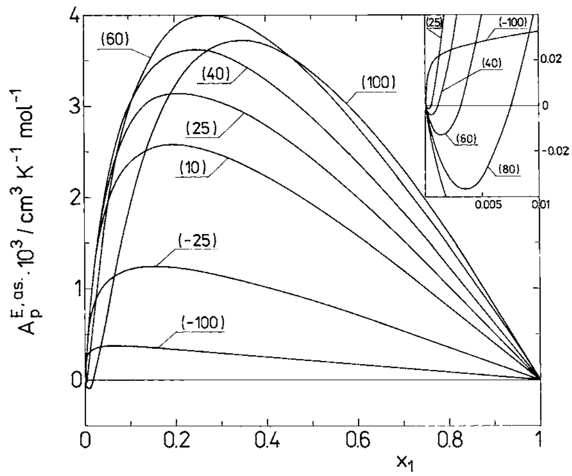

Fig. 5. The model representation of series of isotherms (temperature t (°C) given in parenthesis) of the association contribution $A_p^{\mathrm{E,as}} = (\partial V^{\mathrm{E,as}}/\partial T)_p$ for 1-decanol + n-hexane system vs. 1-decanol mole fractions x_1. The figure added in top right reflects changes of the $A_p^{\mathrm{E,as}}$ in diluted alkanol region.

[19] and formed by n-hexane with 1-alkanols from C_4 to C_{10} [3], all characterized by "S-shaped" A_p^{E}. The 1-decanol + n-hexane system is especially interesting for one more reason, because for this system appears "W-shaped" A_p^{E} curve (see Fig. 4 and compare discussion [4]). The narrow minimum on A_p^{E} curve occurs for this system in high dilution region of alkanol at the room temperature. The minimum quickly decreases with decrease of temperature, which is due to increase asymmetry of the chemical contribution (cf. Fig. 5). The temperature increase leads to enlarge this minimum (cf. Fig. 5) and free volume contribution become more negative. It leads to fast decrease of the maximum and then, to junction of the both minima through series of A_p^{E} isotherms, see Fig. 4. Quite similar behavior is observed for excess isentropic compressibility coefficient κ_S^{E} in series formed by 1-alkanol with homologous n-alkanes in diluted alkanol region [25,26]. This similarity of the shapes of the series of A_p^{E} isotherms for 1-decanol + n-hexane system (Fig. 4) and series of κ_S^{E} curves for systems formed by 1-alkanol with homologous n-alkanes is due to important role of free volume changes in both cases and asymmetry of the association contribution.

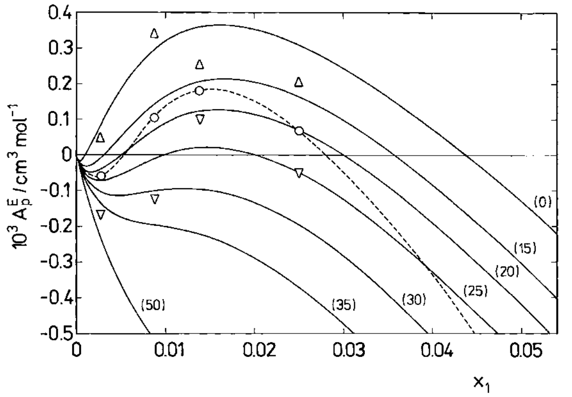

Fig. 4. Series of predicted isotherms (solid line) of the excess molar isobaric thermal expansion $A_p^{\mathrm{E}} = (\partial V^{\mathrm{E}}/\partial T)_p$ for diluted 1-decanol solutions at different temperatures (given in parentheses) in n-hexane vs. molar fraction of alkanol x_1. Points denote A_p^{E} data estimated from V^{E} data [14] by Eq. (6): (△) isotherm at 15°C; (○) isotherm at 25°C and (▽) isotherm at 35°C. Dashed line is drawn through points estimated at 25°C.

Fig. 6 shows predicted temperature dependence A_p^{E} and its contributions: association, non-specific interactions and free volume for 1-decanol + n-hexane system: (a) at mole fraction $x_1 = 0.014$ (corresponding to local maximum in diluted alkanol region at $t = 25°\mathrm{C}$, Fig. 4) and (b) at mole fraction $x_1 = 0.60$ (corresponding to minimum at $t = 25°\mathrm{C}$, Fig. 3).

