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Studies of viscosity and excess molar volume of binary mixtures
5. Characterization of excess molar volume of 1-alkanol with alkylamines, dialkylamines and trialkylamines in terms of the ERAS model

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Abstract

The excess molar volumes V^E of *n*-alkylamine, di-*n*-alkylamine, and tri-*n*-alkylamine with a series of 1-alkanols at 298.15, 303.15 and 313.15 K have been characterized in terms of the ERAS model which accounts for hydrogen bonding effects as well as for free volume effects in associating mixtures. The results obtained by adjusting the model parameters reveal a strong cross-association between the unlike molecules in the mixture resulting from strong negative values for the hydrogen bonding energy and the hydrogen bonding volume.

Keywords: Alkylamine; 1-Alkanols; ERAS model; Excess molar volumes; Hydrogen bonding

1. Introduction

In the previous papers [1–4], we have reported the viscosities η and the excess molar volumes V^E of binary mixtures of *n*-alkylamines, di-*n*-alkylamines and tri-*n*-alkylamines with a series of 1-alkanols over the entire range of composition at 303.15 and 313.15 K. The alkanol (A) and the primary or secondary amine (B) have both, a proton donor and a proton acceptor group. Besides AB and A_mB mixed associates, the species of type A_mB_n also exists [5]. In case of alkanol (A) and tertiary amine (B), they can form mixed multimers with alkanols of the types A_mB, only [6]. The species A_mB_n or A_mB that contain many monomers can be formed with/without the breaking of the H-bonds present in the pure liquids. The hydrogen bonds formed in the mixtures between alkanols and amines are particularly strong as their excess enthalpies are very large negative [7–9].

A theoretical model based on a statistical mechanical derivation, which accounts for self-association and cross-association in hydrogen bonded liquid mixtures is extended real associated solution (ERAS) model due to Heintz and coworkers [10,11]. It combines the effect of association with non-associative intermolecular interaction occurring in liquid mixtures based on equation of state developed originally by Flory et al. [12,13]. The ERAS model has subsequently being successfully applied by many investigators [14–23] to describe the excess thermodynamic properties of alkanol–amine mixtures. Therefore, in this paper we have applied the ERAS model to excess molar volumes for binary mixtures formed from series of 1-alkanols with mono-, di- and tri-*n*-alkylamines.

2. ERAS model

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

$$A_m + A \overset{K_A}{\leftrightarrow} A_{m+1} \quad (1)$$

$$B_n + B \overset{K_B}{\leftrightarrow} B_{n+1} \quad (2)$$

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where m or n are the degree of self-association, ranging from 1 to ∞. The cross-association between A and B molecules is represented by

$$A_m + B_n \overset{K_{AB}}{\Leftrightarrow} A_mB_n \tag{3}$$

The association constants K_i (i = A, B, AB) are assumed to be independent of the chain length. Their temperature dependence is given by

$$K_i = K_0 \exp\left[-\left(\frac{\Delta h_i^*}{R}\right)\left(\frac{1}{T}-\frac{1}{T_0}\right)\right] \tag{4}$$

where K_0 is the equilibrium constant at the standard temperature T_0 (298.15 K), R the gas constant and Δh_i^* the enthalpy for the reactions given by Eqs. (1)–(3), which corresponds to the hydrogen bonding energy. These reactions are also characterized by the volume change Δv_i^* related to the formation of the linear chains.

The essential property of the ERAS model is that the excess functions H^E and V^E are split into a chemical and a physical contribution. The expressions for H^E and V^E of the ERAS model extended to the two-block approach of cross-association [24] are given by [11,17]

$$\begin{aligned} H_c^E = {} & x_A K_A \Delta h_A^* (\phi_{A1} - \phi_{A1}^0) + x_B K_B \Delta h_B^* (\phi_{B1} - \phi_{B1}^0) \\ & + x_A K_{AB} \Delta h_{AB}^* \frac{\phi_{B1}(1-K_A\phi_{A1})}{(V_B/V_A)(1-K_B\phi_{B1}) + K_{AB}\phi_{B1}} \\ & - \frac{P_M^* V_c^E}{\tilde{V}_M^2} \end{aligned} \tag{5}$$

$$H_P^E = (x_A V_A^* + x_B V_B^*)\left(\frac{\phi_A P_A^*}{\tilde{V}_A} + \frac{\phi_B P_B^*}{\tilde{V}_B} - \frac{P_M^*}{\tilde{V}_M}\right) \tag{6}$$

$$H^E = H_c^E + H_P^E \tag{7}$$

$$\begin{aligned} V_c^E = \tilde{V}_M \Bigg\{ & x_A K_A \Delta v_A^* (\phi_{A1} - \phi_{A1}^0) \\ & + x_B K_B \Delta v_B^* (\phi_{B1} - \phi_{B1}^0) + x_A K_{AB} \Delta v_{AB}^* \\ & \times \frac{\phi_{B1}(1-K_A\phi_{A1})}{(V_B/V_A)(1-K_B\phi_{B1}) + K_{AB}\phi_{B1}} \Bigg\} \end{aligned} \tag{8}$$

$$V_P^E = (x_A V_A^* + x_B V_B^*)(\tilde{V}_M - \phi_A \tilde{V}_A - \phi_B \tilde{V}_B) \tag{9}$$

$$V^E = V_c^E + V_p^E \tag{10}$$

K_A and K_B are the equilibrium constants of chain self-association of alkanols and amines, respectively. K_{AB} and Δh_{AB}^* are the association constants and hydrogen bond energy from the cross-association. ϕ_{A1} and ϕ_{B1} are the hard core volume fraction of the monomeric alkanol and amine in the mixture, respectively. They have to be calculated numerically from the solution of the following coupled equations

$$\phi_A = \frac{\phi_{A1}}{(1-K_A\phi_{A1})^2}\left[1 + \frac{V_A K_{AB}\phi_{B1}}{V_B(1-K_B\phi_{B1})}\right] \tag{11}$$

$$\phi_B = \frac{\phi_{B1}}{(1-K_B\phi_{B1})^2}\left[1 + \frac{K_{AB}\phi_{A1}}{(1-K_A\phi_{A1})}\right] \tag{12}$$

Here ϕ_A and ϕ_B are the stoichiometric hard-core volume fractions of alkanol and amine, respectively.

