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Excess enthalpies of alcohol + amine mixtures. Experimental results and theoretical description using the ERAS-model[1]

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Abstract

New experimental data of the molar excess enthalpy H^E of mixtures containing eight liquids – propylamine + methanol, ethanol, propan-1-ol, butan-1-ol, butylamine + methanol, ethanol, propan-1-ol, butan-1-ol – are presented using a quasi-isothermal flow calorimeter. The results are used for testing the ERAS-model which provides a theoretical concept accounting for the self-association and cross-association of alcohol and amine molecules, as well as for non-associative intermolecular interactions. Excess molar volumes V^E are also successfully described by the model. It turns out that the strong cross-association occurring between alcohol and amine molecules is the predominant reason for the remarkably low exothermic values of H^E observed for the mixtures studied. © 1998 Elsevier Science B.V.

Keywords: Molar excess enthalpy; Alkohol+amine mixtures; ERAS-model

1. Introduction

Thermodynamic excess properties of liquid mixtures, such as the molar excess enthalpy H^E and the molar excess volume V^E, provide information about the molecular structure and intermolecular forces in liquid systems. Particularly, mixtures containing molecules which form hydrogen bonds leading to a chainlike association of the molecules are of interest. Alcohols and amines belong to this class of molecules. The self-association of alcohols is a well-known effect which has a pronounced influence on thermodynamic excess properties. The hydrogen bonds formed in the mixtures between alcohols and amines are particularly strong. As a consequence, alcohol +amine mixtures belong to the systems exhibiting the strongest negative excess enthalpies of organic liquid mixtures known in literature [1]. In this work, we present a series of new data of excess enthalpies of alcohol +amine mixtures at 298 K using isothermal flow calorimetry.

A theoretical model based on a statistical mechanical derivation which accounts for self-association and cross-association in hydrogen bonded liquid mixtures is the so-called ERAS-model [2–4]. It combines the effect of association with non-associative intermolecular interactions occurring in liquid mixtures based on an equation of state developed originally by Flory et al. [6]. The ERAS-model has been applied successfully by several other research groups to the mixtures of associating molecules including the alcohol

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+amine mixtures [7–9]. We have applied the ERAS-model to the new H^E data of mixtures containing eight liquids – Propylamine+methanol, ethanol, propanol-1-ol, butan-1-ol, butylamine+methanol, ethanol, propan-1-ol, butan-1-ol – presented in this work. We also use the ERAS-model for describing excess molar volumes V^E of these mixtures.

2. Experimental procedure

A quasi-isothermal flow calorimeter (Model 7501, Hart Scientific) was used for the measurements. Each of the pure components was delivered through stainless steel capillary tubing, at constant flow rate, into a calorimetric flow cell using two precision syringe pumps (Varian 8500). The calorimetric cell is immersed in a large bath at constant temperature. The heating power of the continuous mixing process is compensated by a combined device of a variable control heater and a Peltier cooler working at constant cooling rate. Using a calibration heater with known heating power, the calorimeter can be calibrated. The calibration heater simulates an exothermic mixing process.

Details of the calorimetric equipment are given elsewhere [10]. Exothermic as well as endothermic mixing processes can be studied.

Knowing the volumetric flow rates $\dot{v}_i (i = \mathrm{A, B})$ delivered by the pumps, the molar masses M_i, and the densities of the pure components ϱ_i, the mole fraction x_i of the mixture flowing through the calorimetric cell can be calculated. The excess enthalpy H^E and the mole fraction x_A are given by:

$$x_A = \frac{\dot{v}_A \varrho_A}{M_A} \bigg/ \left(\frac{\dot{v}_A \varrho_A}{M_A} + \frac{\dot{v}_B \varrho_B}{M_B} \right) \quad (1)$$

$$H^E = \dot{q} \bigg/ \left(\frac{\dot{v}_A \varrho_A}{M_A} + \frac{\dot{v}_B \varrho_B}{M_B} \right) \quad (2)$$

where $\dot{q}$ is the measured rate of heat of mixing. The accuracy of the experimental H^E is estimated to be within ±1.5%.

