Densities and Viscosities for Ethyl Acetate + Pentan-1-ol, + Hexan-1-ol, + 3,5,5-Trimethylhexan-1-ol, + Heptan-1-ol, + Octan-1-ol, and + Decan-1-ol at (298.15, 303.15, and 308.15) K

Pandharinath S. Nikam,* Tukaram R. Mahale, and Mehdi Hasan

P.G. Department of Physical Chemistry, M.S.G. College, Malegaon Camp 423 105, India

---

Densities (ρ) and viscosities (η) have been measured at (298.15, 303.15, and 308.15) K for binary mixtures of ethyl acetate with pentan-1-ol, hexan-1-ol, 3,5,5-trimethylhexan-1-ol, heptan-1-ol, octan-1-ol, and decan-1-ol. From these, molar excess volume (V^E) and deviation in viscosity ($\Delta\eta$) have been computed and fitted to the Redlich−Kister polynomial.

Introduction

The variation of density, viscosity, ultrasound velocity, and isentropic compressibility of binary liquid mixtures of protic, aprotic, and associating liquids with changing mole fraction of one of the components has been investigated by some researchers (Marsh and Richards, 1980). The trends of changes, either positive or negative, have been interpreted by these workers in terms of differences in size of molecules and the strength of specific or nonspecific interactions taking place between the components of the mixtures. The effect of molecular size, shape, and molecular association of alkanols have been reported by us (Nikam et al., 1997). In the present study, the densities and viscosities for the binary system of ethyl acetate with pentan-1-ol, hexan-1-ol, 3,5,5-trimethylhexan-1-ol, heptan-1-ol, octan-1-ol, and decan-1-ol over the entire range of compositions at (298.15, 303.15, and 308.15) K have been measured. The V^E and $\Delta\eta$ have been interpreted in terms of intermolecular interactions between constituent molecules of mixtures.

Experimental Section

Alkanols (Merck-Schuchardt, purity >99 mol %) were dried by refluxing over fused calcium oxide for 3−4 h and subsequently fractionally distilled two or three times. Ethyl acetate (E. Merck) with purity >99.5 mol % was used after single distillation.

The gas chromatographic tests of the purified solvents showed a purity of >99.5 mol %. The purities of the solvents were further ascertained by the constancy of their boiling temperatures during distillation and by comparing their densities and viscosities at 298.15, 303.15, and 308.15 K, which agreed reasonably with the corresponding literature values (Table 1).

All mixtures were prepared by mass using a Mettler balance (Switzerland, model AE-240) with a precision of ±0.01 mg. Mixtures were allowed to stand for some time before every measurement so as to avoid air bubbles. The possible error in mole fraction is estimated to be less than $\pm 1 \times 10^{-4}$.

Densities of pure liquids and their mixtures were determined by using a 15-cm^3 double-arm pycnometer as described earlier (Nikam and Sawant, 1997). The pycnometer was calibrated using conductivity water with 0.997 05, 0.995 65, and 0.994 03 g·cm^{-3} as its densities at 298.15, 303.15, and 308.15 K, respectively (Riddick et al., 1986). The pycnometer filled with air bubble free experimental liquids was kept in a transparent-walled water bath, maintained constant to ±0.01 K for 10 to 15 min to attain thermal equilibrium, at the desired temperature as checked by means of specially designed and calibrated thermometer (range 298.15 to 313.15 K only). The positions of the liquid levels in the two arms of pycnometer were recorded with the help of a traveling microscope that could read ±0.01 mm. The density values from triplicate replication at each temperature and composition were reproducible to within $\pm 1 \times 10^{-4}$ g·cm^{-3}.

The viscosities of the binary liquid mixtures were measured using an Ostwald viscometer (Nikam and Sawant, 1997) calibrated with water with 0.8902, 0.7973, and 0.7190 mPa·s as its viscosities at 298.15, 303.15, and 308.15 K, respectively (Riddick et al., 1986). A throughly cleaned and dried viscometer, filled with experimental liquid, was placed vertically in a glass-sided water thermostat maintained constant to ±0.01 K. After attaining thermal equilibrium, the efflux times of flow of liquids were recorded with a digital stop watch correct to ±0.01 s. Since all flow times were greater than 300 s, the kinetic energy corrections were not applied. To evaluate viscometer constants, the length of the capillary of the viscometer (l) term is to be corrected as $l' = l + 0.5r$, r being the radius of the viscometer capillary. Since l is much larger (50−60 mm) as compared to r (0.5 mm), $l = l'$ and hence end effects in viscometer are negligible. The reproducibility in the measurement of viscosity was ±0.001 mPa·s. In all determinations, triplicate experiments were performed at each composition and temperature. The flow times were repeatable within 1%.

