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Volumetric and transport properties of ternary mixtures containing 1-alkanol + ethyl ethanoate + 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 three ternary mixtures 1-butanol + ethyl ethanoate + cyclohexane, 1-pentanol + ethyl ethanoate + cyclohexane, and 1-octanol + ethyl ethanoate + cyclohexane 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 mixture. 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

As a part of our systematic studies on the thermodynamic and transport properties of ternary liquid mixtures containing alkanol, alkyl alkanoate, alkyl amines, and cyclohexane in previous papers [1–4] measurements of densities and viscosities, and related excess or mixing functions have been reported. As an extension in this paper 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 three ternary mixtures 1-butanol (A) + (ethyl ethanoate (B) + cyclohexane (C)), 1-pentanol (A) + (ethyl ethanoate (B) + cyclohexane (C)), 1-octanol (A) + (ethyl ethanoate (B) + cyclohexane (C)) and four binaries 1-octanol (A) + cyclohexane (C), 1-butanol (A) + ethyl ethanoate (B), 1-pentanol (A) + ethyl ethanoate (B), and 1-octanol (A) + (ethyl ethanoate (B)) 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_m^{*E} have been correlated through empirical or semi-theoretical equations due to Redlich and Kister [5], Kohler [6], Rastogi et al. [7], Jacob and Fitzner [8], Tsao and Smith [9], Lark et al. [10], Heric and Brewer [11], and Singh et al. [12]. Further, the Extended Real Associated Solution (ERAS) model [13–15] 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), 1-butanol (C_4H_9OH, BDH AR) 1-pentanol ($C_5H_{11}OH$, Merck-Schuchardt, AG), 1-octanol ($C_8H_{17}OH$, Fluka, AG), and ethyl ethanoate ($C_4H_8O_2$, BDH, AR) were used after further purification and drying by the standard procedures [16]. cC_6H_{12} was dried over molecular sieve type 4 Å (Fluka) and was fractionally distilled over sodium. $C_4H_8O_2$ was kept over anhydrous K_2CO_3 for more than 72 h and fractionally distilled twice. 1-Butanol was washed with sulphuric acid and with sodium bisulphate solution to remove bases, alkanals and alkanones. Alkanoates were removed by boiling for 1.5 h with 20% sodium hydroxide. It was dried with anhydrous potassium carbonate, followed by calcium oxide and finally fractionally distilled through an efficient column. 1-Pentanol and 1-octanol of purity better then 99.3 mol% were used as received without any purification except drying over molecular sieve 4 Å. 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 99.9 mol% for cC_6H_{12} and $C_4H_8O_2$ and 99.3 for C_4H_9OH, $C_5H_{11}OH$ and $C_8H_{17}OH$.

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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	0.76904[a], 0.76915[b]	0.821	0.820[c], 0.821[d]
$C_4H_8O_2$	0.88850	0.88850[c], 0.88851[e]	0.400	0.400[c], 0.401[f]
C_4H_9OH	0.80190	0.80191[g], 0.80193[h]	2.250	2.266[i], 2.271[c]
$C_5H_{11}OH$	0.80711	0.80712[g], 0.8072[i]	2.839	2.841[j], 2.844[c]
$C_8H_{17}OH$	0.81752	0.81830[c], 0.81906[h]	6.190	6.215[c]

[a] Ref. [17].
[b] Ref. [18].
[c] Ref. [16].
[d] Ref. [19].
[e] Ref. [20].
[f] Ref. [21].
[g] Ref. [22].
[h] Ref. [23].
[i] Ref. [24].
[j] Ref. [25].

The pure component properties are in good agreement with literature values [16–25] 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 [26,27]. The details of the experimental procedure have been described earlier [2,28,29].

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-alkanol was added to the known composition of binary mixture of remaining two components, ethyl ethanoate and cyclohexane. 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 ρ and η 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:

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

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

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

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

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

On the basis of theory of absolute reaction rates [30], the excess Gibb's energies of activation of viscous flow were calculated from

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

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 accuracy of $\Delta\eta$ and ΔG^{*E} of viscous flow is 0.002 mPa s and 15 J mol^{-1}, respectively.

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 four binary mixtures at 303.15 K are given in Table 2. 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

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

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 3 together with corresponding standard deviations $\sigma(Y_{ij}^E)$. The coefficients A_p for $C_4H_9OH + cC_6H_{12}$, $C_5H_{11}OH + cC_6H_{12}$ and $C_4H_8O_2 + cC_6H_{12}$ are taken from earlier papers [2,4]. Composition dependence of V_m^E, $\Delta\eta$, and ΔG^{*E} for binary mixtures $C_8H_{17}OH + cC_6H_{12}$, $C_4H_9OH + C_4H_8O_2$, $C_5H_{11}OH + C_4H_8O_2$, and $C_8H_{17}OH + C_4H_8O_2$ is shown in Figs. 1–6.

Densities, viscosities, excess molar volumes, viscosity deviations, and excess Gibbs energies of activation of viscous flow for the ternary mixtures at 303.15 K are given in Tables 4 and 5 . The V_m^E, $\Delta\eta$, and ΔG^{*E} of presently investigated ternary mixtures have been fitted to equations proposed by Heric and Brewer [11] and Singh et al. [12]. These expressions include three terms corresponding to binary contributions evaluated by Redlich–Kister equation [5], adjusted to the binary data.

Heric and Brewer [11] 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. [12] proposed equation is of the following form:

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

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_A 1-octanol + x_C cyclohexane						
0.2008	0.0000	0.78075	1.242	0.204	−0.657	55
0.3755	0.0000	0.78990	1.792	0.294	−1.046	103
0.5205	0.0000	0.79698	2.400	0.303	−1.216	102
0.6054	0.0000	0.80089	2.847	0.290	−1.224	98
0.7044	0.0000	0.80534	3.460	0.242	−1.142	78
0.7758	0.0000	0.80838	3.983	0.206	−1.003	62
0.8541	0.0000	0.81163	4.633	0.151	−0.774	35
0.9010	0.0000	0.81356	5.089	0.107	−0.569	26
0.9553	0.0000	0.81575	5.664	0.051	−0.285	11
x_A 1-butanol + x_B ethyl ethanoate						
0.1411	0.8589	0.87569	0.467	0.147	−0.194	−219
0.3184	0.6816	0.85995	0.563	0.257	−0.426	−517
0.3797	0.6203	0.85467	0.609	0.268	−0.493	−585
0.4659	0.5341	0.84710	0.673	0.291	−0.589	−708
0.5634	0.4366	0.83865	0.766	0.292	−0.677	−807
0.6782	0.3218	0.82880	0.920	0.264	−0.735	−845
0.7595	0.2405	0.82186	1.076	0.229	−0.729	−805
0.8312	0.1688	0.81582	1.287	0.180	−0.651	−668
0.9291	0.0709	0.80764	1.736	0.094	−0.383	−342
x_A 1-pentanol + x_B ethyl ethanoate						
0.1095	0.8905	0.87742	0.474	0.158	−0.193	−109
0.2164	0.7836	0.86746	0.541	0.243	−0.387	−300
0.3291	0.6709	0.85743	0.626	0.305	−0.576	−486
0.4303	0.5697	0.84883	0.722	0.336	−0.726	−624
0.5202	0.4798	0.84150	0.829	0.342	−0.838	−719
0.6103	0.3897	0.83444	0.970	0.328	−0.917	−770
0.7187	0.2813	0.82630	1.211	0.286	−0.940	−746
0.8051	0.1949	0.82009	1.508	0.230	−0.854	−622
0.9009	0.0991	0.81346	2.017	0.149	−0.578	−365
x_A 1-octanol + x_B ethyl ethanoate						
0.0809	0.9191	0.87816	0.537	0.183	−0.331	212
0.1620	0.8380	0.86916	0.680	0.316	−0.658	270
0.3257	0.6743	0.85409	1.028	0.472	−1.258	205
0.4413	0.5587	0.84540	1.314	0.506	−1.641	32
0.5431	0.4569	0.83872	1.596	0.502	−1.949	−184
0.6637	0.3363	0.83183	2.040	0.453	−2.203	−407
0.7062	0.2938	0.82960	2.260	0.430	−2.229	−448
0.8574	0.1426	0.82270	3.545	0.271	−1.820	−385
0.9251	0.0749	0.82007	4.563	0.162	−1.193	−231

where A_{ABC}, B_{ABC} and C_{ABC} are parameters characteristics of the ternary mixtures evaluated by fitting 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 6.

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

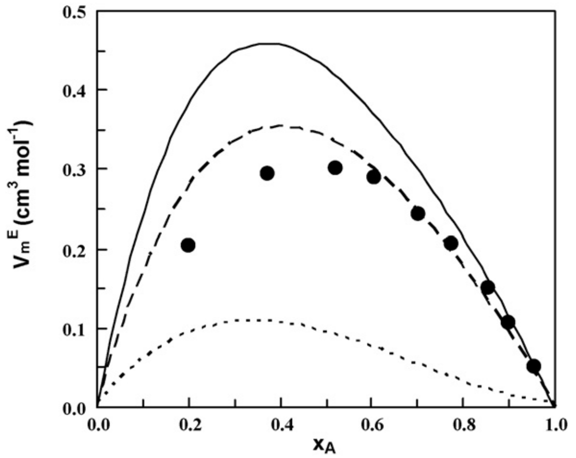

Fig. 1. V_m^E for x_A 1-octanol + x_C cyclohexane at 303.15 K. Experimental points (●), chem (- - - - -), phy (– – –), and ERAS (——).