2.1. ERAS parameters

The physical contribution X_p^E in ERAS model is derived from Flory's equation of state [12,13], which is assumed to be valid not only for pure components but also for the mixture

$$\frac{\tilde{P}_i \tilde{V}_i}{\tilde{T}_i} = \frac{\tilde{V}_i^{1/3}}{\tilde{V}_i^{1/3} - 1} - \frac{1}{\tilde{V}_i \tilde{T}_i} \tag{13}$$

where i = A, B, M (mixture). In Eq. (13), $\tilde{V}_i = V_i/V_i^*$; $\tilde{P}_i = P_i/P_i^*$; $\tilde{T}_i = T_i/T_i^*$; are the reduced volume, pressure, and temperature, respectively. All the reduction parameters V_i^*, P_i^* T_i^* of pure components can be determined knowing the experimental data for molar volume V, thermal expansion coefficient α, isothermal compressibility κ_T, provided suitable association parameters, K_i, Δv_i^*, Δh_i^* are known. The reduction parameters for the mixture P_M^*, T_M^*, and V_M^* are calculated from mixing rules [11,17,19]

$$P_M^* = \phi_A P_A^* + \phi_B P_B^* - X_{AB}\phi_A\theta_B \tag{14}$$

$$T_M^* = \frac{P_M^*}{\phi_A P_A^*/T_M^* + \phi_B P_B^*/T_M^*} \tag{15}$$

$$V_M^* = x_A V_A^* + x_B V_B^* \tag{16}$$

X_{AB} is an interaction parameter characterizing the difference of dispersive intermolecular interaction between A and B. ϕ_i and θ_i are hard-core volume fraction and the surface fraction of the component i [10].

3. Results and discussion

In the literature the reduction parameters for pure amines (propylamine, butylamine, dipropylamine, dibutylamine, tributylamine), and 1-alkanols (ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol and 1-decanol) are mostly available at 298.15 K. For our work we require these parameters at 303.15 and 313.15 K. Properties and parameters as equilibrium constant K, thermal expansion coefficient α, isothermal compressibility κ_T, molar volume V, characteristic volume V^*, characteristic pressure P^*, surface to volume ratio S are listed in Table 1. Further, it was noticed that there are large discrepancies in the literature on the values of reduction parameters for pure alkyl amines that can be seen from Table 2. The values of either α and κ_T or both for propylamine of Heintz and Papaioannou [17], and for butylamine and dibutylamine of Reimann and Heintz [14], Letcher and Gordon [30] and Mohren and Heintz [31], and of dipropylamine of Letcher

Table 1
Properties and parameters of pure alkanols and amines used in the ERAS model

Liquids	T (K)	K	α (kK^{-1})	κ_T (TPa^{-1})	V_M (cm^3 mol^{-1})	V^* (cm^3 mol^{-1})	P^* (J cm^{-3})	S (Å^{-1})	Δh_H (kJ mol^{-1})	Δv_H (cm^3 mol^{-1})
Ethanol	303.15	267	1.110[a]	1189[b]	59.01	47.18	397	1.543[c]	−25.1	−5.6
	313.15	201	1.122[a]	1272[b]	59.69	47.43	390	1.543[c]	−25.1	−5.6
Propanol	303.15	167	1.043[a]	1042[b]	75.51	61.02	416	1.489[c]	−25.1	−5.6
	313.15	121	1.054[a]	1120[b]	76.32	61.32	405	1.489[c]	−25.1	−5.6
Butanol	303.15	148	0.948[a]	973[b]	92.43	75.73	397	1.456[c]	−25.1	−5.6
	313.15	108	0.957[a]	1039[b]	93.35	76.07	389	1.456[c]	−25.1	−5.6
Pentanol	303.15	130	0.939[a]	909[b]	109.18	89.45	425	1.433[c]	−25.1	−5.6
	313.15	95	0.948[a]	965[b]	110.20	89.79	420	1.433[c]	−25.1	−5.6
Hexanol	303.15	102	0.908[a]	863[b]	125.84	103.62	429	1.418[c]	−25.1	−5.6
	313.15	74	0.917[a]	917[b]	127.06	104.05	423	1.418[c]	−25.1	−5.6
Heptanol	303.15	93	0.889[a]	824[b]	142.53	117.63	440	1.405[c]	−25.1	−5.6
	313.15	67	0.896[a]	875[b]	143.64	117.94	433	1.405[c]	−25.1	−5.6
Octanol	303.15	74	0.880[a]	799[b]	159.15	131.20	459	1.396[c]	−23.0	−4.9
	313.15	55	0.887[a]	848[b]	160.41	131.51	453	1.396[c]	−23.0	−4.9
Decanol	303.15	57	0.851[a]	753[b]	192.36	159.16	472	1.382[c]	−21.0	−4.9
	313.15	44	0.858[a]	796[b]	193.97	159.57	469	1.382[c]	−21.0	−4.9
Propylamine	298.15	1.66	1.378[d]	1211[d]	82.97	65.09	447	1.469[c]	−15.2	−4.5
	303.15	1.52	1.387[d]	1275[d]	83.54	65.18	447	1.469[c]	−15.2	−4.5
	313.15	1.25	1.407[d]	1411[d]	84.72	65.34	445	1.469[c]	−15.2	−4.5
Butylamine	298.15	0.96	1.314[d]	1145[d]	99.75	78.51	468	1.441[c]	−15.2	−4.5
	303.15	0.87	1.318[d]	1189[d]	100.41	78.65	467	1.441[c]	−15.2	−4.5
	313.15	0.72	1.322[d]	1288[d]	101.74	78.94	464	1.441[c]	−15.2	−4.5
Dipropylamine	303.15	0.52	1.216[d]	1237[d]	138.39	107.89	466	1.412[c]	−7.5	−4.2
	313.15	0.48	1.246[d]	1356[d]	140.11	108.02	462	1.412[c]	−7.5	−4.2
Dibutylamine	303.15	0.15	1.066[d]	1078[d]	171.88	136.34	467	1.377[c]	−6.5	−3.4
	313.15	0.14	1.079[d]	1162[d]	173.73	136.71	461	1.377[c]	−6.5	−3.4
Tributylamine	303.15	0	0.914[d]	1012[d]	240.57	195.11	416	1.364[c]	0	0
	313.15	0	0.936[d]	1095[d]	242.81	195.15	414	1.364[c]	0	0
n-Hexane	298.15	0	1.387[e]	1689[e]	131.61	99.55	428	1.412[c]	0	0
n-Heptane	298.15	0	1.247[f]	1447[f]	147.42	113.70	432	1.400[c]	0	0

