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Volumetric and transport properties of ternary mixtures containing 1-propanol + ethyl ethanoate + cyclohexane or benzene 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 + ethyl ethanoate + cyclohexane and 1-propanol + ethyl ethanoate + benzene and four 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 interactions between the components of the mixtures. Further, the ERAS model has been examined to estimate V_m^E for the binary and ternary mixtures and the results are compared with the experimental data.

1. Introduction

We are engaged in systematic studies of thermodynamic, acoustic, and transport properties of mixtures involving alkanols, alkyl alkanoates, and hydrocarbons. Speeds of sound, viscosities and excess molar volumes of their binary mixtures have been reported [1–7]. As an extension, study of alkyl alkanoate + alkanols in some third nonpolar solvent would be interesting, important and will throw-light on ternary interactions. This paper reports excess molar volumes $\left(V_m^E\right)$, viscosity deviations ($\Delta\eta$), and excess Gibbs energies of activation (ΔG^{*E}) of viscous flow of two ternary mixtures 1-propanol (A) + ethyl ethanoate (B) + cyclohexane (C) and 1-propanol (A) + ethyl ethanoate (B) + benzene (C) and four binary mixtures ethyl ethanoate (B) + cyclohexane (C), ethyl ethanoate (B) + benzene (C), 1-propanol (A) + benzene (C) and 1-propanol (A) + ethyl ethanoate (B) at 303.15 K and atmospheric pressure over the entire range of composition. The ternary results of V_m^E, $\Delta\eta$, and ΔG_m^{*E} have been correlated through empirical or semi theoretical equations due to Redlich–Kister [8], Kohler [9], Rastogi et al. [10], Jacob–Fitzner [11], Tsao–Smith [12], Lark et al. [13], Heric–Brewer [14], and Singh et al. [15]. Further, the Extended Real Associated Solution (ERAS) model [16,17] has been examined to describe the V_m^E of presently investigated binary and ternary mixtures.

2. Experimental

2.1. Materials

Cyclohexane (cC_6H_{12}, Merck GR), benzene (C_6H_6, BDH AR), 1-propanol (C_3H_7OH, Merck AR), and ethyl ethanoate ($C_4H_8O_2$, BDH, AR) were used after further purification and drying by the standard procedures [18]. cC_6H_{12} was dried over molecular sieve type 4 Å (Fluka) and was fractionally distilled over sodium. C_6H_6 was shaken repeatedly with concentrated H_2SO_4 till free from thiophene, washed with aqueous $NaHCO_3$ then with water, Dried over anhydrous $CaCl_2$ 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. $C_4H_8O_2$ was kept over anhydrous K_2CO_3 for more than 72 h and fractionally distilled twice. 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 and 99.9 mol% for cC_6H_{12}, C_6H_6, and $C_4H_8O_2$. The pure component prop-

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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}	0.76912	0.76915[a]	0.821	0.820[b],0.821[c],
C_6H_6	0.86842	0.86843[d]	0.562	0.562[b], 0.5627[e]
$C_4H_8O_2$	0.88850	0.88850[b]	0.400	0.400[b]
C_3H_7OH	0.79561	0.79561[b]	1.726	1.725[b]

[a] [19].
[b] [18].
[c] [20].
[d] [21].
[e] [22].

erties are in good agreement with literature values [18–22] listed 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 densimeter was calibrated with dry air and with degassed double distilled water. The viscosities were measured with a modified suspended-level Ubbelohde viscometer [23,24]. The details of the experimental procedure have been described earlier [25,26].

The binary 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 component, pure 1-propanol, was added to the known composition of binary mixture of remaining two components, ethyl ethanoate and cyclohexane/benzene. The performance of the densimeter and viscometer was checked by measuring the V_m^E and η within the entire composition range for the test binary mixture benzene + cyclohexane. 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 $\left(V_m^E\right)$ of binary and ternary mixtures at each composition have been calculated using the following expression

$$V_m^E = \frac{\sum_{i=A,B,C} x_i M_i}{\rho} - \sum_{i=A,B,C} \frac{x_i M_i}{\rho_i} \quad (1)$$

where M_i is the molar mass of pure component, ρ and ρ_i represent densities of mixture and pure components i, respectively. The estimated accuracy of V_m^E is $\pm$ 0.005 cm^3 mol^{-1}.

The viscosity deviations ($\Delta\eta$) from linear dependence on mole fraction were calculated by

$$\Delta\eta = \eta - \sum_{i=A,B,C} x_i \eta_i \quad (2)$$

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

On the basis of theory of absolute reaction rates [27], the excess Gibb's energies of activation (ΔG^{*E}) of viscous flow were calculated from

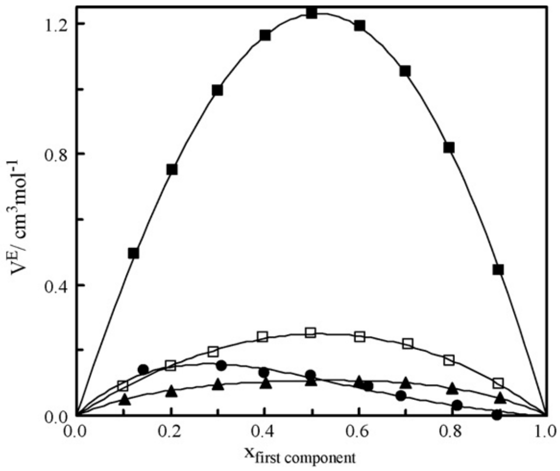

Fig. 1. Excess molar volumes V_m^E for x_B ethyl ethanoate + x_C cyclohexane (■), x_B ethyl ethanoate + x_C benzene (▲), x_A 1-propanol + x_C benzene (●) and x_A 1-propanol + x_B ethyl ethanoate (□) at 303.15 K. Solid curves are calculated Eq. (4) with coefficients in Table 2.

$$\Delta G^{*E} = RT\left[\ln \eta V - \sum_{i=A,B,C} x_i \ln \eta_i V_i\right] \quad (3)$$

where R is a 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 $\Delta\eta$ and ΔG^{*E} are 0.003 mPa s and 15 J mol^{-1}, respectively.

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

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

where $Y_{ij}^E = V_m^E$, $\Delta\eta$, or ΔG^{*E}.

The coefficients A_p of Eq. (4), obtained by the method of least-squares are given in Table 2 together with corresponding standard deviations, $\sigma\left(Y_{ij}^E\right)$. For $C_3H_7OH + cC_6H_{12}$, the coefficients A_p are taken from earlier paper [28]. Composition dependence of V_m^E, $\Delta\eta$, and ΔG^{*E} for binary mixtures $C_4H_8O_2 + cC_6H_{12}$, $C_4H_8O_2 + C_6H_6$, $C_3H_7OH + C_6H_6$, and $C_3H_7OH + C_4H_8O_2$ is shown in Figs. 1–3.

Densities (ρ), viscosities (η), excess molar volumes $\left(V_m^E\right)$, viscosity deviations ($\Delta\eta$), and excess Gibbs energies of activation (ΔG^{*E}) of viscous flow for the ternary mixtures at 303.15 K are given in Tables 3 and 4. The V_m^E, $\Delta\eta$, and ΔG^{*E} of presently investigated ternary mixtures have been fitted to equations proposed by Heric–Brewer [14] and Singh et al. [15]. These expressions include three terms corresponding to binary contributions evaluated by Redlich–Kister equation [8], adjusted to the binary data.

