Density and Viscosity of Binary Mixtures of Ethyl Acetate with Methanol, Ethanol, Propan-1-ol, Propan-2-ol, Butan-1-ol, 2-Methylpropan-1-ol, and 2-Methylpropan-2-ol at (298.15, 303.15, and 308.15) K

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Densities and viscosities have been measured for the binary mixtures of ethyl acetate with linear and branched alkanols (C_1-C_4) at (298.15, 303.15, and 308.15) K. The experimental density (ζ) and viscosity (η) values were used to calculate the excess molar volume (V^E) and viscosity deviation ($\Delta\eta$). The V^E and $\Delta\eta$ values have been fitted to a Redlich−Kister polynomial.

Introduction

The thermodynamic and transport properties of liquid and liquid mixtures (Marsh, 1985; Marsh and Burfitt, 1975; Kim and Marsh, 1988; Sun et al., 1992; Aminabhavi and Gopalkrishna, 1995; Pandey et al., 1993) have been used to understand the molecular interactions between the components of the mixture and also for engineering applications concerning heat transfer, mass transfer, and fluid flow. The density and viscosity of binary liquid mixtures are important from practical and theoretical points of view to understand the liquid theory. In the present study, the densities and viscosities of binary systems of ethyl acetate with linear and branched alkanols (C_1-C_4) over the entire range of composition at (298.15, 303.15, and 308.15) K have been determined. The excess molar volume (V^E) and the viscosity (η) values have been interpreted in terms of the nature of intermolecular interactions between constituent molecules of mixtures.

Experimental Section

Though the V^E measurements are much less sensitive to the purity of substances (So-Jin-Park and Jurgen, 1994), it greatly influences the viscosity of a substance. Hence, all chemicals in the present investigation were used after purification. The spectral grade ethyl acetate (E-Merck) with purity 99.5% was once distilled. Alkanols (E-Merck, 99.7 mol %) were dried by refluxing over fused calcium oxide for 5 h and then distilled fractionally two to three times (Riddick et al., 1986). The purity of these solvents was checked by comparing their density (ζ) and viscosity (η) values, which compared well with the literature data (Table 1). Binary mixtures were prepared, by mass, in airtight stoppered glass bottles with a precision of ±0.01 mg, and care was taken to avoid evaporation and contamination during the mixing process. The possible error in mole fraction is less than 1×10^{-4}.

The densities, ζ, were measured with a double arm pycnometer having a bulb volume of 15 cm^3 and a capillary of an internal diameter of about 0.1 cm. The pycnometer was calibrated with conductivity water using $\zeta = 0.997\ 05$ g·cm^{-3} at 298.15 K. The temperature of the water bath was controlled to ±0.01 K. The density values were reproducible within 5×10^{-5} g·cm^{-3}.

The viscosity of the binary liquid mixtures was measured using an Ostwald viscometer calibrated with conductivity water using $\eta = 0.8937$ mPa·s at 298.15 K. All viscosity measurements were carried out in a glass-sided water thermostat having a thermal stability of ±0.01 K. The flow times of the liquids were recorded with a digital stopwatch correct to ±0.01 s. Since all the flow times were greater than 300 s, the kinetic energy corrections were found to be negligible. The accuracy in the viscosity measurement was ±0.001 mPa·s. The other experimental details of the measurements of density and viscosity are the same as described previously (Nikam et al., 1995).

Table 1. Densities, ζ, and Viscosities, η, of Pure Components and Comparison with Literature Data at 298.15 K

	ζ/g·cm^{-3}		η/mPa·s	
component	exptl	lit. (Riddick et al., 1986)	exptl	lit. (Riddick et al., 1986)
methanol	0.7863	0.7863	0.551	0.5513
ethanol	0.7849	0.7849	1.082	1.0826
propan-1-ol	0.7996	0.7996	1.940	1.943
propan-2-ol	0.7813	0.7813	2.049	2.0436
butan-1-ol	0.8057	0.8057	2.570	2.571
2-methylpropan-1-ol	0.7980	0.7998	3.350	3.333
2-methylpropan-2-ol	0.7812	0.7812	4.332	4.438
ethyl acetate	0.8946	0.8945	0.424	0.426