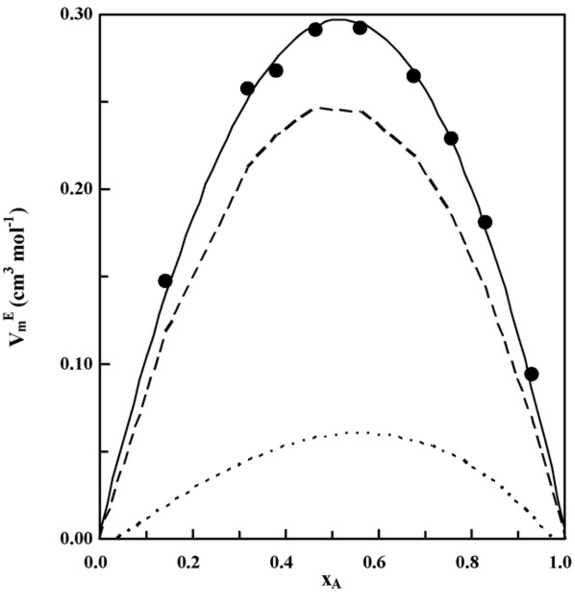

Fig. 2. V_m^E for x_A 1-butanol + x_B ethyl ethanoate at 303.15 K. Experimental points (●), chem (- - - - -), phy (– – –), and ERAS (——).

Table 3
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	$\sigma(Y_{ij}^E)$
x_A 1-octanol + x_C cyclohexane					
V_m^E/cm^3 mol^{-1}	1.230	−0.096	0.023	0.060	0.003
$\Delta\eta$/mPa s	−4.794	−1.463	−0.57	−0.122	0.004
ΔG^{*E}/J mol^{-1}	432	−67	−261	−163	3
x_A 1-butanol + x_B ethyl ethanoate					
V_m^E/cm^3 mol^{-1}	1.163	0.032	0.212	0.102	0.004
$\Delta\eta$/mPa s	−2.477	−1.845	−1.550	−0.955	0.003
ΔG^{*E}/J mol^{-1}	−3037	−2142	−559		14
x_A 1-pentanol + x_B ethyl ethanoate					
V_m^E/cm^3 mol^{-1}	1.342	−0.003	0.443	0.039	0.007
$\Delta\eta$/mPa s	−3.266	−2.361	−1.486	−0.721	0.002
ΔG^{*E}/J mol^{-1}	−2869	−1896	357		14
x_A 1-octano1 + x_B ethyl ethanoate					
V_m^E/cm^3 mol^{-1}	2.023	−0.147	0.508	0.095	0.002
$\Delta\eta$/mPa s	−7.304	−5.989	−4.884	−2.127	0.003
ΔG^{*E}/J mol^{-1}	−476	−4131	209	688	23
x_B ethyl ethanoate + x_C cyclohexane[a]					
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
x_A 1-butanol + x_C cyclohexane[b]					
V_m^E/cm^3 mol^{-1}	1.561	−0.282	0.613	−0.421	0.004
$\Delta\eta$/mPa s	−1.307	−0.471	−0.121	0.298	0.001
ΔG^{*E}/J mol^{-1}	−1068	−106	−137	671	4
x_A 1-pentanol + x_C cyclohexane[b]					
V_m^E/cm^3 mol^{-1}	1.464	−0.057	0.049	−0.179	0.004
$\Delta\eta$/mPa s	−1.787	−0.487	0.019		0.003
ΔG^{*E}/J mol^{-1}	−960	155	224		4

[a] Taken from Ref. [4].
[b] Taken from Ref. [2].

[Eq. (13)], Lark et al. [Eq. (14)] and the standard deviations σ are presented in supporting material as Table ST 1.

Redlich and Kister [5] equation for ternary mixture is

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

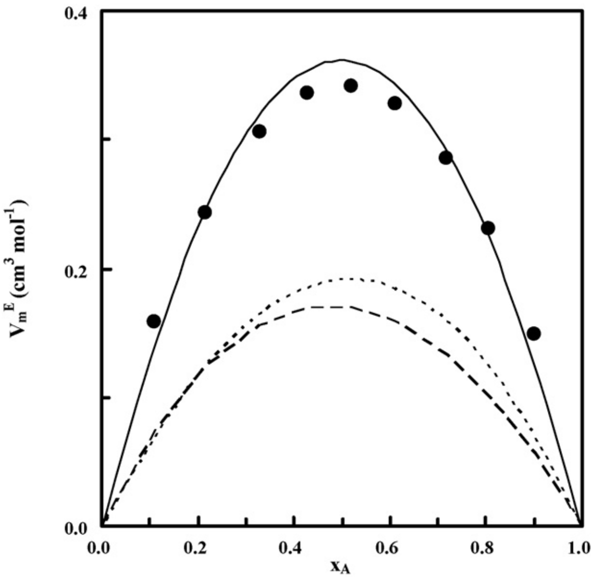

Fig. 3. V_m^E for x_A 1-pentanol + x_B ethyl ethanoate at 303.15 K. Experimental points (●), chem (- - - - -), phy (– – –), and ERAS (——).

Kohler [6] equation is symmetrical in that all three binary mixtures are treated identically and takes the form:

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

In this equation $Y_{ij}{}^E$ refers to the excess properties of $x_i{}^0$, $x_j{}^0$ in the binary mixtures using following equation:

$$x_i^0 = 1 - x_j^0 = \frac{x_i}{x_i + x_j} \tag{9}$$

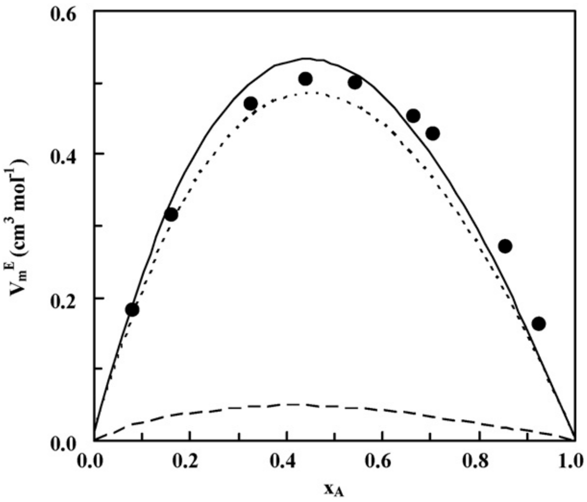

Fig. 4. V_m^E for x_A 1-octanol + x_B ethyl ethanoate at 303.15 K. Experimental points (●), chem (- - - - -), phy (– – –), and ERAS (——).

Table 4
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}
x_A 1-butanol + (x_B ethyl ethanoate + x_C cyclohexane)			
x_B/x_c = 2.7934			
0.1612	0.6177	0.83926	0.909
0.2896	0.5231	0.83358	0.816
0.3404	0.4858	0.83133	0.776
0.4191	0.4278	0.82791	0.697
0.4599	0.3977	0.82617	0.651
0.5343	0.3430	0.82288	0.577
0.6281	0.2739	0.81876	0.468
0.7255	0.2021	0.81441	0.352
0.8268	0.1275	0.80975	0.238
x_B/x_c = 0.8942			
0.1291	0.4112	0.81153	1.097
0.2325	0.3624	0.81038	0.983
0.3371	0.3130	0.80920	0.864
0.4306	0.2688	0.80819	0.749
0.5268	0.2234	0.80709	0.636
0.6393	0.1703	0.80581	0.498
0.7291	0.1279	0.80482	0.380
0.8282	0.0811	0.80370	0.251
0.9029	0.0458	0.80288	0.147
x_B/x_c = 0.3405			
0.1247	0.2223	0.79153	0.828
0.2423	0.1925	0.79248	0.756
0.3414	0.1673	0.79338	0.684
0.3445	0.1665	0.79337	0.686
0.5728	0.1085	0.79562	0.512
0.6417	0.0910	0.79636	0.456
0.7356	0.0672	0.79762	0.353
0.8220	0.0452	0.79885	0.252
0.9169	0.0211	0.80042	0.121
x_A 1-pentanol + (x_B ethyl ethanoate + x_C cyclohexane)			
x_B/x_c = 3.0683			
0.1139	0.6683	0.84303	0.870
0.1941	0.6078	0.83889	0.816
0.2987	0.5289	0.83366	0.731
0.3929	0.4579	0.82909	0.646
0.4612	0.4064	0.82579	0.586
0.5869	0.3116	0.81981	0.477
0.6871	0.2360	0.81512	0.388
0.7932	0.1560	0.81037	0.276
0.8818	0.0891	0.80651	0.173
x_B/x_c = 0.9818			
0.1104	0.4407	0.81397	1.112
0.1998	0.3970	0.81277	0.999
0.2907	0.3519	0.81145	0.889
0.3700	0.3125	0.81026	0.798
0.4327	0.2404	0.80486	0.702
0.5435	0.2265	0.80781	0.587
0.5511	0.2227	0.80769	0.578
0.7053	0.1447	0.80534	0.393
0.7892	0.1046	0.80439	0.285
0.8837	0.0577	0.80309	0.169
x_B/x_c = 0.3412			
0.1212	0.2236	0.79167	0.838
0.1868	0.2069	0.79218	0.810
0.2979	0.1786	0.79327	0.730
0.3878	0.1557	0.79418	0.661
0.5186	0.1225	0.79559	0.549
0.5920	0.1038	0.79643	0.480
0.7022	0.0758	0.79774	0.367
0.7947	0.0522	0.79883	0.272
0.8908	0.0278	0.80014	0.150
x_A 1-octanol + (x_B ethyl ethanoate + x_C cyclohexane)			
x_B/x_c = 3.0463			
0.0342	0.7271	0.84716	0.921
0.0590	0.7084	0.84590	0.912
0.0784	0.6939	0.84497	0.903
0.1059	0.6731	0.84362	0.893
0.1471	0.6421	0.84178	0.868