Results and Discussion

The experimental results for the density (ρ) and viscosity (η) are given in Table 2. The excess volume, V^E, was calculated from

$$V^E/(\text{cm}^3\cdot\text{mol}^{-1}) = \frac{M_1x_1 + M_2x_2}{\rho_{\text{mix}}} - \frac{M_1x_1}{\rho_1} - \frac{M_2x_2}{\rho_2} \quad (1)$$

where ρ_{mix} is the density of the mixture and M_1, x_1, ρ_1 and M_2, x_2, ρ_2 are molecular weight, mole fraction, and density of pure components 1 and 2, respectively. Excess volumes calculated from eq 1 are listed in Table 2.

S0021-9568(97)00253-7 CCC: $15.00

Table 1. Comparison of Experimental Densities (ρ) and Viscosities (η) of Pure Liquids with Literature Values at 298.15, 303.15, and 308.15 K

	$\rho \times 10^{-3}$/(kg·m^{-3})		η/(mPa·s)		$\rho \times 10^{-3}$/(kg·m^{-3})		η/(mPa·s)	
liquid	exptl	lit.	exptl	lit.	exptl	lit.	exptl	lit.
	298.15 K				303.15 K			
pentan-1-ol	0.8110	0.8109[a]	3.510	3.512[b]	0.8068	0.8072[b]	2.961	2.909[b]
hexan-1-ol	0.8155	0.8155[a]	4.574	4.592[b]	0.8119	0.8119[g]	3.781	3.765[b]
3,5,5-trimethylhexan-1-ol	0.8286	n.a.[c]	10.437	n.a.[c]	0.8250	n.a.[c]	10.971	n.a.[c]
heptan-1-ol	0.8209	0.8199[d]	5.937	5.758[d]	0.8172	0.8160[g]	4.995	4.771[g]
octan-1-ol	0.8215	0.82157[b]	7.368	7.633[b]	0.8175	0.8152[b]	6.120	6.125[b]
decan-1-ol	0.8261	0.82623[e]	11.567	11.790[f]	0.8230	0.8227[h]	9.652	n.a.[c]
ethyl acetate	0.8946	0.8945[b]	0.424	0.426[b]	0.8885	0.88855[b]	0.400	0.400[b]
	308.15 K							
pentan-1-ol	0.8034	0.8034[f]	2.518	2.305[b]				
hexan-1-ol	0.8082	0.8083[f]	3.252	3.398[i]				
3,5,5-trimethylhexan-1-ol	0.8216	n.a.[c]	9.608	n.a.[c]				
heptan-1-ol	0.8135	0.8126[f]	4.175	4.266[f]				
octan-1-ol	0.8134	0.81347[b]	5.352	5.250[f]				
decan-1-ol	0.8194	0.8195[f]	7.918	8.124[f]				
ethyl acetate	0.8825	0.88255[b]	0.385	0.387[j]				

[a] Garg et al., 1993. [b] Riddick et al., 1986. [c] Not available. [d] Aminabhavi and Raikar, 1993. [e] Diazpena and Tardajos, 1979. [f] Sastry and Valand, 1996. [g] Aminabhavi et al., 1993. [h] Dewan and Mehta, 1987. [i] TRC Tables, 1996. [j] Aminabhavi et al., 1994.

