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Volumetric and transport properties of ternary mixtures containing 1-propanol, triethylamine or tri-*n*-butylamine and cyclohexane at 303.15 K: Experimental data, correlation and prediction by ERAS model

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ABSTRACT

The excess molar volumes (V_m^E), viscosity deviations ($\Delta\eta$), and excess Gibbs energies of activation (ΔG^{*E}) of viscous flow have been investigated from densities and viscosities measurements for two ternary mixtures 1-propanol + triethylamine + cyclohexane and 1-propanol + tri-*n*-butylamine + cyclohexane and corresponding binaries at 303.15 K and atmospheric pressure over the entire range of composition. The empirical equations due to Redlich–Kister, Kohler, Rastogi et al., Jacob–Fitzner, Tsao–Smith, Lark et al., Heric–Brewer, and Singh et al., have been employed to correlate V_m^E, $\Delta\eta$, and ΔG^{*E} of ternary mixtures with their corresponding binary parameters. The results are discussed in terms of the molecular interaction between the components of the mixture. Further, the Extended Real Associated Solution (ERAS) model has been applied to V_m^E for the present binary and ternary mixtures and the results are compared with the experimental data.

1. Introduction

Excess properties of mixtures provide information about the molecular interactions between the various components and can be used for the development of molecular models describing the thermodynamic behaviour of mixtures. Experimental results of multi-component mixtures are very important for industrial application. Therefore the properties of multi-component mixtures are often estimated from the corresponding data of the constituent binary mixtures but the reliability of such estimation is always questionable and has to be tested.

Mixtures of alkanols with amines have been subject of many investigations [1–14], as they are highly non-ideal systems with large negative excess thermodynamic properties as a result of strong cross-association through formation of hydrogen bonds. Cyclohexane a non-associating inert molecule acts as an order-breaking molecule when mixed with associating components. Since, the excess properties of ternary mixtures are reflecting differences in molecular size, shape, and interaction of three components; it is of interest and significance to study effect of addition of cyclohexane in the mixture formed from alkanol and amine.

We are engaged in systematic studies of thermodynamic, acoustic, and transport properties of mixtures involving alkanols, alkylamines, and hydrocarbons. Speeds of sound, viscosities and excess molar volumes of their binary mixtures have been reported [15–26]. As an extension, in the present work, excess molar volumes (V_m^E), viscosity deviations ($\Delta\eta$), and excess Gibbs energies of activation (ΔG^{*E}) of viscous flow of two ternary mixtures 1-propanol (A) + triethylamine (B) + cyclohexane (C) and 1-propanol (A) + tri-*n*-butylamine (B) + cyclohexane (C) and constituent binary mixtures at 303.15 K and atmospheric pressure over the entire range of composition have been reported. The ternary results of V_m^E, $\Delta\eta$, and ΔG^{*E} have been correlated through empirical or semi theoretical equations due to Redlich–Kister [27], Kohler [28], Rastogi et al. [29], Jacob–Fitzner [30], Tsao–Smith [31], Lark et al. [32], Heric–Brewer [33], and Singh et al. [34]. Further, the Extended Real Associated Solution (ERAS) model [14,35–37] has been applied to describe the excess molar volumes of presently investigated binary and ternary mixtures.

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Table 1
Comparison of densities (ρ) and viscosities (η) of pure liquids at 303.15 K.

Liquid	ρ (g cm^{-3})			η (mPa s)		
	Experimental	Literature		Experimental	Literature	
cC_6H_{12}	0.76916	0.76904[a]	0.76915[b]	0.819	0.820[c]	0.8226[d]
C_3H_7OH	0.79566	0.79561[e]	0.79588[f]	1.727	1.725[c]	
$(C_2H_5)_3N$	0.71845	0.71836[g]	0.7185[h]	0.330	0.323[i]	
$(C_4H_9)_3N$	0.77039	0.7701[h]	0.7706[i]	1.167	1.166[j]	1.17[k]

[a] [40].
[b] [41].
[c] [38].
[d] [42].
[e] [43].
[f] [44].
[g] [45].
[h] [46].
[i] [47].
[j] [48].
[k] [49].

2. Experimental

2.1. Materials

Cyclohexane (cC_6H_{12}, Merck GR), 1-propanol (C_3H_7OH, Merck AR), triethylamine ($(C_2H_5)_3N$, Fluka AG) and tri-*n*-butylamine ($(C_4H_9)_3N$, Fluka AG) were used after further purification and drying by the standard procedures [38]. cC_6H_{12} was dried over molecular sieve type 4 Å (Fluka) and was fractionally distilled over sodium. C_3H_7OH was purified by refluxing over lime for 5 h and then distilling through 1-m column. $(C_2H_5)_3N$ and $(C_4H_9)_3N$ were kept over sodium and fractionally distilled twice [39]. The purity of all the liquid samples was checked by gas–liquid chromatography, and comparing measured normal boiling points. The estimated purity was better than 99.5 mol% for C_3H_7OH, $(C_2H_5)_3N$, and $(C_4H_9)_3N$, and 99.9 mol% for cC_6H_{12}. The pure component properties are in good agreement with literature values [38,40–49] as reported in Table 1.

2.2. Apparatus and procedures

Densities of pure liquid components and investigated binary and ternary mixtures were measured by using an Anton-Paar (DMA 60/602 model) vibrating tube digital densimeter attached with an ultra-thermostat bath (Heto-Birkeroad) controlled to ±0.01 K. The density meter was calibrated with dry air and with degassed double distilled water. The viscosities were measured with a modified suspended-level Ubbelohde viscometer [50]. The viscometer was designed so as to reduce surface tension effects to negligible values [51]. The details of the experimental procedure have been described earlier [15,17].

The mixtures were prepared by mixing known masses of pure liquids in air tight, narrow-mouth ground stoppered bottles taking due precautions to minimize evaporation losses. All the mass measurements were performed on an electronic balance (Mettler AE 163, Switzerland) accurate to 0.01 mg. The samples for the measurement were immediately used after preparation. In case of ternary mixtures the third pure component was added to the known composition of binary mixture of remaining two components. The possible error in the mole fraction is estimated to be less than 1×10^{-4}. The estimated accuracy of presently measured densities and viscosities is within 2×10^{-5} g cm^{-3} and 0.002 mPa s, respectively.

3. Results

The excess molar volumes of binary and ternary mixtures at each composition have been calculated using the following expression

$$V_{\mathrm{m}}^{\mathrm{E}} = \frac{\sum_{i=A,B,C} x_i M_i}{\rho} - \sum_{i=A,B,C} \frac{x_i M_i}{\rho_i} \tag{1}$$

where M_i is the molar mass of pure component, ρ and ρ_i represent densities of mixture and pure components i, respectively. The $V_{\mathrm{m}}^{\mathrm{E}}$ is estimated to be accurate within 0.005 cm^3 mol^{-1}.

The viscosity deviations from linear dependence on mole fraction were calculated by

$$\Delta_{\eta} = \eta - \sum_{i=A,B,C} x_i \eta_i \tag{2}$$

where η and η_i represent viscosities of mixture and pure component i, respectively.

On the basis of theory of absolute reaction rates, the excess Gibb's energies of activation ($\Delta G^{*\mathrm{E}}$) of viscous flow was calculated from Glasstone et al. [52],

$$\Delta G{*}^{\mathrm{E}} = RT[\ln \eta V - \sum_{i=A,B,C} x_i \ln \eta_i V_i] \tag{3}$$

where R is the gas constant, T is absolute temperature, V and V_i are molar volume of the mixture and pure component i, respectively. The estimated errors in $\Delta G^{*\mathrm{E}}$ are 15 J mol^{-1}. Densities (ρ), viscosities (η), excess molar volumes ($V_{\mathrm{m}}^{\mathrm{E}}$), viscosity deviations ($\Delta\eta$), and Gibbs energies of activation ($\Delta G^{*\mathrm{E}}$) of viscous flow for the binary mixtures at 303.15 K are given in Table 2. For the studied binary mixtures, experimental and literature values [13,18,19,22,26,37,39,53–59] of $V_{\mathrm{m}}^{\mathrm{E}}$, $\Delta\eta$, $\Delta G^{*\mathrm{E}}$, and $H_{\mathrm{m}}^{\mathrm{E}}$ interpolated to mole fraction 0.5 are in good agreement as shown in Table 3, except $V_{\mathrm{m}}^{\mathrm{E}}$ values of $(C_2H_5)_3N + cC_6H_{12}$ reported by Suri [53], latter values are lower by 0.060 cm^3 mol^{-1}. The difference may be due to the difference in temperature of two measurements.

