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Excess molar volumes of binary mixtures of alkanols with ethyl acetate from 298.15 to 323.15 K

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Abstract

Excess molar volumes V^E have been investigated from density ρ measurements using vibrating-tube digital densimeter DMA 60/602 for binary mixtures of methanol, 1-propanol, 2-propanol and 1-hexanol with ethyl acetate in the temperature range 298.15–323.15 K. Thermal expansion coefficients α and their excess values α^E were evaluated. The results were analyzed and discussed in terms of dependence of V^E on chain length of alkanol and position of hydroxyl group and effect of temperature. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Alkanol; Association; Ethyl acetate; Binary liquid mixtures; Excess molar volumes; Molecular interactions

1. Introduction

The extensive information on the thermodynamic properties of alkanol + alkanoate binary mixtures is needed not only as their use is increasing in many industrial process as solvent but also for the advancement of theoretical developments through an understanding of the intermolecular forces–solution structure–property relationship [1–8]. The systems of alkanols with alkyl acetate are of considerable interest from the two counts: (i) breaking of H-bonded structures of alkanols and (ii) formation of new H-bonded molecular complexes between alkanol and alkyl acetate. The specific interactions of alkyl acetate with the alkanols can be visualized due to presence of lone pair of electrons on the oxygen atom of alkyl acetate, on account of which it can act as a strong proton-acceptor from the alkanol. Further, these systems are also an ideal choice to examine ideal associated solution models with Flory's interaction term to predict and analyze theoretically the excess molar volumes and their temperature dependence [9,10].

With these considerations, we report in this paper the measurements on excess molar volumes V^E for binary mixtures of methanol, 1-propanol, 2-propanol, and 1-hexanol with ethyl acetate over the entire range of composition and from 298.15 to 323.15 K.

2. Experimental

Ethyl acetate (BDH, AR) was dried over anhydrous K_2CO_3 for more than 72 h, and then was fractionally distilled twice before use [11]. Methanol (Ranbaxy AR, purity >99.5 mol%), was dried over molecular sieve type 4A (Fluka) and fractionally distilled twice, just before use [11]. 1-Propanol (Ranbaxy AR, >99.9 mol%) and 2-propanol (Ranbaxy AR,

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>99.5 mol%) were purified by refluxing over lime for 5 h and then distilling through 1 m column [11]. 1-Hexanol (BDH, Poole England, >98.5 mol%) was dried over molecular sieve 4A and distilled fractionally.

The purity of all the liquids was checked by measuring normal boiling points and through g.l.c. analysis. The experimental densities with the literature values are compared in Table 1. The agreement between the two sets is good. The estimated purity of all the samples was >99.9% except 1-hexanol whose purity was >99.5%

The densities ρ were measured with an Anton Paar vibrating-tube digital densimeter (model DMA 60/602) with a thermostated bath controlled to ±0.01 K. The details of the method used to determine density has been described earlier [12].

Liquid mixtures were prepared by weight, in ground glass narrow-opening stoppered bottles, with a precision digital Mettler Balance (AE 163, Switzerland) possessing an accuracy of 0.01 mg. The possible error in the mole fraction is estimated to be less than $\pm 1 \times 10^4$. The densities ρ were reproducible to within ± 0.02 kg m^{-3}.

3. Results

The densities ρ for pure liquids and for the binary mixtures at number of mole fractions were determined in the temperature range 298.15–323.15 K at intervals of 5 K. The experimental ρ at different temperatures were fitted to a polynomial equation of type

$$\rho = \sum_{i=1}^{m=3} A_i (T - 273.15)^{i-1} \tag{1}$$

The coefficients A_i and the standard deviations σ obtained by the method of least squares using computer programming σ are listed in Table 2.

Table 1
Comparison of densities of pure liquids

Liquids	Temperature (K)	Density (kg m^{-3})	
		Experimental	Literature
Methanol	298.15	786.66	786.37 [25], 786.4 [26], 786.54 [27], 786 64 [28]
	303.15	781.90	781.5 [25], 781.81 [27]
	308.15	777.23	777.16 [27]
	313.15	772.50	772.32 [27]
	318.15	767.68	767.53 [27], 776.59 [29]
	323.15	762.86	
1-Propanol	298.15	799.92	799.60 [25], 799.75 [11], 799.81 [30], 799.91 [29]
	303.15	795.88	795.1 [25]
	308.15	791.84	791.85 [29]
	313.15	787.73	787.46 [30], 787.5 [31], 787.75 [28]
	318.15	783.53	783.59 [29]
2-Propanol	298.15	781.25	780.93 [25]
	303.15	777.04	776.75 [25], 776.90 [11]
	313.15	768.40	
	318.15	763.92	
1-Hexanol	298.15	815.75	815.34 [30], 815.65 [28], 815.9 [28,11], 816.2 [31]
	303.15	812.03	812.01 [11]
	308.15	808.34	808.54 [29], 807.83 [32,33]
	318.15	800.83	801.23 [29]
	323.15	797.08	796.86 [32,33], 797.9 [31]
Ethyl acetate	298.15	894.72	894.45 [11], 894.55 [34]
	303.15	888.55	888.51 [35], 888.6 [11]
	313.15	875.13	876.03[a]
	323.15	863.66	863.75[a]

[a] International critical tables.

Table 2
Coefficients A_i of Eq. (1) and standard deviations for density in kg m^{-3}