3. Experimental results

Molar excess enthalpies of alcohol + amine mixtures, containing eight liquids, have been measured at

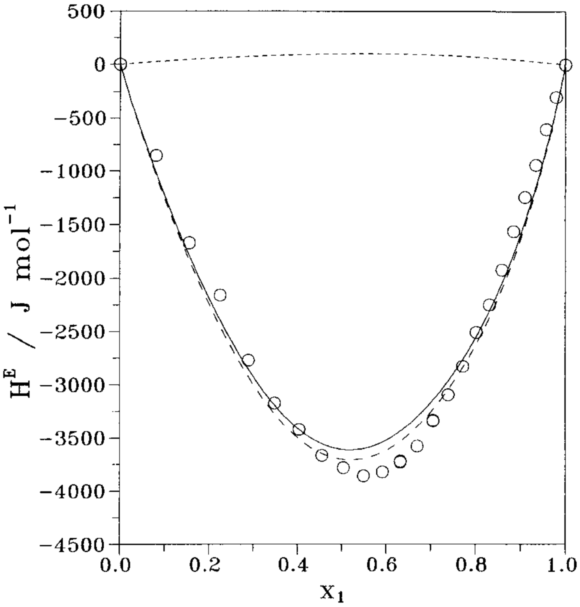

Fig. 1. Molar excess enthalpy H^E of methanol(1) + propylamine(2) at 298.15 K. O, experimental results. Solid line: ERAS-model calculation. - - - chemical contribution to ERAS, · · · physical contribution to ERAS.

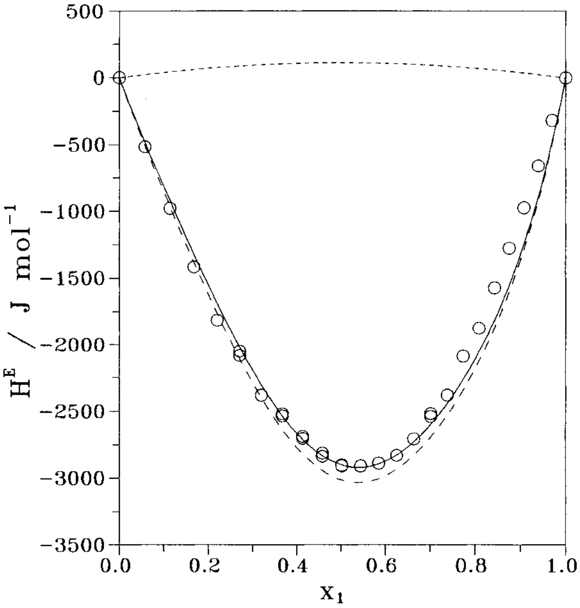

Fig. 2. Molar excess enthalpy H^E of ethanol(1) + propylamine(2) at 298.15 K. O, experimental results. Solid line: ERAS-model calculation. - - - chemical contribution to ERAS, · · · physical contribution to ERAS.

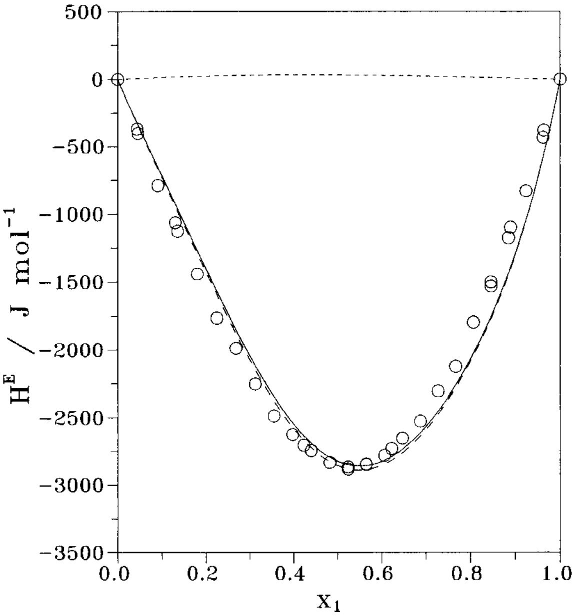

Fig. 3. Molar excess enthalpy H^E of propan – 1 – ol(1)+ propylamine(2) at 298.15 K. O, experimental results. Solid line: ERAS-model calculation. --- chemical contribution to ERAS, ··· physical contribution to ERAS.