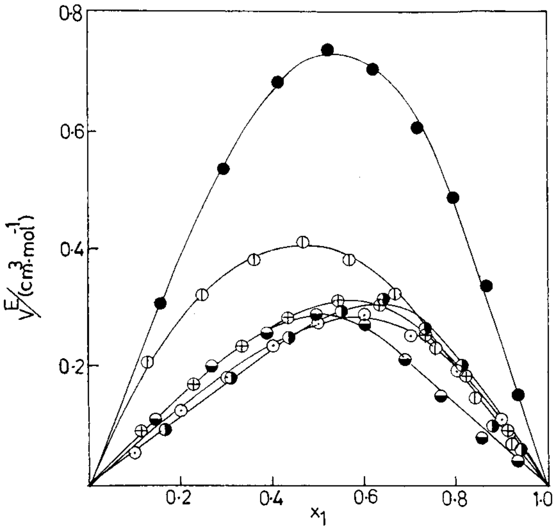

Figure 1. Excess molar volumes, V^E, at 298.15 K for $x_1$ethyl acetate + $(1 - x_1)$alkanol: (⊙) pentan-1-ol, (⊕) hexan-1-ol, (●) 3,5,5-trimethylhexan-1-ol, (⦶) heptan-1-ol, (◒) octan-1-ol, (◑) decan-1-ol.

The experimental values of viscosity given in Table 2 are used to calculate $\Delta\eta$ using the relationship

$$\Delta\eta = \eta_{mix} - x_1\eta_1 - x_2\eta_2 \qquad (2)$$

where η_{mix} is the measured mixture viscosity under question, η_1 and η_2 refer to the viscosities of the pure components of the mixtures, and x_1 and x_2 are mole fractions. The estimated uncertainties are ± 0.002 cm^3·mol^{-1} for V^E and ± 0.0005 mPa·s for $\Delta\eta$. Results of V^E and $\Delta\eta$ were fitted to the Redlich−Kister (1948) polynomial equation;

$$X = V^E \quad \text{or} \quad \Delta\eta = x_1x_2\sum_i^m a_i(x_2 - x_1)^i \qquad (3)$$

where m is the number of coefficients a_i. In each case, the optimum number of coefficients, a_i, is ascertained from an examination of the variation in standard deviation, σ, as given by

$$\sigma = [\sum(X_{obs} - X_{cal})^2/(n - m)]^{1/2} \qquad (4)$$

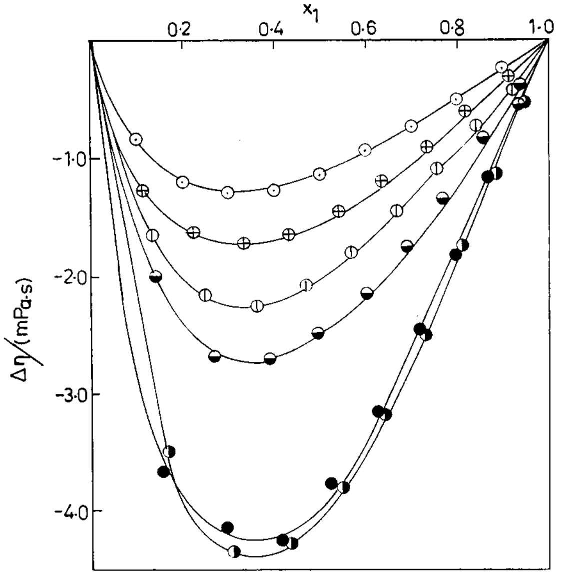

Figure 2. $\Delta\eta$ values at 298.15 K for $x_1$ethyl acetate + $(1 - x_1)$ alkanols: (⊙) pentan-1-ol, (⊕) hexan-1-ol, (●) 3,5,5-trimethylhexan-1-ol, (⦶) heptan-1-ol, (◒) octan-1-ol, (◑) decan-1-ol.

where n is the total number of data points and m is the number of coefficients considered. The coefficients and standard deviations for V^E and $\Delta\eta$, as computed from eqs 3 and 4 respectively, are given in Table 3.

The volume changes arising due to addition of ethyl acetate to an alkanol results from several opposing effects (Paez and Contreras, 1989). The main volume effects accompanying the addition of ethyl acetate to an alkanol result from changes of free volume, interstitial accommodation of the ester within the hydrogen-bonded structure of the alkanol, disruption of the alkanol structure, and the so-called condensation effect (Tereszczanowicz and Benson, 1978) due to restriction of the rotational motion of the alkanol molecules (Mecke, 1950). The breakup of the alkanol structure tends to increase V^E. In the present investigation, positive V^E values for all mixtures (Figure 1) may be attributed to predominance of the declustering of alkanols in the presence of ethyl acetate. The V^E values at equimolar concentration of mixtures follow the order 3,5,5-trimethylhexan-1-ol > heptan-1-ol > hexan-l-ol > pentan-1-ol > decan-1-ol > octan-1-ol.