x_1	A_1	A_2	$A_3 \times 10^3$	σ
Ethyl acetate + methanol mixture				
0.0000	809.603	−0.9026	−0.6429	0.035
0.0443	821.350	−0.9217	−0.6500	0.011
0.0887	831.787	−0.9429	−0.6357	0.014
0.1066	835.737	−0.9527	−0.6286	0.019
0.1335	841.100	−0.9593	−0.6643	0.007
0.1798	849.560	−0.9711	−0.7429	0.013
0.2726	864.654	−1.0140	−0.6571	0.011
0.3693	877.579	−1.0514	−0.5929	0.019
0.4685	888.503	−1.0786	−0.6143	0.021
0.5140	892.956	−1.0925	−0.5857	0.027
0.5197	893.490	−1.0936	−0.5929	0.022
0.5654	897.601	−1.1044	−0.6143	0.031
0.6712	905.947	−1.1304	−0.5786	0.028
0.7759	912.997	−1.1540	−0.5357	0.017
0.8731	918.857	−1.1823	−0.4357	0.009
0.9337	922.046	−1.1959	−0.4286	0.005
1.0000	925.269	−1.2112	−0.4214	0.017
Ethyl acetate + 1-propanol mixture				
0.0000	819.099	−0.7392	−1.1357	0.017
0.0453	824.906	−0.7678	−1.1429	0.011
0.0918	830.860	−0.8011	−1.0571	0.018
0.1090	832.856	−0.8064	−1.1071	0.011
0.1360	836.140	−0.8203	−1.1429	0.020
0.1831	841.847	−0.8474	−1.1214	0.027
0.2761	852.580	−0.8925	−1.1214	0.021
0.3734	863.474	−0.9441	−1.0214	0.010
0.4731	874.250	−0.9924	−0.9643	0.017
0.5196	879.146	−1.0148	−0.9286	0.027
0.5712	884.520	−1.0414	−0.8500	0.011
0.5726	884.626	−1.0396	−0.8857	0.012
0.6727	894.737	−1.0848	−0.7857	0.013
0.7769	904.944	−1.1327	−0.6286	0.060
0.7790	905.094	−1.1326	−0.6357	0.005
0.8840	914.969	−1.1767	−0.4857	0.025
0.8897	915.609	−1.1842	−0.4143	0.016
0.9423	920.259	−1.1982	−0.4143	0.019
1.0000	925.269	−1.2112	−0.4214	0.017
Ethyl acetate + 2-propanol mixture				
0.0000	800.574	−0.7216	−2.0786	0.027
0.0447	806.950	−0.7559	−2.0643	0.015
0.0928	813.676	−0.7929	−1.9643	0.020
0.1107	816.196	−0.8066	−1.9429	0.018
0.1390	820.287	−0.8343	−1.8429	0.008
0.1857	826.577	−0.8631	−1.8286	0.019
0.2792	839.336	−0.9348	−1.5643	0.029
0.3758	851.933	−0.9927	−1.3643	0.051
0.4618	862.850	−1.0398	−1.2071	0.019
0.4762	864.494	−1.0400	−1.2643	0.025
0.5268	870.800	−1.0677	−1.1214	0.023
0.5787	876.894	−1.0787	−1.1786	0.018
0.6805	889.380	−1.1411	−0.7000	0.008
0.7829	901.356	−1.1800	−0.5143	0.028
0.8870	913.351	−1.2164	−0.2714	0.016
0.9379	918.857	−1.2194	−0.3071	0.020
0.9422	919.063	−1.2085	−0.4071	0.007
1.0000	925.269	−1.2112	−0.4214	0.017
Ethyl acetate + 1-hexanol mixture				
0.0000	834.111	−0.7282	−0.2500	0.016
0.0467	837.154	−0.7500	−0.3000	0.013
0.0926	840.061	−0.7657	−0.3571	0.014
0.1103	841.557	−0.7861	−0.2786	0.016
0.1380	843.347	−0.7952	−0.3143	0.013
0.1855	846.773	−0.8208	−0.2929	0.015
0.2812	853.639	−0.8572	−0.3643	0.011
0.3778	861.230	−0.8935	−0.5071	0.025
0.4768	869.619	−0.9394	−0.5357	0.016
0.5231	873.853	−0.9646	−0.4786	0.014
0.5789	878.893	−0.9875	−0.5214	0.017
0.6795	888.786	−1.0402	−0.4929	0.014
0.7830	899.459	−1.0885	−0.4929	0.011
0.8911	912.079	−1.1590	−0.4000	0.016
0.9452	918.390	−1.1805	−0.4714	0.023
1.0000	925.269	−1.2112	−0.4214	0.017

Thermal expansion coefficient α defined as $\alpha = V^{-1}(\mathrm{d}V/\mathrm{d}T)_{\mathrm{P}}$ was calculated at each temperature from the experimental ρ at different temperatures using relation

$$\alpha = -\rho^{-1}\left(\frac{\mathrm{d}\rho}{\mathrm{d}T}\right)_{\mathrm{P}} \tag{2}$$

The V^{E} has been calculated from the molar masses M and the densities of binary mixtures ρ and of pure components ρ_i as

$$V^{\mathrm{E}} = \sum_{i=1}^{2} x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i}\right) \tag{3}$$

The values of excess thermal expansion coefficient α^{E} were calculated as [13]

$$\alpha^{\mathrm{E}} = \alpha - \phi_1\alpha_1 - \phi_2\alpha_2 \tag{4}$$

where ϕ_i represents the volume fraction of component i.

The experimental results for ρ, α, V^{E} and α^{E} for binary mixtures are recorded in Tables 3–6. The estimated accuracy of α, and V^{E} is 1×10^{-3} K^{-1} and 5×10^{-3} cm^3 mol^{-1} for the systems listed in