The values of $V_{\mathrm{m}}^{\mathrm{E}}$, $\Delta\eta$, and $\Delta G^{*\mathrm{E}}$ for presently investigated binary mixtures have been fitted to the Redlich–Kister polynomial equation of the form

$$Y_{ij}^{\mathrm{E}} = x_i x_j \sum_{p=0}^{m} A_p (x_i - x_j)^p \qquad (i, j = A, B, C) \tag{4}$$

where $Y_{ij}^{\mathrm{E}} = V_{\mathrm{m}}^{\mathrm{E}}$, $\Delta\eta$, or $\Delta G^{*\mathrm{E}}$.

Table 2
Densities ρ, viscosities η, excess molar volumes V_m^E, viscosity deviations $\Delta\eta$, and excess Gibbs energies of activation ΔG^{*E} of viscous flow of binary mixtures at 303.15 K.

x_A	x_B	ρ (g cm^{-3})	η (mPa s)	V_m^E (cm^3 mol^{-1})	$\Delta\eta$ (mPa s)	ΔG^{*E} (J mol^{-1})
x_B $(C_2H_5)_3N + x_C$ cC_6H_{12}						
0.0000	0.0000	0.76916	0.819			
0.0000	0.0995	0.76178	0.697	0.157	−0.073	−166
0.0000	0.1947	0.75557	0.614	0.238	−0.110	−262
0.0000	0.2910	0.74984	0.548	0.283	−0.128	−320
0.0000	0.3963	0.74418	0.495	0.287	−0.131	−337
0.0000	0.4999	0.73903	0.453	0.270	−0.122	−322
0.0000	0.5961	0.73460	0.420	0.233	−0.107	−290
0.0000	0.6989	0.73017	0.392	0.179	−0.085	−236
0.0000	0.7968	0.72609	0.374	0.138	−0.056	−136
0.0000	0.8973	0.72221	0.348	0.073	−0.032	−89
0.0000	1.0000	0.71845	0.330			
x_B $(C_4H_9)_3N + x_C$ cC_6H_{12}						
0.0000	0.0000	0.76916	0.819			
0.0000	0.1023	0.76832	0.848	0.174	−0.007	87
0.0000	0.2014	0.76809	0.878	0.267	−0.011	145
0.0000	0.3008	0.76817	0.914	0.308	−0.010	191
0.0000	0.4016	0.76842	0.947	0.311	−0.011	206
0.0000	0.5002	0.76878	0.985	0.279	−0.008	214
0.0000	0.6018	0.76915	1.025	0.234	−0.004	204
0.0000	0.7021	0.76957	1.058	0.163	−0.005	165
0.0000	0.8012	0.76985	1.096	0.116	−0.002	125
0.0000	0.9024	0.77012	1.130	0.063	−0.003	63
0.0000	1.0000	0.77039	1.167			
x_A $C_3H_7OH + x_C$ cC_6H_{12}						
0.0000	0.0000	0.76916	0.819			
0.1021	0.0000	0.76952	0.832	0.216	−0.080	−134
0.2112	0.0000	0.77068	0.872	0.347	−0.139	−204
0.3122	0.0000	0.77237	0.922	0.398	−0.181	−244
0.4211	0.0000	0.77463	0.986	0.416	−0.215	−271
0.5151	0.0000	0.77690	1.053	0.411	−0.234	−281
0.6203	0.0000	0.77994	1.148	0.370	−0.235	−263
0.7208	0.0000	0.78315	1.264	0.324	−0.209	−214
0.8143	0.0000	0.78673	1.398	0.244	−0.161	−147
0.9079	0.0000	0.79083	1.555	0.143	−0.089	−70
1.0000	0.0000	0.79566	1.727			
x_A $C_3H_7OH + x_B$ $(C_2H_5)_3N$						
1.0000	0.0000	0.79566	1.727			
0.7993	0.2007	0.78321	1.189	−1.378	−0.258	−54
0.7050	0.2950	0.77599	1.007	−1.731	−0.308	−64
0.6774	0.3226	0.77373	0.954	−1.796	−0.322	−82
0.6070	0.3930	0.76795	0.845	−1.914	−0.333	−89
0.5148	0.4852	0.76011	0.719	−1.927	−0.330	−109
0.3872	0.6128	0.74928	0.574	−1.741	−0.296	−146
0.2692	0.7308	0.73953	0.470	−1.391	−0.236	−173
0.2363	0.7637	0.73685	0.444	−1.262	−0.216	−182
0.1224	0.8776	0.72789	0.375	−0.742	−0.126	−155
0.0000	1.0000	0.71845	0.330			
x_A $C_3H_7OH + x_B$ $(C_4H_9)_3N$						
1.0000	0.0000	0.79566	1.727			
0.9014	0.0986	0.79171	1.695	−0.299	0.024	246
0.8009	0.1991	0.78831	1.660	−0.525	0.045	413
0.7022	0.2978	0.78547	1.619	−0.688	0.059	512
0.5016	0.4984	0.78018	1.514	−0.753	0.067	550
0.4008	0.5992	0.77782	1.449	−0.683	0.058	500
0.3969	0.6031	0.77775	1.445	−0.683	0.056	495
0.3019	0.6981	0.77571	1.378	−0.566	0.043	410
0.2011	0.7989	0.77378	1.302	−0.413	0.023	285
0.1012	0.8988	0.77194	1.233	−0.199	0.010	152
0.0000	1.0000	0.77039	1.167			

The coefficients A_p of Eq. (4), obtained by the method of least-squares are given in Table 4 together with corresponding standard deviations σ. Composition dependence of V_m^E, $\Delta\eta$, and ΔG^{*E} for binary mixtures is shown in Figs. 1–7.

Densities (ρ), viscosities (η), excess molar volumes (V_m^E), viscosity deviations ($\Delta\eta$), and Gibbs energies of activation (ΔG^{*E}) of viscous flow for the ternary mixtures at 303.15 K are given in Table 5.

3.1. *Correlating equations*

The V_m^E, $\Delta\eta$, and ΔG^{*E} of presently investigated ternary mixtures have been fitted to Heric–Brewer [33] and Singh et al. [34] equations. These expressions include three terms corresponding to binary contributions evaluated by Redlich–Kister equation [27], adjusted to the binary data.

Table 3
Comparison of values of excess molar volume (V_m^E), viscosity deviation ($\Delta\eta$), and Gibbs energy of activation (ΔG^{*E}) of viscous flow at equimolar compositions at 303.15 K along with equimolar excess enthalpy (H_m^E) from literature.