Table 2. Density, ρ, Excess Molar Volume, V^E, and Viscosity, η, for Ethyl Acetate (1) + Alkanols (2) at 298.15, 303.15, and 308.15 K

x_1	$\rho \times 10^{-3}$/ $(kg \cdot m^{-3})$	V^E/ $(cm^3 \cdot mol^{-1})$	η/ (mPa·s)	x_1	$\rho \times 10^{-3}$/ $(kg \cdot m^{-3})$	V^E/ $(cm^3 \cdot mol^{-1})$	η/ (mPa·s)	x_1	$\rho \times 10^{-3}$/ $(kg \cdot m^{-3})$	V^E/ $(cm^3 \cdot mol^{-1})$	η/ (mPa·s)
Ethyl Acetate (1) + Pentan-1-ol (2)											
298.15 K											
0.0000	0.8110	0.000	3.510	0.4001	0.8406	0.229	1.011	0.8001	0.8749	0.190	0.521
0.1000	0.8182	0.057	2.349	0.5001	0.8485	0.268	0.829	0.9000	0.8845	0.109	0.472
0.2000	0.8255	0.126	1.693	0.6036	0.8571	0.286	0.829	1.0000	0.8946	0.000	0.424
0.3000	0.8330	0.182	1.282	0.7001	0.8656	0.249	0.600				
303.15 K											
0.0000	0.8068	0.000	2.961	0.4001	0.8355	0.269	0.924	0.8001	0.8691	0.210	0.486
0.1000	0.8138	0.072	2.079	0.5001	0.8433	0.303	0.766	0.9000	0.8785	0.124	0.446
0.2000	0.8208	0.146	1.530	0.6036	0.8516	0.317	0.644	1.0000	0.8885	0.000	0.400
0.3000	0.8280	0.211	1.161	0.7001	0.8600	0.280	0.561				
308.15 K											
0.0000	0.8034	0.000	2.518	0.4001	0.8308	0.322	0.848	0.8001	0.8634	0.252	0.459
0.1000	0.8100	0.096	1.843	0.5001	0.8382	0.363	0.681	0.9000	0.8726	0.151	0.392
0.2000	0.8167	0.184	1.367	0.6036	0.8463	0.376	0.599	1.0000	0.8885	0.000	0.385
0.3000	0.8236	0.263	1.053	0.7001	0.8544	0.334	0.525				
Ethyl Acetate (1) + Hexan-1-ol (2)											
298.15 K											
0.0000	0.8155	0.000	4.574	0.4360	0.8433	0.279	1.128	0.8227	0.8761	0.183	0.539
0.1142	0.8222	0.090	2.832	0.5370	0.8508	0.310	0.900	0.9125	0.8852	0.091	0.470
0.2247	0.8290	0.172	2.006	0.6350	0.8588	0.296	0.736	1.0000	0.8946	0.000	0.424
0.3320	0.8361	0.231	1.472	0.7301	0.8674	0.238	0.618				
303.15 K											
0.0000	0.8119	0.000	3.781	0.4360	0.8383	0.354	1.027	0.8227	0.8703	0.206	0.506
0.1142	0.8185	0.070	2.481	0.5370	0.8456	0.384	0.824	0.9125	0.8794	0.093	0.448
0.2247	0.8249	0.180	1.775	0.6350	0.8534	0.362	0.692	1.0000	0.8885	0.000	0.400
0.3320	0.8315	0.281	1.334	0.7301	0.8617	0.297	0.574				
308.15 K											
0.0000	0.8082	0.000	3.252	0.4360	0.8335	0.393	0.942	0.8227	0.8645	0.254	0.475
0.1142	0.8145	0.081	2.181	0.5370	0.8406	0.412	0.760	0.9125	0.8733	0.135	0.419
0.2247	0.8206	0.214	1.582	0.6350	0.8482	0.396	0.591	1.0000	0.8825	0.000	0.385
0.3320	0.8269	0.324	1.200	0.7301	0.8561	0.336	0.541				