Table 3
Properties of ethyl acetate + methanol mixture

x_1	ρ (kg m^{-3})	α (kK^{-1})	V^E (cm^3 mol^{-1})	α^E (kK^{-1})
Ethyl acetate + methanol at 298.15 K				
0.0000	786.66	1.188		
0.0443	797.91	1.196	−0.0196	−0.011
0.0887	807.82	1.207	−0.0327	−0.017
0.1066	811.53	1.213	−0.0391	−0.017
0.1335	816.70	1.215	−0.0423	−0.024
0.1798	824.82	1.222	−0.0451	−0.031
0.2726	838.89	1.248	−0.0581	−0.030
0.3693	850.91	1.270	−0.0674	−0.029
0.4685	861.14	1.288	−0.0734	−0.029
0.5140	865.29	1.296	−0.0773	−0.028
0.5197	865.79	1.297	−0.0780	−0.028
0.5654	869.62	1.305	−0.0817	−0.026
0.6712	877.34	1.321	−0.0749	−0.024
0.7759	883.82	1.336	−0.0611	−0.021
0.8731	889.03	1.354	−0.0449	−0.012
0.9337	891.88	1.365	−0.0258	−0.007
1.0000	894.72	1.377		
Ethyl acetate + methanol at 303.15 K				
0 0000	781.90	1.204		
0.0443	793.10	1.211	−0.0244	−0.012
0.0887	802.92	1.222	−0.0397	−0.018
0.1066	806.59	1.228	−0.0466	−0.018
0.1335	811.73	1.231	−0.0521	−0.024
0.1798	819.75	1.239	−0.0556	−0.030
0.2726	833.65	1.264	−0.0703	−0.029
0.3693	845.53	1.286	−0.0819	−0.028
0.4685	855.62	1.304	−0.0887	−0.028
0.5140	859.62	1.312	−0.0854	−0.027
0.5197	860.12	1.313	−0.0866	−0.027
0.5654	863.88	1.321	−0.0891	−0.026
0.6712	871.49	1.337	−0.0823	−0.023
0.7759	877.88	1.351	−0.0689	−0.021
0.8731	882.99	1.369	−0.0502	−0.012
0.9337	885.78	1.379	−0.0291	−0.008
1.0000	888.55	1.392		
Ethyl acetate + methanol at 308.15 K				
0.0000	777.23	1.219		
0.0443	788.30	1.226	−0.0254	−0.012
0.0887	798.02	1.237	−0.0425	−0.018
0.1066	801.62	1.243	−0.0483	−0.018
0.1335	806.71	1.247	−0.0550	−0.023
0.1798	814.66	1.256	−0.0612	−0.028
0.2726	828.36	1.280	−0.0759	−0.028
0.3693	840.04	1.301	−0.0855	−0.028
0.4685	850.00	1.319	−0.0938	−0.027
0.5140	854.03	1.327	−0.0980	−0.026
0.5197	854.51	1.328	−0.0982	−0.026
0.5654	858.23	1.337	−0.1024	−0.024
0.6712	865.67	1.353	−0.0911	−0.022
0.7759	871.96	1.366	−0.0779	−0.020
0.8731	876.95	1.383	−0.0551	−0.012
0.9337	879.67	1.394	−0.0311	−0.007
1.0000	882.38	1.406		
Ethyl acetate + methanol at 313.15 K				
0.0000	772.50	1.235		
0.0443	783.45	1.243	−0.0270	−0.011
0.0887	793.04	1.253	−0.0444	−0.018
0.1066	796.61	1.259	−0.0514	−0.018
0.1335	801.67	1.263	−0.0608	−0.023
0.1798	809.54	1.273	−0.0693	−0.027
0.2726	823.05	1.296	−0.0851	−0.028
0.3693	834.57	1.317	−0.0962	−0.027
0.4685	844.37	1.336	−0.1043	−0.026
0.5140	848.32	1.343	−0.1072	−0.026
0.5197	848.80	1.344	−0.1080	−0.026
0.5654	852.44	1.353	−0.1103	−0.023
0.6712	859.80	1.369	−0.1028	−0.021
0.7759	865.97	1.382	−0.0879	−0.019
0.8731	870.86	1.398	−0.0632	−0.012
0.9337	873.52	1.408	−0.0375	−0.008
1.0000	876.13	1.421		
Ethyl acetate + methanol at 318.15 K				
0.0000	767.68	1.251		
0.0443	778.56	1.259	−0.0310	−0.011
0.0887	788.08	1.269	−0.0519	−0.017
0.1066	791.62	1.275	−0.0600	−0.018
0.1335	796.58	1.279	−0.0676	−0.022
0.1798	804.34	1.290	−0.0760	−0.025
0.2726	817.68	1.312	−0.0932	−0.027
0.3693	829.06	1.333	−0.1064	−0.027
0.4685	838.71	1.352	−0.1141	−0.025
0.5140	842.60	1.359	−0.1169	−0.025
0.5197	843.07	1.360	−0.1175	−0.025
0.5654	846.65	1.370	−0.1194	−0.021
0.6712	853.94	1.385	−0.1157	−0.020
0.7759	860.00	1.398	−0.0994	−0.018
0.8731	864.78	1.413	−0.0712	−0.013
0.9337	867.36	1.423	−0.0411	−0.008
1.0000	869.90	1.436		
Ethyl acetate + methanol at 323.15 K				
0.0000	762.86	1.267		
0.0443	773.64	1.275	−0.0335	−0.011
0.0887	783.05	1.285	−0.0554	−0.017
0.1066	786.52	1.291	−0.0622	−0.017
0.1335	791.48	1.296	−0.0740	−0.021
0.1798	799.15	1.308	−0.0838	−0.023
0.2726	812.32	1.329	−0.1027	−0.026
0.3693	823.53	1.349	−0.1158	−0.026
0.4685	833.05	1.368	−0.1248	−0.024
0.5140	836.87	1.375	−0.1267	−0.024
0.5197	837.33	1.377	−0.1271	−0.023
0.5654	840.85	1.386	−0.1284	−0.021
0.6712	847.96	1.401	−0.1182	−0.019
0.7759	853.95	1.414	−0.1040	−0.017

Table 3 (*Continued*)

x_1	ρ (kg m^{-3})	α (kK^{-1})	V^E (cm^3 mol^{-1})	α^E (kK^{-1})
0.8731	858.65	1.428	−0.0749	−0.013
0.9337	861.18	1.438	−0.0436	−0.008
1.0000	863.66	1.451		

Tables 3–6. The experimental V^E and α^E values were fitted to a Redlich–Kister [14] polynomial equation of the type

$$V^E \text{ or } \alpha^E = x_1 x_2 \sum_{i=1}^{m} A_i (1 - 2x_1)^{i-1} \tag{5}$$

The coefficients A_i of Eq. (5), and the standard deviations σ obtained from the least-squares method are listed in Tables 7 and 8.

4. Discussion

Figs. 1–4 show V^E plotted against x_1 and V^E curves obtained from the smoothing Eq. (5). The V^E are negative for ethyl acetate + methanol and positive for ethyl acetate + 1-propanol, +2-propanol, and + 1-hexanol, over the entire range of composition and at all temperatures. It can be seen from Figs. 1–4 that the magnitude of V^E increases with the rise in temperature. The values of α^E as can be seen from Tables 3–6 and Fig. 5 have the same sign as that of V^E.

We have been able to find published V^E data for all four binary mixtures but only at 298.15 K. Present experimental values and literature values of V^E interpolated to mole fraction 0.5 are listed in Table 9. Our results agree very well with those obtained by various other authors. Thus, at $x_1 = 0.5$, our values for ethyl acetate + methanol −0.0745 cm^3 mol^{-1} may be compared with the −0.072 cm^3 mol^{-1} reported by Ortega et al. [15], −0.073 cm^3 mol^{-1} reported by Nagata et al. [3] and −0.076 cm^3 mol^{-1} by Nakanishi and Shiraj [1]. Our values for ethyl acetate + 1-propanol 0.2358 cm^3 mol^{-1}, ethyl acetate + 2-propanol 0.4750 cm^3 mol^{-1} and for ethyl acetate + 1-hexanol 0.3860 cm^3 mol^{-1} are also very close to 0.2369 cm^3 mol^{-1}, of Ortega et al. [15]; 0.47 cm^3 mol^{-1} of Grolier and Viallard [2] and 0.387 cm^3 mol^{-1} of Ortega et al. [15,16], respectively. There are nevertheless wide discrepancies between the