Binary mixture	V_m^E (cm^3 mol^{-1})	$\Delta\eta$ (mPa s)	ΔG^{*E} (J mol^{-1})	H_m^E (J mol^{-1})
$(C_2H_5)_3N + cC_6H_{12}$	0.267 0.264[a] [39] 0.1974[b] [53]	−0.145	−321	225[a] [56]
$(C_4H_9)_3N + cC_6H_{12}$	0.276 0.273 [19] 0.275 [18] 0.280[a] [39]	−0.008	215 214.7 [19]	151[a] [56]
$C_3H_7OH + cC_6H_{12}$	0.410 0.4183 [22] 0.411[a] [54]	−0.232	−277	562[a,d]
$C_3H_7OH + (C_2H_5)_3N$	−1.917 −1.998[a] [13] −2.002[a] [37] −2.015[a] [55]	−0.329	−113	−1413[a] [37]
$C_3H_7OH + (C_4H_9)_3N$	−0.756 −0.7741 [26]	0.066 0.0649 [26]	549 552.7 [26]	−251[c] [58]
$C_4H_9OH + cC_6H_{12}$	0.390 [59]	−0.327 [59]	−267 [59]	556[a,d]
$C_5H_{11}OH + cC_6H_{12}$	0.366 [59]	−0.447 [59]	−240 [59]	570[a,d]
$C_4H_9OH + (C_2H_5)_3N$	−2.026 [59]	−0.621 [59]	−606 [59]	−1550[a] [55]
$C_5H_{11}OH + (C_2H_5)_3N$	−2.072 [59]	−0.811 [59]	−590 [59]	

[a] At 298.15 K.
[b] At 313.15 K.
[c] At 293.15 K.
[d] The corresponding values at 298.15 were taken from Ref. [57].

Heric–Brewer [33] used the following Eq. (5) for ternary mixture

$$Y_{ABC}^E = Y_{AB}^E + Y_{AC}^E + Y_{BC}^E + x_A x_B x_C [A_{ABC} + B_{ABC} x_A + C_{ABC} x_B] \quad (5)$$

Singh et al. [34] proposed equation is of the following form,

$$Y_{ABC}^E = Y_{AB}^E + Y_{AC}^E + Y_{BC}^E + x_A x_B x_C [A_{ABC} + B_{ABC} x_A (x_B - x_C) + C_{ABC} x_A^2 (x_B - x_C)^2] \quad (6)$$

where A_{ABC}, B_{ABC} and C_{ABC} are parameters characteristics of the ternary mixtures evaluated by fitting the Eqs. (5) and (6) by the method of least-squares. The values of coefficients A_{ABC}, B_{ABC} and C_{ABC} for Heric–Brewer Eq. (5) and Singh et al. Eq. (6) are given in Table 6. The results in Table 6 show that Heric–Brewer equation yields the smaller standard deviations than the Singh et al. equation.

V_m^E, $\Delta\eta$, and ΔG^{*E} for ternary mixtures were predicted using six empirical equations due to Redlich–Kister [Eq. (7)], Kohler [Eq. (8)], Rastogi et al. [Eq. (10)], Jacob–Fitzner [Eq. (11)], Tsao–Smith [Eq. (13)], Lark et al. [Eq. (14)] and the standard deviations σ are presented in Table 7.

Table 4
Coefficients A_p and standard deviations σ of Eq. (4) for excess molar volume (V_m^E), viscosity deviation ($\Delta\eta$), and Gibbs energy of activation (ΔG^{*E}) of viscous flow of binary mixtures at 303.15 K.

Property	A_0	A_1	A_2	A_3	σ
x_B $(C_2H_5)_3N + x_C$ cC_6H_{12}					
V_m^E (cm^3 mol^{-1})	1.066	−0.590	0.315		0.004
$\Delta\eta$ (mPa s)	−0.485	0.289	−0.138		0.002
ΔG^{*E} (J mol^{-1})	−1283	589	−149		11
x_B $(C_4H_9)_3N + x_C$ cC_6H_{12}					
V_m^E (cm^3 mol^{-1})	1.104	−0.856	0.292	0.184	0.006
$\Delta\eta$ (mPa s)	−0.030	0.035	−0.035		0.002
ΔG^{*E} (J mol^{-1})	858	−130	−31		4
x_A $C_3H_7OH + x_C$ cC_6H_{12}					
V_m^E (cm^3 mol^{-1})	1.640	−0.405	0.607		0.004
$\Delta\eta$ (mPa s)	−0.926	−0.283	−0.065	0.263	0.001
ΔG^{*E} (J mol^{-1})	−1109	−25	−73	630	3
x_A $C_3H_7OH + x_B$ $(C_2H_5)_3N$					
V_m^E (cm^3 mol^{-1})	−7.667	−1.577	−0.291	0.612	0.003
$\Delta\eta$ (mPa s)	−1.314	−0.348	−0.217	0.002	
ΔG^{*E} (J mol^{-1})	−453	520	−776	383	4
x_A $C_3H_7OH + x_B$ $(C_4H_9)_3N$					
V_m^E (cm^3 mol^{-1})	−3.024	−0.702	0.354		0.008
$\Delta\eta$ (mPa s)	0.262	0.105	−0.122		0.001
ΔG^{*E} (J mol^{-1})	2194	617	29	125	3

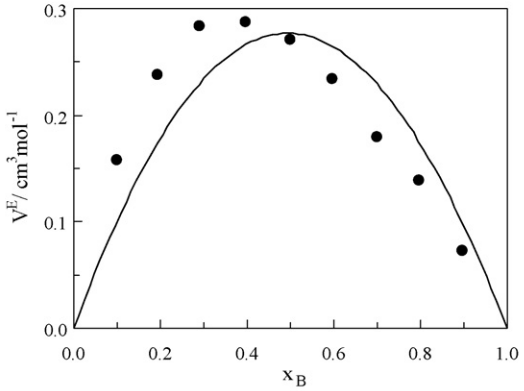

Fig. 1. Excess molar volume V_m^E for x_B triethylamine + x_C cyclohexane at 303.15 K. Experimental points (●) and Flory theory (—).

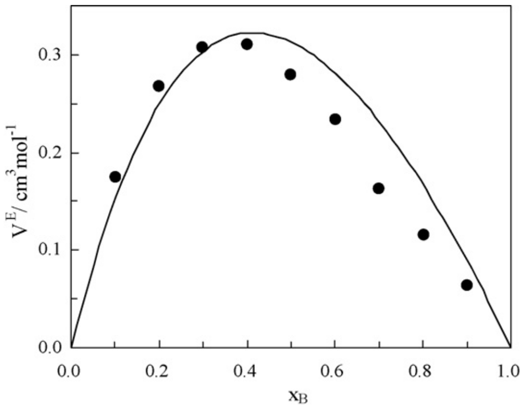

Fig. 2. Excess molar volume V_m^E for x_B tri-*n*-butylamine + x_C cyclohexane at 303.15 K. Experimental points (●) and Flory theory (—).

Redlich and Kister [27] equation for ternary mixture is

$$\begin{aligned} Y_{\mathrm{ABC}}^{\mathrm{E}} &= x_{\mathrm{A}}x_{\mathrm{B}}\sum_{\nu=0}^{m}(A_{\nu})_{\mathrm{AB}}(x_{\mathrm{A}}-x_{\mathrm{B}})^{\nu} + x_{\mathrm{B}}x_{\mathrm{C}}\sum_{\nu=0}^{m}(A_{\nu})_{\mathrm{BC}}(x_{\mathrm{B}}-x_{\mathrm{C}})^{\nu} \\ &\quad + x_{\mathrm{A}}x_{\mathrm{C}}\sum_{\nu=0}^{m}(A_{\nu})_{\mathrm{AC}}(x_{\mathrm{A}}-x_{\mathrm{C}})^{\nu} \equiv Y_{\mathrm{AB}}^{\mathrm{E}} + Y_{\mathrm{BC}}^{\mathrm{E}} + Y_{\mathrm{AC}}^{\mathrm{E}} \end{aligned} \tag{7}$$

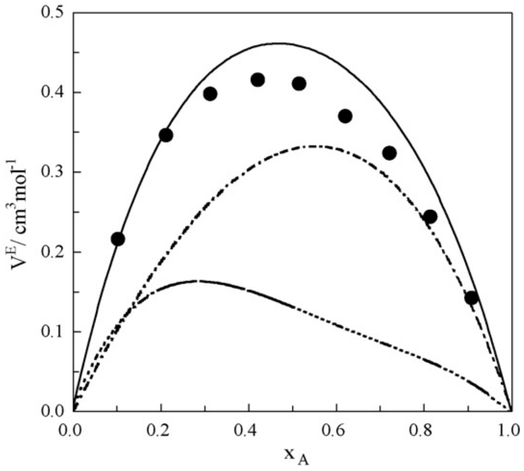

Fig. 3. Excess molar volume V_m^E for x_A 1-propanol + x_C cyclohexane at 303.15 K. Experimental points (●), chemical (-----), physical (– – –), and ERAS (—).