Results and Discussion

The experimental density (ζ) and viscosity (η) are given in Table 2. ζ has been used to calculate the excess volume, V^E, using the following equation:

$$V^E/\text{cm}^3\cdot\text{mol}^{-1} = \frac{M_1x_1 + M_2x_2}{\zeta_{12}} - \frac{M_1x_1}{\zeta_1} - \frac{M_2x_2}{\zeta_2} \quad (1)$$

where ζ_{12} is the density of the mixture and M_1, x_1, ζ_1 and M_2, x_2, ζ_2 are the molecular weight, mole fraction, and density of pure components 1 and 2, respectively. Excess volumes calculated from eq 1 are listed in Table 2.

The results of V^E were fitted to a polynomial of the type

$$V^E/\text{cm}^3\cdot\text{mol}^{-1} = x_1x_2\sum_{i=0}^{m} a_i(x_1 - x_2)^i \quad (2)$$

where m is the number of coefficients a_i. In each case, the optimum number of coefficients is ascertained from an

S0021-9568(96)00090-8 CCC: $12.00

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

	T = 298.15 K			T = 303.15 K			T = 308.15 K		
x_1	ζ/g·cm^{-3}	V^E/cm^3·mol^{-1}	η/mPa·s	ζ/g·cm^{-3}	V^E/cm^3·mol^{-1}	η/mPa·s	ζ/g·cm^{-3}	V^E/cm^3·mol^{-1}	η/mPa·s
				Ethyl Acetate (1) + Methanol (2)					
0.0000	0.7863		0.551	0.7817		0.523	0.7771		0.493
0.0388	0.7967	−0.039	0.529	0.7921	−0.045	0.497	0.7876	−0.059	0.461
0.0833	0.8071	−0.072	0.509	0.8024	−0.083	0.474	0.7977	−0.088	0.439
0.1348	0.8175	−0.091	0.490	0.8127	−0.101	0.458	0.8078	−0.109	0.425
0.1951	0.8280	−0.105	0.475	0.8230	−0.115	0.445	0.8180	−0.125	0.413
0.2667	0.8387	−0.118	0.461	0.8336	−0.128	0.431	0.8285	−0.139	0.401
0.3529	0.8497	−0.126	0.453	0.8444	−0.136	0.424	0.8391	−0.151	0.395
0.4589	0.8607	−0.123	0.446	0.8552	−0.133	0.416	0.8498	−0.114	0.391
0.5924	0.8719	−0.114	0.439	0.8663	−0.122	0.411	0.8607	−0.128	0.387
0.7659	0.8833	−0.078	0.432	0.8774	−0.084	0.406	0.8716	−0.091	0.386
1.0000	0.8946		0.424	0.8885		0.400	0.8825		0.385
				Ethyl Acetate (1) + Ethanol (2)					
0.0000	0.7849		1.082	0.7808		0.988	0.7763		0.893
0.0549	0.7940	0.046	0.955	0.7894	0.059	0.873	0.7848	0.072	0.791
0.1150	0.8034	0.090	0.843	0.7986	0.106	0.767	0.7938	0.124	0.702
0.1849	0.8134	0.139	0.738	0.8084	0.161	0.674	0.8035	0.178	0.615
0.2585	0.8232	0.183	0.670	0.8180	0.207	0.603	0.8129	0.232	0.550
0.3434	0.8335	0.229	0.603	0.8282	0.257	0.544	0.8229	0.282	0.498
0.4396	0.8442	0.273	0.546	0.8387	0.304	0.503	0.8331	0.333	0.462
0.5496	0.8553	0.308	0.494	0.8496	0.338	0.461	0.8439	0.366	0.431
0.6766	0.8675	0.272	0.451	0.8616	0.306	0.424	0.8557	0.338	0.402
0.8247	0.8805	0.180	0.446	0.8745	0.204	0.416	0.8684	0.234	0.395
1.0000	0.8946		0.424	0.8885		0.400	0.8825		0.385
				Ethyl Acetate (1) + Propan-1-ol (2)					
0.0000	0.7996		1.940	0.7956		1.721	0.7912		1.526
0.0704	0.8076	0.057	1.530	0.8032	0.077	1.378	0.7985	0.095	1.237