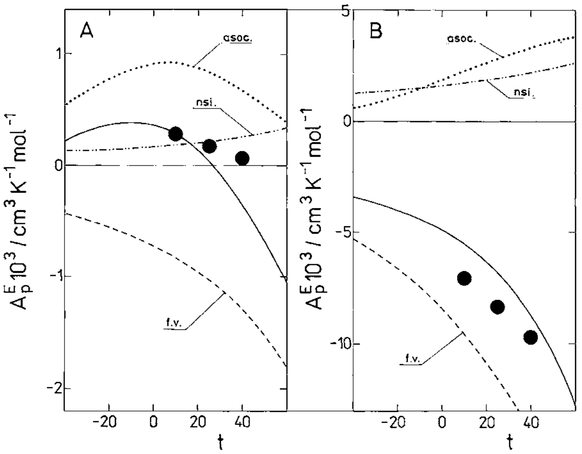

Fig. 6. Excess molar isobaric thermal expansion $A_p^{\rm E} = (\partial V^{\rm E}/\partial T)_p$ for 1-decanol + n-hexane system vs. temperature t (°C) for concentrations close to: (A) maximum of the positive lobe at $x_1 \cong 0.014$ and (B) minimum of the negative lobe at $x_1 \cong 0.60$ mole fraction of 1-decanol. The lines denote: (—), total $A_p^{\rm E}$; (···), association contribution $A_p^{\rm E,as}$; (- - -), free volume contribution $A_p^{\rm E,f,v}$ and (–··–), non-specific interactions contribution $A_p^{\rm E,nsi}$. Points denote experimental data calculated by Eq. (6) from smoothed data [14].

These contributions were calculated as follows: (1) association contribution was calculated from Eq. (2) omitting equation of state contribution; (2) free volume contribution was calculated omitting association contribution and putting Flory interaction parameter $X_{12} = 0$, in equation of state contribution; (3) non-specific interactions contribution was calculated as difference between equation of state contribution and free volume contribution. The $A_p^{\rm E}$ at $x_1 = 0.014$, presented in Fig. 6A as temperature function shows maximum due to distinct maximum on the association contribution. The temperature rise leads to increase free volume effect and decrease $A_p^{\rm E}$ values. The $A_p^{\rm E}$ at $x_1 = 0.60$, presented in Fig. 6B, is negative and quickly decrease with temperature rise. The association contribution shows indistinct maximum but negative free volume contribution predominates over positive ones. In both cases, the model predicts $A_p^{\rm E}$ and its temperature changes very well. The analysis of these figures indicate on possibility to find temperature range, where maximum increases and minimum decreases with temperature rise, leading to more sharp "S-shape" of $A_p^{\rm E}$ curve as a function of concentration [5] and even to appearance common intersection point of $A_p^{\rm E}$ isotherms. Such behavior is also characteristic for excess volume [5].

4. Conclusions

The review of literature data for excess volume 1-alkanol + alkane mixtures measured at three or more temperatures was done. The set of 29 binary systems formed by 1-alkanols from ethanol to dodecanol and alkanes from butane to tetradecane [8–24] (see Table 2) was used for estimation $A_p^{\rm E} = (\partial V^{\rm E}/\partial T)_p$ and $(\partial^2 V^{\rm E}/\partial T^2)_p$. These results were used to test predictive ability of the model proposed by Treszczanowicz and Benson. This simple model taking into account association and packing effects predicts correctly excess volume, its first temperature derivative and also sign of second temperature derivative. The model is able to predict these properties even in diluted alkanol region. Moreover, the model predicts also appearance of a double minimum on $A_p^{\rm E}$ curve and their junction with temperature rise observed for 1-decanol + n-hexane system. It is interesting that double minimum can be observed for excess isentropic compressibility curves in series of systems formed by given alkanol with alkanes differing in molecular length and shape [25,26]. Moreover, the model predicts possibility appearance of the common intersection point for the series $A_p^{\rm E}$ isotherms. These results indicate also for interesting changes of the pressure derivative of the excess enthalpy $(\partial H^{\rm E}/\partial P)_T = V^{\rm E} - T(\partial V^{\rm E}/\partial T)_p$ and excess molar isobaric heat capacity $(\partial C_p^{\rm E}/\partial P)_T = -T(\partial^2 V^{\rm E}/\partial T^2)_p$ and suggest an interesting area for experimental research.

Acknowledgements

Authors are very indebted to Prof. G.C. Benson for valuable discussion.

Appendix A.