[a] [25].
[b] [26].
[c] Estimated from shape of molecule [27].
[d] [28].
[e] [29].
[f] [10].

Table 2
Comparison of ERAS parameters of pure amines available in the literature

Liquids	T (K)	α (kK^{-1})	κ_T (TPa^{-1})	V^* (cm^3 mol^{-1})	P^* (J cm^{-3})	Δh_H (kJ mol^{-1})	Δv_H (TPa^{-1})	Reference
Propylamine	298.15	1.683	1173	61.58	719.9	−13.2	−2.8	[17]
	298.15	1.378	1211	65.09	447	−15.2	−4.5	[28][a]
Butylamine	298.15	0.81	1110	84.2	269.7	−13.2	−2.8	[14]
	298.15	1.310	1055	77.59	565.7	−13.2	−2.8	[17]
	298.15	1.31	1173	77.57	508.5	−13.2	−2.8	[30]
	298.15	1.257	1055	77.59	562.4	−13.2	−2.8	[31]
	298.15	1.303	1158.5	77.6	511.7			[32]
	298.15	1.314	1145	78.51	468	−15.2	−4.5	[28][a]
	313.15	1.19	1180	79.4	475.2			[14]
	313.15			78.00	351.1			[19]
	313.15	1.318	1288	78.94	464	−15.2	−4.5	[28][a]
Dipropylamine	298.15	1.31	1220	106.5	516	−7.5	−4.2	[15]
	298.15	1.201	1183	107.85	466	−7.5	−4.2	[28][a]
	298.15			106.5	546	−7.5	−4.2	[20]
Dibutylamine	293.15	0.7	970	144.70	283.5			[14]
	298.15	0.78	1020	143	319.1	−6.5	−3.4	[14]
	298.15	1.07	1020	135.86	466.2	−4.5	2.8	[33]
	313.15	1.14	1140	137.7	432.2			[14]
	298.15	1.059	1039	136.19	469	−6.5	−3.4	[28][a]
	313.15	1.079	1162	136.71	461	−6.5	−3.4	[28][a]

[a] Values obtained in our work [28].

Table 3
The ERAS model binary mixture parameters

Mixtures	T (K)	X_{AB} (J cm^{-3})	K_{AB}	Δh^*_{AB} (kJ mol^{-1})	Δv^*_{AB} (cm^3 mol^{-1})	Reference
Propylamine + n-hexane	298.15	12.5	0	0	0	[40,42]
Butylamine + n-heptane	298.15	15.0	0	0	0	[40]
Propylamine + ethanol	298.15	10.39	1470	−40.9	−11.2	[17]
	303.15	11.3	1420	−41.1	−11.16	
	313.15	11.3	844	−41.1	−11.32	
Propanol	298.15	5.34	1417	−39.4	−11.0	[17]
	303.15	11.0	880	−40.8	−11.06	
	313.15	11.0	525	−40.8	−11.18	
Butanol	298.15	4.61	894	−39.3	−11.6	[17]
	303.15	11.0	740	−40.4	−11.15	
	313.15	11.0	444	−40.4	−11.26	
Pentanol	303.15	11.0	400	−39.5	−10.72	
	313.15	11.0	242	−39.5	−10.77	
Heptanol	303.15	11.0	380	−38.4	−10.31	
	313.15	11.0	233	−38.4	−10.23	
Octanol	303.15	11.0	83	−37.8	−9.87	
	313.15	11.0	51	−37.8	−9.98	
Decanol	303.15	11.0	42	−37.5	−9.82	
	313.15	11.0	26	−37.5	−10.17	
Butylamine + ethanol	298.15	11.60	488	−41.5	−11.9	[14]
	298.15	8.79	834	−40.5	−10.5	[17]
	303.15	10.5	1454	−39.8	−11.03	
	313.15	10.5	878	−39.8	−10.83	
	313.15	13.9	247	−41.5	−11.2	[14]
Propanol	298.15	7.23	794	−39.5	−10.2	[17]
	303.15	10.5	762	−39.8	−10.72	
	313.15	10.5	460	−39.8	−10.88	
Butanol	298.15	5.3	775	−38.6	−10.2	[17]
	303.15	10.5	720	−39.5	−10.85	
	313.15	10.5	436	−39.5	−10.94	
	313.15	5.3	368	−38.6	−10.2	[19]
Pentanol	303.15	10.5	624	−39.5	−10.58	
	313.15	10.5	378	−39.5	−10.52	
Hexanol	303.15	10.5	433	−39.4	−10.56	
	313.15	10.5	263	−39.4	−10.51	
Heptanol	298.15	13.3	444	−38.5	−9.8	[14]
	303.15	10.5	388	−39.2	−10.42	
	313.15	10.5	236	−39.2	−10.39	
	313.15	12.3	222	−38.5	−9.32	[14]
Octanol	303.15	10.5	132	−35.0	−9.82	
	313.15	10.5	85	−35.0	−9.78	
Decanol	303.15	10.5	50	−35.0	−10.28	
	313.15	10.5	32	−35.0	−10.46	
Dipropylamine + ethanol	298.15	5	1400	−37.0	−11.2	[20]
	303.15	10.0	1480	−35.0	−11.44	
	313.15	10.0	950	−35.0	−11.24	
Propanol	298.15	5	835	−34.5	−11.2	[20]
	303.15	10.0	685	−35.0	−11.45	
	313.00	10.0	440	−35.0	−11.37	
Butanol	298.15	5	800	−34.5	−11.2	[20]
	303.15	10.0	505	−35.0	−11.78	
	313.15	10.0	324	−35.0	−11.68	
Pentanol	298.15	5	785	−34.5	−11.2	[20]
	303.15	10.0	410	−35.0	−11.44	
	313.15	10.0	263	−35.0	−11.33	
Hexanol	298.15	5	600	−34.5	−11.2	[20]
Heptanol	298.15	5	500	−34.5	−11.2	[20]
	303.15	10.0	188	−35.0	−11.45	
	313.15	10.0	121	−35.0	−11.33	
Octanol	298.15	5	450	−34.5	−11.2	[20]
	303.15	10.0	64	−35.0	−11.68	
	313.15	10.0	41	−35.0	−11.64	
Decanol	303.15	10.0	30	−35.0	−12.09	