0.1455	0.8158	0.107	1.217	0.8111	0.143	1.091	0.8061	0.176	0.979
0.2260	0.8243	0.157	0.981	0.8194	0.199	0.893	0.8142	0.236	0.816
0.3124	0.8331	0.194	0.809	0.8279	0.243	0.740	0.8227	0.276	0.684
0.4052	0.8424	0.207	0.694	0.8369	0.262	0.649	0.8316	0.290	0.594
0.5053	0.8521	0.191	0.608	0.8466	0.234	0.566	0.8410	0.271	0.535
0.6137	0.8624	0.150	0.548	0.8566	0.197	0.509	0.8507	0.239	0.472
0.7315	0.8728	0.104	0.494	0.8669	0.149	0.460	0.8608	0.197	0.434
0.8597	0.8836	0.058	0.454	0.8776	0.075	0.429	0.8714	0.118	0.405
1.0000	0.8946		0.424	0.8885		0.400	0.8825		0.385
				Ethyl Acetate (1) + Propan-2-ol (2)					
0.0000	0.9813		2.049	0.7712		1.781	0.7725		1.551
0.0704	0.7906	0.076	1.460	0.7860	0.103	1.275	0.7808	0.145	1.158
0.1454	0.7996	0.195	1.141	0.7949	0.225	0.982	0.7897	0.264	0.905
0.2259	0.8092	0.298	0.914	0.8042	0.343	0.822	0.7989	0.371	0.746
0.3122	0.8192	0.340	0.754	0.8140	0.430	0.688	0.8087	0.458	0.634
0.4051	0.8298	0.439	0.640	0.8245	0.485	0.593	0.8189	0.524	0.550
0.5052	0.8411	0.459	0.567	0.8357	0.493	0.527	0.8301	0.521	0.490
0.6138	0.8532	0.439	0.513	0.8475	0.470	0.483	0.8417	0.502	0.448
0.7313	0.8659	0.376	0.470	0.8600	0.414	0.442	0.8541	0.436	0.416
0.8599	0.8796	0.248	0.449	0.8735	0.275	0.425	0.8672	0.326	0.401
1.0000	0.8946		0.424	0.8885		0.400	0.8825		0.385
				Ethyl Acetate (1) + Butan-1-ol (2)					
0.0000	0.8057		2.570	0.8018		2.268	0.7981		1.982
0.0862	0.8132	0.080	1.868	0.8089	0.096	1.673	0.8049	0.115	1.413
0.1739	0.8209	0.127	1.400	0.8165	0.146	1.263	0.8122	0.178	1.138
0.2650	0.8290	0.161	1.126	0.8245	0.176	1.023	0.8197	0.227	0.931
0.3594	0.8374	0.184	0.897	0.8326	0.203	0.825	0.8276	0.260	0.756
0.4569	0.8461	0.196	0.767	0.8411	0.209	0.710	0.8358	0.272	0.654
0.5579	0.8552	0.184	0.654	0.8499	0.198	0.605	0.8444	0.264	0.564
0.6625	0.8645	0.160	0.573	0.8591	0.175	0.532	0.8534	0.231	0.499
0.7708	0.8742	0.120	0.507	0.8685	0.140	0.488	0.8626	0.187	0.462
0.8833	0.8842	0.072	0.547	0.8782	0.087	0.431	0.8722	0.125	0.409
1.0000	0.8946		0.424	0.8885		0.400	0.8825		0.385
				Ethyl Actate (1) + 2-Methylpropan-1-ol (2)					
0.0000	0.7980		3.350	0.7941		2.997	0.7902		2.499
0.0855	0.8063	0.045	2.049	0.8019	0.084	2.073	0.7978	0.095	1.713
0.1738	0.8147	0.107	1.595	0.8100	0.158	1.551	0.8054	0.195	1.242
0.2650	0.8232	0.173	1.217	0.8184	0.212	1.221	0.8136	0.262	0.986
0.3593	0.8321	0.216	0.935	0.8272	0.256	0.979	0.8220	0.311	0.782
0.4568	0.8413	0.252	0.757	0.8362	0.290	0.785	0.8308	0.357	0.655
0.5579	0.8533	0.275	0.648	0.8455	0.314	0.660	0.8399	0.374	0.560
0.6625	0.8614	0.214	0.571	0.8556	0.260	0.562	0.8498	0.333	0.506
0.7710	0.8735	0.131	0.512	0.8664	0.175	0.495	0.8602	0.242	0.447
0.8833	0.8839	0.051	0.463	0.8774	0.731	0.438	0.8714	0.111	0.412
1.0000	0.8946		0.424	0.8885		0.400	0.8825		0.385