Heric–Brewer [14] used the following equation 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. [15] 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 square. 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 2
Coefficients A_p and standard deviations σ of Eq. (4) for V_m^E, $\Delta\eta$, and ΔG^{*E} of binary mixtures at 303.15 K.

Property	A_0	A_1	A_2	A_3	$\sigma\left(Y_{ij}^E\right)$
Ethyl ethanoate + cyclohexane					
V_m^E (cm^3 mol^{-1})	4.921	0.412	−0.338	−0.387	0.002
$\Delta\eta$ (mPa s)	−0.573	0.289	−0.238	0.155	0.002
ΔG^{*E} (J mol^{-1})	−1941	661	−490	327	8
Ethyl ethanoate + benzene					
V_m^E (cm^3 .mol^{-1})	0.424	0.038	0.226	−0.015	0.002
$\Delta\eta$ (mPa s)	−0.119	0.049	−0.009	0.026	0.001
ΔG^{*E} (J mol^{-1})	−480	176	21	126	4
1-Propanol + benzene					
V_m^E (cm^3 mol^{-1})	0.460	−0.418	0.296	−0.604	0.004
$\Delta\eta$ (mPa s)	−1.631	−0.269	−0.485	−0.280	0.002
ΔG^{*E} (J mol^{-1})	−2903	1399	−1042	−376	11
1-Propanol + ethyl ethanoate					
V_m^E (cm^3 .mol^{-1})	0.992	0.094	0.026	−0.079	0.004
$\Delta\eta$ (mPa s)	−1.666	−0.538	0.076	0.225	0.003
ΔG^{*E} (J mol^{-1})	−2375	873	490	277	6
1-Propanol + cyclohexane*					
V_m^E /cm^3 mol^{-1}	1.640	−0.405	0.607		0.004
$\Delta($/mPa s	−0.926	−0.283	−0.065	0.263	0.001
ΔG^{*E}/J mol^{-1}	−1109	−25	−73	630	3

* Taken from reference [28].

Table 5. The results in Table 5 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 also correlated 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 6.

Redlich and Kister [8] equation for ternary mixture is

$$Y_{ABC}^E = x_A x_B \sum_{\nu=0}^{m} (A_\nu)_{AB}(x_A - x_B)^\nu + x_A x_C \sum_{\nu=0}^{m} (A_\nu)_{AC}(x_A - x_C)^\nu + x_B x_C \sum_{\nu=0}^{m} (A_\nu)_{BC}(x_B - x_C)^\nu \equiv Y_{AB}^E + Y_{AC}^E + Y_{BC}^E \qquad (7)$$

Kohler [9] equation is symmetrical in that all three binary mixtures are treated identically and takes the form

$$Y_{ABC}^E = (x_A + x_B)^2 Y_{AB}^E + (x_A + x_C)^2 Y_{AC}^E + (x_B + x_C)^2 Y_{BC}^E \qquad (8)$$

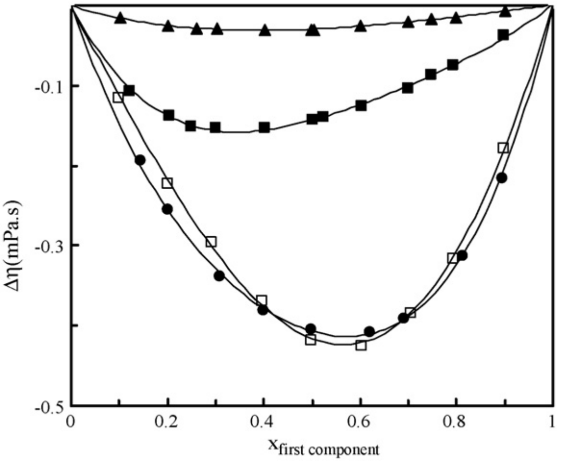

Fig. 2. Viscosity deviation $\Delta\eta$ for x_B ethyl ethanoate + x_C cyclohexane (■), x_B ethyl ethanoate + x_C benzene (▲), x_A 1-propanol + x_C benzene (●) and x_A 1-propanol + x_B ethyl ethanoate (□) at 303.15 K. Solid curves are calculated Eq. (4) with coefficients in Table 2.

In this equation Y_{ij}^E refers to the excess properties of x_i^o, x_j^o in the binary mixtures using following equation:

$$x_i^o = 1 - x_j^o = \frac{x_i}{x_i + x_j} \qquad (9)$$

Rastogi et al. [10] proposed Eq. (10) for correlating the excess properties of a ternary mixture

$$Y_{ABC}^E = (1/2)[(x_A + x_B)Y_{AB}^E + (x_A + x_C)Y_{AC}^E + (x_B + x_C)Y_{BC}^E] \qquad (10)$$

In which Y_{ij}^E represents the excess properties of the binary mixtures at composition x_i^o, x_j^o which refers using Eq. (9).

Jacob and Fitzner [11] suggested an equation for estimating the properties of a ternary solution based on the binary data at compo-

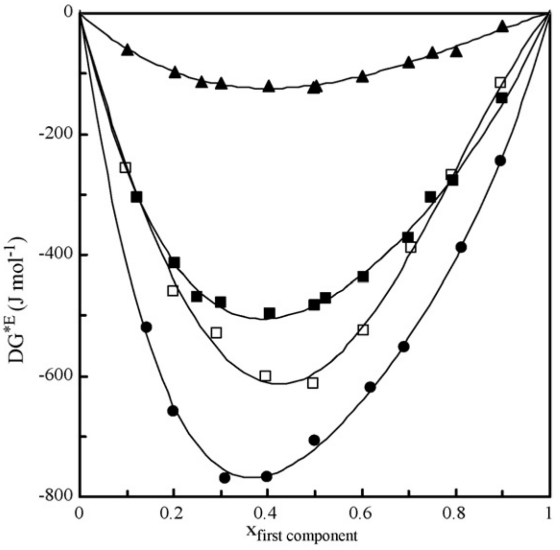

Fig. 3. Excess Gibbs energy of activation ΔG^{*E} of viscous flow for x_B ethyl ethanoate + x_C cyclohexane (■), x_B ethyl ethanoate + x_C benzene (▲), x_A 1-propanol + x_C benzene (●) and x_A 1-propanol + x_B ethyl ethanoate (□) at 303.15 K. Solid curves are calculated Eq. (4) with coefficients in Table 2.