Table 4 (*Continued*)

x_A	x_B	ρ/g cm^{-3}	V_m^E/cm^3 mol^{-1}
0.1814	0.6163	0.84032	0.844
0.4489	0.4149	0.83061	0.638
0.5248	0.3578	0.82827	0.578
0.6836	0.2382	0.82390	0.440
0.7523	0.1865	0.82224	0.370
0.8613	0.1044	0.81990	0.235
x_B/x_c = 0.9916			
0.0359	0.4800	0.81604	1.190
0.0728	0.4616	0.81613	1.145
0.1094	0.4434	0.81618	1.103
0.1751	0.4107	0.81632	1.021
0.2314	0.3827	0.81644	0.951
0.3555	0.3209	0.81669	0.792
0.4111	0.2932	0.81681	0.719
0.4533	0.2722	0.81691	0.662
0.5120	0.2430	0.81693	0.601
0.6628	0.1679	0.81702	0.435
0.7523	0.1233	0.81704	0.341
0.8613	0.0691	0.81711	0.219
x_B/x_c = 0.3448			
0.0325	0.2481	0.79208	0.880
0.0648	0.2398	0.79320	0.863
0.1037	0.2298	0.79455	0.838
0.1297	0.2231	0.79535	0.831
0.1735	0.2119	0.79683	0.796
0.4142	0.1502	0.80406	0.598
0.4620	0.1379	0.80535	0.554
0.5087	0.1260	0.80659	0.510
0.5622	0.1123	0.80791	0.466
0.5869	0.1059	0.80851	0.443
0.6888	0.0798	0.81088	0.352
0.7452	0.0653	0.81213	0.299
0.8730	0.0326	0.81485	0.168

Rastogi et al. [7] proposed Eq. (10) for predicting 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^0, x_j^0 which refers using Eq. (9).

Jacob and Fitzner [8] suggested an equation for estimating the properties of a ternary solution based on the binary data at composition nearest the ternary composition taking the

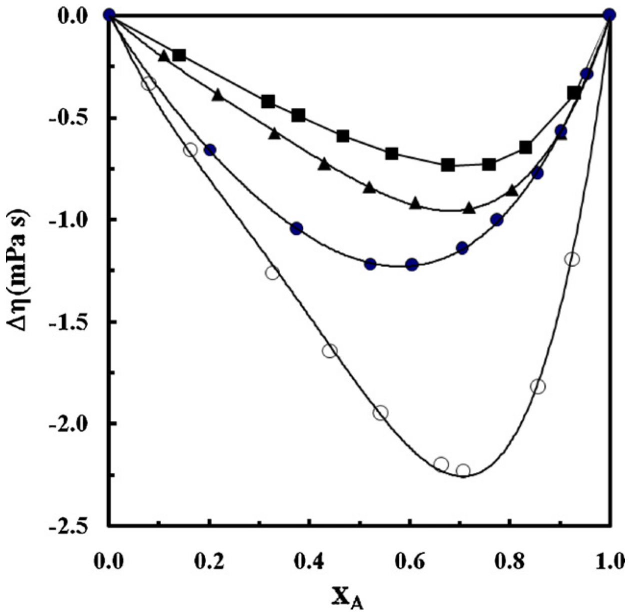

Fig. 5. Viscosity deviation $\Delta\eta$ for x_A 1-octanol + x_C cyclohexane (■), x_A 1-butanol + x_B ethyl ethanoate (▲), x_A 1-pentanol + x_B ethyl ethanoate (●) and x_A 1-octanol + x_B ethyl ethanoate (○) at 303.15 K. Solid curves are calculated Eq. (4) with coefficients in Table 3.

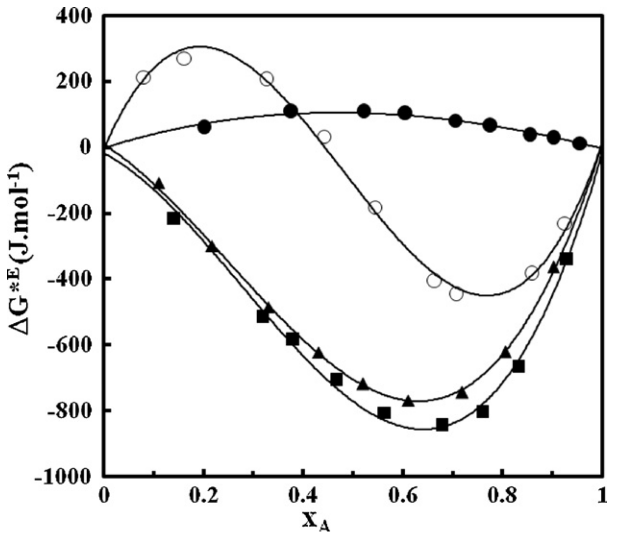

Fig. 6. Excess Gibbs energy of activation ΔG^{*E} of viscous flow for x_A 1-octanol + x_C cyclohexane (■), x_A 1-butanol + x_B ethyl ethanoate (▲), x_A 1-pentanol + x_B ethyl ethanoate (●) and x_A 1-octanol + x_B ethyl ethanoate (○) at 303.15 K. Solid curves are calculated Eq. (4) with coefficients in Table 3.

Table 5
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}
x_A 1-butanol + (x_B ethyl ethanoate + x_C cyclohexane)				
$x_B/x_c = 2.9920$				
0.0544	0.7088	0.450	−0.150	−341
0.1030	0.6723	0.475	−0.210	−394
0.1535	0.6345	0.503	−0.270	−448
0.1959	0.6027	0.514	−0.333	−559
0.2584	0.5559	0.564	−0.393	−572
0.3313	0.5012	0.610	−0.473	−658
0.3935	0.4546	0.665	−0.527	−685
0.4272	0.4293	0.695	−0.556	−706
0.4883	0.3835	0.763	−0.594	−709
0.6281	0.2788	0.938	−0.663	−736
0.8268	0.1298	1.385	−0.563	−532
$x_B/x_c = 1.0072$				
0.0538	0.4748	0.476	−0.222	−619
0.1047	0.4493	0.498	−0.283	−678
0.3127	0.3449	0.647	−0.476	−743
0.2632	0.3697	0.611	−0.431	−715
0.2883	0.3571	0.629	−0.454	−728
0.3146	0.3439	0.648	−0.478	−744
0.3954	0.3034	0.729	−0.529	−728
0.4473	0.2773	0.778	−0.566	−744
0.4856	0.2581	0.819	−0.587	−747
0.6393	0.1810	1.047	−0.611	−660
0.8282	0.0862	1.489	−0.479	−435
$x_B/x_c = 0.3154$				
0.0611	0.2246	0.602	−0.212	−494
0.0901	0.2177	0.615	−0.244	−540
0.1692	0.1988	0.665	−0.315	−578
0.2088	0.1893	0.703	−0.336	−551
0.2866	0.1707	0.770	−0.389	−556
0.3258	0.1613	0.788	−0.430	−613
0.4021	0.1430	0.862	−0.473	−616
0.4658	0.1278	0.940	−0.493	−587
0.5008	0.1194	0.980	−0.507	−582
0.6417	0.0857	1.198	−0.504	−506
0.8220	0.0426	1.616	−0.362	−294
x_A 1-pentanol + (x_B ethyl ethanoate + x_C cyclohexane)				
$x_B/x_c = 3.0899$				
0.0525	0.7158	0.483	−0.142	−178
0.0909	0.6868	0.522	−0.193	−157
0.1348	0.6536	0.562	−0.256	−171
0.1673	0.6291	0.590	−0.303	−189
0.2403	0.5739	0.633	−0.431	−349
0.2964	0.5316	0.673	−0.522	−440
0.3373	0.5007	0.698	−0.592	−537
0.3958	0.4565	0.743	−0.684	−642
0.4658	0.4036	0.814	−0.776	−730
0.6871	0.2364	1.209	−0.898	−720
0.8818	0.0893	1.994	−0.567	−337
$x_B/x_c = 0.9956$				
0.0612	0.4683	0.531	−0.217	−411
0.0837	0.4571	0.556	−0.241	−385
0.1442	0.4269	0.601	−0.331	−435
0.1853	0.4064	0.631	−0.393	−479
0.2642	0.3671	0.692	−0.507	−563
0.3012	0.3486	0.715	−0.566	−633
0.3621	0.3182	0.757	−0.660	−740
0.4036	0.2975	0.818	−0.691	−711
0.4588	0.2700	0.882	−0.750	−743
0.5511	0.2239	1.023	−0.815	−736
0.7892	0.1052	1.679	−0.688	−450
$x_B/x_c = 0.3168$				
0.0561	0.2271	0.628	−0.211	−397
0.0900	0.2189	0.653	−0.257	−439
0.1623	0.2015	0.711	−0.352	−484
0.2114	0.1897	0.757	−0.410	−500
0.2759	0.1742	0.806	−0.497	−568
0.3187	0.1639	0.854	−0.541	−581
0.3886	0.1471	0.932	−0.611	−613
0.4028	0.1437	0.952	−0.621	−610