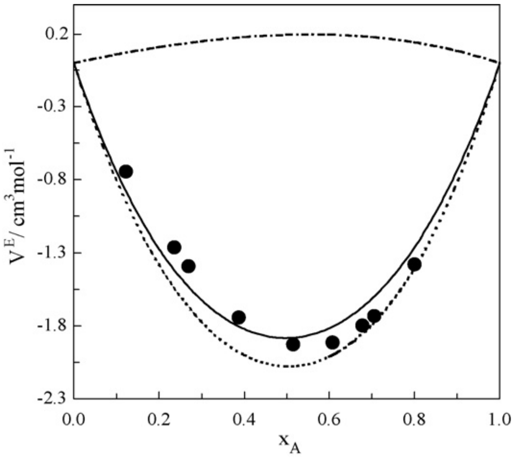

Fig. 4. Excess molar volume V_m^E for x_A 1-propanol + x_B triethylamine at 303.15 K. Experimental points (●), chemical (-----), physical (– – –), and ERAS (—).

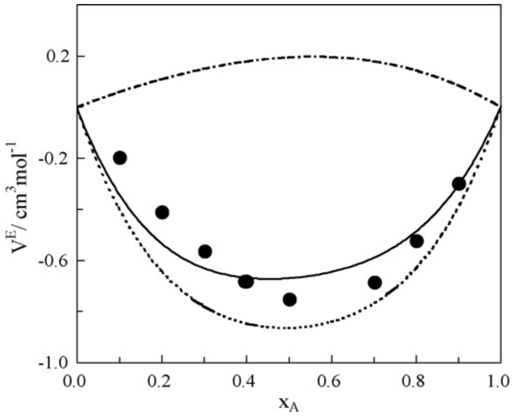

Fig. 5. Excess molar volume V_m^E for x_A 1-propanol + x_B tri-*n*-butylamine at 303.15 K. Experimental points (●), chemical (------), physical (– – –), and ERAS (—).

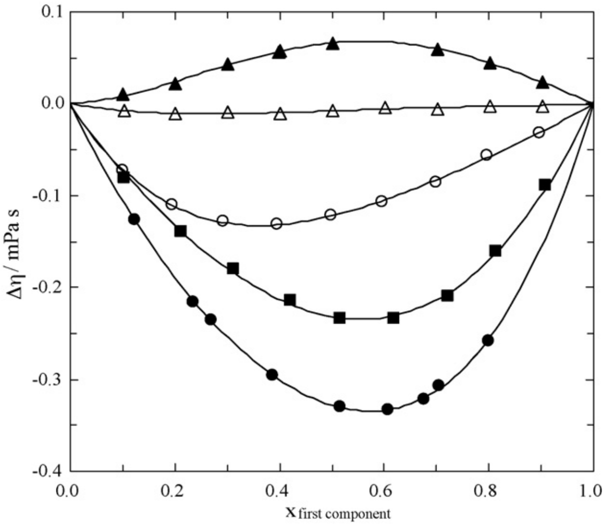

Fig. 6. Viscosity deviation $\Delta\eta$ for x_B triethylamine + x_C cyclohexane (○), x_B tri-*n*-butylamine + x_C cyclohexane (△), x_A 1-propanol + x_C cyclohexane (■), x_A 1-propanol + x_B triethylamine (●) and x_A 1-propanol + x_B tri-*n*-butylamine (▲) at 303.15 K.

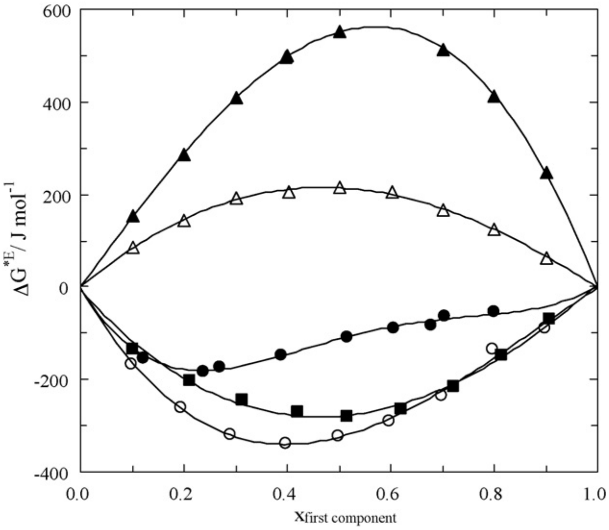

Fig. 7. Gibbs energy of activation ΔG^{*E} of viscous flow for x_B triethylamine + x_C cyclohexane (○), x_B tri-*n*-butylamine + x_C cyclohexane (△), x_A 1-propanol + x_C cyclohexane (■), x_A 1-propanol + x_B triethylamine (●) and x_A 1-propanol + x_B tri-*n*-butylamine (▲) at 303.15 K.

Kohler [28] equation is symmetrical in that all three binary mixtures are treated identically and takes the form

$$Y^E_{ABC} = (x_A + x_B)^2 Y^E_{AB} + (x_B + x_C)^2 Y^E_{BC} + (x_A + x_C)^2 Y^E_{AC} \tag{8}$$

In this equation Y^E_{ij} refers to the excess properties at x^0_i, x^0_j in the binary mixtures using following equation:

$$x^0_i = 1 - x^0_j = \frac{x^0_i}{x^0_i + x^0_j} \tag{9}$$

Rastogi et al. [29] proposed Eq. (10) for predicting the excess property of a ternary mixture

$$Y^E_{ABC} = (1/2)[(x_A + x_B)Y^E_{AB} + (x_A + x_C)Y^E_{AC} + (x_B + x_C)Y^E_{BC}] \tag{10}$$

In which Y^E_{ij} represents the excess properties of the binary mixtures at composition x^0_i, x^0_j which refers using Eq. (9).

Jacob and Fitzner [30] suggested an equation for estimating the properties of a ternary solution based on the binary data at composition nearest the ternary composition taking the form

$$Y^E_{ABC} = \frac{x_A x_B Y^E_{AB}}{\left(x_A + \frac{x_C}{2}\right)\left(x_B + \frac{x_C}{2}\right)} + \frac{x_A x_C Y^E_{AC}}{\left(x_A + \frac{x_B}{2}\right)\left(x_C + \frac{x_B}{2}\right)} + \frac{x_B x_C Y^E_{BC}}{\left(x_B + \frac{x_A}{2}\right)\left(x_C + \frac{x_A}{2}\right)} \tag{11}$$

Such that for the binary mixture at composition x^0_i, x^0_j.

$$x_i - x_j = x^0_i - x^0_j \tag{12}$$

Tsao and Smith [31] equation is

$$Y^E_{ABC} = \left(\frac{x_B}{1 - x_A}\right) Y^E_{AB} + \left(\frac{x_C}{1 - x_A}\right) Y^E_{AC} + (1 - x_A) Y^E_{BC} \tag{13}$$

In which the Y^E_{ij} refers the excess property of the binary mixtures at composition x^0_i, x^0_j such that $x^0_i = (1 - x^0_j) = x_A$ for the AB and AC binary mixtures and $x^0_B = x_B/(x_B + x_C)$ for the BC binary mixture.