Table 3
Densities (ρ) and excess molar volume (V_m^E) for ternary mixtures at 303.15 K.

x_A	x_B	ρ (g cm^{-3})	V_m^E (cm^3 mol^{-1})
1-Propanol + ethyl ethanoate + cyclohexane			
$x_B/x_C = 2.9637$			
0.1553	0.6316	0.84108	0.902
0.2765	0.5410	0.83559	0.809
0.4086	0.4423	0.82940	0.682
0.5112	0.3655	0.82439	0.566
0.6065	0.2943	0.81949	0.455
0.6717	0.2455	0.81592	0.383
0.7641	0.1764	0.81057	0.284
0.8427	0.1176	0.80583	0.191
0.9193	0.0603	0.80098	0.099
$x_B/x_C = 1.1038$			
0.1247	0.4593	0.81671	1.108
0.2567	0.3900	0.81415	0.952
0.3785	0.3261	0.81164	0.804
0.4828	0.2714	0.80942	0.668
0.5794	0.2207	0.80716	0.548
0.6718	0.1722	0.80493	0.426
0.7671	0.1222	0.80245	0.302
0.8447	0.0815	0.80025	0.207
0.9258	0.0389	0.79786	0.102
$x_B/x_C = 0.3333$			
0.1460	0.2135	0.79053	0.796
0.2702	0.1825	0.79078	0.721
0.3834	0.1542	0.79109	0.643
0.4897	0.1276	0.79155	0.553
0.5867	0.1033	0.79192	0.479
0.6794	0.0801	0.79248	0.390
0.7641	0.0590	0.79302	0.309
0.8570	0.0358	0.79379	0.208
0.9311	0.0172	0.79472	0.098
1-Propanol + ethyl ethanoate + benzene			
$x_B/x_C = 2.9770$			
0.1875	0.6082	0.86841	0.209
0.2460	0.5644	0.86384	0.221
0.4212	0.4333	0.84964	0.231
0.4676	0.3986	0.84574	0.228
0.5222	0.3577	0.84106	0.221
0.7009	0.2239	0.82505	0.174
0.7461	0.1901	0.82083	0.155
0.7549	0.1834	0.82005	0.146
0.8120	0.1407	0.81462	0.115
0.8613	0.1038	0.80980	0.088
0.8627	0.1028	0.80967	0.086
0.9121	0.0658	0.80471	0.058
0.9569	0.0323	0.80013	0.029
$x_B/x_C = 1.0127$			
0.1925	0.4062	0.86382	0.196
0.2362	0.3843	0.86055	0.205
0.4010	0.3013	0.84798	0.204
0.4572	0.2733	0.84361	0.191
0.4963	0.2533	0.84048	0.183
0.6377	0.1822	0.82887	0.141
0.6854	0.1584	0.82476	0.128
0.7531	0.1242	0.81885	0.101
0.7964	0.1024	0.81498	0.084
0.8370	0.0821	0.81127	0.068
0.8483	0.0763	0.81023	0.063
0.9618	0.0192	0.79939	0.017

sition nearest the ternary composition taking the form

$$Y_{ABC}^E = \frac{x_A x_B Y_{AB}^E}{(x_A + x_C/2)(x_B + x_C/2)} + \frac{x_A x_C Y_{AC}^E}{(x_A + x_B/2)(x_C + x_B/2)} + \frac{x_B x_C Y_{BC}^E}{(x_B + x_A/2)(x_C + x_A/2)} \tag{11}$$

Such that for the binary mixture at composition x_i^o, x_j^o.

$$x_i - x_j = x_i^o - x_j^o \tag{12}$$

Table 4
Viscosities (η), viscosity deviations ($\Delta\eta$), and excess Gibbs energies of activation (ΔG^{*E}) of viscous flow for ternary mixtures at 303.15 K.

x_A	x_B	η (mPa s)	$\Delta\eta$ (mPa s)	ΔG^{*E} (J mol^{-1})
1-Propanol + ethyl ethanoate + cyclohexane				
$x_B/x_C = 2.9651$				
0.0666	0.6980	0.460	−0.128	−291
0.1309	0.6499	0.494	−0.172	−315
0.1923	0.6040	0.511	−0.230	−426
0.2496	0.5611	0.521	−0.290	−564
0.3085	0.5171	0.538	−0.345	−671
0.3684	0.4723	0.554	−0.402	−787
0.3886	0.4572	0.561	−0.420	−813
0.4539	0.4084	0.605	−0.455	−838
0.5216	0.3577	0.666	−0.477	−818
0.6717	0.2455	0.887	−0.439	−581
0.8427	0.1176	1.279	−0.256	−226
$x_B/x_C = 1.1039$				
0.0736	0.4861	0.504	−0.179	−439
0.1441	0.4491	0.528	−0.234	−517
0.2091	0.4150	0.552	−0.284	−579
0.2592	0.3887	0.571	−0.322	−641
0.3187	0.3575	0.593	−0.366	−713
0.3664	0.3325	0.611	−0.402	−772
0.4346	0.2967	0.657	−0.433	−784
0.4802	0.2727	0.693	−0.448	−776
0.5295	0.2469	0.738	−0.459	−761
0.6718	0.1722	0.941	−0.416	−558
0.8447	0.0815	1.326	−0.226	−201
$x_B/x_C = 0.3333$				
0.0722	0.2319	0.600	−0.188	−457
0.1302	0.2175	0.621	−0.226	−511
0.2062	0.1985	0.644	−0.280	−592
0.2637	0.1841	0.676	−0.306	−598
0.3202	0.1700	0.696	−0.343	−652
0.3407	0.1648	0.707	−0.353	−661
0.4314	0.1422	0.767	−0.384	−665
0.4907	0.1273	0.816	−0.396	−648
0.5510	0.1123	0.885	−0.388	−579
0.6794	0.0801	1.057	−0.345	−444
0.8570	0.0359	1.404	−0.177	−160
1-Propanol + ethyl ethanoate + benzene				
$x_B/x_C = 2.9777$				
0.1875	0.6083	0.485	−0.197	−357
0.2460	0.5645	0.513	−0.244	−417
0.4212	0.4333	0.628	−0.354	−513
0.4676	0.3986	0.671	−0.371	−507
0.5222	0.3577	0.730	−0.382	−484
0.7009	0.2239	0.981	−0.361	−364
0.7461	0.1901	1.063	−0.336	−318
0.7549	0.1834	1.081	−0.330	−308
0.8120	0.1407	1.203	−0.281	−240
0.8613	0.1038	1.318	−0.230	−186
0.8627	0.1028	1.322	−0.228	−182
0.9121	0.0658	1.453	−0.161	−121
0.9569	0.0323	1.586	−0.085	−59
$x_B/x_C = 1.0124$				
0.1925	0.4062	0.520	−0.200	−379
0.2362	0.3843	0.544	−0.230	−405
0.4010	0.3013	0.660	−0.319	−443
0.4572	0.2733	0.710	−0.340	−445
0.4963	0.2533	0.748	−0.351	−441
0.6377	0.1822	0.910	−0.364	−409
0.6854	0.1584	0.980	−0.354	−381
0.7531	0.1242	1.092	−0.326	−331
0.7964	0.1024	1.175	−0.298	−291
0.8370	0.0821	1.264	−0.260	−242
0.8483	0.0763	1.288	−0.249	−231
0.9618	0.0192	1.600	−0.079	−63
$x_B/x_C = 0.3506$				
0.2175	0.2031	0.535	−0.246	−564
0.3828	0.1603	0.646	−0.335	−571
0.4913	0.1321	0.747	−0.365	−538
0.5444	0.1183	0.803	−0.373	−518
0.6579	0.0888	0.945	−0.369	−457

Table 4 (*Continued*)

x_A	x_B	η (mPa s)	$\Delta\eta$ (mPa s)	ΔG^{*E} (J mol^{-1})
0.7339	0.0691	1.058	−0.347	−406
0.7479	0.0655	1.083	−0.339	−390
0.7860	0.0556	1.151	−0.317	−356
0.8187	0.0471	1.219	−0.288	−312
0.8443	0.0404	1.278	−0.261	−273
0.9090	0.0236	1.437	−0.180	−179
0.9544	0.0118	1.567	−0.104	−101

Tsao and Smith [12] 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^o_i, x^o_j such that $x^o_i = 1 - x^o_j = x_A$ for the AB and AC binary mixtures and $x^o_B = x_B/(x_B + x_C)$ for the BC binary mixture.