Table 5 (*Continued*)

x_A	x_B	η/mPa s	$\Delta\eta$/mPa s	ΔG^{*E}/J mol^{-1}
0.4593	0.1301	1.033	−0.659	−593
0.5986	0.0966	1.295	−0.692	−523
0.7947	0.0494	1.875	−0.527	−293
x_A 1-octanol + (x_B ethyl ethanoate + x_C cyclohexane)				
x_B/x_c = 3.0463				
0.0342	0.7271	0.473	−0.225	−210
0.0590	0.7084	0.514	−0.326	−158
0.0784	0.6939	0.542	−0.408	−143
0.1059	0.6731	0.590	−0.517	−104
0.1471	0.6421	0.661	−0.679	−73
0.1814	0.6163	0.725	−0.811	−59
0.4489	0.4149	1.357	−1.700	−190
0.5248	0.3578	1.584	−1.904	−292
0.6836	0.2382	2.281	−2.110	−413
0.7523	0.1865	2.741	−2.040	−403
0.8617	0.1041	3.824	−1.579	−289
x_B/x_c = 0.9916				
0.0359	0.4800	0.544	−0.268	−310
0.0728	0.4616	0.617	−0.401	−209
0.1094	0.4434	0.690	−0.532	−140
0.1751	0.4107	0.828	−0.760	−65
0.2314	0.3827	0.953	−0.949	−43
0.3555	0.3209	1.240	−1.355	−118
0.4111	0.2932	1.391	−1.514	−160
0.4533	0.2722	1.516	−1.624	−198
0.5120	0.2430	1.716	−1.752	−239
0.7523	0.1233	3.016	−1.793	−282
0.8613	0.0691	4.082	−1.334	−189
x_B/x_c = 0.3448				
0.0325	0.2481	0.640	−0.251	−313
0.0648	0.2398	0.717	−0.351	−201
0.1037	0.2298	0.807	−0.474	−112
0.1297	0.2231	0.866	−0.557	−75
0.1735	0.2119	0.967	−0.696	−36
0.4142	0.1502	1.621	−1.361	−59
0.4620	0.1379	1.784	−1.460	−84
0.5087	0.1260	1.966	−1.533	−100
0.5622	0.1123	2.196	−1.596	−120
0.5869	0.1059	2.315	−1.612	−126
0.6888	0.0798	2.901	−1.585	−133
0.8730	0.0326	4.491	−1.003	−79

form:

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

Such that for the binary mixture at composition x_i^0, x_j^0.

$$x_i - x_j = x_i^0 - x_j^0 \qquad (12)$$

Tsao and Smith [9] equation is

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

Table 6

Values of coefficients A_{ABC}, B_{ABC}, C_{ABC} of Heric–Brewer Eq. (5) and Singh et al. Eq. (6) for V^E_m (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)			σ	Singh et al. Eq. (6)			σ
	A_{ABC}	B_{ABC}	C_{ABC}		A_{ABC}	B_{ABC}	C_{ABC}	
x_A 1-butanol + x_B ethyl ethanoate + x_C cyclohexane								
V^E_m	−6.195	8.271	11.772	0.005	1.094	14.222	−32.535	0.017
$\Delta\eta$	−2.151	3.792	3.012	0.009	0.041	6.121	23.739	0.010
ΔG^{*E}	−6542	8663	8250	35	−1420	15,462	105,535	34
x_A 1-pentanol + x_B ethyl ethanoate + x_C cyclohexane								
V^E_m	−0.320	−1.003	−0.068	0.004	−0.706	0.163	−14.975	0.006
$\Delta\eta$	−0.132	−3.782	5.964	0.005	1.020	10.039	−70.025	0.025
ΔG^{*E}	−3229	−5563	22,984	65	4602	30,341	−333,305	115
x_A 1-octanol + x_B ethyl ethanoate + x_C cyclohexane								
V^E_m	0.519	−5.447	−3.897	0.004	−2.423	−6.411	−81.069	0.014
$\Delta\eta$	8.109	−5.561	−8.824	0.002	3.347	−12.261	−28.065	0.013
ΔG^{*E}	22,264	−28,817	−25,567	31	5544	−30,563	−427,094	78

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_m^E/J mol^{-1}	κ_S^E/T Pa^{-1}
$C_8H_{17}OH + cC_6H_{12}$	0.307	−1.199	109		
	0.334[a]			615[b]	−4[a]
	0.342[c,d]				
$C_4H_9OH + C_4H_8O_2$	0.291	−0.619	−759		
	0.292[c,e]	−0.671[f]		1694[g]	
	0.201[h]				
$C_5H_{11}OH + C_4H_8O_2$	0.335	−0.817	−717		
	0.341[c,e]	−0.915[f]		1804[g]	
$C_8H_{17}OH + C_4H_8O_2$	0.505	−1.826			
	0.500[c,e]				
	0.246[f]	−1.811[f]		2003[g]	
$C_3H_7OH + cC_6H_{12}$	0.410[i]	−0.232[i]	−277[i]	562[b]	
$C_4H_9OH + cC_6H_{12}$	0.390[j]	−0.327[j]	−267[j]	556[b]	
$C_5H_{11}OH + cC_6H_{12}$	0.366[j]	−0.447[j]	−240[j]	570[b]	
$C_4H_8O_2 + cC_6H_{12}$	1.230[k]	−0.143[k]	−485[k]	1342[c,l]	

[a] Ref. [42].
[b] Ref. [47].
[c] 298.15 K.
[d] Ref. [43].
[e] Ref. [44].
[f] Ref. [46].
[g] Ref. [48].
[h] Ref. [45].
[i] Ref. [3].
[j] Ref. [2].
[k] Ref. [4].
[l] Ref. [49].

in which the Y_{ij}^E refers the excess property of the binary mixtures at composition $x_i{}^0, x_j{}^0$ such that $x_i{}^0 = (1 - x_j{}^0) = x_A$ for the AB and AC binary mixtures and $x_B{}^0 = x_B/(x_B + x_C)$ for the BC binary mixture.The proposed equation by Lark et al. [10] for ternary mixtures is expressed as:

$$Y_{ABC}^E = [(n_A)_{AB} + (n_B)_{AB}]Y_{AB}^E + [(n_C)_{AC} + (n_A)_{AC}]Y_{AC}^E + [(n_B)_{BC} + (n_C)_{BC}]Y_{BC}^E \qquad (14)$$

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

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

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

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

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

3.1. ERAS model

The ERAS model due to Heintz and co-workers [13,14] combines the linear chain association model with Flory's equation of state [31] 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_m^E), excess molar Gibbs energies (G_m^E), and excess molar volumes (V_m^E) and accounts for the competing effects present in the binary mixtures [32–36]. The ERAS model has also been used to predict excess properties of ternary mixtures [2–4,15,37–40] from the parameters of the binary constituents. Here, the ERAS model has been examined to predict V_m^E of ternary mixtures C_4H_9OH or $C_5H_{11}OH$ or $C_8H_{17}OH + (C_4H_8O_2 + cC_6H_{12})$ consisting of one associating component (A, 1-alkanol), 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 for ternary mixtures are given elsewhere [15,37,41]. Here we shall present only those results which are relevant to the volumetric behaviour of 1-alkanol + ethyl ethanoate + cyclohexane solutions. In accordance to that, the expressions for calculating the physical and chemical contributions (V_{phy}^E) and (V_{chem}^E) to excess molar volumes (V_m^E) of ternary mixtures can be expressed as follows:

$$V_{phy}^E = (x_A V_A^* + x_B V_B^* + x_C V_C^*)\ (\tilde{v}_M - \phi_A \tilde{v}_A - \phi_B \tilde{v}_B - \phi_C \tilde{v}_C) \qquad (18)$$

$$V_{chem}^E = \tilde{v}_M \left\{ x_A K_A\ \Delta v_A^* (\phi_{A1} - \phi_{A1}^0) + x_B K_B\ \Delta v_B^* (\phi_{B1} - \phi_{B1}^0) + x_A K_{AB} \Delta v_{AB}^* \frac{\phi_{B1}(1 - K_A \phi_{A1})}{(V_B/V_A)(1 - K_B \phi_{B1}) K_{AB} \phi_{B1}} \right\} \qquad (19)$$

Physical contributions contain the reduction and reduced parameters of the pure substances. P_i^*, V_i^*, T_i^*, and $\tilde{v}_i$ are obtained from pure component properties. X_{ij} parameters account for non-polar van der Waals interactions and must be adjusted to binary H_m^E data [31]. Chemical contributions contain the association constants K_i and K_{ij} and the corresponding association enthalpies Δh_i^* and Δh_{ij}^*, and association volumes Δv_i^* and Δv_{ij}^*. ϕ_{A1} and ϕ_{B1} are the hard core volume fractions of the monomer molecules A and B, respectively. The values of unknown cross-parameters X_{AB}, K_{AB}, Δh_{AB}^* and Δv_{AB}^* appearing in ERAS model equations were adjusted simultaneously to H_m^E and V_m^E for binary mixture data. Once all the binary parameters were known, the V_m^E of three ternary mixtures 1-alkanol (C_4H_9OH or $C_5H_{11}OH$ or $C_8H_{17}OH$) + ($C_4H_8O_2 + cC_6H_{12}$) were calculated.