Table 2 (Continued)

	T = 298.15 K			T = 303.15 K			T = 308.15 K		
x_1	ζ/g·cm^{-3}	V^E/cm^3·mol^{-1}	η/mPa·s	ζ/g·cm^{-3}	V^E/cm^3·mol^{-1}	η/mPa·s	ζ/g·cm^{-3}	V^E/cm^3·mol^{-1}	η/mPa·s
				Ethyl Acetate (1) + 2-Methylpropan-2-ol (2)					
0.0000	0.7812		4.332	0.7754		3.372	0.7643		2.687
0.0855	0.7894	0.217	2.461	0.7841	0.164	2.013	0.7736	0.130	1.668
0.1738	0.7980	0.431	1.598	0.7928	0.348	1.371	0.7832	0.274	1.180
0.2650	0.8071	0.599	1.155	0.8020	0.511	1.021	0.7929	0.426	0.905
0.3594	0.8168	0.732	0.926	0.8116	0.646	0.809	0.8031	0.553	0.732
0.4569	0.8272	0.809	0.738	0.8219	0.733	0.675	0.8138	0.644	0.618
0.5578	0.8385	0.810	0.618	0.8332	0.732	0.570	0.8258	0.640	0.528
0.6625	0.8511	0.709	0.548	0.8458	0.638	0.512	0.8386	0.571	0.505
0.7708	0.8643	0.569	0.496	0.8590	0.497	0.465	0.8524	0.418	0.438
0.8896	0.8796	0.330	0.453	0.8739	0.283	0.428	0.8678	0.226	0.418
1.0000	0.8946		0.424	0.8885		0.400	0.8825		0.385

examination of the variation in standard deviation, σ, as given by

$$\sigma = [(x_{obsd} - x_{calcd})^2/(n - m)]^{1/2} \quad (3)$$

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 as computed from eqs 2 and 3, respectively, are presented in Table 3.

The viscosity deviations, $\Delta\eta$, were obtained by

$$\Delta\eta = \eta_m - x_1\eta_1 - x_2\eta_2 \quad (4)$$

where η_m is the viscosity of the mixture and η_1 and η_2 are the viscosities of pure components 1 and 2, respectively.

The coefficients, a_i, and standard deviation, σ, for $\Delta\eta$ as obtained from equations similar to eqs 2 and 3 are listed in Table 3.

Excess molar volumes are positive for mixtures of ethyl acetate with all the alkanols except methanol (Figure 1).

The observed excess molar volume values in the present investigation may be discussed in terms of several effects which may be arbitrarily divided into physical, chemical, and geometrical contributions. The physical interactions involve mainly dispersion forces, giving a positive contribution to V^E (Aminabhavi et al., 1993). The chemical or

Table 3. Parameters and Standard Deviations, σ, of Eqs 2 and 3 for Ethyl Actate + Alkanols