Ethyl Acetate (1) + 3,5,5-Trimethylhexan-1-ol (2)											
298.15 K											
0.0000	0.8286	0.000	10.430	0.5219	0.8492	0.737	1.443	0.8677	0.8779	0.331	0.574
0.1539	0.8332	0.304	5.471	0.6208	0.8556	0.705	1.075	0.9364	0.8862	0.151	0.486
0.2904	0.8381	0.534	3.367	0.7106	0.8626	0.606	0.879	1.0000	0.8946	0.000	0.424
0.4122	0.8433	0.680	2.072	0.7925	0.8700	0.483	0.672				
303.15 K											
0.0000	0.8250	0.000	10.971	0.5219	0.8451	0.670	1.305	0.8677	0.8730	0.267	0.526
0.1539	0.8297	0.246	4.696	0.6208	0.8501	0.822	0.975	0.9364	0.8807	0.199	0.475
0.2904	0.8345	0.455	2.968	0.7106	0.8581	0.553	0.789	1.0000	0.8885	0.000	0.400
0.4122	0.8396	0.594	1.837	0.7925	0.8653	0.421	0.631				
308.15 K											
0.0000	0.8216	0.000	9.608	0.5219	0.8412	0.598	1.181	0.8677	0.8679	0.224	0.495
0.1539	0.8263	0.205	4.016	0.6208	0.8460	0.749	0.934	0.9364	0.8753	0.084	0.439
0.2904	0.8310	0.385	2.452	0.7106	0.8538	0.478	0.724	1.0000	0.8825	0.000	0.385
0.4122	0.8359	0.524	1.646	0.7925	0.8607	0.354	0.586				
Ethyl Acetate (1) + Heptan-1-ol (2)											
298.15 K											
0.0000	0.8209	0.000	5.937	0.4677	0.8460	0.408	1.284	0.8406	0.8776	0.145	0.569
0.1277	0.8265	0.207	3.587	0.5686	0.8534	0.380	1.000	0.9222	0.8860	0.070	0.410
0.2478	0.8326	0.317	2.423	0.6673	0.8614	0.318	0.823	1.0000	0.8946	0.000	0.424
0.3609	0.8392	0.379	1.721	0.7546	0.8693	0.229	0.663				
303.15 K											
0.0000	0.8172	0.000	4.995	0.4677	0.8412	0.457	1.184	0.8406	0.8718	0.184	0.529
0.1277	0.8225	0.222	3.130	0.5686	0.8482	0.438	0.914	0.9222	0.8801	0.086	0.473
0.2478	0.8282	0.374	2.144	0.6673	0.8559	0.379	0.752	1.0000	0.8885	0.000	0.400
0.3609	0.8344	0.442	1.543	0.7546	0.8636	0.290	0.627				
308.15 K											
0.0000	0.8135	0.000	4.175	0.4677	0.8362	0.522	1.065	0.8406	0.8660	0.224	0.496
0.1277	0.8183	0.276	2.724	0.5686	0.8431	0.490	0.839	0.9222	0.8741	0.115	0.462
0.2478	0.8238	0.428	1.904	0.6673	0.8506	0.428	0.696	1.0000	0.8825	0.000	0.385
0.3609	0.8298	0.494	1.410	0.7546	0.8580	0.344	0.576				
Ethyl Acetate (1) + Octan-1-ol (2)											
298.15 K											
0.0000	0.8215	0.000	7.368	0.4964	0.8474	0.286	1.449	0.8552	0.8783	0.081	0.585
0.1410	0.8277	0.112	4.383	0.5965	0.8546	0.271	1.088	0.9301	0.8664	0.040	0.496
0.2701	0.8340	0.200	2.825	0.6891	0.8623	0.212	0.841	1.0000	0.8946	0.000	0.424
0.3878	0.8406	0.256	1.985	0.7641	0.8692	0.150	0.712				