4. Discussion

Table 7 shows that for the studied four binary mixtures, experimental and literature values [42–46] of $V_{\mathrm{m}}^{\mathrm{E}}$ interpolated to mole fraction 0.5 are in good agreement. The values of $\Delta\eta$ at equimolar composition reported by Nikam et al. [45,46] are in good agreement for $C_8H_{17}OH + C_4H_8O_2$ but are more negative than the present results for $C_4H_9OH + C_4H_8O_2$ and $C_5H_{11}OH + C_4H_8O_2$. The values of $V_{\mathrm{m}}^{\mathrm{E}}$ (Fig. 1) are positive and $\Delta\eta$ (Fig. 5) negative for $C_8H_{17}OH + cC_6H_{12}$ due to the breaking of hydrogen bonds in 1-octanol and non-specific interactions [41,42]. Comparing the values of $V_{\mathrm{m}}^{\mathrm{E}}$ and $\Delta\eta$ for 1-alkanol + cyclohexane (Table 7), it can be seen that $V_{\mathrm{m}}^{\mathrm{E}}$ and $\Delta\eta$ values decrease with chain length of 1-alkanol from 1-propanol to 1-octanol. By the addition of cyclohexane molecules, the polymeric alkanol molecules dissociate and have greater mobility than the pure alkanols due to greatly reduced cohesive forces of polymeric alkanol molecules upon mixing [50]. For the higher alkanol i.e., 1-octanol, the expected negative values of $\Delta G^{*\mathrm{E}}$ because of the depolymerization are masked by the positive contributions to $\Delta G^{*\mathrm{E}}$ [28,51,52] arising due to the large size difference between the two unlike components 1-octanol and cyclohexane as a result net values of $\Delta G^{*\mathrm{E}}$ are small positive.

Figs. 2–4 show that the values of $V_{\mathrm{m}}^{\mathrm{E}}$ for three binary mixtures $C_4H_9OH + C_4H_8O_2$ and $C_5H_{11}OH\ C_4H_8O_2$ and $C_8H_{17}OH + C_4H_8O_2$ are positive and $\Delta\eta$ are negative. The magnitude and sign of $V_{\mathrm{m}}^{\mathrm{E}}$ 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 [53]. It can be seen from Figs. 2–4, that the positive $V_{\mathrm{m}}^{\mathrm{E}}$ values increase systematically as the chain length of alkyl group in 1-alkanol is increased and the values of $\Delta\eta$ (Fig. 5) decrease.

In order to see the influence of variation of 1-alkanol composition in ternary mixtures, the $V_{\mathrm{m}}^{\mathrm{E}}$, $\Delta\eta$, and $\Delta G^{*\mathrm{E}}$ were studied by adding C_4H_9OH or $C_5H_{11}OH$ or $C_8H_{17}OH$ to pseudo-binary mixture ($C_4H_8O_2 + cC_6H_{12}$) of different fixed compositions for each ternary mixture (Tables 4 and 5). Tables 6 and ST1 summarize the results of different correlating equations. It is found that Eq. (7) due to Redlich–Kister gave smaller values of σ in correlating the $V_{\mathrm{m}}^{\mathrm{E}}$, $\Delta\eta$, and $\Delta G^{*\mathrm{E}}$ 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. The values of σ for $V_{\mathrm{m}}^{\mathrm{E}}$, $\Delta\eta$, and $\Delta G^{*\mathrm{E}}$ are in the range of 0.016–0.245 $\mathrm{cm^3\,mol^{-1}}$, 0.013–0.731 mPa s and 49–336 $\mathrm{J\,mol^{-1}}$ for different empirical equations. The correlating ability was improved using the correlating equations containing ternary contributory terms (Table 6). The correlation due to Heric–Brewer Eq. (5) is comparatively better than that of Singh et al. Eq. (6).

The values of $V_{\mathrm{m}}^{\mathrm{E}}$ for three ternary mixtures 1-butanol or 1-pentanol or 1-octanol + (ethyl ethanoate + cyclohexane) are large and positive (Figs. 7–9). For the equimolar composition (i.e. $x_A = x_B = x_C = 1/3$), $V_{\mathrm{m}}^{\mathrm{E}}$ values of ternary mixtures $C_4H_9OH + C_4H_8O_2 + cC_6H_{12}$, $C_5H_{11}OH + C_4H_8O_2 + cC_6H_{12}$ and $C_8H_{17}OH + C_4H_8O_2 + cC_6H_{12}$ are 0.868, 0.832 and 0.812 $\mathrm{cm^3\,mol^{-1}}$, respectively. It is observed that by the addition of 1-alkanol to pseudo-binary mixture ($C_4H_8O_2 + cC_6H_{12}$) the values of $V_{\mathrm{m}}^{\mathrm{E}}$ decrease. This is attributed to the occurrence of specific interactions between alkanol and alkanoate molecules and the dilution effect on breaking of dipolar-structure in alkanoate.

Values of equimolar, maximum and minimum $V_{\mathrm{m}}^{\mathrm{E}}$ for different ternary mixtures formed from alkanol, alkyl alkanoate and hydrocarbons are compared in supporting material as Table ST2. Mostly $V_{\mathrm{m}}^{\mathrm{E}}$ values are large and positive for ternary mixtures alkanol + alkyl alkanoate + cycloalkane. The expansive region in the ternary mixtures 1-propanol + ethyl ethanoate + cyclohexane [4], 1-butanol + ethyl ethanoate + cyclohexane, 1-pentanol + ethyl ethanoate + cyclohexane, 1-octanol + ethyl ethanoate + cyclohexane, 1-propanol + propyl propanoate + cyclohexane [54], methyl butanoate + heptane + cyclooctane [55], and propyl propanoate + hexane + cyclohexane [56], 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.

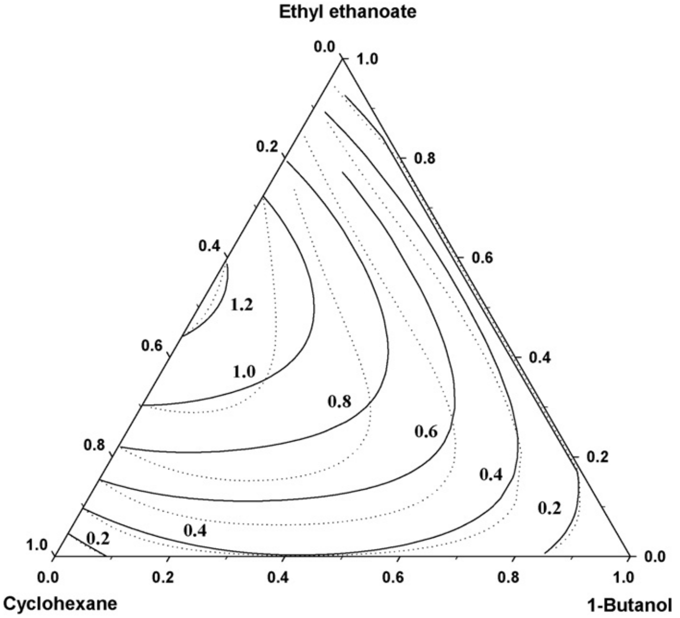

Fig. 7. Isolines at constant excess molar volumes, $V_{\mathrm{m}}^{\mathrm{E}}$ ($\mathrm{cm^3\,mol^{-1}}$) for ternary mixture of 1-butanol + ethyl ethanoate + cyclohexane correlated with Eq. (5) (——) and ERAS model (. . . .) at 303.15 K.

The values of viscosity deviations $\Delta\eta$ for all the three ternary mixtures are negative (Figs. 10–12). The values of $\Delta\eta$ for the equimolar composition are in sequence: 1-butanol + ethyl ethanoate + cyclohexane (−0.480 mPa s) > 1-pentanol + ethyl ethanoate + cyclohexane (−0.602 mPa s) > 1-octanol + ethyl ethanoate + cyclohexane (−1.285 mPa s). The

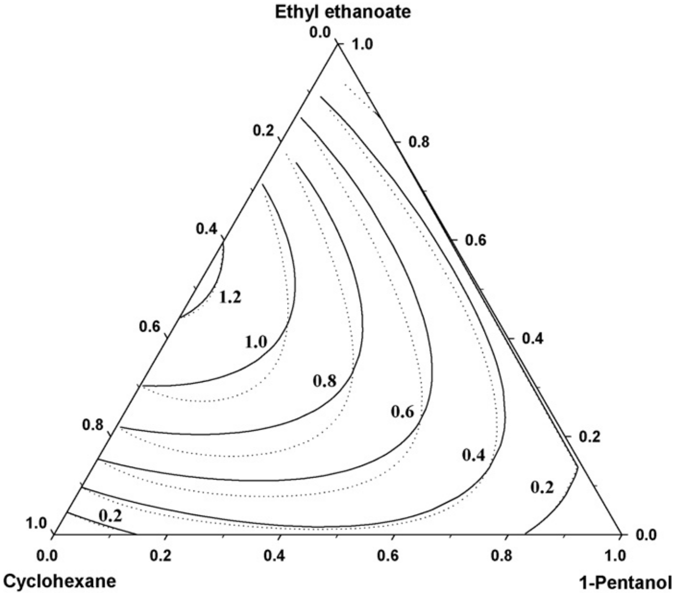

Fig. 8. Isolines at constant excess molar volumes, $V_{\mathrm{m}}^{\mathrm{E}}$ ($\mathrm{cm^3\,mol^{-1}}$) for ternary mixture of 1-pentanol + ethyl ethanoate + cyclohexane correlated with Eq. (5) (——) and ERAS model (. . . .) at 303.15 K.