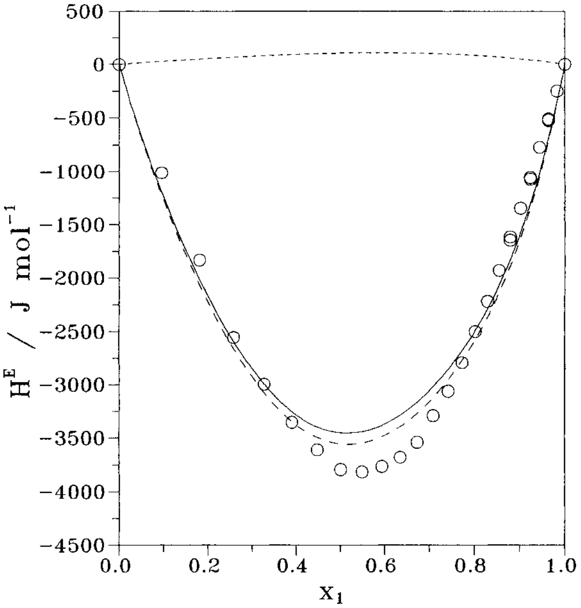

Fig. 5. Molar excess enthalpy H^E of methanol(1) + butylamine(2) at 298.15 K. O, experimental results. Solid line: ERAS-model calculation. --- chemical contribution to ERAS, ··· physical contribution to ERAS.

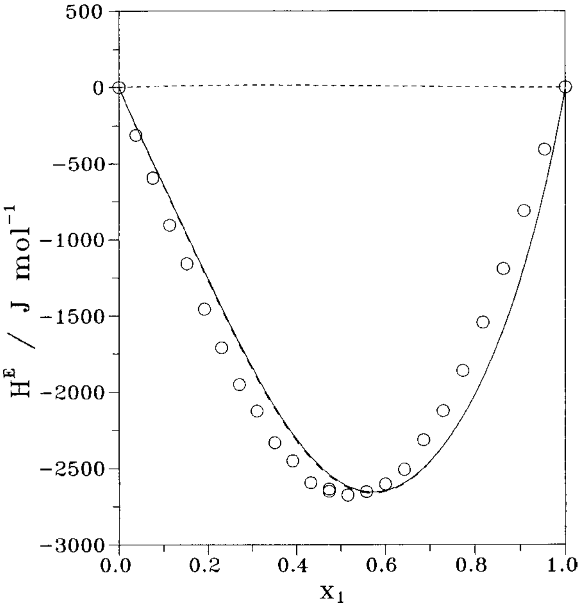

Fig. 4. Molar excess enthalpy H^E of butan – 1 – ol(1)+ propylamine(2) at 298.15 K. O, experimental results. Solid line: ERAS-model calculation. --- chemical contribution to ERAS, ··· physical contribution to ERAS.

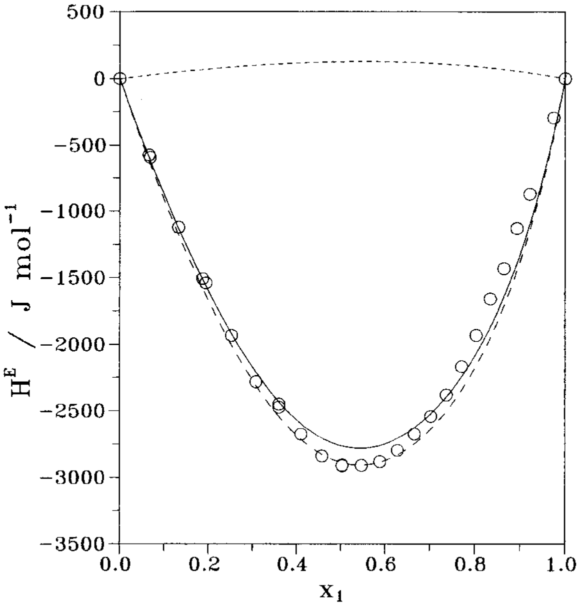

Fig. 6. Molar excess enthalpy H^E of ethanol(1) + butylamine(2) at 298.15 K. O, experimental results. Solid line: ERAS-model calculation. --- chemical contribution to ERAS, ··· physical contribution to ERAS.