The proposed equation by Lark et al. [13] for ternary mixtures is expressed as

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

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.

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

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

ERAS model*:* The ERAS model due to Heintz and coworkers [16,17] combines the linear chain association model with Flory's equation of state [29] and is applicable to mixtures consisting of one highly associating component and other weakly associated/polar component, which forms cross-association complex (AB). This model provides a quantitative treatment of excess molar enthalpies H^E_m, excess molar Gibbs energies G^E_m, and excess molar volumes V^E_m and accounts for the competing effects present in the binary mixtures [6,30–32]. The ERAS model has also been used to predict excess properties of ternary mixtures [28,33–35] from the parameters of the binary constituents. Here, the ERAS model has been examined to predict V^E_m of ternary mixture $C_3H_7OH + C_4H_8O_2 + cC_6H_{12}$ consisting of one associating component (A, 1-propanol), second weakly associated polar (B, ethyl ethanoate) component that can form a cross-association complex (AB) and third non-polar inert component (C, cyclohexane)**.** In the frame work 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 [17,28,33]. The ERAS model is characterized by the enthalpy for the reactions corresponding to the hydrogen bonding energy Δh^*_i and the volume change (reaction volume) Δv^*_i, related to the formation of the linear chains in associated molecules. 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 V^E_m of $C_3H_7OH + C_4H_8O_2 + cC_6H_{12}$ ternary mixture were calculated.

4. Discussion

Table 7 shows that for the studied binary mixtures, experimental and literature values [36,39,41,43] of V^E_m interpolated to mole fraction 0.5 are in good agreement. $\Delta\eta$ for $C_3H_7OH + C_4H_8O_2$ reported by Nikam et al. [43] are more negative than the present results. The large and positive values of V^E_m (Fig. 1) and large negative values of $\Delta\eta$ and ΔG^{*E} (Figs. 2 and 3) for $C_4H_8O_2 + cC_6H_{12}$ may be attributed to the operation of dispersion forces and to the disruption of dipolar order in ethyl ethanoate by the addition of cyclohexane molecules. These results are also consistent with large positive excess molar enthalpy H^E_m and isentropic compressibility κ^E_S values (Table 7) for $C_4H_8O_2 + cC_6H_{12}$ [36–38]. On the other hand for $C_4H_8O_2 + C_6H_6$, the values of V^E_m are small and positive and of $\Delta\eta$ and ΔG^{*E} are small and negative. The main reason for relatively small deviations from the ideal values in case of $C_4H_8O_2 + C_6H_6$ may be that either the different contributions arising from mixing the components are small or that opposite contributions largely balance each other. The results suggest that the weak specific interactions appear to occur in alkanoate + benzene mixture. The interaction may be due to n–π complex formation between free electrons of the carboxylic group and aromatic ring. As the V^E_m values for $C_3H_7OH + C_6H_6$ are moderate positive, points to the fact that the effects contributing to the positive V^E_m values outweigh the effects responsible for negative contributions. The negative values of $\Delta\eta$ and ΔG^{*E} for $C_3H_7OH + C_6H_6$ also supports this graded behavior. Figs. 1 and 2 show that the values of V^E_m for $C_3H_7OH + C_4H_8O_2$ mixtures are positive while $\Delta\eta$ are negative. The magnitude and sign of V^E_m and $\Delta\eta$ suggest that declustering of alkanol and dipolar disordering of ethanoate in the system is dominating over the structure formed by alkanol + ethanoate pair [46].

In order to see the influence of variation of C_3H_7OH composition in ternary mixtures, the V^E_m, $\Delta\eta$, and ΔG^{*E} were studied by adding C_3H_7OH to pseudo binary mixture ($C_4H_8O_2 + cC_6H_{12}$ or $C_4H_8O_2 + C_6H_6$) of different fixed compositions for each ternary mixture (Tables 3 and 4). Tables 5 and 6 summarize the results of different correlating equations. Examination of Table 6 shows that Eq. (7) due to Redlich–Kister gave smaller values of σ in correlating the V^E_m and $\Delta\eta$ while comparatively higher values of σ were obtained with the other equations proposed by Kohler, Rastogi et al., Jacob–Fitzner, Tsao–Smith, and Lark et al. In the case of ΔG^{*E}, the values of σ are in the range of 57–235 J mol^{-1} for different empirical equations, least being 57 J mol^{-1} for 1-propanol + ethyl ethanoate + benzene with Rastogi et al. Eq. (10), while 111 J mol^{-1} for 1-propanol + ethyl ethanoate + cyclohexane when the Taso–Smith Eq. (13) is used. The correlating ability was improved using the correlating equations containing ternary contributory terms (Table 5). The correlation due to Heric–Brewer Eq. (5) is comparatively better than that of Singh et al. Eq. (6).

The values of V^E_m for ternary mixtures $C_3H_7OH + C_4H_8O_2 + cC_6H_{12}$ are large and positive while for $C_3H_7OH + C_4H_8O_2 + C_6H_6$ small and positive (Figs. 4 and 5). For the equimolar composition (i.e. $x_A = x_B = x_C = 1/3$), V^E_m values of ternary mixtures $C_3H_7OH + C_4H_8O_2 + cC_6H_{12}$ and $C_3H_7OH + C_4H_8O_2 + C_6H_6$ are 0.854 cm^3 mol^{-1} and 0.220 cm^3 mol^{-1}, respectively. It is observed that by the addition of C_3H_7OH to pseudo binary mixture ($C_4H_8O_2 + cC_6H_{12}$) the values of V^E_m decrease. This may be inferred as the occurrence of specific interactions between alkanol and alkanoate molecules and the dilution effect on breaking of dipolar-structure in alkanoate. Nagata et al. [47] have determined equilibrium constant for alkanol–ethanoate mixtures through H^E_m consistent with the present results. The large and positive values of V^E_m for $C_3H_7OH + C_4H_8O_2 + cC_6H_{12}$ further indicate that the positive contributions due to dispersion interactions and disruption of H-bonds in 1-propanol molecules and dipolar order in ethyl ethanoate

Table 5
Values of coefficients A_{ABC}, B_{ABC}, C_{ABC} of Heric–Brewer Eq. (5) and Singh et al. Eq. (6) for V_m^E (cm^3 mol^{-1}), $\Delta\eta$ (mPa s) and ΔG^{*E} (J mol^{-1}) of 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
1-Propanol + ethyl ethanoate + cyclohexane								
V_m^E	−7.835	6.975	17.688	0.008	−0.382	22.087	50.194	0.019
$\Delta\eta$	0.177	−7.266	3.836	0.007	−0.892	4.071	−91.402	0.033
ΔG^{*E}	−571	−18441	12006	58	−1222	5841	−438971	115
1-Propanol + ethyl ethanoate + benzene								
V_m^E	1.990	−4.106	−0.932	0.007	−1.273	−0.995	87.903	0.020
$\Delta\eta$	1.422	2.866	0.242	0.004	3.483	0.490	−32.083	0.018
ΔG^{*E}	4610	−881	1720	20	4156	1650	36989	22

Table 6
The values of standard deviations σ of V_m^E (cm^3 mol^{-1}), $\Delta\eta$ (mPa s) and ΔG^{*E} (J mol^{-1}) calculated by different empirical equations.