Table 3 (*Continued*)

Mixtures	T (K)	X_{AB} (J cm^{-3})	K_{AB}	Δh^*_{AB} (kJ mol^{-1})	Δv^*_{AB} (cm^3 mol^{-1})	Reference
	313.15	10.0	19	−35.0	−12.27	
Dibutylamine + ethanol	298.15	10.0	540	−37.0	−10.8	[21]
	303.15	10.0	476	−36.6	−10.29	
	313.15	10.0	299	−36.6	−10.35	
Propanol	298.15	12.7	395	−36.0	−10.45	[14]
	298.15	10.0	250	−34.5	−10.8	[21]
	303.15	10.0	238	−34.4	−10.45	
	313.15	10.0	154	−34.4	−10.49	
	313.15	12.7	221	−36.0	−9.77	[14]
Butanol	298.15	10.0	230	−34.5	−10.8	[21]
	303.15	10.0	218	−34.4	−10.68	
	313.15	10.0	141	−34.4	−10.69	
Pentanol	298.15	10.0	195	−34.5	−10.8	[21]
	303.15	10.0	190	−34.4	−10.37	
	313.15	10.0	123	−34.4	−10.67	
Hexanol	298.15	10.0	130	−34.5	−10.8	[21]
	303.15	10.0	128	−34.4	−10.72	
	313.15	10.0	83	−34.4	−10.69	
Heptanol	298.15	10.0	95	−34.5	−10.80	[19]
	298.15	10.0	95	−34.5	−11.0	[21]
	303.15	10.0	90	−34.4	−11.04	
	313.15	10.0	58	−34.4	−11.02	
Octanol	298.15	10.0	85	−34.5	−10.8	[21]
	303.15	10.0	54	−34.4	−11.11	
	313.15	10.0	33	−34.4	−11.19	
Decanol	303.15	10.0	27	−34.4	−12.00	
	313.15	10.0	17	−34.4	−12.00	
Tributylamine + propanol	303.15	6.9	12.6	−32.4	−12.95	
	313.15	6.9	8.4	−32.4	−13.48	
Butanol	303.15	6.9	11.8	−32.4	−13.89	
	313.15	6.9	7.8	−32.4	−14.22	
Pentanol	303.15	7.0	11.4	−32.4	−14.07	
	313.15	7.0	7.6	−32.4	−14.02	
Heptanol	303.15	7.6	9.6	−32.4	−14.65	
	313.15	7.6	6.4	−32.4	−13.97	
Octanol	303.15	7.6	7.1	−32.4	−14.72	
	313.15	7.6	4.7	−32.4	−14.55	
Decanol	303.15	7.6	6.0	−32.4	−14.78	
	313.15	7.6	4.0	−32.4	−14.60	

and Bricknell [15] are different than the our values [28] as well as other literature values [32–36].

To determine reduction parameters additional data required are K_i, Δh_i^*, and Δv_i^* for associated components. Different sets of values of association constant K_i, Δh_i^*, and Δv_i^* are available in the literature [10,11,29,37,38]. The values of Δh_i^* and Δv_i^* for alkanols used by Heintz and coworkers [10,11,29,37] are $-25.1\,\text{kJ mol}^{-1}$ and $-5.6\,\text{cm}^3\,\text{mol}^{-1}$, respectively, irrespective of the chain length of alkanol. If these values are used, especially for the higher alkanols, then the calculated values of the heat of vaporization ΔH_{vap} employing Eq. (17), are much higher compared to the experimental values [39]

$$\Delta H_{\text{vap}} = RT - \Delta h_i^* K \phi_i^0 + \frac{P_i^* V_i^*}{\tilde{V}_i} \tag{17}$$