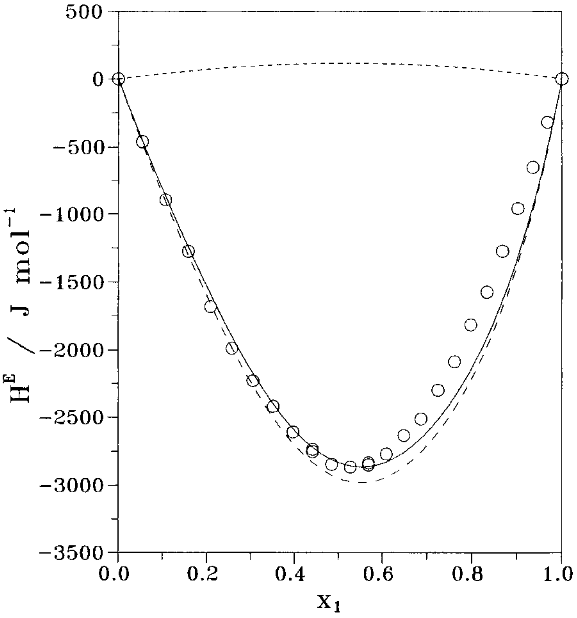

Fig. 7. Molar excess enthalpy H^E of propan – 1 – ol(1)+ butylamine(2) at 298.15 K. O, experimental results. Solid line: ERAS-model calculation. - - - chemical contribution to ERAS, · · · physical contribution to ERAS.

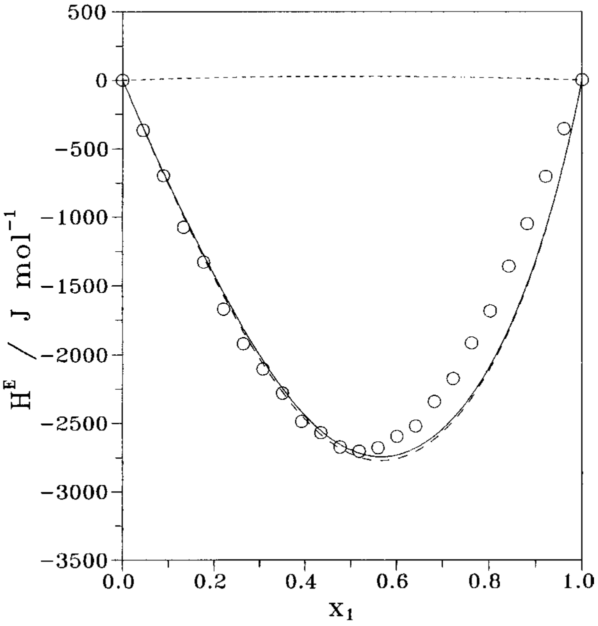

Fig. 8. Molar excess enthalpy H^E of butan – 1 – ol(1)+ butylamine(2) at 298.15 K. O, experimental results. Solid line: ERAS-model calculation. - - - chemical contribution to ERAS, · · · physical contribution to ERAS.

298.15 K. For each system 20 to 25 data points have been obtained, covering the entire range of composition. The experimental data are shown in Figs. 1–8. Accurate representation is provided by using the Redlich–Kister polynomial fit:

$$H^E = (1 - x_1)x_1 \sum_{k=0}^{m} A_k(2x_1 - 1)^k \tag{3}$$

where x_1 is the mole fraction of the alcohol.

The coefficients A_k are listed for all the systems in Table 1 along with the standard deviation σ, presenting the averaged deviation of experimental H^E data from those calculated with the help of Eq. (3) according to

$$\sigma = \sqrt{\frac{1}{n}\sum^{n}(H^E_{\text{exp}} - H^E_{\text{eq.(3)}})^2} \tag{4}$$

where n is the number of experimental points per mixture. Eq. (3) describes H^E within the experimental error. All H^E curves are negative showing minimum values between -2500 and $-4000\,\text{J mol}^{-1}$. (see Figs. 1–8).

4. ERAS-model calculations

The assumption made in frame of the ERAS-model include the self-association of alcohols (A) and amines (B) according to the following reaction scheme:

$$A_m + A_1 \rightleftharpoons A_{m+1}$$

$$B_m + B_1 \rightleftharpoons B_{m+1}$$

with m being the degree of self-association, ranging from $m = 1$ to ∞. The equilibria are described by a single equilibrium constant $K_i (i = \text{A}, \text{B})$ independent of the chain length m:

$$K_i = \frac{c_{i,m+1}}{c_{i,mc_i,1}} \frac{1}{V_i^*} \tag{5}$$

The corresponding cross-association between alcohol and amine molecules is described by:

$$A_m + B_n \rightleftharpoons A_mB_n$$

with

$$K_{AB} = \frac{c_{A_mB_n}}{c_{A_m}c_{B_n}} \frac{1}{V_A^*} \tag{6}$$

Table 1
Coefficients of the Redlich–Kister equation (Eq. (3)) and the standard deviation σ