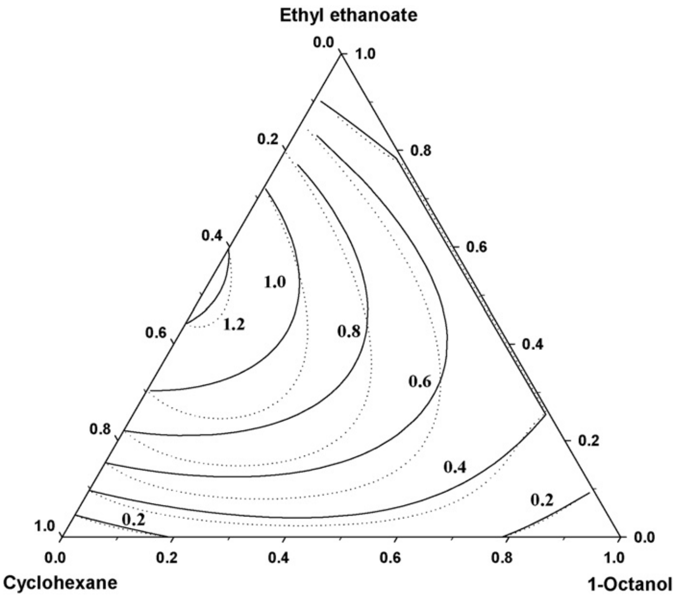

Fig. 9. Isolines at constant excess molar volumes, V_m^E (cm^3 mol^{-1}) for ternary mixture of 1-octanol + ethyl ethanoate + cyclohexane correlated with Eq. (5) (——) and ERAS model (. . . .) at 303.15 K.

negative deviations increase with the increase of chain length of alkanol from 1-propanol [4] to 1-octanol in ternary mixture 1-alkanol + ethyl ethanoate + cyclohexane. The negative values of viscosity deviations are consistent with the destruction of hydrogen bonds in 1-alkanols and dilution of dipolar order in alkanoate. The negative values of $\Delta\eta$ were also observed for methyl butanoate + heptane + cyclooctane [55], methyl pentanoate or methyl heptanoate + octane + 1-hexanol [57], and 1-hexanol + propyl propanoate + benzene [58]. The negative values observed for viscosity deviations $\Delta\eta$ of the ternary mixtures under study could be explained by the breaking of the hydrogen bonding in 1-alkanols and disruption of dipolar order that makes the mixture flow more easily. This is in accordance with the conclusions of

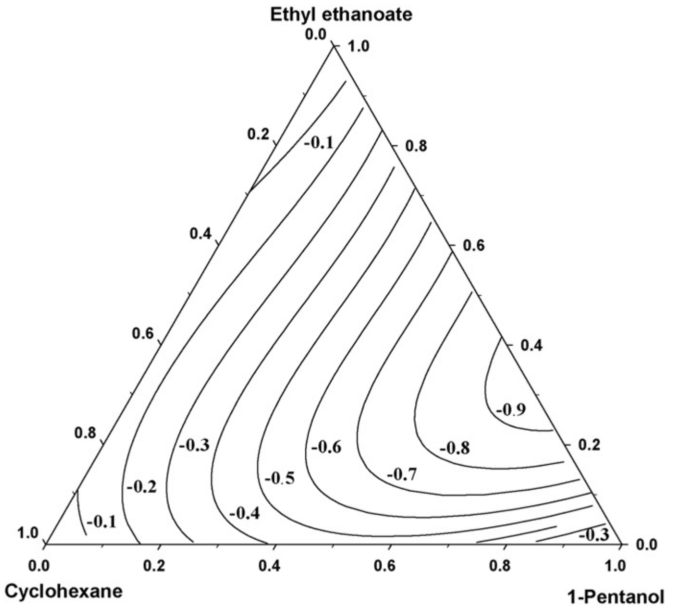

Fig. 11. Isolines at constant viscosity deviations, $\Delta\eta$ (mPa s) for ternary mixture of 1-pentanol + ethyl ethanoate + cyclohexane correlated with Eq. (5) at 303.15 K.

Fort and Moore [50] about the behaviour of systems containing an associated component.

The Gibbs energies of activation of viscous flow are negative for all three investigated mixtures (Figs. 13–15). The dependence of ΔG^{*E} on composition is complex, depending upon the different contributions in the mixture. The values of ΔG^{*E} for equimolar 1-alkanol + (ethyl ethanoate + cyclohexane) mixtures, increase with the increase in chain length of 1-alkanol.

ERAS model. Out of seven binary pairs needed to examine present three ternary mixtures, three pairs $C_4H_8O_2 + cC_6H_{12}$, $C_4H_9OH + cC_6H_{12}$ and $C_5H_{11}OH + c\ cC_6H_{12}$ have been analyzed in our previous papers [2,4]. The remaining four pairs $C_8H_{17}OH + cC_6H_{12}$, $C_4H_9OH + C_4H_8O_2$, $C_5H_{11}OH$, $C_4H_8O_2$ and $C_8H_{17}OH + C_4H_8O_2$ have been considered here. The required pure

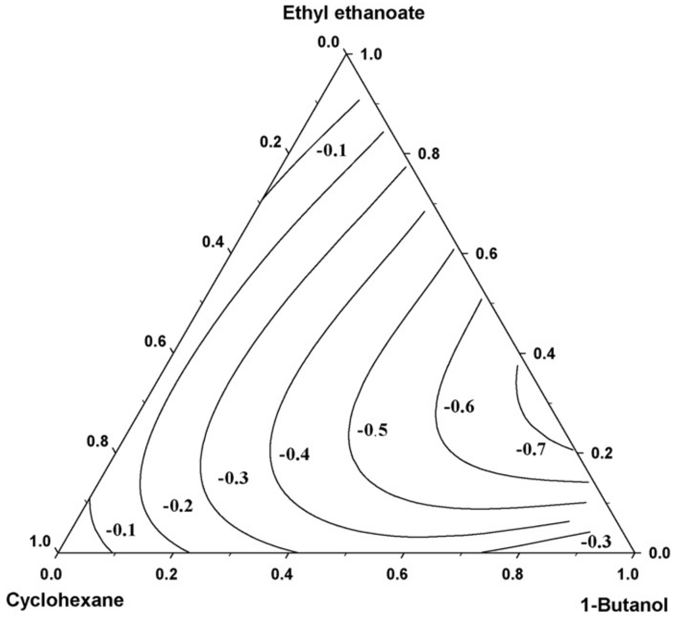

Fig. 10. Isolines at constant viscosity deviations, $\Delta\eta$ (mPa s) for ternary mixture of 1-butanol + ethyl ethanoate + cyclohexane correlated with Eq. (5) at 303.15 K.

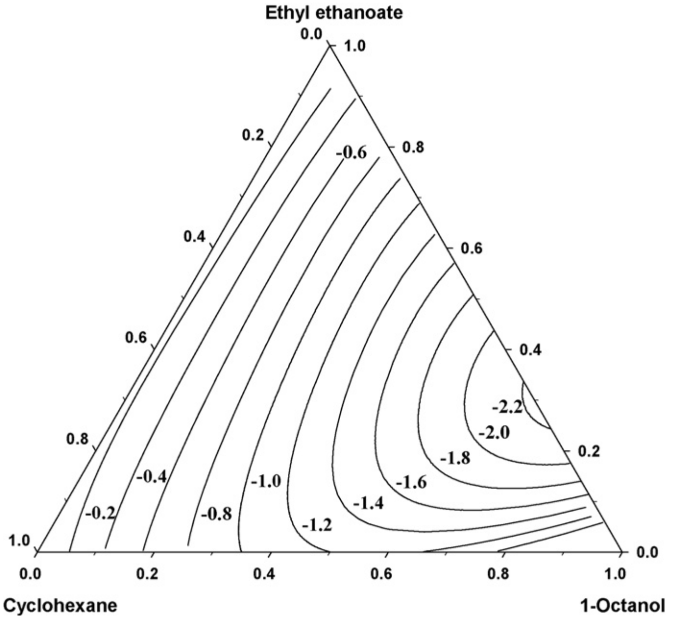

Fig. 12. Isolines at constant viscosity deviations, $\Delta\eta$ (mPa s) for ternary mixture of 1-octanol + ethyl ethanoate + cyclohexane correlated with Eq. (5) at 303.15 K.

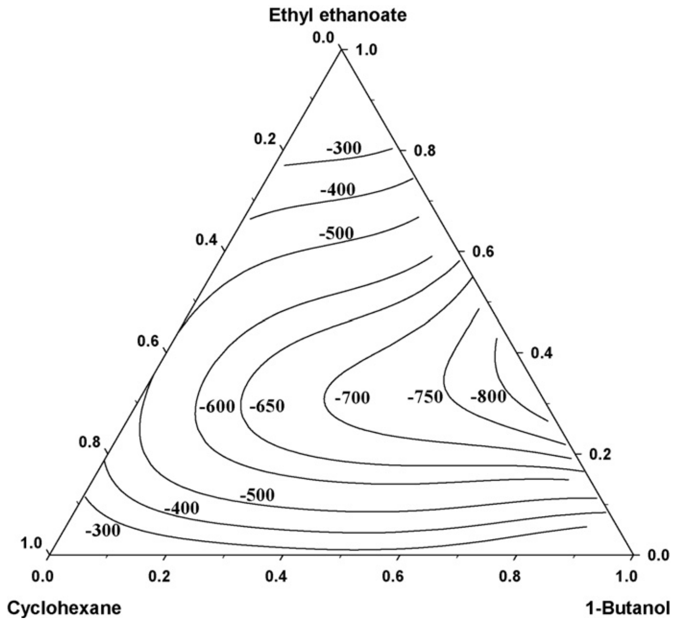

Fig. 13. Isolines at constant excess Gibbs energy of activation ΔG^{*E} (J mol^{-1}) of viscous flow for ternary mixture of 1-butanol + ethyl ethanoate + cyclohexane correlated with Eq. (5) at 303.15 K.