Table 2. (Continued)

x_1	$\rho \times 10^{-3}$/ (kg·m^{-3})	V^E/ (cm^3·mol^{-1})	η/ (mPa·s)	x_1	$\rho \times 10^{-3}$/ (kg·m^{-3})	V^E/ (cm^3·mol^{-1})	η/ (mPa·s)	x_1	$\rho \times 10^{-3}$/ (kg·m^{-3})	V^E/ (cm^3·mol^{-1})	η/ (mPa·s)
Ethyl Acetate (1) + Octan-1-ol (2) (Continued)											
303.15 K											
0.0000	0.8175	0.000	6.120	0.4964	0.8428	0.259	1.292	0.8552	0.8728	0.068	0.542
0.1410	0.8236	0.089	3.809	0.5965	0.8499	0.237	0.992	0.9301	0.8806	0.029	0.468
0.2701	0.8298	0.169	2.512	0.6891	0.8574	0.179	0.798	1.0000	0.8885	0.000	0.400
0.3878	0.8362	0.223	1.777	0.7641	0.8640	0.124	0.653				
308.15 K											
0.0000	0.8134	0.000	5.352	0.4964	0.8382	0.228	1.152	0.8552	0.8674	0.053	0.510
0.1410	0.8194	0.070	3.324	0.5965	0.8452	0.208	0.907	0.9301	0.8749	0.026	0.446
0.2701	0.8256	0.135	2.215	0.6891	0.8524	0.148	0.724	1.0000	0.8825	0.000	0.385
0.3878	0.8318	0.186	1.596	0.7641	0.8589	0.099	0.606				
Ethyl Acetate (1) + Decan-1-ol (2)											
298.15 K											
0.0000	0.8261	0.000	11.567	0.5450	0.8504	0.290	1.698	0.8778	0.8793	0.093	0.657
0.1664	0.8320	0.095	6.200	0.6423	0.8570	0.311	1.238	0.9418	0.8867	0.060	0.521
0.3099	0.8380	0.175	3.758	0.7293	0.8641	0.256	0.936	1.0000	0.8946	0.000	0.424
0.4348	0.8441	0.246	2.442	0.8073	0.8714	0.170	0.809				
303.15 K											
0.0000	0.8230	0.000	9.652	0.5450	0.8460	0.339	1.533	0.8778	0.8737	0.115	0.613
0.1664	0.8287	0.080	5.263	0.6423	0.8522	0.357	1.235	0.9418	0.8811	0.047	0.497
0.3099	0.8344	0.178	3.279	0.7293	0.8591	0.295	0.864	1.0000	0.8885	0.000	0.400
0.4348	0.8401	0.273	2.171	0.8073	0.8663	0.199	0.719				
308.15 K											
0.0000	0.8194	0.000	7.918	0.5450	0.8413	0.379	1.384	0.8778	0.8681	0.133	0.583
0.1664	0.8249	0.094	4.520	0.6423	0.8473	0.397	1.032	0.9418	0.8753	0.058	0.477
0.3099	0.8303	0.203	2.876	0.7293	0.8539	0.329	0.796	1.0000	0.8825	0.000	0.385
0.4348	0.8357	0.306	1.935	0.8073	0.8608	0.242	0.647				

Table 3. Parameters and Standard Deviations, σ, of Eqs 3 and 4 for Ethyl Acetate + Alkanols