Property	σ					
	Eq. (7)	Eq. (8)	Eq. (10)	Eq. (11)	Eq. (13)	Eq. (14)
1-Propanol + ethyl ethanoate + cyclohexane						
V^E	0.040	0.055	0.171	0.053	0.209	0.129
$\Delta\eta$	0.041	0.087	0.147	0.083	0.075	0.113
ΔG^{*E}	151	133	248	138	111	219
1-Propanol + ethyl ethanoate + benzene						
V^E	0.012	0.068	0.044	0.061	0.068	0.054
$\Delta\eta$	0.051	0.060	0.129	0.059	0.064	0.057
ΔG^{*E}	93	251	57	235	234	165

by cyclohexane molecules are dominating over the specific interactions between alkanol + ethanoate pair.

The value of equimolar V_m^E for $C_3H_7OH + C_4H_8O_2 + cC_6H_{12}$ is considerably reduced from 0.854 to 0.220 cm^3 mol^{-1} when cC_6H_{12} molecules in the mixture are replaced by C_6H_6. Highly diminished equimolar V_m^E value indicates beside disruption of alkanol and ethanoate structures and the specific interactions between pairs of alkanol, ethanoate and benzene are significant.

In Table 8 we compare values of equimolar, maximum and minimum V_m^E for different ternary mixtures formed from alkanol, alkyl alkanoate and hydrocarbons. Mostly V_m^E values are large positive for ternary mixtures alkanol + alkyl alkanoate + cycloalkane, and it reduces when n-alkane or benzene is replaced for cyclohexane. The expansive region in the ternary mixtures 1-propanol + ethyl ethanoate + cyclohexane, 1-propanol + propyl propanoate + cyclohexane [48], methyl butanoate + heptane + cyclooctane [49], propyl propanoate + hexane + cyclohexane [50], and 1-butanol + dioxane + cyclohexane [35] can probably be ascribed to the inefficient packing in the mixtures of these components as a result of their incompatible structures, cyclohexane with an arm-chair structure. Alkane and 1-alkanol with flexible-chain structures in 1-propanol + propyl propanoate + hexane [48], 1-propanol + ethyl propanoate + hexane [51], 1-butanol + ethyl propanoate + hexane [51], 1-heptanol + ethyl propanoate + hexane [52], 1-octanol + ethyl propanoate + hexane [52], 1-hexanol + methyl pentanoate + octane [53], 1-hexanol + methyl heptanoate + octane [53], 1-octanol + methyl butanoate + heptane [54], 1-octanol + butyl butanoate + octane [55], 1-octanol + butyl butanoate + decane [56], 1-octanol + butyl butanoate + dodecane [57] mixtures, the packing effects are

Table 7
Values of V_m^E, $\Delta\eta$, ΔG^{*E}, H^E, and κ_S^E at equimolar compositions.

Mixture	V_m^E (cm^3 mol^{-1})	$\Delta\eta$ (mPa s)	ΔG^{*E} (J mol^{-1})	H^E (J mol^{-1})	κ_S^E (TPa^{-1})
$C_4H_8O_2 + cC_6H_{12}$	1.230 1.17[*,a]	−0.143	−485	1342[*,a] 1307[c]	62[b]
$C_4H_8O_2 + C_6H_6$	0.106 0.117[*,d]	−0.030	−120	84[d]	−9[b]
$C_3H_7OH + C_6H_6$	0.115 0.098[f]	−0.408	−726	746[e]	8[f]
$C_3H_7OH + C_4H_8O_2$	0.248 0.241[h] 0.2367[*,i]	−0.416 −0.495[h]	−594	1627[g]	
$C_3H_7OH + cC_6H_{12}$	0.410[j]	−0.232[j]	−277[j]	562[k]	

[*] 298.15 K.
[a] [36].
[b] [37].
[c] [38].
[d] [39].
[e] [40].
[f] [41].
[g] [42].
[h] [43].
[i] [44].
[j] [28].
[k] [45].

Table 8
Comparison of equimolar, ternary contribution $\left(V^{E}_{m,ABC}-V^{E}_{m,bin}\right)$, maximum and minimum values of excess molar volumes of several ternary mixtures.

Ternary mixture	$V^{E}_{m,ABC}$ (cm^3 mol^{-1})					Reference
	Temperature (K)	I	II	III	IV	
1-Propanol + ethyl ethanoate + cyclohexane	303.15	0.854	0.014	1.232	0	This work
1-Propanol + propyl propanoate + cyclohexane	298.15	0.625	0.009	0.775	0	48
1-Butanol + dioxane + cyclohexane	298.15	0.758	0.042	0.95	0	35
Methyl butanoate + heptane + cyclooctane	313.15	0.573	−0.019	0.842	−0.307	49
Propyl propanoate + hexane + cyclohexane	298.15	0.505	−0.038	0.818	0	50
1-Propanol + propyl propanoate + hexane	298.15	0.080	−0.076	0.363	−0.18	50
1-Propanol + ethyl propanoate + hexane	298.15	0.425	0.005	0.631	0	51
1-Butanol + ethyl propanoate + hexane	298.15	0.350	−0.022	0.631	−0.039	51
1-Heptanol + ethyl propanoate + hexane	298.15	0.180	−0.080	0.631	−0.372	52
1-Octanol + ethyl propanoate + hexane	298.15	0.176	−0.059	0.631	−0.472	52
1-Hexanol + methyl pentanoate + octane	303.15	0.446	0.010	0.647	−0.013	53
1-Hexanol + methyl pentanoate + octane	313.15	0.473	−0.003	0.676	−0.010	53
1-Hexanol + methyl heptanoate + octane	303.15	0.185	−0.084	0.353	−0.013	53
1-Hexanol + methyl heptanoate + octane	313.15	0.345	0.050	0.425	−0.010	53
1-Octanol + methyl butanoate + heptane	283.15	0.276	−0.191	0.655	−0.204	54
1-Octanol + methyl butanoate + heptane	313.15	0.296	−0.114	0.791	−0.271	54
1-Octanol + butyl butanoate + octane	308.15	0.252	0.005	0.378	−0.105	55
1-Octanol + butyl butanoate + decane	308.15	0.431	0.014	0.559	−0.009	56
1-Octanol + butyl butanoate + dodecane	308.15	0.534	0.019	0.652	0	57
1-Propanol + ethyl ethanoate + benzene	303.15	0.220	0.012	0.249	0	This work
1-Hexanol + propyl propanoate + benzene	298.15	0.235	0.007	0.341	−0.044	58
1-Hexanol + propyl propanoate + benzene	308.15	0.207	−0.023	0.360	−0.055	59
Propyl propanoate + hexane + benzene	298.15	0.161	−0.148	0.399	−0.044	60