The proposed equation by Lark et al. [32] for ternary mixtures is expressed as

$$Y^E_{ABC} = [(n_A)_{AB} + (n_B)_{AB}]Y^E_{AB} + [(n_B)_{BC} + (n_C)_{BC}]Y^E_{BC} + [(n_C)_{AC} + (n_A)_{AC}]Y^E_{AC} \tag{14}$$

where $(n_i)_{ij}$ is the number of mole of the component (i) in the binary mixture (ij) so that

$$(n_A)_{AB} + (n_A)_{AC} = x_A \tag{15}$$

and x_A distributes itself proportionally between the component (B) and (C) i.e.

$$(n_A)_{AB} = \frac{x_B}{x_B + x_C} x_A \tag{16}$$

$$(n_A)_{AC} = \frac{x_C}{x_B + x_C} x_A \tag{17}$$

4. ERAS model

The ERAS model due to Heintz and co-workers [35,36] combines the linear chain association model with Flory's equation of state [60] and is applicable to mixtures consisting of one associating component (A, alkanol) and other weakly associating component (B, alkylamine), which forms cross-association complex (A_iB). This model provides a quantitative treatment of H^E_m, G^E_m, and V^E_m and accounts for the competing effects present in the binary mixtures [10–13,61–69]. The ERAS model has also been used to predict excess properties of ternary mixtures [14,37,70–74] from the parameters of the binary constituents. The ERAS model has been examined to predict the excess molar volumes of present ternary mixtures consisting of one associating component (A, alkanol), second non-associating (B, trialkylamine) component that can form a cross-association complex (A_iB) and third non-polar inert component. In the framework of the ERAS model, the thermodynamic excess properties of binary and ternary mixtures can be expressed as the addition of a physical and a chemical contribution. The details of the ERAS model equations are given elsewhere [36,37,59].

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

$$K_i = K_o \exp\left[-\left(\frac{\Delta h^*_i}{R}\right)\left(\frac{1}{T} - \frac{1}{T_o}\right)\right] \tag{18}$$

where K_0 is the equilibrium constant at the standard temperature T_0 (298.15 K), R is the gas constant and Δh^*_i is the enthalpy for the reactions corresponding to the hydrogen bonding energy. These reactions are also characterized by the volume change (reaction volume) Δv^*_i, related to the formation of the linear chains. The values of unknown cross-parameters: X_{AB} (the Flory's contact interaction parameter), K_{AB} (the cross-association constant), Δh^*_{AB} (the association energy per mole of hydrogen bonds due cross-association) and Δv^*_{AB} (the reaction volume per mole of hydrogen bonds due to cross-association) were adjusted simultaneously to H^E_m and V^E_m for binary mixture data. Once all the binary parameters were known, the excess molar volumes of $C_3H_7OH + (C_2H_5)_3N + cC_6H_{12}$ and $C_3H_7OH + (C_4H_9)_3N + cC_6H_{12}$ were calculated.

5. Discussion

The values of V^E_m (Figs. 1–3) are positive while $\Delta\eta$ (Fig. 6) negative for $(C_2H_5)_3N + cC_6H_{12}$, $(C_4H_9)_3N + cC_6H_{12}$ and $C_3H_7OH + cC_6H_{12}$ due to disruption of dipolar order in trialkylamine or breaking of hydrogen bonds in 1-propanol [15,22]. This is in agreement with the positive H^E_m values of these solutions [56,57].

Table 5

Densities (ρ), viscosities (η), excess molar volume (V_m^E), viscosity deviations ($\Delta\eta$), and Gibbs energies of activation (ΔG^{*E}) of viscous flow for ternary mixtures at 303.15 K.

x_A	x_B	ρ (g cm^{-3})	η (mPa s)	V_m^E (cm^3 mol^{-1})	$\Delta\eta$ (mPa s)	ΔG^{*E} (J mol^{-1})
x_A $C_3H_7OH + x_B$ $(C_2H_5)_3N + x_C$ cC_6H_{12}						
$x_A/x_C = 2.3102$						
0.6578	0.0575	0.77977	1.141	−0.048	−0.247	−215
0.6102	0.1257	0.77637	1.034	−0.444	−0.277	−211
0.5586	0.1996	0.77233	0.928	−0.795	−0.300	−212
0.4920	0.2950	0.76660	0.811	−1.123	−0.311	−207
0.4325	0.3803	0.76111	0.714	−1.303	−0.311	−218
0.3684	0.4721	0.75493	0.616	−1.383	−0.306	−261
0.2914	0.5825	0.74718	0.535	−1.321	−0.263	−224
0.2087	0.7010	0.73879	0.451	−1.099	−0.215	−240
0.1063	0.8477	0.72855	0.381	−0.635	−0.119	−153
$x_A/x_C = 0.9944$						
0.4716	0.0542	0.77464	0.981	0.046	−0.239	−251
0.4279	0.1418	0.77091	0.879	−0.428	−0.259	−244
0.3917	0.2144	0.76724	0.801	−0.717	−0.269	−243
0.3435	0.3111	0.76177	0.714	−0.971	−0.265	−221
0.2982	0.4019	0.75622	0.631	−1.091	−0.262	−239
0.2510	0.4966	0.75009	0.559	−1.097	−0.245	−244
0.1980	0.6029	0.74312	0.492	−0.998	−0.212	−225
0.1371	0.7250	0.73515	0.425	−0.769	−0.164	−211
0.0745	0.8506	0.72721	0.370	−0.441	−0.101	−171
$x_A/x_C = 0.4320$						
0.2793	0.0742	0.76959	0.848	−0.019	−0.189	−224
0.2563	0.1505	0.76624	0.778	−0.332	−0.200	−224
0.2337	0.2254	0.76250	0.708	−0.550	−0.213	−247
0.2061	0.3169	0.75744	0.640	−0.705	−0.211	−241
0.1755	0.4183	0.75139	0.574	−0.751	−0.200	−225
0.1463	0.5151	0.74548	0.518	−0.710	−0.182	−210
0.1135	0.6238	0.73890	0.462	−0.596	−0.155	−188
0.0792	0.7375	0.73225	0.413	−0.429	−0.117	−155
0.0414	0.8628	0.72537	0.363	−0.224	−0.071	−130
x_A $C_3H_7OH + x_B$ $(C_4H_9)_3N + x_C$ cC_6H_{12}						
$x_A/x_C = 2.1867$						
0.6683	0.0261	0.78168	1.239	0.277	−0.196	−142
0.6257	0.0881	0.78098	1.261	0.127	−0.156	13
0.5898	0.1406	0.78037	1.275	0.016	−0.129	116
0.5529	0.1942	0.77984	1.301	−0.098	−0.088	232
0.5016	0.2690	0.77909	1.320	−0.237	−0.048	339
0.4395	0.3595	0.77816	1.351	−0.372	0.008	456
0.3741	0.4549	0.77704	1.368	−0.449	0.051	522
0.2909	0.5761	0.77551	1.353	−0.463	0.070	511
0.1696	0.7529	0.77317	1.282	−0.323	0.047	348
$x_A/x_C = 0.9853$						
0.4687	0.0555	0.77650	1.068	0.276	−0.196	−134
0.4497	0.0940	0.77649	1.085	0.190	−0.175	−51
0.4235	0.1468	0.77642	1.107	0.079	−0.148	48
0.3893	0.2156	0.77627	1.151	−0.054	−0.096	193
0.3547	0.2853	0.77596	1.188	−0.158	−0.052	304
0.3097	0.3760	0.77553	1.231	−0.275	−0.001	411
0.2545	0.4873	0.77471	1.263	−0.336	0.043	473
0.1935	0.6101	0.77363	1.275	−0.323	0.068	466
0.1146	0.7690	0.77214	1.232	−0.205	0.041	304
$x_A/x_C = 0.4296$						
0.2904	0.0337	0.77244	0.927	0.324	−0.168	−181
0.2697	0.1024	0.77287	0.957	0.192	−0.142	−55
0.2533	0.1570	0.77309	0.982	0.099	−0.122	30
0.2335	0.2228	0.77311	1.030	0.022	−0.078	164
0.2119	0.2948	0.77308	1.067	−0.053	−0.047	254
0.2020	0.3277	0.77303	1.089	−0.080	−0.027	302
0.1869	0.3780	0.77292	1.110	−0.114	−0.010	339
0.1127	0.6251	0.77197	1.182	−0.151	0.044	376
0.0689	0.7707	0.77126	1.182	−0.092	0.033	262