Table 4
Properties of ethyl acetate + 1-propanol mixture

x_1	ρ (kg m^{-3})	α (kK^{-1})	V^E (cm^3 mol^{-1})	α^E (kK^{-1})
Ethyl acetate + 1-propanol at 298.15 K				
0.0000	799.92	0.995		
0.0453	805.00	1.025	0.0446	0.008
0.0918	810.18	1.054	0.0793	0.014
0.1090	812.01	1.061	0.0967	0.013
0.1360	814.93	1.077	0.1157	0.017
0.1831	819.98	1.102	0.1421	0.020
0.2761	829.57	1.143	0.1915	0.021
0.3734	839.23	1.186	0.2263	0.023
0.4731	848.84	1.226	0.2369	0.024
0.5196	853.19	1.244	0.2373	0.025
0.5712	857.95	1.263	0.2318	0.025
0.5726	858.08	1.263	0.2314	0.025
0.6727	867.13	1.296	0.2019	0.022
0.7769	876.24	1.329	0.1537	0.021
0.7790	876.38	1.329	0.1568	0.020
0.8840	885.24	1.357	0.0923	0.015
0.8897	885.75	1.360	0.0843	0.016
0.9423	890.04	1.370	0.0490	0.010
1.0000	894.72	1.377		
Ethyl acetate + 1-propanol at 303.15 K				
0.0000	795.88	1.014		
0.0453	800.84	1.044	0.0455	0.008
0.0918	805.87	1.073	0.0838	0.015
0.1090	807.66	1.081	0.1012	0.015
0.1360	810.48	1.097	0.1238	0.018
0.1831	815.39	1.122	0.1532	0.022
0.2761	824.78	1.164	0.2015	0.024
0.3734	834.23	1.205	0.2359	0.025
0.4731	843.60	1.245	0.2491	0.026
0.5196	847.86	1.263	0.2488	0.027
0.5712	852.51	1.281	0.2437	0.026
0.5726	852.64	1.282	0.2430	0.027
0.6727	861.47	1.314	0.2152	0.024
0.7769	870.35	1.345	0.1696	0.021
0.7790	870.55	1.345	0.1659	0.020
0.8840	879.23	1.371	0.0989	0.013
0.8897	879.69	1.374	0.0951	0.015
0.9423	883.94	1.384	0.0533	0.009
1.0000	888.55	1.392		
Ethyl acetate + 1-propanol at 308.15 K				
0.0000	791.84	1.034		
0.0453	796.62	1.064	0.0522	0.008
0.0918	801.51	1.092	0.0933	0.014
0.1090	803.27	1.100	0.1097	0.014
0.1360	806.02	1.117	0.1330	0.019
0.1831	810.80	1.142	0.1643	0.023
0.2761	819.98	1.184	0.2126	0.026
0.3734	829.19	1.225	0.2497	0.028
0.4731	838.35	1.264	0.2626	0.029
0.5196	842.52	1.282	0.2615	0.030
0.5712	847.04	1.300	0.2589	0.029

Table 4 (*Continued*)

x_1	ρ (kg m^{-3})	α (kK^{-1})	V^E (cm^3 mol^{-1})	α^E (kK^{-1})
0.5726	847.17	1.300	0.2579	0.029
0.6727	855.82	1.332	0.2276	0.026
0.7769	864.61	1.361	0.1693	0.022
0.7790	864.68	1.361	0.1794	0.021
0.8840	873.22	1.387	0.1055	0.015
0.8897	873.67	1.389	0.1016	0.015
0.9423	877.83	1.398	0.0587	0.009
1.0000	882.38	1.406		
Ethyl acetate + 1-propanol at 313.15 K				
0.0000	787.73	1.054		
0.0453	792.37	1.084	0.0551	0.008
0.0918	797.15	1.111	0.0959	0.014
0.1090	798.83	1.120	0.1162	0.015
0.1360	801.52	1.138	0.1391	0.021
0.1831	806.18	1.162	0.1714	0.024
0.2761	815.10	1.205	0.2246	0.028
0.3734	824.07	1.245	0.2643	0.030
0.4731	833.02	1.284	0.2768	0.031
0.5196	837.06	1.301	0.2791	0.031
0.5712	841.50	1.318	0.2737	0.030
0.5726	841.62	1.319	0.2734	0.031
0.6727	850.08	1.350	0.2417	0.028
0.7769	858.59	1.378	0.1914	0.023
0.7790	858.77	1.378	0.1889	0.022
0.8840	867.10	1.402	0.1158	0.014
0.8897	867.57	1.403	0.1084	0.014
0.9423	871.64	1.413	0.0644	0.008
1.0000	876.13	1.421		
Ethyl acetate + 1-propanol at 318.15 K				
0.0000	783.53	1.074		
0.0453	788.05	1.105	0.0566	0.010
0.0918	792.67	1.131	0.1027	0.014
0.1090	794.34	1.141	0.1202	0.017
0.1360	796.91	1.158	0.1490	0.022
0.1831	801.46	1.183	0.1820	0.026
0.2761	810.12	1.226	0.2412	0.031
0.3734	818.91	1.265	0.2786	0.032
0.4731	827.62	1.304	0.2951	0.034
0.5196	831.57	1.321	0.2972	0.034
0.5712	835.92	1.337	0.2906	0.032
0.5726	836.04	1.339	0.2900	0.034
0.6727	844.33	1.369	0.2557	0.030
0.7769	852.68	1.395	0.2015	0.024
0.7790	852.84	1.395	0.2008	0.023
0.8840	861.02	1.417	0.1227	0.014
0.8897	861.48	1.418	0.1153	0.013
0.9423	865.51	1.428	0.0649	0.008
1.0000	869.90	1.436		
Ethyl acetate + 1-propanol at 323.15 K				
0.0000	779.30	1.094		
0.0453	783.65	1.126	0.0632	0.011
0.0918	788.16	1.150	0.1098	0.014
0.1090	789.76	1.161	0.1305	0.017
0.1360	792.26	1.180	0.1605	0.024
0.1831	796.66	1.204	0.1982	0.028
0.2761	805.16	1.248	0.2536	0.034
0.3734	813.72	1.286	0.2940	0.035
0.4731	822.23	1.324	0.3105	0.036
0.5196	826.10	1.341	0.3114	0.037
0.5712	830.33	1.357	0.3069	0.035
0.5726	830.44	1.358	0.3071	0.036
0.6727	838.53	1.387	0.2739	0.032
0.7769	846.75	1.412	0.2124	0.025
0.7790	846.88	1.412	0.2147	0.024
0.8840	854.93	1.433	0.1296	0.014
0.8897	855.36	1.433	0.1244	0.013
0.9423	859.31	1.443	0.0723	0.008
1.0000	863.66	1.451		

values obtained in the present work and certain other published values. The values reported by Grolier and Viallard [2] differ by 17 and 14% with our values for ethyl acetate + methanol and for ethyl acetate + 1-propanol, respectively.

Fig. 6 shows that the V^E increase with increasing length of the hydrocarbon chain of the alkanol. In Fig. 6, we have also included the equimolar values of V^E for mixtures of ethyl acetate with ethanol, 1-butanol and 1-pentanol from literature [15] for the purpose of comparison and completeness of 1-alkanol series up to hexanol. This behavior is consistent with that observed in other ester + 1-alkanol mixtures series [6,7].

The values of excess properties depend on the type and extent of intermolecular interactions and on the difference in size and shape of unlike molecules [17–19]. In the systems considered here, we can recognize four different effects as being important. (i) The reduction of intermolecular associations (hydrogen bonds in alkanols and dipole–dipole interaction in esters) in the pure liquids. (ii) Unfavorable interactions between different groups such as $-CH_3$, $-CH_2-$, $>C=O$, $-OH$, etc. (iii) Change in free volumes and interstitial accommodation depending upon the size of component molecules. (iv) Formation of new ester–alkanol polymers. The positive contribution to V^E is expected from first two effects while opposite contribution from remaining two.