I = Equimolar values of $V^{E}_{m,ABC}$, II = ternary contribution ($V^{E}_{m,ABC}-V^{E}_{m,bin}$), III = maximum value of $V^{E}_{m,ABC}$ and IV = minimum value of $V^{E}_{m,ABC}$.

more relevant resulting small positive or negative values of V^{E}_{m}. In case of mixtures, 1-propanol + ethyl ethanoate + benzene, 1-hexanol + propyl propanoate + benzene [58,59], and propyl propanoate + hexane + benzene [60] involving benzene, the specific interactions of n...HO, −OH. . .π and or n. . .π types lead to reduction in V^{E}_{m}.

The values of viscosity deviations $\Delta\eta$ for both ternary mixtures are negative (Figs. 6 and 7). The values of $\Delta\eta$ for the equimolar composition of ternary mixtures $C_3H_7OH + C_4H_8O_2 + cC_6H_{12}$ and $C_3H_7OH + C_4H_8O_2 + C_6H_6$ are −0.388 and -0.288 mPa s, respectively. The negative values of viscosity deviations are consistent with the destruction of hydrogen bonds in 1-propanol. The negative values of $\Delta\eta$ were also observed for methyl butanoate + heptane + cyclo-octane [49], methyl pentanoate or methyl heptanoate + octane + 1-hexanol [53], and 1-hexanol + propyl propanoate + benzene [58,59]. On comparing the equimolar values of $\Delta\eta$ of $C_3H_7OH + C_4H_8O_2 + C_6H_6$ (−0.288 mPa s) with $C_3H_7OH + C_4H_8O_2 + cC_6H_{12}$ (−0.388 mPa s), the values of $\Delta\eta$ are decreased when cyclohexane is replaced by benzene in the mixture.

The viscosity of a mixture strongly depends on the entropy of mixture [61], 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 [62] 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

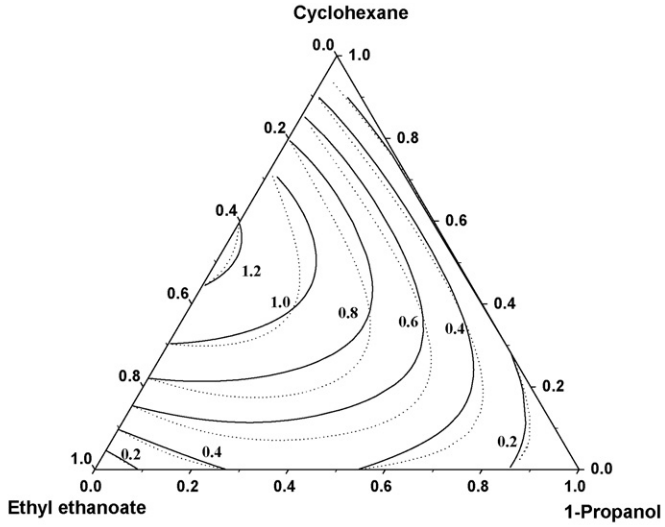

Fig. 4. Isolines at constant excess molar volumes, V^{E}_{m} (cm^3 mol^{-1}) for ternary mixture of 1-propanol + ethyl ethanoate + cyclohexane correlated with Eq. (5) (——) and ERAS model (- - - - - -) at 303.15 K.

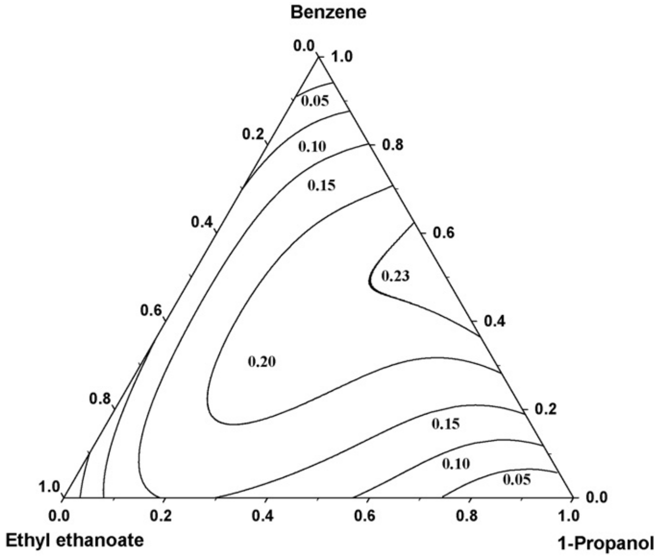

Fig. 5. Isolines at constant excess molar volumes, V^{E}_{m} (cm^3 mol^{-1}) for ternary mixture of 1-propanol + ethyl ethanoate + benzene correlated with Eq. (5) (——) at 303.15 K.

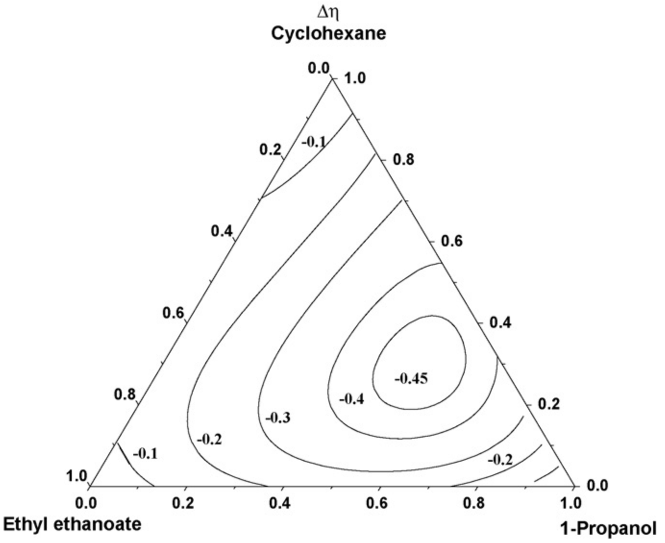

Fig. 6. Isolines at constant viscosity deviations, $\Delta\eta$ (mPa s) for ternary mixture of 1-propanol + ethyl ethanoate + cyclohexane correlated with Eq. (5) at 303.15 K.

values observed for viscosity deviations $\Delta\eta$ of the ternary mixtures under study point out the easier flow of the mixture when compared with the behaviour of its pure components. This could be explained by the breaking of the hydrogen bonding in 1-propanol and disruption of dipolar order that makes the mixture flow more easily. This is also in accordance with the conclusions of Fort and Moore [63] about the behaviour of systems containing an associated component.

The values of ΔG^{*E} are large and negative for both investigated ternary mixtures. The dependence of ΔG^{*E} on composition is complex (Figs. 8 and 9), depending upon the different contributions in the mixture. However, these negative values of ΔG^{*E} are consistent with the negative values of $\Delta\eta$ and positive values of V_m^E, which arise due to the structure breaking of both propanol and ethanoate molecules.