System	A_0 (J/mol)	A_1 (J/mol)	A_2 (J/mol)	A_3 (J/mol)	A_4 (J/mol)	σ (J/mol)
Methanol + Propylamine	−15174.47	−3845.802	2549.988	2570.389	−406.2955	24.722
Ethanol + Propylamine	−11557.61	−2111.680	859.553	1539.893	697.3341	19.147
Propanol + Propylamine	−11396.97	−1670.636	2098.246	487.798	−947.6687	15.892
Butanol + Propylamine	−10677.48	−1173.536	1748.233	806.032	677.8402	10.414
Methanol + Butylamine	−15070.70	−3561.815	2308.403	2210.221	63.1960	17.443
Ethanol + Butylamine	−11558.63	−2296.975	1494.758	1059.249	-502.0037	16.652
Propanol + Butylamine	−11377.81	−1582.550	2020.958	1002.916	−109.8840	15.445
Butanol + Butylamine	−10725.69	−1314.400	2021.423	972.236	−35.8499	17.559

The c_i in Eqs. (5) and (6) are molar concentrations and V_i^* is the so-called hard core volumes of the molecule i. It has been shown by Flory [5] that this definition of equilibrium constants is consistent with statistical–mechanical considerations within the frame of lattice models.

The behavior of self-association and cross-association is combined with the ERAS equation of state

$$\frac{\tilde{p}\tilde{V}}{\tilde{T}} = \frac{\tilde{V}^{1/3}}{\tilde{V}^{1/3}-1} - \frac{1}{\tilde{V}\tilde{T}} \tag{7}$$

which is essentially identical with Flory's equation of state [6]. The difference lies in another definition of the reduction parameters p^*, V^* and T^* for the reduced pressure $\tilde{p} = p/p^*$, the reduced volume $\tilde{V} = V^{\mathrm{mol}}/V^*$ and the reduced temperature $\tilde{T} = T/T^*$. These quantities for pure liquids with self-association are defined as follows:

$$V_i^* = V_i^{\mathrm{mol}}\left(\frac{1+(\alpha_i-\alpha_i^*)T}{1+4/3(\alpha_i-\alpha_i^*)T}\right)^3 \tag{8}$$

$$\alpha_i^* = \Delta\nu_i^*\Delta h_i^*\,\frac{(4K_i+1)^{1/2}-2K_i(4K_i+1)^{-1/2}-1}{2K_iV_i^*RT^2} \tag{9}$$

$$P_i^* = (\alpha_i-\alpha_i^*)T\tilde{V}_i^2\left(\kappa_i-\alpha_i^*T\frac{\Delta\nu^*}{\Delta h^*}\right)^{-1} \tag{10}$$

$$T_i^* = \frac{\tilde{V}_i^{4/3}}{\tilde{V}_i^{1/3}-1}T \tag{11}$$

Knowing the molar volume V_i^{mol}, the thermal expansion coefficient α_i, and the compressibility κ_i from experimental p–V–T data all reduction parameters can be determined provided suitable association parameters K_i, Δh_i^*, and $\Delta\nu_i^*$ are known from other sources, where Δh_i^* and $\Delta\nu_i^*$ are the reaction enthalpy and the reaction volume of the hydrogen bond, respectively. Mixtures can also be treated using Eq. (7) by applying certain mixing rules. Details are described in the literature [2–4].

The essential property of the ERAS-model is that the excess functions such as H^{E} and V^{E} are split into a physical and a chemical contribution:

$$H^{\mathrm{E}} = H^{\mathrm{E}}_{\mathrm{phys}} + H^{\mathrm{E}}_{\mathrm{chem}} \tag{12}$$

with

$$H^{\mathrm{E}}_{\mathrm{phys}} = (x_{\mathrm{A}}V_{\mathrm{A}}^* + x_{\mathrm{B}}V_{\mathrm{B}}^*)\left\{\frac{\Phi_{\mathrm{A}}P_{\mathrm{A}}^*}{\tilde{V}_{\mathrm{A}}} + \frac{\Phi_{\mathrm{B}}P_{\mathrm{B}}^*}{\tilde{V}_{\mathrm{B}}} - \frac{P_M^*}{\tilde{V}_M}\right\} \tag{13}$$

where

$$P_M^* = \Phi_{\mathrm{A}}P_{\mathrm{A}}^* + \Phi_{\mathrm{B}}P_{\mathrm{B}}^* - \Phi_{\mathrm{A}}\vartheta_{\mathrm{B}}X_{\mathrm{AB}} \tag{14}$$