Comparing the values of V_m^E and $\Delta\eta$ for 1-alkanol + cyclohexane (Table 3), it is seen that V_m^E and $\Delta\eta$ values decrease with chain length of 1-alkanol from 1-propanol to 1-pentanol. In case of $C_3H_7OH + (C_2H_5)_3N$ and $C_3H_7OH + (C_4H_9)_3N$ mixtures, the large negative values of V_m^E (Figs. 4 and 5) are due to hydrogen bonding in 1-propanol molecules and cross-association between unlike components [13,14,25,37]. This cross-hydrogen bonding is stronger than those formed between the molecules of 1-propanol (OH...OH) [74]. This is also corroborated from exothermic H_m^E (Table 6). For $C_3H_7OH + (C_2H_5)_3N$ values of V_m^E are significantly more negative than $C_3H_7OH + (C_4H_9)_3N$ mixture, this indicate that cross-association is more pronounced in the mixture of triethy-

Table 6

Values of coefficients A_{ABC}, B_{ABC}, C_{ABC} of Heric–Brewer Eq. (5) and Singh et al. Eq. (6) for excess molar volume (V_m^E) in $cm^3\ mol^{-1}$, viscosity deviation ($\Delta\eta$) in mPa s, and Gibbs energy of activation (ΔG^{*E}) of viscous flow in $J\ mol^{-1}$ units for ternary mixtures at 303.15 K.

	Heric–Brewer Eq. (5)				Singh et al. Eq. (6)			
	A_{ABC}	B_{ABC}	C_{ABC}	σ	A_{ABC}	B_{ABC}	C_{ABC}	σ
x_A $C_3H_7OH + x_B$ $(C_2H_5)_3N + x_C$ cC_6H_{12}								
V_m^E	−32.406	41.704	18.267	0.005	−13.420	9.372	101.768	0.104
$\Delta\eta$	3.225	−3.526	−2.915	0.005	1.009	−4.542	−4.725	0.006
ΔG^{*E}	8614	−10642	−7199	19	2800	−10584	−38142	26
x_A $C_3H_7OH + x_B$ $(C_4H_9)_3N + x_C$ cC_6H_{12}								
V_m^E	−14.004	21.233	4.831	0.005	−5.810	−4.700	30.128	0.063
$\Delta\eta$	−0.518	0.348	6.071	0.005	1.683	14.013	31.592	0.015
ΔG^{*E}	−1471	4673	13117	15	4593	24911	52008	30

Table 7

The values of standard deviations (σ) of excess molar volume (V_m^E) in $cm^3\ mol^{-1}$, viscosity deviation ($\Delta\eta$) in mPa s, and Gibbs energy of activation (ΔG^{*E}) of viscous flow in $J\ mol^{-1}$ units calculated by different empirical equations[a].

Property	σ					
	Eq. (7)	Eq. (8)	Eq. (10)	Eq. (11)	Eq. (13)	Eq. (14)
x_A $C_3H_7OH + x_B$ $(C_2H_5)_3N + x_C$ cC_6H_{12}						
V_m^E	0.315	0.298	0.455	0.297	0.301	0.384
$\Delta\eta$	0.025	0.057	0.059	0.051	0.075	0.040
ΔG^{*E}	65	73	38	68	104	36
x_A $C_3H_7OH + x_B$ $(C_4H_9)_3N + x_C$ cC_6H_{12}						
V_m^E	0.144	0.140	0.179	0.135	0.164	0.138
$\Delta\eta$	0.043	0.042	0.060	0.042	0.042	0.032
ΔG^{*E}	110	102	167	101	54	136

[a] Eqs. (7), (8), (10), (11), (13) and (14) represent equations due to Redlich–Kister [27], Kohler [28], Rastogi et al. [29], Jacob–Fitzner [30], Tsao–Smith [31], and Lark et al. [32], respectively.

lamine than that in tri-*n*-butylamine. However, on comparing the V_m^E for 1-alkanols + triethylamine (Table 3), the values of V_m^E are not much affected by the change in the length of alkanol from 1-propanol to 1-pentanol.

In order to see the influence of variation of trialkylamine composition in ternary mixtures $C_3H_7OH + (C_2H_5)_3N + cC_6H_{12}$ and $C_3H_7OH + (C_4H_9)_3N + cC_6H_{12}$, the V_m^E, $\Delta\eta$, and ΔG^{*E} were studied by adding trialkylamine to binary mixture ($C_3H_7OH + cC_6H_{12}$) of three different fixed compositions for each ternary mixture (Table 5). In both ternary mixtures, an inversion of sign of V_m^E from positive to negative occurs when amount of trialkylamine is increased in $C_3H_7OH + cC_6H_{12}$ mixtures (Figs. 8 and 9). The V_m^E is the result of the sum of several effects: chemical, structural, and physical. In the mixtures under investigation, the results can be mainly explained in terms of the association of components in the mixtures. The negative deviations in V_m^E are consistent with formation of A_iB complex between 1-propanol + trialkylamine. Negative values of V_m^E were observed for ethanol or 1-butanol + triethylamine + *n*-hexane [70] and 1-butanol + tri-*n*-butylamine or tri-*n*-octylamine + *n*-hexane [14] mixtures and were also explained through the complex formation between alkanol and amine. The smaller the ratio of cyclohexane, V_m^E is more negative, while an increase in the amount of cyclohexane results in the destruction of hydrogen bonds and increase in V_m^E, which subsequently becomes positive in the region corresponding to high mole fraction of cyclohexane and low mole fractions of 1-propanol/amine. For the equimolar composition (i.e. $x_A = x_B = x_C = 1/3$), V_m^E values for $C_3H_7OH + (C_2H_5)_3N + cC_6H_{12}$ ($-1.011\ cm^3\ mol^{-1}$) less than that for $C_3H_7OH + (C_4H_9)_3N + cC_6H_{12}$ ($-0.228\ cm^3\ mol^{-1}$). The negative value of equimolar V_m^E for $C_3H_7OH + (C_2H_5)_3N + cC_6H_{12}$ is significantly reduced when $(C_2H_5)_3N$ in the mixture is replaced by $(C_4H_9)_3N$. This is consistent with the fact that the strength of complex formation A_iB is greater in $C_3H_7OH + (C_2H_5)_3N$ than that in $C_3H_7OH + (C_4H_9)_3N$.

The values of viscosity deviations $\Delta\eta$ in $C_3H_7OH + (C_2H_5)_3N + cC_6H_{12}$ are large and negative over the entire range of composition while in $C_3H_7OH + (C_4H_9)_3N + cC_6H_{12}$ an inversion of sign occurs from negative to positive as composition of amine is increased (Figs. 10 and SF1). For latter mixture, the $\Delta\eta$ values are negative in the poor tri-*n*-butylamine regions, but

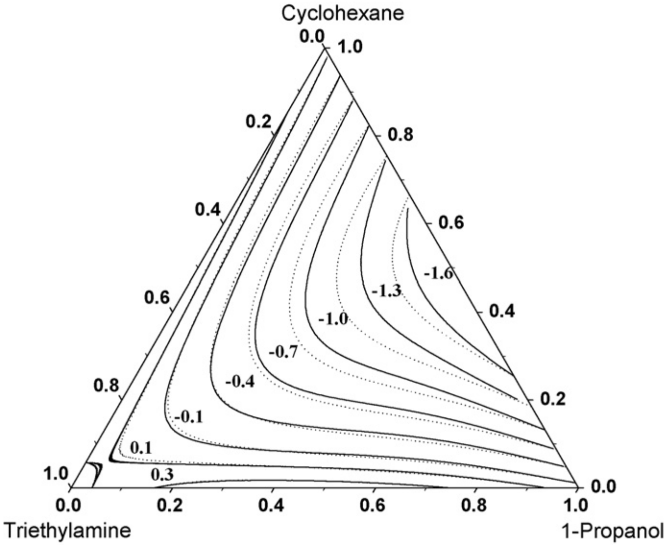

Fig. 8. Isolines at constant excess molar volumes, V_m^E ($cm^3\ mol^{-1}$) for ternary mixture of x_A 1-propanol + x_B triethylamine + x_C cyclohexane correlated with Eq. (5) (——) and ERAS model (------) at 303.15 K.