Table 5
Properties of ethyl acetate + 2-propanol mixture

x_1	ρ (kg m^{-3})	α (kK^{-1})	V^E (cm^3 mol^{-1})	α^E (kK^{-1})
Ethyl acetate + 2-propanol at 298.15 K				
0.0000	781.25	1.057		
0.0447	786.77	1.092	0.0884	0.017
0.0928	792.64	1.124	0.1741	0.030
0.1107	794.82	1.137	0.2022	0.036
0.1390	798.28	1.161	0.2407	0.049
0.1857	803.87	1.187	0.3041	0.058
0.2792	815.00	1.243	0.3933	0.080
0.3758	826.29	1.284	0.4475	0.088
0.4618	836.11	1.316	0.4714	0.091
0.4762	837.72	1.317	0.4747	0.088
0.5268	843.42	1.332	0.4722	0.087
0.5787	849.20	1.340	0.4616	0.079
0.6805	860.42	1.367	0.4100	0.076
0.7829	871.52	1.383	0.3226	0.063
0.8870	882.76	1.393	0.1839	0.045
0.9379	888.18	1.390	0.1050	0.029
0.9422	888.59	1.383	0.1030	0.021
1.0000	894.72	1.377		
Ethyl acetate + 2-propanol at 303.15 K				
0.0000	777.04	1.089		
0.0447	782.41	1.124	0.0942	0.018
0.0928	788.10	1.156	0.1882	0.032
0.1107	790.25	1.168	0.2157	0.037
0.1390	793.60	1.191	0.2595	0.050
0.1857	799.02	1.217	0.3308	0.059
0.2792	809.87	1.270	0.4298	0.080
0.3758	820.89	1.309	0.4926	0.088
0.4618	830.56	1.339	0.5150	0.091
0.4762	832.13	1.341	0.5196	0.089
0.5268	837.74	1.355	0.5165	0.088
0.5787	843.46	1.363	0.5018	0.081
0.6805	854.51	1.385	0.4478	0.074
0.7829	865.53	1.399	0.3481	0.061
0.8870	876.63	1.406	0.2031	0.041
0.9379	882.01	1.403	0.1180	0.026
0.9422	882.45	1.397	0.1118	0.019
1.0000	888.55	1.392		
Ethyl acetate + 2-propanol at 308.15 K				
0.0000	772.75	1.122		
0.0447	777.95	1.157	0.1026	0.019
0.0928	783.52	1.187	0.1994	0.032
0.1107	785.56	1.200	0.2346	0.039
0.1390	788.82	1.221	0.2821	0.050
0.1857	794.12	1.248	0.3567	0.062
0.2792	804.67	1.298	0.4687	0.082
0.3758	815.49	1.334	0.5337	0.088
0.4618	824.96	1.363	0.5606	0.092
0.4762	826.55	1.365	0.5603	0.090
0.5268	832.04	1.378	0.5602	0.089
0.5787	837.69	1.386	0.5428	0.083
0.6805	848.58	1.402	0.4861	0.072
0.7829	859.40	1.415	0.3880	0.059
0.8870	870.45	1.419	0.2275	0.039
0.9379	875.79	1.417	0.1365	0.025
0.9422	876.26	1.412	0.1261	0.019
1.0000	882.38	1.406		
Ethyl acetate + 2-propanol at 313.15 K				
0.0000	768.40	1.156		
0.0447	773.43	1.191	0.1110	0.020
0.0928	778.82	1.220	0.2168	0.033
0.1107	780.84	1.232	0.2505	0.039
0.1390	783.97	1.252	0.3059	0.050
0.1857	789.14	1.279	0.3848	0.063
0.2792	799.47	1.326	0.5015	0.082
0.3758	810.05	1.360	0.5728	0.088
0.4618	819.34	1.387	0.6019	0.092
0.4762	820.87	1.390	0.6052	0.091
0.5268	826.32	1.401	0.5993	0.089
0.5787	831.86	1.410	0.5835	0.085
0.6805	842.62	1.421	0.5205	0.071
0.7829	853.33	1.431	0.4137	0.057
0.8870	864.25	1.433	0.2460	0.036
0.9379	869.58	1.430	0.1453	0.022
0.9422	870.07	1.426	0.1317	0.017
1.0000	876.13	1.421		
Ethyl acetate + 2-propanol at 318.15 K				
0.0000	763.92	1.190		
0.0447	768.76	1.225	0.1225	0.021
0.0928	774.04	1.253	0.2310	0.034
0.1107	775.97	1.265	0.2708	0.041
0.1390	779.02	1.284	0.3295	0.052
0.1857	784.05	1.311	0.4148	0.065
0.2792	794.11	1.355	0.5432	0.083
0.3758	804.56	1.387	0.6108	0.090
0.4618	813.63	1.412	0.6480	0.093
0.4762	815.16	1.415	0.6487	0.092
0.5268	820.49	1.424	0.6466	0.089
0.5787	825.99	1.434	0.6253	0.087
0.6805	836.62	1.439	0.5576	0.069
0.7829	847.22	1.447	0.4435	0.055
0.8870	858.05	1.446	0.2655	0.032
0.9379	863.38	1.444	0.1546	0.020
0.9422	863.85	1.441	0.1423	0.016
1.0000	869.90	1.436		
Ethyl acetate + 2-propanol at 323.15 K				
0.0000	759.28	1.224		
0.0447	763.99	1.260	0.1288	0.023
0.0928	769.11	1.286	0.2461	0.036
0.1107	771.00	1.298	0.2873	0.043
0.1390	773.96	1.316	0.3509	0.053
0.1857	778.84	1.343	0.4445	0.067
0.2792	788.67	1.384	0.5823	0.084
0.3758	798.85	1.413	0.6631	0.090
0.4618	807.83	1.437	0.6958	0.094

Table 5 (*Continued*)

x_1	ρ (kg m^{-3})	α (kK^{-1})	V^E (cm^3 mol^{-1})	α^E (kK^{-1})
0.4762	809.32	1.441	0.6985	0.095
0.5268	814.60	1.448	0.6932	0.090
0.5787	820.00	1.459	0.6742	0.090
0.6805	830.57	1.458	0.5952	0.068
0.7829	841.07	1.464	0.4742	0.053
0.8870	851.86	1.460	0.2814	0.029
0.9379	857.11	1.458	0.1702	0.018
0.9422	857.62	1.457	0.1524	0.016
1.0000	863.66	1.451		