The model equations for the excess properties are expressed as a sum of the association and equation of state contributions (see [1,3])

$$Z^{\rm E} = Z^{\rm E,as} + Z^{\rm E,EOS} \tag{A.1}$$

where $Z^{\mathrm{E}} = H^{\mathrm{E}}, V^{\mathrm{E}}, C_p^{\mathrm{E}}, A_p^{\mathrm{E}}$. The relations for association contributions are described by athermal associated model with the Mecke–Kempter mode of continuous self-association of alkanol. The association contribution to excess volume and excess enthalpy are given by the same functional dependence on association constant and concentration, as it was pointed out by Kehiaian [27] and for regarded model are expressed by

$$\frac{V^{\mathrm{E,as}}}{\Delta v} = \frac{H^{\mathrm{E,as}}}{\Delta h} = h(K^{(\varphi)}, \varphi_1) \qquad \text{(A.2)}$$

Therefore, the association contribution to excess molar isobaric thermal expansion and excess molar isobaric heat capacity also exhibit the same functional shape

$$\frac{A_p^{\mathrm{E,as}}}{\Delta h\,\Delta v/RT^2} = \frac{C_p^{\mathrm{E,as}}}{\Delta h^2/RT^2} = f(K^{(\varphi)}, \varphi_1) \qquad \text{(A.3)}$$

where, for Mecke and Kempter mode of alkanol self-association

$$h(K^{(\varphi)}, \varphi_1) = x_1\left[\frac{1}{X_{\mathrm{A}}^0} - \frac{1}{X_{\mathrm{A}}}\right],$$

$$f(K^{(\varphi)}, \varphi_1) = x_1\left[\varphi_{\mathrm{A}}^0 - \frac{\varphi_{\mathrm{A}}}{\varphi_1}\right] - h(K^{(\varphi)}, \varphi_1) \qquad \text{(A.4)}$$

where $X_{\mathrm{A}}^0, X_{\mathrm{A}}$ are the average degree of self-association and $\varphi_{\mathrm{A}}^0, \varphi_{\mathrm{A}}$ the segment fraction of monomer of the self-associated component in pure liquid 1 and in mixture, respectively, are given by relations

$$\frac{1}{X_{\mathrm{A}}^0} = \frac{\ln(1 + K^{(\varphi)})}{K^{(\varphi)}}, \qquad \frac{1}{X_{\mathrm{A}}} = \frac{\ln(1 + K^{(\varphi)}\varphi_1)}{K^{(\varphi)}\varphi_1} \qquad \text{(A.5)}$$

$$\varphi_{\mathrm{A}}^0 = \frac{1}{1 + K^{(\varphi)}}, \qquad \varphi_{\mathrm{A}} = \frac{\varphi_1}{1 + K^{(\varphi)}\varphi_1} \qquad \text{(A.6)}$$

and where $K^{(\varphi)}$ is an alkanol association constant given by Eq. (3).

The equation of state (EOS) contributions to excess enthalpy, $H^{\mathrm{E,EOS}}$, volume, $V^{\mathrm{E,EOS}}$, isobaric molar thermal expansion, $A_p^{\mathrm{E,EOS}}$, and heat capacity, $C_p^{\mathrm{E,EOS}}$ are given by the Flory equation of state theory

$$V^{\mathrm{E,EOS}} = V_{\mathrm{m}}^*[\tilde{v} - (\tilde{v}_1\varphi_1 + \tilde{v}_2\varphi_2)] \qquad \text{(A.7)}$$

$$A_p^{\mathrm{E,EOS}} = V_{\mathrm{m}}^*\left[\left(\frac{\partial\tilde{v}}{\partial T}\right)_p - \sum_{i=1}^{2}\varphi_i\tilde{v}_i\alpha_{p,i}^0\right] \qquad \text{(A.8)}$$

$$H^{\mathrm{E,EOS}} = x_1\theta_2V_1^*\tilde{\rho}^2X_{12} - \sum_{i=1}^{2}x_iP_i^*V_i^*(\tilde{\rho}_i - \tilde{\rho}) \qquad \text{(A.9)}$$

$$C_p^{\mathrm{E}} = x_1\theta_2V_1^*\tilde{\rho}^2X_{12} + \sum_{i=1}^{2}x_iP_i^*V_i^*\left[\tilde{\rho}_i^2\left(\frac{\partial\tilde{v}_i}{\partial T}\right)_p - \tilde{\rho}^2\left(\frac{\partial\tilde{v}}{\partial T}\right)_p\right] \qquad \text{(A.10)}$$

where $\tilde{v}_i = V_i^0/V_i^* = 1/\tilde{\rho}_i$ and $\tilde{v} = V/V_{\mathrm{m}}^* = 1/\tilde{\rho}$ are the reduced volumes of pure liquid i and mixture, and their temperature derivatives are given by relation

$$\left(\frac{\partial\tilde{v}_i}{\partial T}\right)_p = \frac{3\tilde{v}_i^{7/3}}{T_i^*(4 - 3\tilde{v}_i^{1/3})}, \qquad \left(\frac{\partial\tilde{v}}{\partial T}\right)_p = \frac{3\tilde{v}^{7/3}}{T^*(4 - 3\tilde{v}^{1/3})} \qquad \text{(A.11)}$$

where P_i^*, T_i^*, V_i^* are the characteristic pressure, temperature and volume of pure liquid i, V_i^* and T^* are characteristic volume and temperature of a mixture, X_{12} is interaction parameter in the equation of state contribution given by Eq. (4). More details and derivation of the model equations, see [1,3].