It is known that for the higher alkanols, the values of enthalpy and volume of hydrogen bond formation decrease with the chain length [24,38,40]. Considering this fact, we have used the values of Δh_i^* and Δv_i^* as $-25.1\,\text{kJ mol}^{-1}$ and $-5.6\,\text{cm}^3\,\text{mol}^{-1}$ for ethanol to heptanol as recommended by Heintz et al. [10,11,29], but for the higher alkanols from octanol and decanol, the values of Δh_i^* and Δv_i^* have been selected from a recent paper by Pineiro et al. [38], in which the ERAS model and its parameters have been reviewed and examined critically. As the values of K_{B}, Δh_{B}^* and Δv_{B}^* for propylamine and butylamine reported in the literature were based on incorrect values of reduction parameters, we have redetermined the values of Δh_{B}^* and Δv_{B}^* for propylamine and butylamine from the excess enthalpies and excess volume data of propylamine + *n*-hexane and butylamine + *n*-heptane mixtures [41–43]. The present values of Δh^* and Δv^* are $-15.2\,\text{kJ mol}^{-1}$ and $-4.5\,\text{cm}^3\,\text{mol}^{-1}$, respectively for propylamine and butylamine. Heintz et al. [11,14,17] have always used $-13.2\,\text{kJ mol}^{-1}$ and $-2.8\,\text{cm}^3\,\text{mol}^{-1}$. The values of Δh_i^*

Table 4
Comparison of experimental excess molar volume ($cm^3\,mol^{-1}$) [1–4] with ERAS model calculations at $x = 0.5$ and standard deviation $\sigma(V^E, cm^3\,mol^{-1})$ for entire range of composition

	T (K)	$V^E_c(0.5)$	$V^E_p(0.5)$	$V^E_{ERAS}(0.5)$	$V^E_{exp}(0.5)$	$\sigma(V^E)$	Reference
Propylamine + ethanol	298.15	−1.935	0.640	−1.295	−1.337		[17]
	303.15	−1.549	0.172	−1.376	−1.375	0.036	
	313.15	−1.634	0.197	−1.438	−1.435	0.038	
Propanol	298.15	−1.959	0.699	−1.260	−1.314		[17]
	303.15	−1.511	0.167	−1.344	−1.334	0.009	
	313.15	−1.605	0.207	−1.397	−1.400	0.014	
Butanol	298.15	−2.101	0.828	−1.273	−1.244		[17]
	303.15	−1.519	0.207	−1.312	−1.298	0.033	
	313.15	−1.574	0.223	−1.351	−1.364	0.020	
Pentanol	303.15	−1.391	0.146	−1.245	−1.249	0.081	
	313.15	−1.441	0.132	−1.310	−1.325	0.045	
Heptanol	303.15	−1.324	0.082	−1.242	−1.228	0.117	
	313.15	−1.350	0.052	−1.298	−1.297	0.071	
Octanol	303.15	−1.186	0.034	−1.152	−1.194	0.099	
	313.15	−1.226	−0.010	−1.217	−1.272	0.057	
Decanol	303.15	−1.013	−0.025	−1.037	−1.098	0.088	
	313.15	−1.039	−0.104	−1.143	−1.203	0.056	
Butylamine + ethanol	298.15	−1.770	0.483	−1.287	−1.284		[14]
	298.15	−1.497	0.236	−1.261	−1.288		[17]
	303.15	−1.637	0.208	−1.429	−1.342	0.068	
	313.15	−1.672	0.207	−1.464	−1.391	0.056	
	313.15	−1.555	0.236	−1.318	−1.316		[14]
Propanol	298.15	−1.493	0.289	−1.209	−1.223		[17]
	303.15	−1.548	0.196	−1.352	−1.292	0.049	
	313.15	−1.652	0.223	−1.429	−1.345	0.066	
Butanol	298.15	−1.535	0.329	−1.206	−1.201		[17]
	303.15	−1.587	0.259	−1.328	−1.256	0.094	
	313.15	−1.668	0.287	−1.381	−1.298	0.085	
Pentanol	303.15	−1.480	0.195	−1.285	−1.231	0.084	
	313.15	−1.506	0.205	−1.300	−1.259	0.088	
Hexanol	303.15	−1.444	0.179	−1.265	−1.216	0.172	
	313.15	−1.477	0.191	−1.287	−1.241	0.124	
Heptanol	298.15	−1.405	0.317	−1.088	−1.094		[14]
	303.15	−1.383	0.134	−1.248	−1.207	0.132	
	313.15	−1.429	0.143	−1.285	−1.227	0.130	
	313.15	−1.303	0.123	−1.168	−1.161		[14]
Octanol	303.15	−1.343	0.098	−1.245	−1.203	0.116	
	313.15	−1.379	0.100	−1.279	−1.227	0.116	
Decanol	303.15	−1.209	0.020	−1.189	−1.185	0.104	
	313.15	−1.224	0.012	−1.211	−1.207	0.089	
Dipropylamine + ethanol	298.15	−1.911	0.209	−1.702	−1.559	0.110	[20]
	303.15	−2.129	0.209	−1.919	−1.755	0.154	
	313.15	−2.125	0.232	−1.893	−1.713	0.141	
Propanol	298.15	−1.896	0.247	−1.649	−1.550	0.076	[20]
	303.15	−2.033	0.213	−1.821	−1.726	0.089	
	313.15	−2.020	0.241	−1.780	−1.694	0.082	
Butanol	298.15	−1.903	0.328	−1.575	−1.558	0.049	[20]
	303.15	−2.065	0.288	−1.777	−1.701	0.083	
	313.15	−2.041	0.315	−1.726	−1.660	0.054	
Pentanol	298.15	−1.941	0.421	−1.519	−1.600	0.100	[20]
	303.15	−1.912	0.204	−1.708	−1.655	0.063	
	313.15	−1.882	0.209	−1.673	−1.622	0.059	
Hexanol	298.15	−1.938	0.385	−1.553	−1.597	0.080	[20]
Heptanol	298.15	−1.921	0.434	−1.487	−1.618	0.170	[20]
	303.15	−1.740	0.121	−1.618	−1.597	0.085	
	313.15	−1.710	0.116	−1.594	−1.573	0.077	
Octanol	298.15	−1.912	0.276	−1.636	−1.608	0.110	[20]
	303.15	−1.593	0.080	−1.514	−1.552	0.074	
	313.15	−1.537	0.064	−1.474	−1.514	0.064	
Decanol	303.15	−1.418	−0.017	−1.435	−1.517	0.097	
	313.15	−1.360	−0.055	−1.415	−1.481	0.073	
Dibutylamine + ethanol	298.15	−1.751	0.326	−1.425	−1.334	0.085	[21]