system		T/K	a_0	a_1	a_2	a_3	σ
ethyl acetate + methanol	V^E/cm^3·mol^{-1}	298.15	−0.491	0.050	−0.149	0.491	0.003
		303.15	−0.528	0.027	−1.171	0.660	0.004
		308.15	−0.580	−0.109	−0.092	1.175	0.011
	$\Delta\eta$/mPa·s	298.15	−0.176	0.160	−0.131	0.034	0.001
		303.15	−0.191	0.120	−0.122	0.217	0.001
		308.15	−0.204	0.068	−0.107	0.453	0.003
ethyl acetate + ethanol	V^E/cm^3·mol^{-1}	298.15	1.169	0.412	−0.228	−0.367	0.005
		303.15	1.295	0.496	−0.153	−0.544	0.004
		308.15	1.405	0.594	0.006	−0.683	0.005
	$\Delta\eta$/mPa·s	298.15	−0.967	0.459	−0.209	0.349	0.005
		303.15	−0.882	0.537	−0.249	0.085	0.005
		308.15	−0.882	0.537	−0.249	0.085	0.003
ethyl acetate + propan-1-ol	V^E/cm^3·mol^{-1}	298.15	0.757	−0.460	−0.148	0.320	0.004
		303.15	0.962	−0.488	−0.125	0.209	0.005
		308.15	1.107	−0.420	0.184	0.237	0.004
	$\Delta\eta$/mPa·s	298.15	−2.279	1.625	−1.015	0.316	0.002
		303.15	−1.981	1.443	−0.789	0.105	0.008
		308.15	−1.711	1.276	−0.686	−0.094	0.010
ethyl acetate + propan-2-ol	V^E/cm^3·mol^{-1}	298.15	1.856	−0.092	−0.153	0.976	0.006
		303.15	2.002	−0.101	0.079	0.885	0.005
		308.15	2.073	0.006	0.683	0.640	0.010
	$\Delta\eta$/mPa·s	298.15	−3.300	1.053	−4.722	8.152	0.089
		303.15	−2.174	1.278	−1.895	2.360	0.019
		308.15	−1.869	1.175	−1.341	1.367	0.007
ethyl acetate + butan-1-ol	V^E/cm^3·mol^{-1}	298.15	0.752	−0.115	0.122	−0.110	0.004
		303.15	0.803	−0.099	0.309	−0.171	0.005
		308.15	1.049	−0.103	0.388	−0.036	0.007
	$\Delta\eta$/mPa·s	298.15	−3.117	2.190	−1.735	0.907	0.010
		303.15	−2.684	1.866	−1.390	0.614	0.009
		308.15	−2.205	1.155	−1.666	1.806	0.025
ethyl acetate + 2-methylpropan-1-ol	V^E/cm^3·mol^{-1}	298.15	1.049	0.032	−0.839	−0.230	0.009
		303.15	1.206	0.132	−0.545	−0.638	0.007
		308.15	1.486	0.192	−0.526	−0.510	0.007
	$\Delta\eta$/mPa·s	298.15	−4.446	2.176	−4.603	6.176	0.083
		303.15	−3.782	2.217	−2.643	2.529	0.021
		308.15	−3.262	2.249	−2.303	1.754	0.015
ethyl acetate + 2-methylpropan-2-ol	V^E/cm^3·mol^{-1}	298.15	3.227	−0.009	−0.226	0.551	0.009
		303.15	2.913	0.087	−0.642	0.561	0.010
		308.15	2.559	0.259	−0.932	0.137	0.010
	$\Delta\eta$/mPa·s	298.15	−6.534	4.866	−7.246	6.775	0.048
		303.15	−4.879	3.549	−5.008	4.688	0.035
		308.15	−3.642	2.329	−4.076	4.601	0.049