system		temp/K	a_0	a_1	a_2	a_3	σ
ethyl acetate + pentan-1-ol	V^E/(cm^3·mol^{-1})	298.15	1.075	0.418	−0.240	−0.104	0.006
		303.15	1.212	0.404	−0.214	−0.081	0.005
		308.15	1.447	0.429	−0.146	−0.101	0.006
	$\Delta\eta$/(mPa·s)	298.15	−4.507	2.956	−2.565	1.778	0.012
		303.15	−3.660	2.332	−1.530	0.822	0.006
		308.15	−3.001	2.021	−1.074	−0.372	0.010
ethyl acetate + hexan-1-ol	V^E/(cm^3·mol^{-1})	298.15	1.220	0.444	−0.869	−0.357	0.002
		303.15	1.516	0.451	−0.910	−0.155	0.003
		308.15	1.659	0.330	−0.668	0.416	0.004
	$\Delta\eta$/(mPa·s)	298.15	−5.977	3.735	−3.774	2.834	0.031
		303.15	−4.734	2.825	−2.267	1.578	0.013
		308.15	−3.986	2.112	−1.755	1.248	0.017
ethyl acetate + 3,5,5-trimethylhexan-1-ol	V^E/(cm^3·mol^{-1})	298.15	3.076	0.917	0.955	0.990	0.068
		303.15	2.783	1.047	−1.270	−1.240	0.065
		308.15	2.483	1.088	−1.425	−1.495	0.065
	$\Delta\eta$/(mPa·s)	298.15	−15.301	9.691	−6.344	3.220	0.066
		303.15	−17.413	12.135	−8.619	4.290	0.055
		308.15	−14.550	11.332	−13.334	9.150	0.077
ethyl acetate + heptan-1-ol	V^E/(cm^3·mol^{-1})	298.15	1.576	−0.392	−0.235	−0.229	0.009
		303.15	1.847	−0.360	−0.333	−0.179	0.006
		308.15	2.055	−0.374	0.031	−0.296	0.004
	$\Delta\eta$/(mPa·s)	298.15	−7.819	5.545	−4.389	0.590	0.046
		303.15	−6.421	3.863	−2.597	1.726	0.011
		308.15	−5.160	2.723	−1.604	1.507	0.012
ethyl acetate + octan-1-ol	V^E/(cm^3·mol^{-1})	298.15	1.115	−0.139	−0.594	0.017	0.010
		303.15	0.984	−0.129	−0.667	0.043	0.011
		308.15	0.841	−0.091	−0.672	0.026	0.013
	$\Delta\eta$/(mPa·s)	298.15	−9.050	8.809	−1.762	0.819	0.085
		303.15	−7.242	6.661	−5.941	2.316	0.074
		308.15	−6.279	5.780	−0.698	0.497	0.065
ethyl acetate + decan-1-ol	V^E/(cm^3·mol^{-1})	298.15	1.147	0.893	−0.839	−0.997	0.009
		303.15	1.285	0.999	−0.814	−1.052	0.010
		308.15	1.434	1.134	0.804	−1.171	0.008
	$\Delta\eta$/(mPa·s)	298.15	−16.074	9.467	−4.880	2.352	0.029
		303.15	−12.915	7.501	−4.258	2.322	0.042
		308.15	−10.254	5.179	2.546	2.046	0.012

The higher V^E values for 3,5,5-trimethylhexan-1-ol + ethyl acetate mixtures indicate that the effect of interaction between these two components becomes more and more sterically hindered when the alkyl group in the alkanol (3,5,5-trimethylhexan-1-ol) becomes more and more branched (Narayanswamy et al., 1981).

In the case of l-alkanols (C_5-C_7), clustering decreases with increase of chain length of alkanols owing to less proton-donating tendency of higher alkanols. Therefore, heteroassociation effects decrease in the binary mixtures with an increase of chain length of linear alkanols.

Interstitial accommodation and orientational ordering lead to a more compact structure and tend to decrease V^E values. With increasing alkanol size (octan-1-ol and decan-1-ol), the interstitial accommodation becomes increasingly important (Kiyohara and Benson, 1979); thus, V^E values of mixtures containing octan-1-ol and decan-1-ol become less positive.

The increase of V^E with increase of temperature suggests the breaking of interactions and aggregates of alkanols and ethyl acetate at elevated temperature (Paez and Contreras, 1989).

The $\Delta\eta$ values at equimolar concentrations of mixtures follow the order pentan-1-ol > hexan-1-ol > heptan-1-ol > octan-1-ol > 3,5,5-trimethylhexan-1-ol > decan-1-ol (Figure 2).

The molecular size effect of alkanols from pentan-l-ol to decan-1-ol is quite considerable on values of $\Delta\eta$. It changes from −0.011 to −0.032 mPa·s at 298.15 K. The minima of the $\Delta\eta$ versus x_1 curves lie in the low-fraction region of ethyl acetate.

Literature Cited

Aminabhavi, T. M.; Raikar, S. K. A Study on Mixing Properties of Binary Mixtures of Bromoform with Aliphatic Alcohols. *J. Chem. Eng. Data* **1993**, *38*, 310−319.