Table 6
Properties of ethyl acetate + 1-hexanol mixture

x_1	ρ (kg m^{-3})	α (kK^{-1})	V^E (cm^3 mol^{-1})	α^E (kK^{-1})
Ethyl acetate + 1-hexanol at 298.15 K				
0.0000	815.75	0.908		
0.0467	818.21	0.935	0.0710	0.010
0.0926	820.69	0.955	0.1384	0.012
0.1103	821.74	0.974	0.1523	0.024
0.1380	823.27	0.985	0.1932	0.025
0.1855	826.07	1.011	0.2435	0.032
0.2812	831.98	1.052	0.3318	0.034
0.3778	838.59	1.096	0.3675	0.036
0.4768	845.81	1.142	0.3860	0.038
0.5231	849.44	1.164	0.3767	0.039
0.5789	853.88	1.187	0.3712	0.035
0.6795	862.47	1.235	0.3274	0.034
0.7830	871.94	1.277	0.2628	0.022
0.8911	882.86	1.335	0.1419	0.021
0.9452	888.58	1.355	0.0806	0.010
1.0000	894.72	1.377		
Ethyl acetate + 1-hexanol at 303.15 K				
0.0000	812.03	0.915		
0.0467	814.39	0.943	0.0741	0.010
0.0926	816.77	0.964	0.1443	0.013
0.1103	817.70	0.982	0.1714	0.025
0.1380	819.21	0.994	0.2076	0.026
0.1855	821.89	1.020	0.2623	0.032
0.2812	827.60	1.062	0.3519	0.035
0.3778	833.95	1.108	0.3948	0.039
0.4768	840.94	1.155	0.4134	0.041
0.5231	844.48	1.176	0.4010	0.040
0.5789	848.80	1.200	0.3928	0.037
0.6795	857.15	1.248	0.3454	0.035
0.7830	866.35	1.291	0.2775	0.023
0.8911	876.93	1.349	0.1567	0.021
0.9452	882.56	1.370	0.0851	0.011
1.0000	888.55	1.392		
Ethyl acetate + 1-hexanol at 308.15 K				
0.0000	808.34	0.923		
0.0467	810.55	0.951	0.0847	0.010
0.0926	812.84	0.973	0.1560	0.014
0.1103	813.71	0.990	0.1873	0.024
0.1380	815.14	1.003	0.2277	0.026
0.1855	817.67	1.029	0.2911	0.032
0.2812	823.18	1.072	0.3813	0.035
0.3778	829.32	1.120	0.4239	0.040
0.4768	836.08	1.168	0.4422	0.043
0.5231	839.50	1.189	0.4304	0.042
0.5789	843.70	1.214	0.4192	0.040
0.6795	851.78	1.262	0.3714	0.037
0.7830	860.77	1.305	0.2921	0.024
0.8911	871.03	1.363	0.1687	0.022
0.9452	876.50	1.384	0.0945	0.011
1.0000	882.38	1.406		

The volumetric behavior of the ethyl acetate + 1-propanol, and ethyl acetate + 1-hexanol, mixtures shows that effects (i) and (ii) which leads to an expansion in volumes, predominates over the other two (iii) and (iv), which contribute to contraction. The effect of interstitial accommodation of the molecules decreases as the length of the 1-alkanol chain increase and does not appear to have an excessive influence on the volumetric behavior of these mixtures, i.e. less efficient packing with the larger molecules of 1-alkanol. On the other hand, the effect of interaction among the components produces a greater steric impediment as the chain length of the 1-alkanol increases. For these mixtures excess Gibbs energy of mixing G^E, excess enthalpy H^E and excess entropy S^E are also positive [4] which support this graded behavior. Deshpande et al. [20] have determined the volumetric equilibrium constant for 1-alkanol–ester mixtures through the measurement of molar heat capacities and have shown that their values decrease with alkanol chain length, consistent with the present result.

The behavior of the branched alkanols brings about other differences. The values of V^E are comparatively larger for 2-propanol than the corresponding 1-propanol mixtures. Similar difference in behavior was also observed between ethyl acetate + 1-hexanol and ethyl acetate + 2-hexanol mixtures [16]. The difference in the V^E values for the alkanol isomers may be considered on two counts: first, auto-association equilibrium constant K of alkanol and second, formation of new ester–alkanol complex.

It is known that the depolymerization of alkanols leads to increase in volume. This increase will depend on the value of K, larger the value of K large will be the increase in the volume due to depolymerization. The K

Table 6 (*Continued*)

x_1	ρ (kg m^{-3})	α (kK^{-1})	V^E (cm^3 mol^{-1})	α^E (kK^{-1})
Ethyl acetate + 1-hexanol at 313.15 K				
0.0000	804.57	0.930		
0.0467	806.66	0.960	0.0908	0.012
0.0926	808.85	0.982	0.1648	0.015
0.1103	809.67	0.998	0.1988	0.024
0.1380	811.02	1.011	0.2435	0.026
0.1855	813.47	1.038	0.3052	0.033
0.2812	818.78	1.083	0.3965	0.037
0.3778	824.69	1.133	0.4420	0.044
0.4768	831.19	1.182	0.4645	0.046
0.5231	834.52	1.202	0.4493	0.044
0.5789	838.54	1.227	0.4433	0.041
0.6795	846.39	1.276	0.3899	0.038
0.7830	855.12	1.319	0.3056	0.025
0.8911	865.09	1.377	0.1761	0.022
0.9452	870.39	1.400	0.1006	0.012
1.0000	876.13	1.421		
Ethyl acetate + 1-hexanol at 318.15 K				
0.0000	800.83	0.937		
0.0467	802.79	0.968	0.0985	0.012
0.0926	804.87	0.991	0.1766	0.017
0.1103	805.62	1.007	0.2164	0.025
0.1380	806.94	1.020	0.2578	0.027
0.1855	809.26	1.047	0.3253	0.034
0.2812	814.32	1.093	0.4246	0.038
0.3778	820.02	1.145	0.4698	0.046
0.4768	826.28	1.195	0.4933	0.049
0.5231	829.46	1.215	0.4828	0.046
0.5789	833.42	1.241	0.4655	0.044
0.6795	840.99	1.290	0.4131	0.040
0.7830	849.48	1.334	0.3207	0.027
0.8911	859.10	1.391	0.1922	0.022
0.9452	864.34	1.415	0.1021	0.013
1.0000	869.90	1.436		
Ethyl acetate + 1-hexanol at 323.15 K				
0.0000	797.08	0.945		
0.0467	798.91	0.976	0.1062	0.012
0.0926	800.89	1.001	0.1870	0.018
0.1103	801.55	1.016	0.2359	0.026
0.1380	802.80	1.030	0.2799	0.028
0.1855	804.99	1.056	0.3533	0.033
0.2812	809.87	1.103	0.4501	0.038
0.3778	815.27	1.158	0.5080	0.048
0.4768	821.30	1.209	0.5309	0.051
0.5231	824.43	1.228	0.5112	0.047
0.5789	828.21	1.255	0.4988	0.046
0.6795	835.54	1.304	0.4418	0.041
0.7830	843.80	1.348	0.3398	0.028
0.8911	853.13	1.405	0.2049	0.021
0.9452	858.18	1.430	0.1156	0.013
1.0000	863.66	1.451		