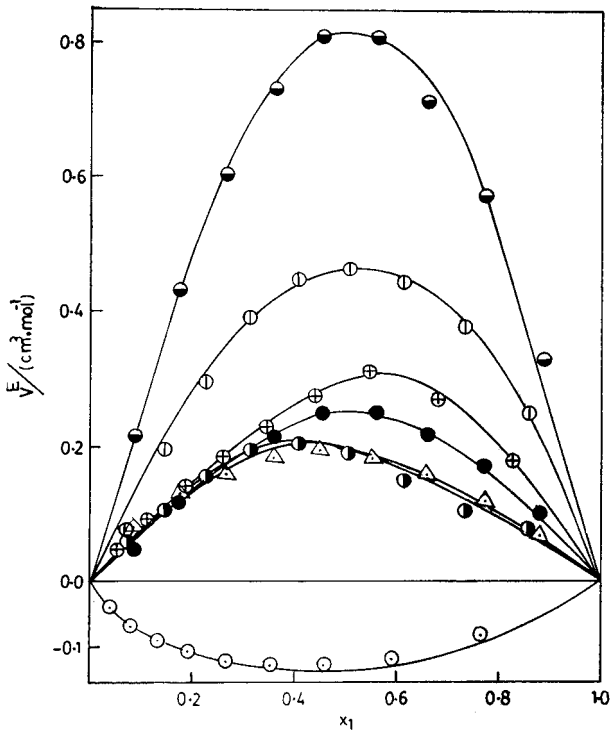

Figure 1. Excess molar volumes, V^E, at 298.15 K for x_1 ethyl acetate + $(1 - x_1)$ alkanols: (⊙) methanol, (⊕) ethanol, (◑) propan-1-ol, (Φ)propan-2-ol, (●) 2-methylpropan-1-ol, (◒) 2-methylpropan-2-ol, and (◬) butan-1-ol.

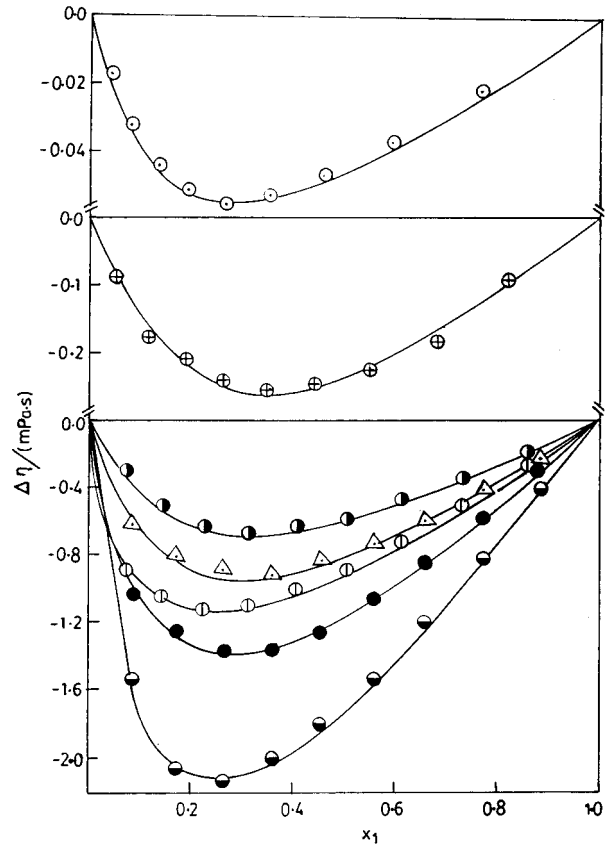

Figure 2. $\Delta\eta$ values at 298.15 K for x_1 ethyl acetate + $(1 + x_1)$ alkanols: (⊙) methanol, (⊕) ethanol, (◑) propan-1-ol, (Φ) propan-2-ol, (●) 2-methylpropan-1-ol, (◒) 2-methylpropan-2-ol, and (◬) butan-1-ol.

specific interactions between constituent molecules of the mixture result in a volume decrease. In the present investigation the negative V^E values for binary mixtures of ethyl acetate with methanol may be attributed to hydrogen bond formation through dipole−dipole interactions between methanol and ethyl acetate molecules or to structural contributions arising from the geometrical fitting of one component (methanol) into the other (ethyl acetate) due to differences in the molar volumes between components. With higher alkanols (C_2−C_4) the geometrical contribution is negligible and clustering decreases with an increase in chain length of the alkanols. Therefore, the mixtures containing higher alkanols give positive V^E values. The higher alkanols possess less proton donating ability than the lower ones and hence heteroassociation effects decrease in the binary mixtures with an increase of chain length of linear alkanols. Thus, positive V^E values are observed in the mixtures of ethyl acetate with higher alkanols. V^E values of branched alkanols are higher than those of their corresponding straight chain alkanols, probably due to increased steric hindrance of branched alkanols.

V^E values of all binary systems increase with an increase of temperature. This is attributed to decreased ester−ester and alkanol−alkanol contacts with an increase of temperature.

Figure 2 shows that the deviations in viscosity are negative in all the systems and become more negative with an increase in chain length and branching of alkanols.

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Received for review March 4, 1996. Accepted May 15, 1996.[⊗]

JE960090G

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1996.