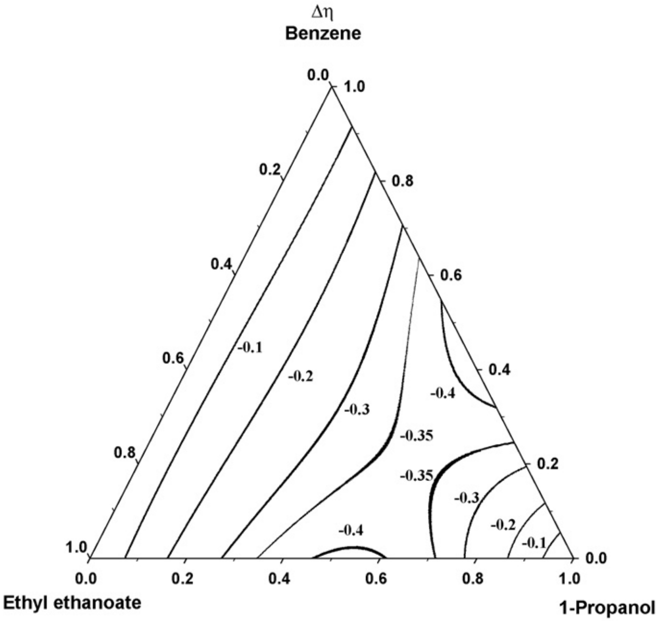

Fig. 7. Isolines at constant viscosity deviations, $\Delta\eta$ (mPa s) for ternary mixture of 1-propanol + ethyl ethanoate + benzene correlated with Eq. (5) at 303.15 K.

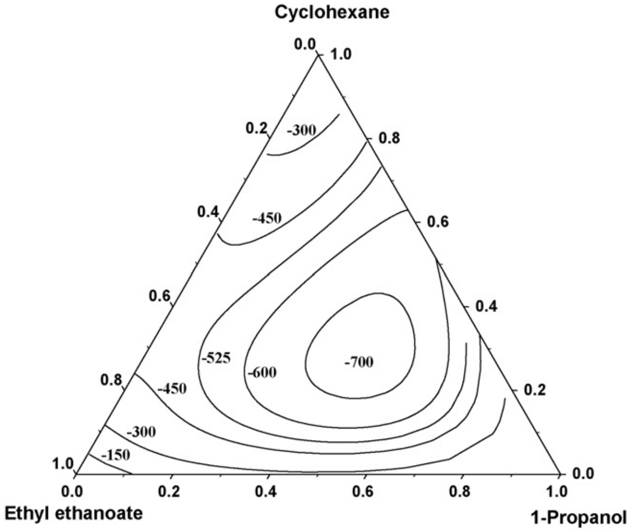

Fig. 8. Isolines at constant excess Gibbs energy of activation ΔG^{*E} (J mol^{-1}) of viscous flow for ternary mixture of 1-propanol + ethyl ethanoate + cyclohexane correlated with Eq. (5) at 303.15 K.

ERAS model: The required pure component properties and the ERAS parameters are listed in Table 9. The values of surface to volume ratio (S) were taken from Bondi [64]. There is no self-association in ethyl ethanoate molecules as existed in alkanols through hydrogen bonds. However, the mixtures methyl ethanoate + alkane [67], THF + alkane [34], tetrahydropyran (THP) + alkane [67], and alkanol + methyl ethanoate [31], have been analyzed in frame-work of the ERAS model considering weak polar-association for alkyl alkanoate, THF, and THP. This weak self-association in these molecules was considered as a formal result of the model calculation rather than evidence that a real association occurs in latter molecules. It has to be interpreted as preferential interaction among alkyl alkanoate, THF, and THP molecules due to their dipole moments. Accordingly, we have treated ethyl ethanoate as a weak dipolar-associated molecule with $K_i = 1$. The values of Δh_{ij}^* and Δv_{ij}^* for ethyl ethanoate were estimated from the experimental H_m^E [36] and V_m^E data of ethyl ethanoate + cyclohexane by

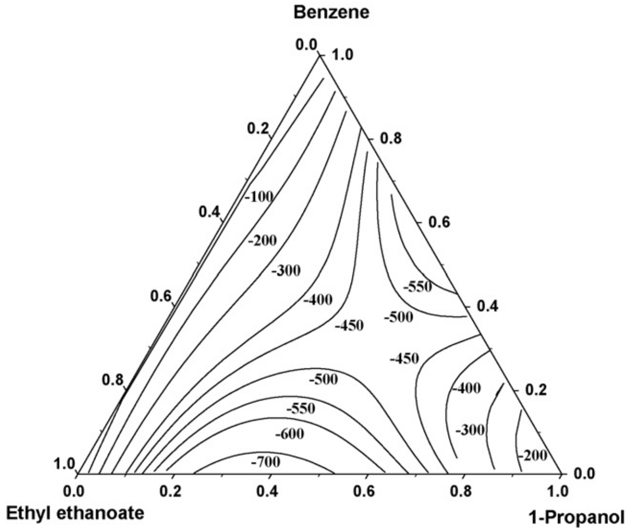

Fig. 9. Isolines at constant excess Gibbs energy of activation ΔG^{*E} (J mol^{-1}) of viscous flow for ternary mixture of 1-propanol + ethyl ethanoate + benzene correlated with Eq. (5) at 303.15 K.

Table 9
Properties and parameters of pure components at 303.15 K used in 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[c]	167[d]	61.22	395	−25.1[e]	−5.6[e]	1.489
$C_4H_8O_2$	99.16	1.392[f]	1245[f]	1	76.48	503	−10.0	−5.7	1.393
cC_6H_{12}	109.42	1.233[g]	1171[g]	–	84.33	534	–	–	1.315
C_6H_6	89.14	1.223[g]	1280[g]	–	69.76	623	–	–	1.243

[a] Calculated in accordance with reference [64].
[b] [2].
[c] [65].
[d] [6].
[e] [16].
[f] [66].
[g] [19].

Table 10
Parameters for binary mixtures and comparison of equimolar experimental and ERAS model results at 303.15 K.

Mixture	X_{ij} (J cm^{-3})	K_{ij}	Δh^*_{ij} (kJ mol^{-1})	Δv^*_{ij} (cm^3 mol^{-1})	V^E_m (cm^3 mol^{-1})				
					Experimental	Physical	Chemical	Total	σ
$C_4H_8O_2 + cC_6H_{12}$	40.0	–	–		1.230	0.752	0.453	1.205	0.058
$C_3H_7OH + cC_6H_{12}$ *	6.5	–	–	–	0.410	0.328	0.134 0.462	0.039	
$C_3H_7OH + C_6H_6$	7.0	9	−14.2	−7.3	0.115	0.414	−0.265	0.149	0.054
$C_4H_8O_2 + C_6H_6$	2.0	15	−5.7	−2.1	0.106	0.000	0.116	0.116	0.014
$C_3H_7OH + C_4H_8O_2$	4.0	10	−9.5	−8.7	0.248	0.182	0.074	0.256	0.010

* Reference [28].

the ERAS model. The values of Δh^*_{ij} and Δv^*_{ij} were found to be −10.0 kJ mol^{-1} and −5.7 cm^3 mol^{-1}. In mixtures $C_4H_8O_2 + C_6H_6$ and $C_3H_7OH + C_6H_6$, the optimum values of cross parameters X_{ij}, K_{ij}, Δh^*_{ij} and Δv^*_{ij}, were obtained by simultaneously adjusting to the experimental equimolar H^E_m [36,39,40] and the whole composition range V^E_m.