Table 7
Coefficients A_i of Eq. (5) and standard deviations σ for excess molar volumes in cm^3 mol^{-1}

Temperature (K)	A_1	A_2	A_3	A_4	σ
Ethyl acetate + methanol mixture					
298.15	−0.2988	0.1087	−0.1598	−0.1627	0.0028
303.15	−0.3399	0.0813	−0.2050	−0.1590	0.0031
308.15	−0.3793	0.1160	−0.1946	−0.2003	0.0027
313.15	−0.4198	0.1026	−0.2305	−0.1313	0.0019
318.15	−0.4595	0.1410	−0.2815	−0.2049	0.0019
323.15	−0.4950	0.1093	−0.2902	−0.1678	0.0027
Ethyl acetate + 1-propanol mixture					
298.15	0.9434	0.0615	−0.0093		0.0025
303.15	0.9953	0.0492	0.0129	−0.0136	0.0015
308.15	1.0415	0.0518	0.0808	0.0173	0.0039
313.15	1.1036	0.0242	0.0994	0.0221	0.0031
318.15	1.1787	0.0324	0.0659	0.0221	0.0023
323.15	1.2383	0.0328	0.1379	0.0337	0.0032
Ethyl acetate + 2-propanol mixture					
298.15	1.9002	0.0653	0.0796	0.0873	0.0024
303.15	2.0768	0.1024	0.0664		0.0019
308.15	2.2494	0.0972	0.1426	−0.0751	0.0023
313.15	2.4162	0.0962	0.1443	−0.0303	0.0022
318.15	2.5917	0.0969	0.1787		0.0034
323.15	2.7864	0.1506	0.1638	−0.1107	0.0030
Ethyl acetate + 1-hexanol mixture					
298.15	1.5440	0.1446	0.0303	−0.1368	0.0052
303.15	1.6469	0.2031	0.0400	−0.2257	0.0040
308.15	1.7574	0.2590	0.1227	−0.2737	0.0034
313.15	1.8366	0.2577	0.1671	−0.2507	0.0042
318.15	1.9529	0.2571	0.1743	−0.1857	0.0037
323.15	2.0818	0.3456	0.2510	−0.3395	0.0058

for 1-propanol, 197 is comparatively higher than that for 2-propanol, 131 at 25°C. When mixture is formed this should result into more positive value of V^E for 1-propanol than corresponding 2-propanol. But, the experimental observation is opposite to this. On the other hand, the second effect due to formation of new ester–alkanol polymer leads to decrease in the V^E and H^E. From the experimental results, we may say that ester–2-propanol complex formation is relatively weaker due to the steric hindrance than the formation of complex between ester and 1-propanol.

Nagata [21] analyzed G^E and H^E data for ester–alkanol mixtures on the basis of ideal associated solution model considering cross-association between ester–alkanol in addition to the depolymerization of alkanol. The value of cross-association constant K_{AB}

Table 8
Coefficients A_i of Eq. (5) and standard deviations σ for excess thermal expansion coefficient α^E

Temperature (K)	A_1	A_2	A_3	σ
Ethyl acetate + methanol mixture				
298.15	−0.1139	−0.0634	−0.0800	0.0020
303.15	−0.1083	−0.0628	−0.1024	0.0018
308.15	−0.1035	−0.0637	−0.0997	0.0016
313.15	−0.1240	0.0186	0.0525	0.0008
318.15	−0.0959	−0.0539	−0.1061	0.0011
323.15	−0.0907	−0.0502	−0.1105	0.0012
Ethyl acetate + 1-propanol mixture				
298.15	0.0936	−0.0026	0.0995	0.0013
303.15	0.1047	0.0118	0.0781	0.0009
308.15	0.1145	0.0118	0.0675	0.0009
313.15	0.1240	0.0186	0.0525	0.0008
318.15	0.1346	0.0293	0.0465	0.0012
323.15	0.1462	0.0382	0.0385	0.0016
Ethyl acetate + 2-propanol mixture				
298.15	0.3544	−0.0207	0.0784	0.0045
303.15	0.3561	0.0095	0.0618	0.0034
308.15	0.3575	0.0245	0.0598	0.0030
313.15	0.3589	0.0510	0.0410	0.0022
318.15	0.3610	0.0771	0.0303	0.0021
323.15	0.3632	0.1006	0.0319	0.0027
Ethyl acetate + 1-hexanol mixture				
298.15	0.1502	0.0107	0.0740	0.0032
303.15	0.1554	0.0137	0.0776	0.0030
308.15	0.1638	0.0084	0.0685	0.0029
313.15	0.1695	0.0088	0.0822	0.0030
318.15	0.1771	0.0111	0.0843	0.0029
323.15	0.1845	0.0114	0.0782	0.0031

for ester (B) + alkanol (A) $\Leftrightarrow$ ester–alkanol complex (AB), was found to be 70 for ethyl acetate–1-propanol compared to only 50 for ethyl acetate–2-propanol at 298.15 K. The smaller value of K_{AB} for ethyl acetate–2-propanol results into less contraction as a result the net V^E is more compared to the ethyl acetate–1-propanol mixture. This clearly explains why V^E for ethyl acetate–2-propanol is larger than that for the ethyl acetate–1-propanol mixture.

The increase of V^E with temperature may be attributed to more depolymerization of alkanol molecules as well as to destabilization of dipolar order of ester, hence increase in volume of mixture.

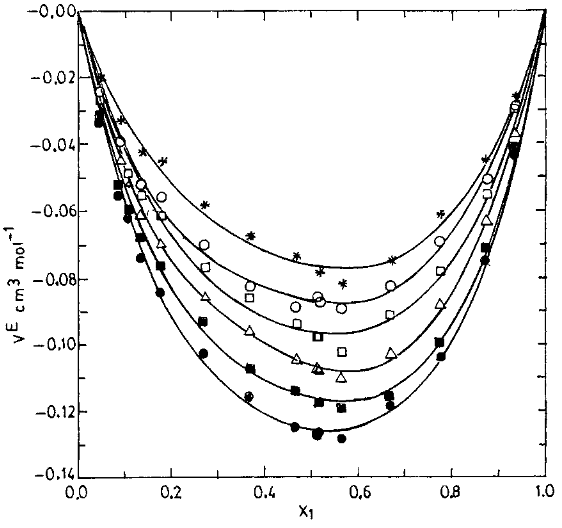

Fig. 1. Excess molar volumes of ethyl acetate + methanol. Experimental points: at 298.15 K (*); 303.15 K (○); 308.15 K (□); 313.15 K (△); 318.15 K (■); 323.15 K (●); — calculated with Eq. (5).

For the ethyl acetate + methanol mixture, V^E (Fig. 1) are negative over the entire range of composition and at all temperatures and become more negative as temperature is raised. The negative values of V^E are invariably observed for all other esters including methyl and butyl acetates [2,6] and methyl, ethyl and butyl formates [5,7,8] when mixed with methanol at 298.15 K.