Table 4 (*Continued*)

	T (K)	$V^{\mathrm{E}}_{\mathrm{c}}(0.5)$	$V^{\mathrm{E}}_{\mathrm{p}}(0.5)$	$V^{\mathrm{E}}_{\mathrm{ERAS}}(0.5)$	$V^{\mathrm{E}}_{\mathrm{exp}}(0.5)$	$\sigma(V^{\mathrm{E}})$	Reference
	303.15	−1.640	0.173	−1.467	−1.423	0.068	
	313.15	−1.620	0.189	−1.427	−1.397	0.067	
Propanol	298.15	−1.715	0.392	−1.323	−1.321		[14]
	298.15	−1.644	0.329	−1.315	−1.315	0.048	[21]
	303.15	−1.625	0.212	−1.413	−1.397	0.044	
	313.15	−1.625	0.234	−1.391	−1.384	0.047	
	313.15	−1.497	0.239	−1.258	−1.255		[14]
Butanol	298.15	−1.663	0.317	−1.345	−1.325	0.049	[21]
	303.15	−1.705	0.296	−1.409	−1.395	0.035	
	313.15	−1.699	0.321	−1.373	−1.364	0.038	
Pentanol	298.15	−1.658	0.314	−1.344	−1.379	0.028	[21]
	303.15	−1.618	0.249	−1.369	−1.386	0.021	
	313.15	−1.608	0.262	−1.346	−1.361	0.024	
Hexanol	298.15	−1.601	0.306	−1.295	−1.401	0.060	[21]
	303.15	−1.671	0.251	−1.420	−1.431	0.036	
	313.15	−1.649	0.263	−1.387	−1.406	0.031	
Heptanol	298.15	−1.538	0.210	−1.328	−1.403	0.046	[21]
	303.15	−1.658	0.216	−1.442	−1.463	0.048	
	313.15	−1.630	0.223	−1.407	−1.428	0.046	
Octanol	298.15	−1.522	0.326	−1.197	−1.388	0.093	[21]
	303.15	−1.678	0.190	−1.488	−1.497	0.036	
	313.15	−1.640	0.193	−1.447	−1.454	0.030	
Decanol	303.15	−1.684	0.113	−1.571	−1.589	0.036	
	313.15	−1.552	0.024	−1.528	−1.557	0.033	
Tributylamine + propanol	303.15	−0.827	0.124	−0.703	−0.774	0.091	
	313.15	−0.767	0.133	−0.634	−0.695	0.093	
Butanol	303.15	−0.979	0.153	−0.826	−0.887	0.095	
	313.15	−0.899	0.177	−0.712	−0.773	0.108	
Pentanol	303.15	−1.069	0.146	−0.933	−1.003	0.091	
	313.15	−0.945	0.152	−0.793	−0.854	0.109	
Heptanol	303.15	−1.188	0.134	−1.054	−1.142	0.098	
	313.15	−1.028	0.135	−0.894	−0.991	0.102	
Octanol	303.15	−1.237	0.117	−1.120	−1.200	0.103	
	313.15	−1.037	0.112	−0.961	−1.042	0.122	
Decanol	303.15	−1.286	0.062	−1.223	−1.298	0.108	
	313.15	−1.096	0.037	−1.059	−1.149	0.120	

and Δv^*_i for the pure self-associated components alkanols as well as for the alkylamines used in the present work are also included in Table 1.

Unknown parameters K_{AB}, Δh^*_{AB}, Δv^*_{AB},and X_{AB} appearing in Eqs. (5)–(10) are cross-parameters. The values of unknown cross-parameters K_{AB}, Δh^*_{AB}, Δv^*_{AB} and X_{AB} can be determined by simultaneously adjusting the theoretical expressions (5)–(10) of the ERAS model to the experimental H^{E} and V^{E} data. There can be several sets of these parameters. The optimum values of cross-parameters can be obtained to give minimum deviations for H^{E} and V^{E} data, subject to the additional restriction $2 < X_{\mathrm{AB}} < 12\,\mathrm{J\,cm^{-3}}$ [10,17].

In the present study first we have obtained optimum values of K_{AB}, Δh^*_{AB}, Δv^*_{AB} and X_{AB} for alkanol + alkyl amine systems at 303.15 K by simultaneously adjusting the theoretical expressions (5)–(10) to experimental equimolar H^{E} and whole composition range V^{E}. Then for 313.15 K, the values of Δh^*_{AB} and X_{AB} were regarded as temperature independent and K_{AB} calculated consistent with Eq. (4). Using these values of K_{AB}, Δh^*_{AB}, X_{AB}, the optimum values of Δv^*_{AB} were obtained to adjust experimental V^{E} (whole concentration range). The optimum values of the cross-parameters for alkanol + alkyl amine systems are given in Table 3. The values of excess enthalpy H^{E} for alkanol + alkyl amine were taken from literature [6,17–21,44–47].

Results of calculated excess molar volumes are compared with the experimental data at equimolar composition in Table 4 along with the standard deviation $\sigma(V^{\mathrm{E}})$ between experimental and ERAS V^{E} for whole concentration range. The physical and chemical contributions to the excess molar volume V^{E} are also presented. We have also included the literature experimental and ERAS model data of excess molar volumes at 298.15 K. It may be mentioned that use of incorrect equation for calculation of $V^{\mathrm{E}}_{\mathrm{c}}$ by Reimann and Heintz [14] gave incorrect values of Δv^*_{AB} for ethanol + butylamine, heptanol + butylamine and propanol + dibutylamine at 298.15 and 313.15 K. The corrected values of these parameters are also reported in the present work. For few selected mixtures experimental and theoretical values of V^{E} are compared graphically in Figs. 1–5 over the entire range of composition.