Aminabhavi, T. M.; Aralguppi, M. I.; Shivaputrappa B.; Harogoppad, B.; Balundgi, R. H. Densities, Viscosities, Refractive Indices, and Speeds of Sound for Methyl Acetoacetate + Aliphatic Alcohols (C1−C8) *J. Chem. Eng. Data* **1993**, *38*, 31−39.

Aminabhavi, T. M.; Phayade, H. T. S.; Khinnavar, R. S.; Gopalakrishnan, B.; Hansen, K. C. Densities, Refractive Indices, Speeds of Sound, and Shear Viscosities of Diethylene Glycol, Dimethyl Ether with Ethyl Acetate, Methyl Benzoate, Ethyl Benzoate, and Diethyl Succinate in the Temperature Range from 298.15 to 318.15 K. *J. Chem. Eng. Data* **1994**, *39*, 251−260.

Dewan, R. K.; Mehta, S. K. Excess Volumes of (Ethylbenzene + an Alkanol). *J. Chem. Thermodyn.* **1987**, *19*, 819−822.

Diazpena, M.; Tradajos G. Isothermal Compressibilities of *n*-l-Alcohols from Methanol to 1-Dodecanol at 298.15, 308.15, 318.15, 333.15 K. *J. Chem. Thermodyn.* **1979**, *11*, 441−445.

Kiyohara, O.; Benson, G. C. Ultrasonic Speed and Isentropic Compressibilities of *n*-Alkanol + *n*-Heptane Mixtures at 298.15 K. *J. Chem. Thermodyn.* **1979**, *11*, 861−873.

Marsh, K. N.; Richards, A. B. Excess Volumes for Ethanol + Water Mixtures at 10-K Intervals from 278.15 to 338.15 K. *Aust. J. Chem.* **1980**, *33*, 2121−2132.

Mecke, R. Infrared Spectra of Hydroxylic Compounds. *Discuss Faraday Soc.* **1950**, *9*, 161−177.

Narayanswamy, G.; Dharmaraju, G.; Raman, G. K. Excess Volumes and Isentropic Compressibilities of Acetonitrile + *n*-Propanol, + *i*-Propanol, + *n*-Butanol, + *i*-Butanol, and Cyclohexanol at 303.15 K. *J. Chem. Thermodyn.* **1981**, *13*, 327−331.

Nikam, P. S.; Sawant, A. B. Viscosity of Potassium Halides and Symmetrical Tetraalkylammonium Bromides in Acetronitrile + Water Mixtures at 298.15 K. *J. Chem. Eng. Data* **1997**, *42*, 1151−1156.

Nikam, P. S.; Jadhav, M. C.; Mehdi Hasan. Volumetric, Viscometric and Ultrasonic Behaviour of Diemethylsulfoxide with Normal Alcohol (C_1−C_4) at 308.15K. *J. Mol. Liq.* **1997**, in press.

Paez, S.; Contreras, M. Densities and Viscosities of Binary Mixtures of 1-Propanol and 2-Propanol with Acetonitrile. *J. Chem Eng. Data* **1989**, *34*, 455−459.

Redlich, O.; Kister, A. T. Algebric Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345−348.

Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents; Physical Properties and Methods of Purifications*, 4th ed.; Wiley-Interscience: New York, 1986.

Sastry, N. V.; Valand, M. K. Viscosities and Densities for Heptane + 1-Pentanol, + 1-Hexanol, + 1-Heptanol, + 1-Octanol, + 1-Decanol, and 1-Dodecanol at 298.15 K and 308.15 K. *J. Chem. Eng. Data* **1996**, *41*, 1426−1428.

TRC Tables, Source Data Base−Experimental Data, Ver. 1.1, 1994, and Data Base for Chemistry and Engineering, Ver. 1996−1, 1997; Texas A&M University, College Station, TX.

Treszczanowicz, A. J.; Benson, G. C. Excess Volume for *n*-Alkanols + *n*-Alkanes II. Binary Mixtures of *n*-Pentanol, *n*-Hexanol, *n*-Octanol and *n*-Decanol, + *n*-Heptane. *J. Chem. Thermodyn.* **1978**, *10*, 967−974.

Received for review October 23, 1997. Accepted February 17, 1998.

JE970253G