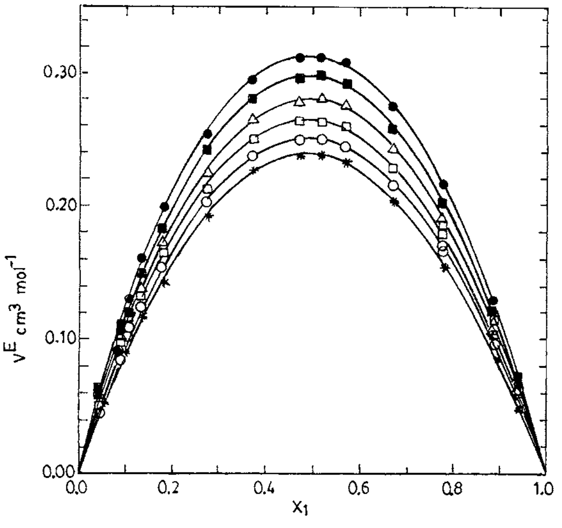

Fig. 2. Excess molar volumes of ethyl acetate + 1-propanol. Symbols same as in Fig. 1; — calculated with Eq. (5).

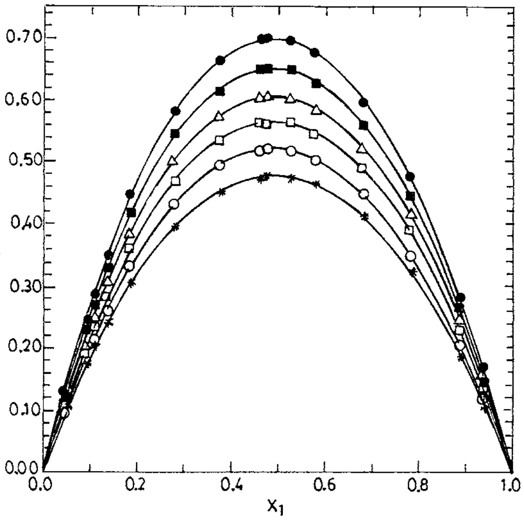

Fig. 3. Excess molar volumes of ethyl acetate + 2-propanol. Symbols same as in Fig. 1; — calculated with Eq. (5).

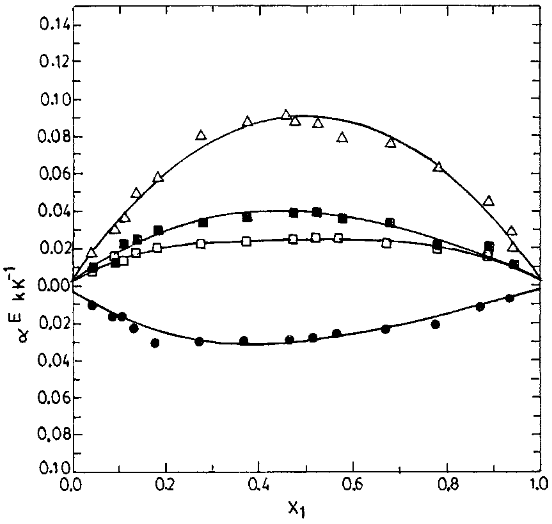

Fig. 5. Excess thermal expansion coefficient of ethyl acetate + alkanols at 298.15 K. Experimental points: methanol (●); 1-propanol (□); 2-propanol (△) and 1-hexanol (■); — calculated with Eq. (5).

It is interesting to note that H^E and S^E [4] for ethyl acetate + methanol are positive, while V^E are negative. Positive H^E and S^E definitely indicate dominance of rupture of H-bonded structure of methanol and disappearance of dipolar order of ester molecules by each other over the formation of new ester–alkanol species. The molar enthalpy of H-bond formation in the pure alkanol is approximately −25 to −30 kJ mol^{-1} where as that of the H-bond between ester and alkanol as determined is only −18.4 kJ mol^{-1} [21]. Therefore, the negative values of V^E for ethyl acetate + methanol may be attributed to the dominance of interstitial accommodation of small methanol molecules into the free volumes of ethyl acetate and formation of ester–alkanol complex over the other two (i) and (ii) effects mentioned above.

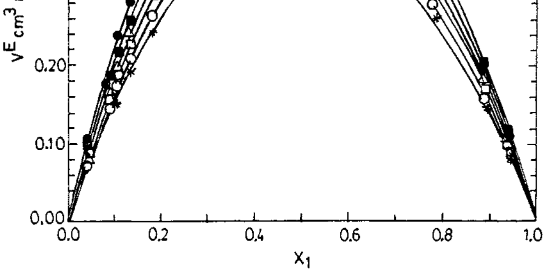

Fig. 4. Excess molar volumes of ethyl acetate + 1-hexanol. Symbols same as in Fig. 1; — calculated with Eq. (5).

Table 9
Comparison of present V^E with literature values at 298.15 K

System	V^E (cm^3 mol^{-1})		
	Experimental	Literature	Reference
Ethyl acetate + methanol	−0.0745	−0.072	[15]
		−0.073	[3]
		−0.077	[1]
		−0.09	[2]
1-Propanol	0.2358	0.2367	[15]
		0.29	[2]
2-Propanol	0.4750	0.47	[2]
1-Hexanol	0.3860	0.387	[15]

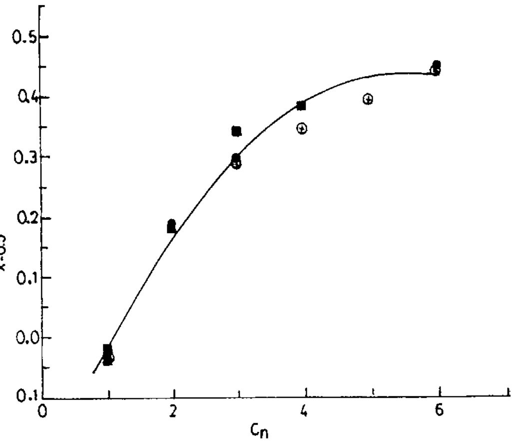

Fig. 6. Dependence of equimolar excess molar volumes for ethyl acetate + 1-alkanol at 298.15 K on number of C atoms in alkanols. This work (●); ref. [15] (⊕); ref. [3] (△); ref. [2] (■);

Further, it may be said that on increasing the temperature, the free volume increases and results into more efficient packing of methanol molecules into the free volume or cavities of ethyl acetate.

The $(\partial V^E/\partial T)_P$ and α^E are related by [22]

$$\alpha^E = V^{-1}\left[\left(\frac{\partial V^E}{\partial T}\right)_P - \alpha_{id} V^E\right] \quad (6)$$

As $(\partial V^E/\partial T)_P$ and α^E have the same sign in the present mixtures, the $(\partial V^E/\partial T)_P$ is dominant in Eq. (6).

Further analysis of the results on the basis of ERAS model [23,24] will be presented in next paper.

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