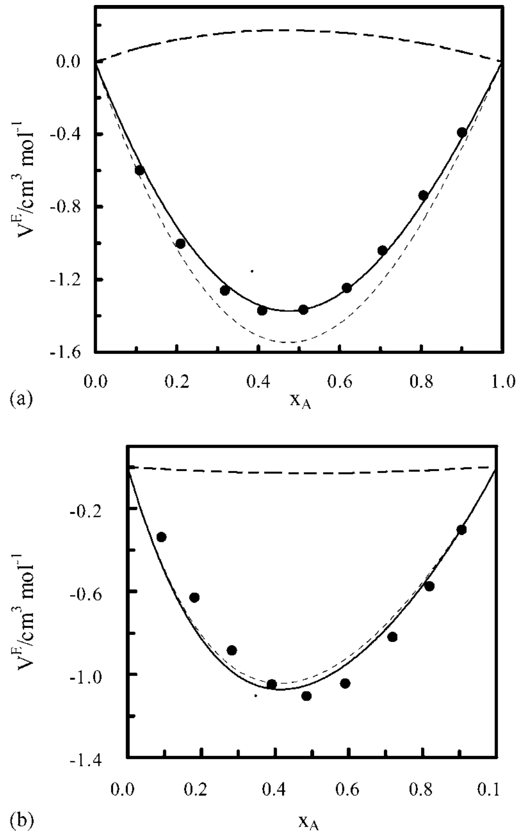

Fig. 1. Excess molar volumes of (a) ethanol + propylamine, (b) decanol + propyl amine at 303.15 K. (●) V^E_{exp} [1]; (—) V^E_{ERAS}; (- - -) V^E_c; (— — —) V^E_p.

We shall analyze the ERAS results considering three groups of mixtures involving:(i) primary amine, (ii) secondary amine, and (iii) tertiary amine.

(i) It can be seen from Table 3 that the values of Δh^*_{AB} and Δv^*_{AB} are from -35.0 to -41.5 kJ mol^{-1} and from -9.78 to -11.32 cm^3 mol^{-1} for alkanol + primary amine mixtures. These values are comparable with the values for butylamine mixtures with ethanol [14], propanol [11,17] and heptanol [14] studied previously. The estimated values of Δh^*_{AB} (O–H$\cdots$N hydrogen bond) are from -33.5 to -42.7 kJ mol^{-1} from calorimetry measurements [44,48–50]. Thus the ERAS model values are in agreement with the method which is free of a molecular model. The magnitudes of cross-parameters K_{AB}, Δh^*_{AB} and Δv^*_{AB}, for alkanol + primary amine are much larger than those of pure amines and alkanols self-association. The values of standard deviation $\sigma(V^E)$ for present alkanol + primary amine (Table 4) are in the range from 0.014 to 0.132 cm^3 mol^{-1}.

(ii) The Δh^*_{AB} and Δv^*_{AB} values for the alkanol + secondary amine mixtures (Table 3) are in the range from -34.4 to -36.6 kJ mol^{-1} and from -10.29 to -12.27 cm^3 mol^{-1}. The estimated Δh^*_{AB} are very

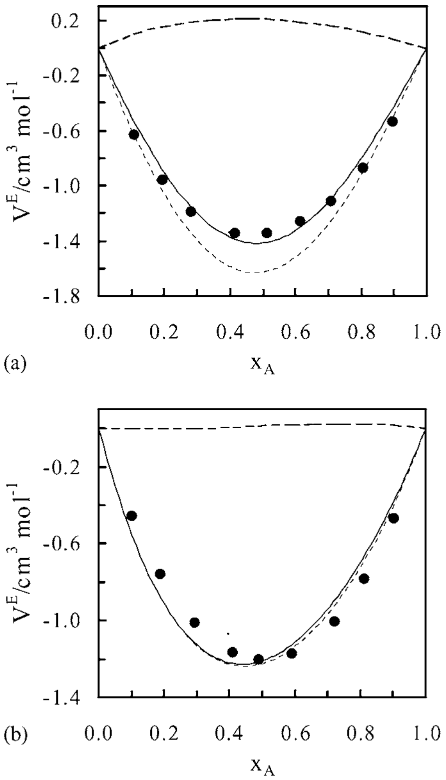

Fig. 2. Excess molar volumes of (a) ethanol + butylamine, (b) decanol + butylamine at 303.15 K. (●) V^E_{exp} [2]; (—) V^E_{ERAS}; (- - -) V^E_c; (— — —) V^E_p.

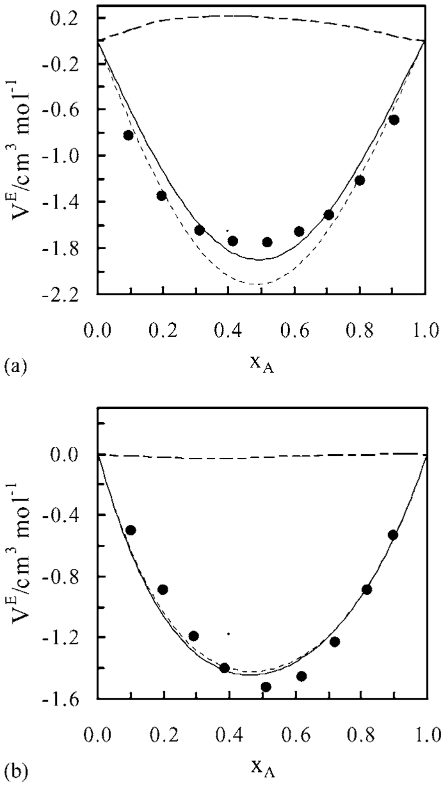

Fig. 3. Excess molar volumes of (a) ethanol + dipropylamine, (b) decanol + dipropyl amine at 303.15 K. (●) V^E_{exp} [3]; (—) V^E_{ERAS}; (- - -) V^E_c; (— — —) V^E_p.