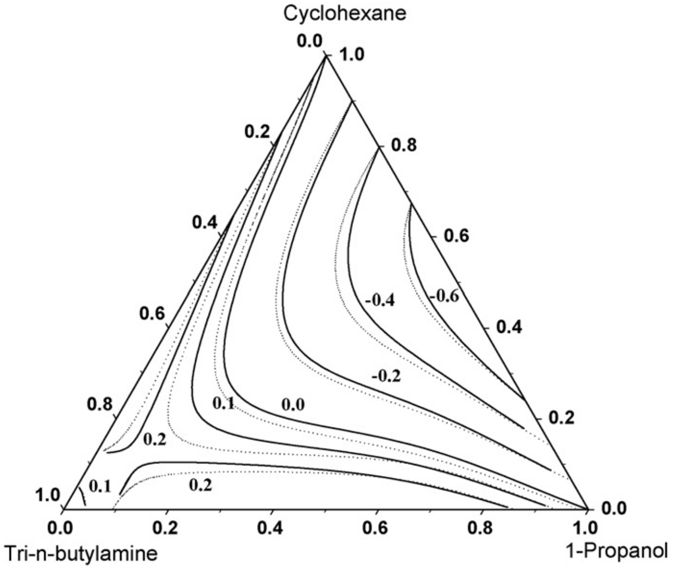

Fig. 9. Isolines at constant excess molar volumes, V_m^E ($cm^3\ mol^{-1}$) for ternary mixture of x_A 1-propanol + x_B tri-*n*-butylamine + x_C cyclohexane correlated with Eq. (5) (—–) and ERAS model (------) at 303.15 K.

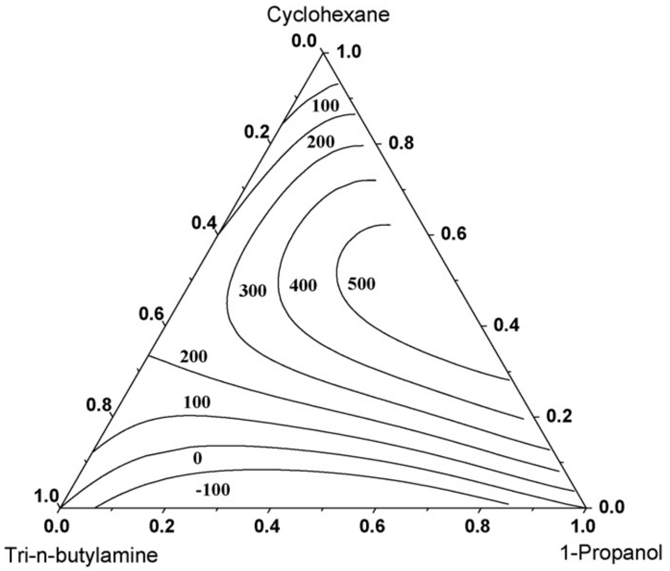

Fig. 11. Isolines at constant Gibbs energy of activation ΔG^{*E} ($J\ mol^{-1}$) of viscous flow for ternary mixture of x_A 1-propanol + x_B tri-*n*-butylamine + x_C cyclohexane correlated with Eq. (5) at 303.15 K.

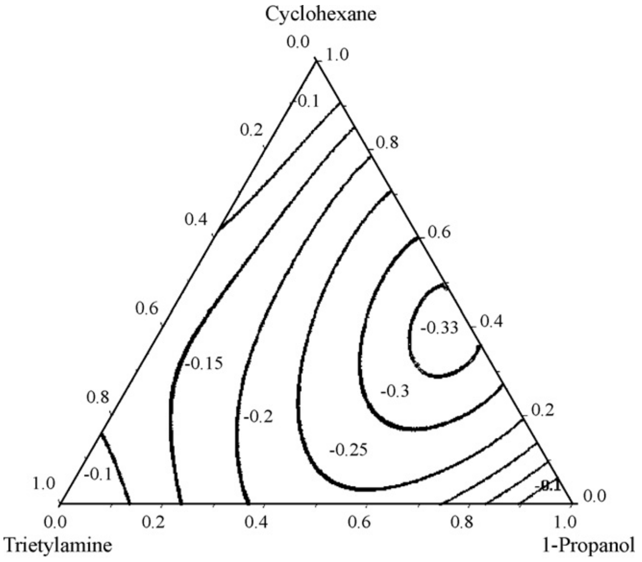

Fig. 10. Isolines at constant viscosity deviations, $\Delta\eta$ (mPa s) for ternary mixture of x_A 1-propanol + x_B triethylamine + x_C cyclohexane correlated with Eq. (5) at 303.15 K.

become slightly positive when the amount of tri-*n*-butylamine is increased. The values of $\Delta\eta$ for the equimolar composition of ternary mixtures calculated using Heric–Brewer Eq. (5) are more negative for $C_3H_7OH + (C_2H_5)_3N + cC_6H_{12}$ (−0.263 mPa s) than for $C_3H_7OH + (C_4H_9)_3N + cC_6H_{12}$ (−0.017 mPa s). The negative values of viscosity deviations are consistent with the destruction of hydrogen bonds in 1-propanol.

The viscosity of a mixture strongly depends on the entropy of mixture [75], which is related with the structure of the liquid and the enthalpy (and consequently with molecular interaction between the components of the mixture). Vogel and Weiss [76] affirm that mixtures with strong interaction between different molecules present positive viscosity deviations; whereas for mixtures without specific interactions, the viscosity deviations are negative. So the viscosity deviations are functions of molecular interaction as well as of size and shape of molecules. The negative values observed for viscosity deviations $\Delta\eta$ of the ternary mixtures under study cannot explain the graded behaviour of complex formation between alkanol + amine (A_iB). This reveals that the strength of the intermolecular hydrogen bonding is not the only factor influencing the viscosity deviation of liquid mixtures. The molecular sizes and shapes of the components are equally important factors.

The Gibbs energy of activation ΔG^{*E} of viscous flow (Figs. 11 and SF2) is negative for $C_3H_7OH + (C_2H_5)_3N + cC_6H_{12}$ while it has both positive and negative values for $C_3H_7OH + (C_4H_9)_3N + cC_6H_{12}$. The

Table 8
Properties and parameters of pure components, molar volume (V), thermal expansion coefficient (α), isothermal compressibility (κ_T), equilibrium constant (K_A), characteristic volume (V^*), characteristic pressure (P^*), enthalpy change (Δh^*), volume change (Δv^*) and surface to volume ratio (S) at 303.15 K used in Flory theory and ERAS model.