In mixture $C_3H_7OH + C_4H_8O_2$, to account for the complex formation C_3H_7OH-$C_4H_8O_2$ (AB), the values of cross parameters X_{ij}, K_{ij}, Δh^*_{ij}, and Δv^*_{ij} were obtained by simultaneously adjusting to the experimental equimolar H^E_m [42] and the whole composition range V^E_m. The values of the cross parameters for binary mixtures are given in Table 10.

Table 11
The ERAS excess molar volumes along with chemical and physical contributions to ERAS model and difference $\delta V \left(= V^E_{m,exp} - V^E_{m,ERAS}\right)$ for 1-propanol + ethyl ethanoate + cyclohexane at 303.15 K.

x_A	x_B	V^E_{chem} (cm^3 mol^{-1})	V^E_{phy} (cm^3 mol^{-1})	V^E_{ERAS} (cm^3 mol^{-1})	δV (cm^3 mol^{-1})
1-Propanol + ethyl ethanoate + cyclohexane					
$x_B/x_C = 2.9637$					
0.1553	0.6316	0.275	0.535	0.811	0.091
0.2765	0.5410	0.256	0.490	0.746	0.064
0.4086	0.4423	0.226	0.440	0.666	0.017
0.5112	0.3655	0.196	0.392	0.587	−0.021
0.6065	0.2943	0.161	0.339	0.500	−0.045
0.6717	0.2455	0.134	0.298	0.431	−0.049
0.7641	0.1764	0.091	0.230	0.322	−0.038
0.8427	0.1176	0.054	0.164	0.217	−0.026
0.9193	0.0603	0.020	0.086	0.106	−0.007
$x_B/x_C = 1.1038$					
0.1247	0.4593	0.394	0.690	1.084	0.024
0.2567	0.3900	0.336	0.624	0.960	−0.008
0.3785	0.3261	0.280	0.556	0.836	−0.032
0.4828	0.2714	0.230	0.484	0.714	−0.046
0.5794	0.2207	0.181	0.418	0.599	−0.051
0.6718	0.1722	0.134	0.347	0.481	−0.055
0.7671	0.1222	0.087	0.263	0.350	−0.047
0.8447	0.0815	0.050	0.186	0.236	−0.029
0.9258	0.0389	0.019	0.091	0.110	−0.008
$x_B/x_C = 0.3333$					
0.1460	0.2135	0.360	0.545	0.905	−0.109
0.2702	0.1825	0.303	0.524	0.827	−0.106
0.3834	0.1542	0.249	0.499	0.748	−0.106
0.4897	0.1276	0.199	0.462	0.661	−0.108
0.5867	0.1033	0.154	0.414	0.568	−0.089
0.6794	0.0801	0.114	0.354	0.467	−0.078
0.7641	0.0590	0.079	0.284	0.363	−0.054
0.8570	0.0358	0.044	0.190	0.234	−0.027
0.9311	0.0172	0.019	0.095	0.114	−0.016

Results of calculated V_m^E and their comparison with the experimental data at equimolar mixture are given in Table 10 along with the physical and chemical contributions. The ERAS model V_m^E is in good qualitative agreement with the experimental data. The standard deviations $\sigma(V_\mathrm{m}^\mathrm{E})$ between experiment and theory are from 0.010 to 0.058 cm^3 mol^{-1} (Table 10). In $C_4H_8O_2 + cC_6H_{12}$ mixture both the physical and chemical contributions to total V_m^E are positive as expected. The physical contribution is dominating over the chemical contribution, which is reflected in to the large positive value of X_{ij} that is required for the ERAS model calculations. The values of $K_{ij} = 15$, $\Delta h_{ij}^* = -5.7\,\mathrm{kJ\,mol^{-1}}$ and $\Delta v_{ij}^* = -2.1\,\mathrm{cm^3\,mol^{-1}}$ needed to fit H_m^E and V_m^E of $C_4H_8O_2 + C_6H_6$ are consistent with the weak specific-interactions speculated between ethyl ethanoate and benzene molecules. In case of $C_3H_7OH + C_6H_6$, the values of $X_{ij} = 7.0\,\mathrm{J\,cm^{-3}}$, $\mathrm{K_{ij}} = 9$, $\Delta h_{ij}^* = -14.2\,\mathrm{kJ\,mol^{-1}}$ and $\Delta v_{ij}^* = -7.3\,\mathrm{cm^3\,mol^{-1}}$ are in accordance with the weak specific-interactions between alkanol and benzene molecules.

Comparison of experimental and the ERAS model V_m^E data for the ternary mixture $C_3H_7OH + C_4H_8O_2 + cC_6H_{12}$ are presented in Table 11. Excess molar volumes for present ternary mixtures were calculated using binary parameters of constituent pairs and the results are compared in Fig. 4. The values of $\sigma(V_\mathrm{m}^\mathrm{E})$ for the present ternary mixture is 0.061 cm^3 mol^{-1}. Thus good agreement between experimental and ERAS model values is obtained. However, prediction of V_m^E at lower mole fraction of alkanol is not as good as at higher concentration.

The physical and chemical contributions to total V_m^E are positive for 1-propanol + ethyl ethanoate + cyclohexane. The magnitude of each contribution depends on composition. e.g. physical contribution in 1-propanol + ethyl ethanoate + cyclohexane is dominating over the chemical contribution.

5. Conclusions

In this work, V_m^E, $\Delta\eta$, and $\Delta G^{*\mathrm{E}}$ have been determined from densities and viscosities measurements for two ternary mixtures 1-propanol + ethyl ethanoate + cyclohexane and 1-propanol + ethyl ethanoate + benzene and four binaries ethyl ethanoate + cyclohexane, ethyl ethanoate + benzene, 1-propanol + benzene and 1-propanol + ethyl ethanoate at 303.15 K.

The large and positive values of V_m^E are observed for 1-propanol + ethyl ethanoate + cyclohexane which are reduced when benzene is replaced for cyclohexane. The expansive region in the ternary mixtures 1-propanol + ethyl ethanoate + cyclohexane can be ascribed to the inefficient packing in the mixtures of these components as a result of their incompatible structures. In case of mixture 1-propanol + ethyl ethanoate + benzene, specific interactions of *n*...HO, –OH. . .π and or n. . .π types leads to reduction in V_m^E.

Large standard deviations are observed when the V_m^E, $\Delta\eta$, and $\Delta G^{*\mathrm{E}}$ 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 an almost quantitative representation of V_m^E of the ternary mixture $C_3H_7OH + C_4H_8O_2 + cC_6H_{12}$ using model parameters obtained from data of the constituting binaries.

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