and

$$\begin{aligned} H^{\mathrm{E}}_{\mathrm{chem}} &= x_{\mathrm{A}}\Delta h_{\mathrm{A}}^*K_{\mathrm{A}}\left(\phi_{\mathrm{A1}}-\phi_{\mathrm{A1}}^0\right) \\ &\quad + x_{\mathrm{B}}\Delta h_{\mathrm{B}}^*K_{\mathrm{B}}\left(\phi_{\mathrm{B1}}-\phi_{\mathrm{B1}}^0\right) + x_{\mathrm{A}}\Delta h_{\mathrm{AB}}^*K_{\mathrm{AB}} \\ &\quad \times \frac{\phi_{\mathrm{B1}}(1-K_{\mathrm{A}}\phi_{\mathrm{A1}})}{(V_{\mathrm{B}}/V_{\mathrm{A}})(1-K_{\mathrm{B}}\phi_{\mathrm{B1}})+K_{\mathrm{AB}}\phi_{\mathrm{B1}}} \\ &\quad - \frac{P_M^*V^{\mathrm{E}}_{\mathrm{chem}}}{(\tilde{V}_M)^2} \end{aligned} \tag{15}$$

The surface fraction, ϑ_i, and the volume fraction, Φ_i, are defined as

$$\vartheta_i = s_i\Phi_i\Big/\sum_j s_j\Phi_j \tag{16}$$

$$\Phi_i = V_i^*x_i\Big/\sum_j V_j^*x_j \tag{17}$$

where s_i is the so-called surface-to-volume ratio of molecule i. ϕ_{A1} and ϕ_{B1} are the volume fractions of monomeric species of A and B in the mixture. They have to be calculated from the following equations using a numerical procedure:

$$\Phi_A = \frac{\phi_{A1}}{(1 - K_A\phi_{A1})^2}\left\{1 + \frac{V_A K_{AB}\phi_{B1}}{V_B(1 - K_B\phi_{B1})}\right\} \tag{18}$$

$$\Phi_B = \frac{\phi_{B1}}{(1 - K_B\phi_{B1})^2}\left\{1 + \frac{K_{AB}\phi_{A1}}{(1 - K_A\phi_{A1})}\right\} \tag{19}$$

The molar excess volume is also split into a physical and chemical contribution:

$$V^E = V^E_{phys} + V^E_{chem} \tag{20}$$

with

$$V^E_{phys} = \left(x_A V_A^* + x_B V_B^*\right)\left\{\tilde{V}_M - \Phi_A \tilde{V}_A - \Phi_B \tilde{V}_B\right\} \tag{21}$$

and

$$\begin{aligned} V^E_{chem} = \tilde{V}_M \Bigg\{ & x_A \Delta\nu_A^* K_A(\phi_{A1} - \phi^0_{A1}) \\ & + x_B \Delta\nu_B^* K_B(\phi_{B1} - \phi^0_{B1}) + x_A \Delta\nu_{AB}^* K_{AB} \\ & \times \frac{\phi_{B1}(1 - K_A\phi_{A1})}{(V_B/V_A)(1 - K_B\phi_{B1}) + K_{AB}\phi_{B1}} \Bigg\} \end{aligned}$$

where $\Delta\nu_A^*$ and $\Delta\nu_B^*$ are the reaction volumes of the hydrogen bond.

Parameters adjustable to excess properties are K_A, K_B, K_{AB}, Δh_A^*, Δh_B^*, Δh_{AB}^*, $\Delta\nu_A^*$, $\Delta\nu_B^*$ and X_{AB}.

The number of these parameters is reduced by the following conditions:

- values of K_A and K_B and of Δh_A^* and Δh_B^* are known for all alcohols and amines from excess enthalpies of alcohol + alkane and amine + alkane mixtures and from the heat of vaporization of the pure substances [2–4].
- $\Delta\nu_A^*$ and $\Delta\nu_B^*$ are evaluated by adjusting these parameters to V^E of alcohol + alkane and amine + alkane mixtures [4,11]

The remaining parameters adjustable to H^E and V^E of the systems studied here are K_{AB}, Δh_{AB}^*, $\Delta\nu_{AB}^*$ and X_{AB}, where X_{AB} is subject to the additional restriction

$$2 < X_{AB} < 12\,\mathrm{J\,cm^{-3}}$$

All parameters used for describing H^E and V^E are simultaneously listed in Tables 2 and 3. Values of V^{mol}, α, and x have been obtained by new experimental studies performed in this work using a vibrating tube densimeter (A. Paar, DMA 602 HT). They agree well with the data of methanol, ethanol, propan-1-ol and propylamine, obtained in previous studies with the exception of κ for butylamine [4]. The calculated curves are presented in Figs. 1–8 for H^E and for selected number of examples also for V^E in Figs. 9–12, where the experimental data of V^E have been taken from literature [12,13].