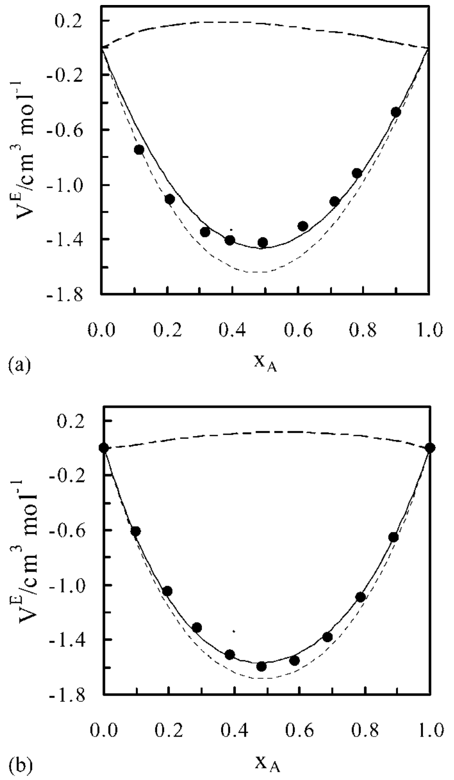

Fig. 4. Excess molar volumes of (a) ethanol + dibutylamine, (b) decanol + dibutyl mine at 303.15 K. (●) V^E_{exp} [3]; (—) V^E_{ERAS}; (- - -) V^E_c; (— — —) V^E_p.

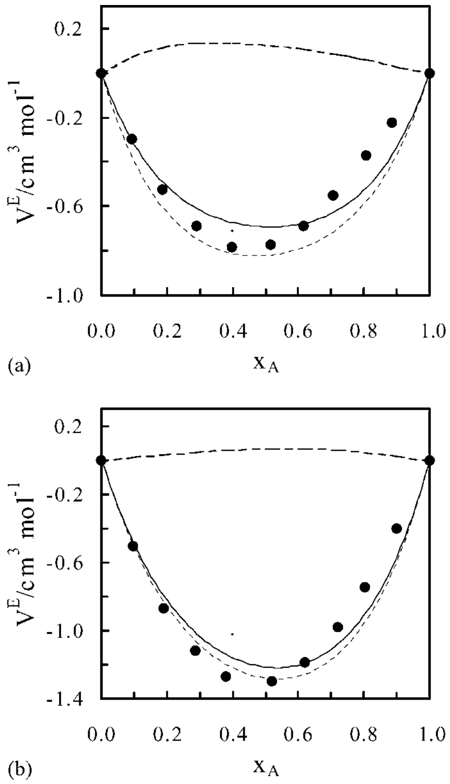

Fig. 5. Excess molar volumes of (a) propanol + tributylamine, (b) decanol + tributylamine at 303.15 K. (●) V^E_{exp} [1]; (—) V^E_{ERAS}; (- - -) V^E_c; (— — —) V^E_p.

close to calorimetric values $= -38.4 \pm 0.40$ [51]. The values of $\sigma(V^E)$ for present alkanol + secondary amine (Table 4) are in the range from 0.021 to 0.170 $cm^3\ mol^{-1}$.

(iii) The K_{AB} values for the alkanols + tributylamine mixtures (Table 3) are comparatively much smaller than those involving mono- and di-amines. The values of K_{AB} are in the range from 4.0 to 12.6 for present alkanol + tributylamine and decrease from 1-propanol to 1-decanol. The values of K_{AB} for alkanol (propanol to 1-octanol) + triethylamine are in the range from 180 to 70 at 298.15 K [11,23] and for propanol + tripropylamine are 140 at 298.15 K [15]. Thus for a given alkanol the values of K_{AB} for triethylamine are approximately 6–12 times larger than those for tributylamine mixtures. The values of Δh^*_{AB} and Δv^*_{AB} are -32.4 kJ mol^{-1} and from -12.95 to -14.78 $cm^3\ mol^{-1}$. These values are similar to those observed for alkanol + triethylamine [11,23]. The experimental values for O–H···N hydrogen-bonding observed are -32.6 kJ mol^{-1} (spectroscopically [52]) and -34.8 ± 0.4 kJ mol^{-1} (calorimetrically [15]). Thus, the present value of -32.4 kJ mol^{-1} is a reasonable estimate of H-bonding. The present values of Δv^*_{AB} are almost three-times the value $\Delta v^*_A = -5.6$ $cm^3\ mol^{-1}$ of pure alkanols. Sawamura et al. [53] has reported $\Delta v^*_{AB} = -10.7$ $cm^3\ mol^{-1}$ measured directly by pressure dependence of UV light absorption of phenol/triethylamine system. The very large negative values of Δh^*_{AB} and Δv^*_{AB} for alkanol + trialkylamine suggest very strong O–H···N bond formation but the small values of K_{AB} also suggest that the number of such bond formed in the mixture is small. The values of $\sigma(V^E)$ for present alkanol + tributylamine (Table 4) are in the range from 0.091 to 0.122 $cm^3\ mol^{-1}$.

4. Conclusions

From this study following conclusions can be drawn:

(i) The ERAS model is able to represent satisfactorily V^E for alkanol + alkylamine mixtures.

(ii) The results obtained by the adjustment of the model parameters reveal that the strong negative values of V^E for alkanol + alkylamine can only be explained by the assumption of strong hydrogen bonding effects between the unlike components.

(iii) The values of Δh^*_{AB} indicate that H-bond energy (O–H···N) for a given alkanol decreases in the order primary amine > secondary amine > tertiary amine, but for a given amine, they do not vary significantly with the size of alkanol. Further, The values of Δh^*_{AB} indicate that H-bond energy (O–H···N) for a given amine does not vary significantly with the size of alkanol.

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