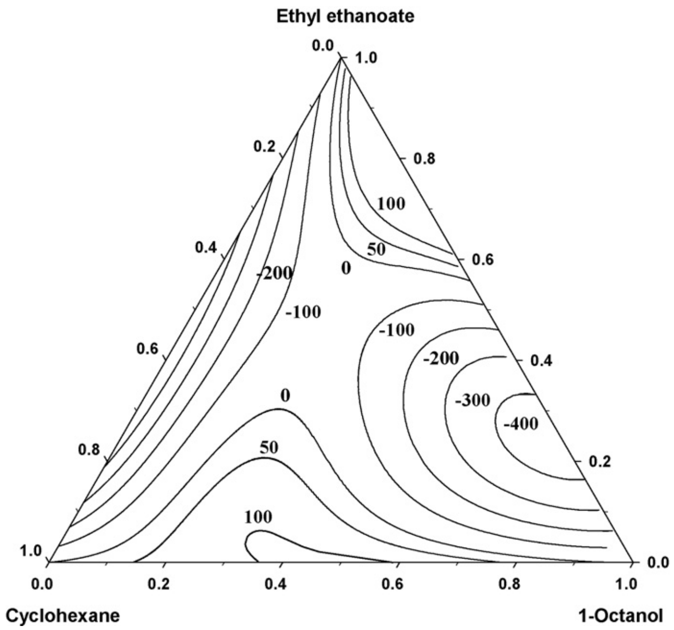

Fig. 15. Isolines at constant excess Gibbs energy of activation ΔG^{*E} (J mol^{-1}) of viscous flow for ternary mixture of 1-octanol + ethyl ethanoate + cyclohexane correlated with Eq. (5) at 303.15 K.

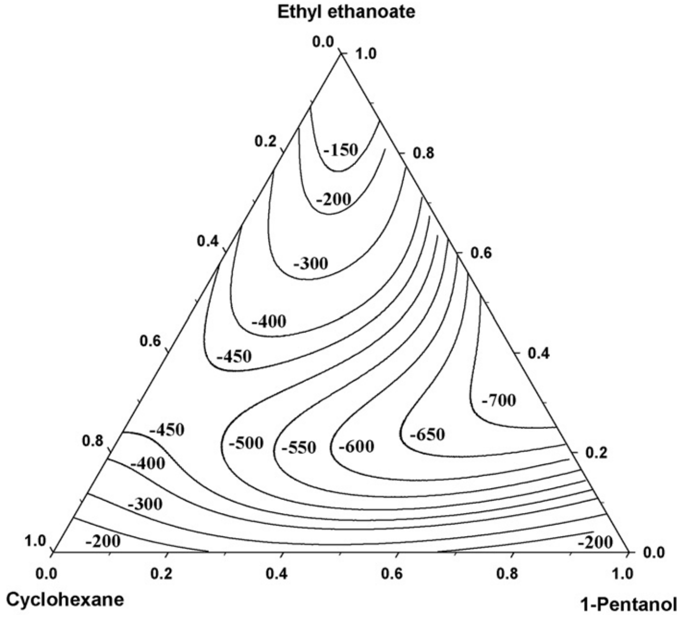

Fig. 14. Isolines at constant excess Gibbs energy of activation ΔG^{*E} (J mol^{-1}) of viscous flow for ternary mixture of 1-pentanol + ethyl ethanoate + cyclohexane correlated with Eq. (5) at 303.15 K.

component properties and the ERAS parameters are listed in Table 8. The values of surface to volume ratio (S) were taken from Bondi [59]. There is no self-association in ethyl ethanoate molecules as existed in alkanols through hydrogen bonds. However, the mixtures with ethyl ethanoate [4] have been analyzed in frame-work of the ERAS model considering weak polar-association in ethyl ethanoate. This weak self-association in the alkanoate 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 between alkyl alkanoate molecules due to their dipole moments. Accordingly, here also ethyl ethanoate was treated as a weak dipolar-associated molecule with $K_i = 1$. The values of Δh_i^* and Δv_i^* for ethyl ethanoate were estimated from the experimental H_m^E [49,62] and V_m^E data of ethyl ethanoate + cyclohexane by the ERAS model. The values of Δh_i^* and Δv_i^* were found to be −10.0 kJ mol^{-1} and −5.7 cm^3 mol^{-1} [4].

The 1-butanol, 1-pentanol, and 1-octanol interact with ethyl ethanoate to form alkanol–ethanoate complex [63]. To account for complex formation (AB), the values of cross-parameters X_{ij}, K_{ij}, Δh_{ij}^*, and Δv_{ij}^* were obtained by simultaneously adjusting the theoretical expressions of ERAS model to the experimental equimolar H_m^E [48] and the whole composition range V_m^E. The values of the cross-parameters for binary mixtures are given in Table 9.

Table 8
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}
$C_4H_8O_2$	99.16	1.392[b]	1245[b]	1	76.48	503	−10.0	−5.7	1.393
cC_6H_{12}	109.42	1.233[c]	1171[c]	–	84.33	534	–	–	1.315
C_4H_9OH	92.43	0.976[d]	976[d]	148[d]	75.73	396	−25.1[e]	−5.6[e]	1.456
$C_5H_{11}OH$	109.22	0.924[d]	918[d]	130[d]	89.48	421	−25.1[e]	−5.6[e]	1.433
$C_8H_{17}OH$	159.14	0.865[d]	799[d]	74[d]	131.55	448	−23.0[d]	−4.9[d]	1.388

[a] Calculated in accordance with Ref. [59].
[b] Ref. [60].
[c] Ref. [18].
[d] Ref. [61].
[e] Ref. [12].

Table 9
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	Phy	Chem	Total	σ
$C_4H_8O_2 + cC_6H_{12}$[a]	40.0	–	–		1.230	0.752	0.453	1.205	0.058
$C_4H_9OH + C_4H_8O_2$	7.0	5.6	−5.8	−12.4	0.290	0.294	0.008	0.302	0.023
$C_5H_{11}OH + C_4H_8O_2$	15.0	4.0	−5.8	−13.6	0.335	0.366	0.002	0.364	0.030
$C_8H_{17}OH + C_4H_8O_2$	16.6	4.0	−5.8	−9.4	0.505	0.284	0.212	0.496	0.050
$C_4H_9OH + cC_6H_{12}$[b]	9.6	–	–	–	0.392	0.119	0.440	0.559	0.125
$C_5H_{11}OH + cC_6H_{12}$[b]	11.0	–	–	–	0.363	0.110	0.378	0.488	0.112
$C_8H_{17}OH + cC_6H_{12}$	13.8	–	–	–	0.307	0.087	0.340	0.427	0.099

[a] Taken from Ref. [4].
[b] Taken from Ref. [2].

The ERAS model results are compared in Figs. 1–4. Results of calculated and their comparison with the experimental data at equimolar mixture are given in Table 9 along with the physical and chemical contributions. The values of standard deviations $\sigma(V^E_m)$ for the ERAS model are also included in Table 9. The standard deviations $\sigma(V^E_m)$ between experiment and theory are from 0.023 to 0.099 cm^3 mol^{-1}. The values of cross-parameters K_{ij}, Δh^*_{ij}, and Δv^*_{ij} for 1-alkanol + ethyl ethanoate mixtures are consistent with weak complex formation between unlike components. The physical contribution is dominating over the chemical contribution, which is reflected in to the large positive values of X_{ij} required for the ERAS model calculations.

The ERAS model is applied to three ternary mixtures: $C_4H_9OH + C_4H_8O_2 + cC_6H_{12}$, $C_5H_{11}OH + C_4H_8O_2 + cC_6H_{12}$, and $C_8H_{17}OH + C_4H_8O_2 + cC_6H_{12}$. V^E_m of ternary mixtures were calculated using binary parameters of constituent pairs and the results are presented in supporting material as Table ST 3. The results are compared graphically in Figs. 7–9. The values of $\sigma(V^E_m)$ for the present ternary mixtures are in the range from 0.044 to 0.071 cm^3 mol^{-1}. Thus adequate agreement between experimental and ERAS model values is obtained. However, prediction of V^E_m at lower mole fraction of alkanol is not as good as at higher concentration. The physical and chemical contributions to total V^E_m are positive for all the three ternary mixtures of 1-alkanol with (ethyl ethanoate + cyclohexane). The magnitude of each contribution depends on composition and size of 1-alkanol involved, e.g. physical contribution in $C_4H_9OH + C_4H_8O_2 + cC_6H_{12}$ and $C_5H_{11}OH + C_4H_8O_2 + cC_6H_{12}$ is dominating over the chemical contribution while in case of $C_8H_{17}OH + C_4H_8O_2 + cC_6H_{12}$ both are of equal significance.