5. Discussion

The H^E curves of all 8-liquid systems are negative showing remarkably low values in the minimum range from −2.5 to −4.0 kJ mol^{-1}. The chemical contribution to H^E is the dominant one, H^E_{phys} is very small and positive in all cases. It is obvious that H^E is determined by the strong cross-association between alcohols and

Table 2
ERAS-model parameters of the pure substances at 298.15 K

Substance	K	P^* (J/cm^3)	V^{mol} (cm^3/mol)	V^* (cm^3/mol)	α (10^{-4}/K)	κ (10^{-4}/MPa)	Δh^* (kJ/mol)	Δv^* (cm^3/mol)
Methanol	986	443.6	40.732	32.13	11.89	11.92	−25.1	−5.6
Ethanol	317	426.4	58.673	47.11	10.95	10.79	−25.1	−5.6
Propanol	197	433.9	75.159	61.22	10.07	9.79	−25.1	−5.6
Butanol	175	422.7	91.973	75.70	9.32	8.84	−25.1	−5.6
Propylamine	1.00	719.9	83.105	61.58	16.83	11.73	−13.2	−2.8
Butylamine	0.96	565.7	99.891	77.59	13.10	10.55	−13.2	−2.8

Table 3
ERAS-model parameters characterizing mixture properties of 1 − Alkanol + 1 − Amine systems at 298.15 K

System	K_{AB}	Δh^*_{AB} (kJ/mol)	Δv^*_{AB} (cm^3/mol)	X_{AB} (J/cm^3)
Methanol + Propylamine	2124	−46.3	−12.3	10.23
Ethanol + Propylamine	1470	−40.9	−11.2	10.39
Propanol + Propylamine	1417	−39.4	−11.0	5.34
Butanol + Propylamine	894	−39.3	−11.6	4.61
Methanol + Butylamine	1504	−45.6	−12.0	9.20
Ethanol + Butylamine	834	−40.5	−10.5	8.79
Propanol + Butylamine	794	−39.5	−10.2	7.23
Butanol + Butylamine	775	−38.6	−10.2	5.30

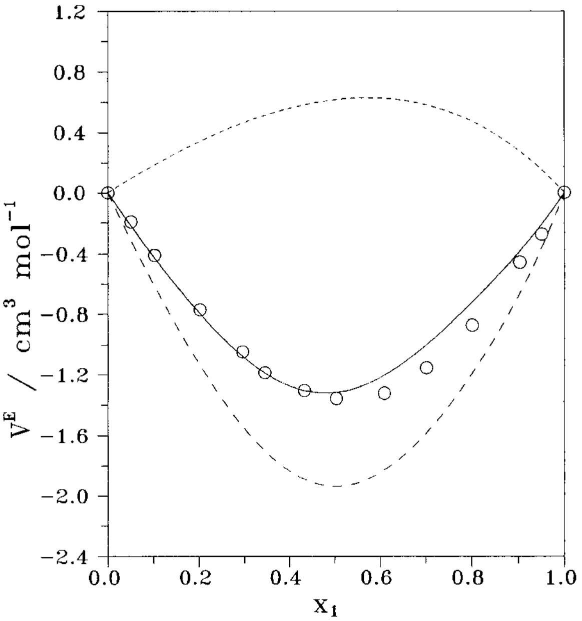

Fig. 9. Molar excess volume V^E of ethanol(1) + propylamine(2) at 298.15 K. O, experimental results taken from [12]. Solid line: ERAS-model calculation. - - - chemical contribution to ERAS · · · physical contribution to ERAS.