Liquid	V ($cm^3\ mol^{-1}$)	α (kK^{-1})	κ_T (TPa^{-1})	K_A	V^* ($cm^3\ mol^{-1}$)	P^* ($J\ cm^{-3}$)	Δh^* ($kJ\ mol^{-1}$)	Δv^* ($cm^3\ mol^{-1}$)	S^a ($Å^{-1}$)
C_3H_7OH	75.53	1.025[b]	1071[b]	167[b]	61.22	395	−25.1[c]	−5.6[c]	1.489
$(C_2H_5)_3N$	140.85	1.355[d]	1493[d]	–	106.61	475	–	–	1.369
$(C_4H_9)_3N$	240.60	0.914[d]	1012[d]	–	195.11	416	–	–	1.364
cC_6H_{12}	109.42	1.233[e]	1171[e]	–	84.33	534	–	–	1.315

[a] Calculated in accordance with Ref. [77].
[b] Ref. [78].
[c] Ref. [36].
[d] Ref. [79].
[e] Ref. [40].

Table 9

Binary interaction parameter (X_{ij}) binary association constant (K_{AB}), association enthalpy (Δh^*_{AB}), and association volume (Δv^*_{AB}) of ERAS model and comparison of equimolar excess molar enthalpy and excess molar volume.

Mixture	T (K)	X_{ij} (J cm^{-3})	K_{AB}	Δh^*_{AB} (kJ mol^{-1})	Δv^*_{AB} (cm^3 mol^{-1})	H^E_m (J mol^{-1})		$\sigma(H^E_m)$ (J mol^{-1})	V^E_m (cm^3 mol^{-1})		$\sigma(V^E_m)$ (cm^3 mol^{-1})
						Experiment	Theory		Experiment	Theory	
$(C_2H_5)_3N + cC_6H_{12}$	303.15	14.6	–	–	–				0.270	0.277	0.042
$(C_4H_9)_3N + cC_6H_{12}$	303.15	6.0	–	–	–				0.276	0.313	0.036
$C_3H_7OH + cC_6H_{12}$	303.15	6.5	–	–	–				0.410	0.462	0.039
$C_3H_7OH + (C_2H_5)_3N$	298.15	5.0	135	−31.2	−12.4	−1412[a]	−1318	93	−2.002[a]	−1.901	0.101
	303.15	4.2	110	−31.2	−12.4		−1362		−1.917	−1.878	0.120
	298.15[b]	6.9	100	−32.4	−15.2						
	298.15[a]	8.0	100	−32.4	−15.4	−1412	−1324	98	−2.002	−1.966	0.103
	298.15[c]	10.0	100	−33.2	−13.8	−1500	−1424	98			
	313.15[c]	10.0	53	−33.2	−13.8	−1411	−1443	97			
	298.15[d]	5.0	180	−31.5	−12.2	−1473	−1492	98	−1.998	−2.140	0.15
$C_3H_7OH + (C_4H_9)_3N$	293.15	5.0	18	−30.0	−12.3	−252[e]	−246	31	−0.853[f]	−0.757	0.084
	303.15	4.0	12	−30.0	−12.3		−139		−0.756	−0.640	0.080

[a] Ref. [54].

[b] Ref. [36].

[c] Ref. [10].

[d] Ref. [13].

[e] Ref. [58].

[f] Extrapolated from V^E_m at 303.15 and 313.15 K [26].

dependence of ΔG^{*E} on composition is complex, depending upon the different contributions in the mixture.

The properties and parameters as equilibrium constant K, thermal expansion coefficient α, isothermal compressibility κ_T, molar volume V, characteristic volume V^*, characteristic pressure P^*, and surface to volume ratio S for 1-propanol, triethylamine, tri-*n*-butylamine and cyclohexane are listed in Table 8. The values of surface to volume ratio (S) were taken from Bondi [77]. There is no association effect at all in mixtures $(C_2H_5)_3N + cC_6H_{12}$ and $(C_4H_9)_3N + cC_6H_{12}$, in this case, the ERAS model reduces to the Flory theory and therefore the only adjustable mixing parameter in the model calculations is the Flory interaction parameter X_{BC} characterizing the difference of dispersive intermolecular interactions, which was calculated from experimental equimolar H^E_m [56]. For $C_3H_7OH + cC_6H_{12}$ mixtures only self-association in 1-propanol is present, therefore, the ERAS model was applied without any cross-association, and the required Flory interaction parameter X_{AC} was adjusted to equimolar experimental H^E_m [57]. The optimum values of parameters X_{AB}, K_{AB}, Δh^*_{AB}, and Δv^*_{AB}, were first obtained at 298.15 K for $C_3H_7OH + (C_2H_5)_3N$ and at 293.15 K for $C_3H_7OH + (C_4H_9)_3N$, by simultaneously adjusting to the experimental H^E_m and V^E_m [26,37,58], since the values of H^E_m for the mixtures are available at the mentioned temperature. Then at 303.15, the values of Δh^*_{AB} and Δv^*_{AB} were regarded as temperature independent and K_{AB} calculated consistent with Eq. (18). Using these values of K_{AB}, Δh^*_{AB}, Δv^*_{AB}, the optimum values of X_{AB} were obtained to adjust experimental V^E_m. The values of the cross-parameters for binary mixtures are given in Table 9. The present values of cross-parameters X_{AB}, K_{AB}, Δh^*_{AB}, and Δv^*_{AB}, are also compared with literature values along with experimental and theoretical ERAS values of equimolar H^E_m and V^E_m in Table 9. The theoretical results are compared in Figs. 1–5. The standard deviations $\sigma(V^E_m)$ between experiment and theory are from 0.036 to 0.120 cm^3 mol^{-1}.

To characterize $C_3H_7OH + (C_2H_5)_3N$ mixture, the ERAS model has been applied earlier by Funke el al. [36], Bender et al. [37] and Villa et al. [13] at 298.15 K and Gonzalez et al. [10] at 298.15 and 313.15 K. These authors have used different values for the binary interaction parameter X_{AB} and cross-association parameters K_{AB}, Δh^*_{AB}, and Δv^*_{AB}. With these parameters adjusted to experimental data the agreement between calculated and experimental results is not much improved. The values of K_{AB} at 303.15 K are 110 for $C_3H_7OH + (C_2H_5)_3N$ and 12 for $C_3H_7OH + (C_4H_9)_3N$. The value of K_{AB} involving $(C_2H_5)_3N$ is approximately 9 times larger than those for $(C_4H_9)_3N$ mixtures. This fact is consistent with the formation of strong cross-associates in a mixture of short-chain tertiary amine.

The V^E_m as per the ERAS model for present ternary mixtures $C_3H_7OH + (C_2H_5)_3N + cC_6H_{12}$ and $C_3H_7OH + (C_4H_9)_3N + cC_6H_{12}$ were calculated using binary parameters of constituent pairs. The experimental and ERAS model V^E_m results are compared graphically in Figs. 8 and 9. The values of $\sigma(V^E_m)$ for $C_3H_7OH + (C_2H_5)_3N + cC_6H_{12}$ and $C_3H_7OH + (C_4H_9)_3N + cC_6H_{12}$ mixtures are 0.061 and 0.072 cm^3 mol^{-1}, respectively. Thus good agreement between experimental and ERAS model values is obtained. The ERAS model for mixed association between the molecules of three-component mixtures requires exactly the same binary parameters and no additional parameters were needed to predict the ternary excess molar volumes.

6. Conclusions

The values of V^E_m are positive while $\Delta\eta$ negative for binary mixtures of trialkylamine or 1-propanol with cyclohexane, due to disruption of dipolar order or breaking of hydrogen bonds. Large negative values of V^E_m result from cross-hydrogen bonding between the molecules of 1-propanol and trialkylamine in their binary mixtures.

Large standard deviations are observed when the V^E_m, $\Delta\eta$, and ΔG^{*E} of viscous flow were correlated with the empirical equations containing only binary parameters. The Heric–Brewer equation with ternary contributory terms provides the small standard deviations.

The ERAS model gives a quantitative representation of V^E_m of present binary mixtures involving 1-propanol, trialkylamine, and cyclohexane. The ERAS model for mixed association between the molecules of three-component mixtures requires constituent binary parameters and no additional parameter is necessary to estimate V^E_m of present two ternary mixtures.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2008.09.006.

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