References

[1] A.J. Treszczanowicz, G.C. Benson, Fluid Phase Equilib. 23 (1985) 117.

[2] A.J. Treszczanowicz, Interpretation of the Excess Volumes of Associated Mixtures in Terms of Association Model with an Equation of State Term, Polish Academy of Sciences, Institute of Physical Chemistry, 1992, Warsaw.

[3] A.J. Treszczanowicz, T. Treszczanowicz, Thermochim. Acta 237 (1994) 277.

[4] A.J. Treszczanowicz, T. Treszczanowicz, Thermochim. Acta 255 (1995) 379.

[5] A.J. Treszczanowicz, T. Treszczanowicz, Fluid Phase Equilib. 135 (1997) 179.

[6] A.J. Treszczanowicz, H. Kehiaian, Bull. Acad. Polon. Sci., Ser. Sci. Chim. 18 (1970) 729.

[7] A.J. Treszczanowicz, Bull. Acad. Polon. Sci., Ser. Sci. Chim. 21 (1973) 197.

[8] J.T. Sipowska, J.B. Ott, L.R. Lemon, B.G. Marchant, P.R. Brown, J. Chem. Thermodyn. 27 (1995) 1355.

[9] K.N. Marsh, C. Burfitt, J. Chem. Thermodyn. 7 (1975) 955.

[10] C. Ormanoudis, C. Dakos, C. Panayotou, J. Chem. Eng. Data 36 (1991) 39.

[11] D. Papaloannou, D. Zakias, C. Panayotou, J. Chem. Eng. Data 36 (1991) 39.

[12] C.B. Kretschmer, J. Nowakowska, R. Wiebe, J. Am. Chem. Soc. 70 (1948) 1785.

[13] L.R. Lemon, J.D. Moore, P.R. Brown, J.B. Ott, J. Chem. Thermodyn. 28 (1996) 187.

[14] A. Heintz, B. Schmittecker, D. Wagner, R.N. Lichtenthaler, J. Chem. Eng. Data 31 (1986) 487.

[15] L. Romani, J. Peleteiro, T.P. Inglesias, E. Carballo, R. Escudero, J.L. Legido, J. Chem. Eng. Data 39 (1994) 821.

[16] D. Wagner, A. Heintz, J. Chem. Eng. Data 31 (1986) 483.

[17] J. Ortega, J.S. Matos, J.A. Pena, M.I. Paz-Andrade, L. Pias, J. Fernandez, Thermochim. Acta 131 (1988) 57.

[18] J. Ortega (author of data verification), in: H.V. Kehiaian (Ed.), Selected Data for Mixtures, Vol. 3, International Data Series, Ser. [A], 1988, pp. 183–184.

[19] J.T. Sipowska, L.R. Lemon, J.B. Ott, P.R. Brown, B.G. Marchant, J. Chem. Thermodyn. 26 (1994) 1275.

[20] A. Kumar, Indian J. Chem. 23A (1984) 943.

[21] J.A. Gates, R.H. Wood, J.C. Cobos, C. Casanova, A.H. Roux, G. Roux-Desgranges, J.-P.E. Grolier, Fluid Phase Equilib. 27 (1986) 137.

[22] A.H. Al-Dujaili, A. Awwad, Fluid Phase Equilib. 55 (1990) 355.

[23] A. D'Aprano, I.D. Donato, V.T. Livieri, J. Sol. Chem. 19 (1990) 711.

[24] G. de la Fuente, J.F. Rodrigez, J.A. Gonzalez, J.C. Cobos, C. Casanova, J. Chem. Thermodyn. 24 (1992) 23.

[25] Y.P. Handa, C.J. Halpin, G.C. Benson, J. Chem. Thermodyn. 13 (1981) 875.

[26] G.C. Benson, Y.P. Handa, J. Chem. Thermodyn. 13 (1981) 887.

[27] H. Kehiaian, Bull. Acad. Polon. Sci., Ser. Sci. Chim. 16 (1968) 165.