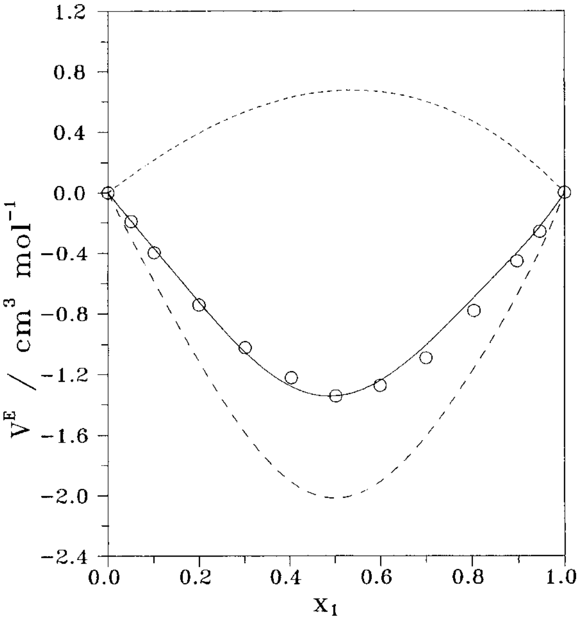

Fig. 10. Molar excess volume V^E of propan − 1 − ol(1)+ propylamine(2) at 298.15 K. O, experimental results taken from [12]. Solid line: ERAS-model calculation. - - - chemical contribution to ERAS · · · physical contribution to ERAS.

amines leading to strong exothermic H^E values. The situation is similar with V^E, however, the physical contribution is larger and the resulting curve predicted by the ERAS-model is the result of a compensating effect of the chemical and the physical contribution (see Figs. 9–12).

The parameters listed in Tables 2 and 3 reveal some of the reasons for the obtained results from the point of view of molecular interactions. The self-association of amines is weak as compared to the self-association of alcohols which is reflected by small values of K_B, Δh^*_B and Δv^*_B.

Particularly high values are found for K_{AB}, Δh^*_{AB} and Δv^*_{AB} which again demonstrates the strong hydrogen bond –O–H· · ·N– between alcohol and amine molecules. Values of Δh^*_{AB} and Δv^*_{AB} are found which are almost double, as high as those observed for the self-association of alcohols, and three to four times higher than those of the self-association of amines.

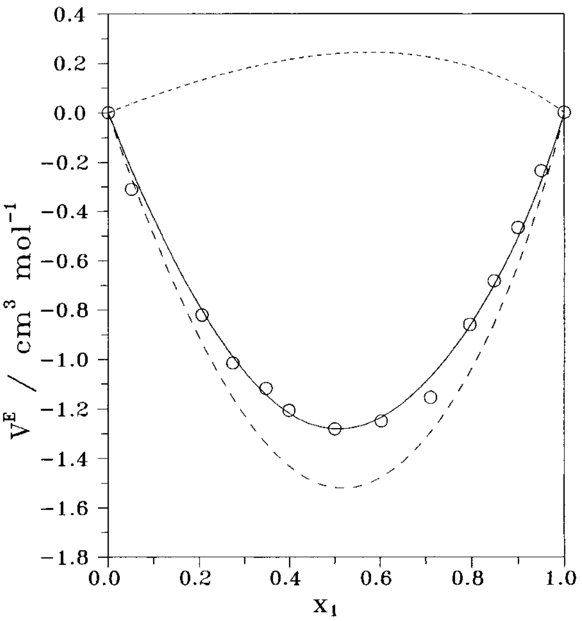

Fig. 11. Molar excess volume V^E of ethanol(1)+butylamine(2) at 298.15 K. O, experimental results taken from [13]. Solid line: ERAS-model calculation. - - - chemical contribution to ERAS · · · physical contribution to ERAS.

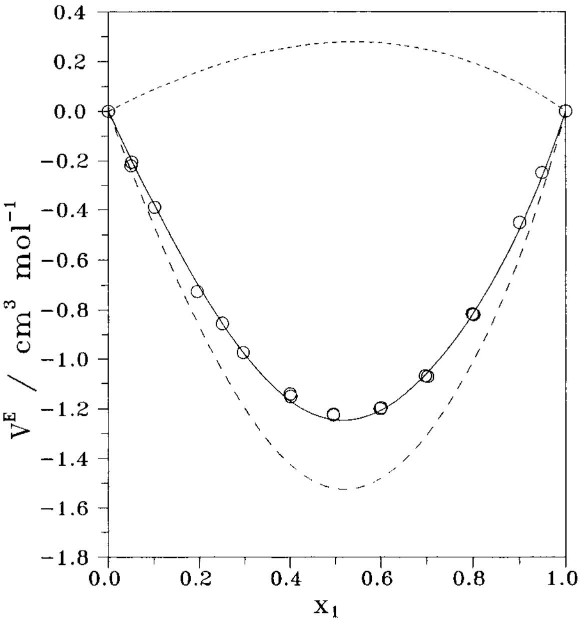

Fig. 12. Molar excess volume V^E of propan − 1 − ol(1)+ butylamine(2) at 298.15 K. O, experimental results taken from [13]. Solid line: ERAS-model calculation. - - - chemical contribution to ERAS · · · physical contribution to ERAS.

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