5. Conclusions

In this work, V^E_m, $\Delta\eta$, and ΔG^{*E} have been determined from densities and viscosities measurements for three ternary mixtures C_4H_9OH or $C_5H_{11}OH$ or $C_8H_{17}OH + C_4H_8O_2 + cC_6H_{12}$ and four binaries $C_4H_9OH + C_4H_8O_2$, $C_5H_{11}OH + C_4H_8O_2$, $C_8H_{17}OH + C_4H_8O_2$, and $C_8H_{17}OH + cC_6H_{12}$ at 303.15 K.

The large and positive values of V^E_m for 1-alkanol + ethyl ethanoate + cyclohexane indicate that the positive contributions due to dispersion interactions and disruption of H-bonds in 1-alkanols and dipolar-order in ethyl ethanoate by cyclohexane molecules are dominating over the specific interaction between alkanol and ethanoate pair.

The Heric–Brewer equation with ternary contributory terms provides the good correlation of ternary data.

The ERAS model gives an adequate quantitative representation of V^E_m except at lower mole fraction of alkanol in the investigated ternary mixtures using model parameters obtained from data of the constituting binaries.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2009.02.022.

References

[1] S.L. Oswal, S.G. Patel, J. Chem. Soc., Faraday Trans. 90 (1995) 1083–1088.
[2] R.L. Gardas, S.L. Oswal, J. Solution Chem. 37 (2008) 1449–1470.
[3] R.L. Gardas, S.L. Oswal, Thermochim. Acta 479 (2008) 17–27.
[4] S.L. Oswal, N.Y. Ghael, R.L. Gardas, Thermochim. Acta 484 (2009) 11–21.
[5] O. Redlich, A.T. Kister, Ind. Eng. Chem. 40 (1948) 341–345.
[6] F. Kohler, Monatsh. Chem. 91 (1960) 738–740.
[7] R.P. Rastogi, J. Nath, S.S. Das, J. Chem. Eng. Data 22 (1977) 249–252.
[8] K.T. Jacob, K. Fitzner, Thermochim. Acta 18 (1977) 197–206.
[9] C.C. Tsao, J.M. Smith, Chem. Eng. Prog. Symp. Ser. 49 (7) (1953) 107–117.
[10] B. Lark, S. Kaur, S. Singh, Indian J. Chem. 26A (1987) 1109–1114.
[11] E.L. Heric, J.G. Brewer, J. Chem. Eng. Data 14 (1969) 55–63.
[12] P.P. Singh, R.K. Nikam, S.P. Sharma, S. Aggarwal, Fluid Phase Equilibr. 18 (1984) 333–344.
[13] A. Heintz, Ber. Bunsenges. Phys. Chem. 89 (1985) 172–181.
[14] H. Funke, M. Wetzel, A. Heintz, Pure Appl. Chem. 61 (1989) 1429–1439.
[15] M. Bender, J. Hauser, A. Heintz, Ber. Bunsenges. Phys. Chem. 95 (1991) 801–811.
[16] J.A. Riddick, W.B. Bunger, T.K. Sakano, Organic Solvents Physical Properties and Methods of Purification, Wiley Interscience, New York, 1986.
[17] R.H. Stokes, J. Chem. Thermodyn. 5 (1973) 379–385.
[18] K. Tamura, S. Murakami, S. Doi, J. Chem. Thermodyn. 17 (1985) 325–333.
[19] C. Yang, Z. Liu, H. Lai, P. Ma, J. Chem. Thermodyn. 39 (2007) 28–38.
[20] J. Timmermans, Physico Chemical Constant of Pure Organic Compounds, vol. 2, Elsevier Publ. Co., 1965.
[21] N.N. Wankhede, D.S. Wankhede, M.K. Lande, B.R. Arbad, J. Chem. Thermodyn. 38 (2006) 1664–1668.
[22] J.L. Hales, J.H. Ellender, J. Chem. Thermodyn. 8 (1976) 1177–1184.
[23] M. Diaz-Pena, G. Tardajos, J. Chem. Thermodyn. 11 (1979) 441–445.
[24] B. Garcia, C. Herrera, J.M. Lead, J. Chem. Eng. Data 36 (1991) 269–274.
[25] T.M. Aminabhavi, M.I. Aralaguppi, S.B. Harogoppad, R.H. Balundgi, J. Chem. Eng. Data 38 (1993) 310–319.
[26] L. Ubbelohde, Ind. Eng. Chem. Anal. 9 (1937) 85–90.
[27] F.A. Goncalves, J. Kestin, J.V. Senger, Int. J. Thermophys. 12 (1991) 1013–1028.
[28] S.L. Oswal, A.T. Patel, Int. J. Thermophys. 12 (1991) 821–835.
[29] S.G. Patel, S.L. Oswal, J. Chem. Soc., Faraday Trans. 88 (1992) 2497–2502.
[30] S. Glasstone, K.J. Laidler, H. Eyring, The Theory of Rate Process, McGraw-Hill, New York, 1941, pp. 514–516.
[31] P.J. Flory, R.A. Orwoll, A. Vrij, J. Am. Chem. Soc. 86 (1964) 3507–3515.
[32] M. Bender, A. Heintz, Fluid Phase Equilibr. 89 (1993) 197–215.
[33] M. Iglesias, B. Orge, J.M. Canosa, A. Rodrıguez, M. Domınguez, M.M. Pineiro, J. Tojo, Fluid Phase Equilibr. 147 (1998) 285–300.
[34] B. Orge, M. Iglesias, G. Marino, M. Domınguez, M.M. Pineiro, J. Tojo, Fluid Phase Equilibr. 170 (2000) 151–163.
[35] S.L. Oswal, Thermochim. Acta 425 (2005) 59–68.
[36] S.L. Oswal, K.D. Prajapati, N.Y. Gahel, S. Ijardar, Fluid Phase Equilibr. 218 (2004) 131–140.
[37] M. Keller, S. Schnabel, A. Heintz, Fluid Phase Equilibr. 110 (1995) 231–265.
[38] I. Gascon, S. Martin, B. Giner, M. Haro, C. Lafuente, Can. J. Chem. 81 (2003) 357–363.
[39] M. Haro, I. Gascon, P. Cea, C. Lafuente, F.M. Royo, J. Thermal Anal. Calorim. 79 (2005) 51–57.

[40] M. Kwaterski, E.N. Rezanova, R.N. Lichtenthaler, J. Chem. Thermodyn. 38 (2006) 1199–1213.
[41] N.Y. Ghael, Ph.D. Thesis, V.N. South Gujarat University, Surat (2004).
[42] S.L. Oswal, K.D. Prajapati, J. Chem. Eng. Data 43 (1998) 367–372.
[43] J.M. Jansens, M. Ruel, Can. J. Chem. Eng. 50 (1972) 591–594.
[44] J. Ortega, J.A. Pena, M.I. Paz-Andrade, Aust. J. Chem. 39 (1986) 1685–1690.
[45] S. Nikam, R.M. Tukaram, M. Hasan, J. Chem. Eng. Data 41 (1996) 1055–1058.
[46] S. Nikam, R.M. Tukaram, M. Hasan, J. Chem. Eng. Data 43 (1998) 436–440.
[47] J.J. Christensen, R.W. Hanks, R.M. Izatt, Handbook of Heats of Mixing, Wiley Interscience, N.Y., 1982.
[48] J.L. Legido, J. Vijande, B.E. de Cominges, J. Garcia, T.P. Iglesias, S. Garcia-Garabal, J. Fernandez, Fluid Phase Equilibr. 148 (1998) 49–68.
[49] O. Dusart, J.P.E. Grolier, A. Viallard, Bull. Soc. Chim. Fr. (1977) 587–592.
[50] R.J. Fort, W.R. Moore, Trans. Faraday Soc. 62 (1966) 1112–1116.
[51] G. Delmas, P. Purves, P. de Saint Romain, J. Phys. Chem. 79 (1975) 1970–1974.
[52] A. Aucejo, M.C. Burguet, R. Munoz, J.L. Marques, J. Chem. Eng. Data 40 (1995) 141–147.
[53] S.L. Oswal, S.R. Putta Sharmila, Thermochim. Acta 373 (2001) 141–152.
[54] C. Franjo, M.T. Lorenzana, J.L. Legido, M.I. Paz Andrade, E. Jimenez, J. Chem. Thermodyn. 26 (1994) 1025–1030.
[55] J.L. Trenzado, J.S. Matos, R. Alcalde, Fluid Phase Equilibr. 200 (2002) 295–315.
[56] M.J. Souza, E. Jimenez, J.L. Legido, J. Fernandez, E. Perez-Martell, M.I. Paz Andrade, J. Chem. Thermodyn. 24 (1992) 119–128.
[57] J.L. Trenzado, J.S. Matos, E. Gonzalez, E. Romano, M.N. Caro, J. Chem. Eng. Data 48 (2003) 1004–1014.
[58] H. Casas, S. García-Garabal, L. Segade, O. Cabeza, C. Franjo, E. Jimenez, J. Chem. Thermodyn. 35 (2003) 1129–1137.
[59] A. Bondi, Physical Properties of Molecular Crystals, Liquids and Glasses, Wiley, New York, 1968.
[60] S.L. Oswal, P. Oswal, P.S. Modi, J.P. Dave, R.L. Gardas, Thermochim. Acta 410 (2004) 1–14.
[61] S.L. Oswal, K.D. Prajapati, P. Oswal, N.Y. Ghael, S.P. Ijardar, J. Mol. Liq. 116 (2005) 73–82.
[62] D.D. Deshpande, C.S. Prabhu, Indian J. Chem. Sec. A 16 (1978) 95–98.
[63] I. Nagata, Fluid Phase Equilibr. 1 (1977) 93–111.