Densities and Excess Volumes of Binary Liquid Mixtures of PEG 200, PEG 400 and PEG 600 with Toluene at Three Temperatures

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Densities for the systems PEG 200 + toluene, PEG 400 + toluene and PEG 600 + toluene at three different temperatures have been studied. Excess volumes (V^E) are calculated over the entire range of composition at three different temperatures using the standard relation. The data are fitted into an empirical equation.

$$V^E = X_1X_2[a + b(2X_1 - 1) + c(2X_1 - 1)^2]$$

and the values of constants a, b and c are evaluated by the least squares method along with standard deviation (σ). The marked reduction in (V^E) with increase in C—C chain length of PEG has been studied in the light of interaction phenomena.

INTRODUCTION

Many researchers[1–6] have studied densities and excess volumes of binary liquid systems to understand the specific interactions between components in binary systems with polar and non-polar solvents. Several workers have studied binary systems with alcohol[7, 8] to understand the specific interaction between the components. There is some work done[9] on binary systems of PEG 200 and PEG 400 in polar and nonpolar solvents. In this paper densities and excess volumes for binary liquid mixtures of PEG 200 + toluene, PEG 400 + toluene and PEG 600 + toluene at 303, 313 and 323 K are being reported.

EXPERIMENTAL

Toluene (E. Merck), PEG 200, PEG 400 and PEG 600 were further purified by standard method[10] and used. Purity of liquids was checked by measuring densities and refractive indices compared with literature values[11, 12] at 303 K. The details of the apparatus and procedure have been discussed elsewhere[9]. The density data are corrected to $\pm 1 \times 10^{-4}$ units. Mixtures were prepared by weighing the liquids in ground stoppered weighing flasks on a balance accurate to 1×10^{-3} units taking due precautions to minimise evaporations. The experiments were repeated for various mixtures with varying mole fractions. The thermostat baths were controlled to ± 0.1 K.

RESULTS AND DISCUSSION

The densities were measured at 303, 313 and 323 K over the entire range of compostion for all the binary systems. The excess volumes (V^E) were calculated from the density data using the relation

$$V^E = [(M_1X_1 + M_2X_2)/d_{12}] - [M_1X_1/d_1 + M_2X_2/d_2] \quad (1)$$

where M, X and d represent molecular weight, mole fraction and density respectively. Subscripts 1, 2 and 12 refer to pure components and mixtures respectively. The density and excess volume are reported in Tables 1–3.

The excess volumes (V^E) were calculated using the empirical relation

$$V^E = X_1X_2[a + b(2X_1 - 1) + c(2X_1 - 1)^2] \quad (2)$$

TABLE-1
DENSITIES (d) (g cm^{-3}) AND EXCESS VOLUMES (V^E) (cm^3 mol^{-1}) OF PEG 200 + TOLUENE AT THREE TEMPERATURES

X_1	303 K			313 K			323 K		
	d	V^E_{expt}	V^E_{cal}	d	V^E_{expt}	V^E_{cal}	d	V^E_{expt}	V^E_{cal}
0.0000	0.8577	—	—	0.8450	—	—	0.8369	—	—
0.1438	0.9130	–0.0941	–0.1302	0.9020	–0.1940	–0.2243	0.8946	–0.2515	–0.2822
0.2197	0.9398	–0.2572	–0.2289	0.9294	–0.3615	–0.3381	0.9220	–0.4203	–0.4074
0.3012	0.9661	–0.3982	–0.3308	0.9562	–0.5005	–0.4420	0.9492	–0.5884	–0.5167
0.4904	1.0180	–0.4746	–0.4698	1.0094	–0.5632	–0.5665	1.0028	–0.6661	–0.6489
0.5379	1.0293	–0.4456	–0.4732	1.0211	–0.5453	–0.5668	1.0144	–0.6204	–0.6520
0.6613	1.0566	–0.3759	–0.4182	1.0493	–0.4790	–0.5064	1.0429	–0.5621	–0.5991
0.7610	1.0765	–0.2994	–0.3150	1.0697	–0.3782	–0.3981	1.0635	–0.4629	–0.4908
0.8551	1.0937	–0.2085	–0.1883	1.0875	–0.2782	–0.2571	1.0814	–0.3592	–0.3354
0.9125	1.1033	–01085	–0.1076	1.0973	–0.1577	–0.1583	1.0912	–0.2174	–0.2159
1.0000	1.1174	—	—	1.1116	—	—	1.1053	—	—

TABLE-2
DENSITIES (d) (g cm^{-3}) AND EXCESS VOLUMES (V^E) (cm^3 mol^{-1}) OF PEG 400 + TOLUENE AT THREE TEMPERATURES

X_1	303 K			313 K			323 K		
	d	V^E_{expt}	V^E_{cal}	d	V^E_{expt}	V^E_{cal}	d	V^E_{expt}	V^E_{cal}
0.0000	0.8577	—	—	0.8450	—	—	0.8369	—	—
0.1125	0.9320	–0.1517	–0.1575	0.9216	–0.2805	–0.2851	0.9142	–0.3465	–0.3639
0.2296	0.9842	–0.2822	–0.3006	0.9752	–0.4446	–0.4647	0.9683	–0.5571	–0.5584
0.3095	1.0112	–0.4111	–0.3810	1.0029	–0.5701	–0.5417	0.9960	–0.6700	–0.6310
0.4059	1.0369	–0.4822	–0.4540	1.0292	–0.6248	–0.6010	1.0225	–0.7315	–0.6856
0.5046	1.0579	–0.5271	–0.4959	1.0507	–0.6665	–0.6313	1.0441	–0.7529	–0.7215
0.6112	1.0758	–0.4774	–0.4971	1.0693	–0.6157	–0.6295	1.0629	–0.7249	–0.7390
0.7076	1.0892	–0.4184	–0.4528	1.0831	–0.5565	–0.5875	1.0768	–0.6652	–0.7180
0.7950	1.0995	–0.3441	–0.3709	1.0937	–0.4667	–0.5014	1.0875	–0.5796	–0.6400
0.9116	1.1111	–0.2081	–0.1926	1.1056	–0.2978	–0.2810	1.0995	–0.4106	–0.3810
1.0000	1.1183	—	—	1.1128	—	—	1.1064	—	—

The values of constants a, b and c are evaluated by the least squares method at temperatures 303, 313 and 323 K and are given in Table-4 along with standard deviation (σ) defined by the equation

$$\sigma^2 = \Sigma (V^E_{expt} - V^E_{col})^2/(n - 3) \quad (3)$$

where n is the total number of measurements.

TABLE-3

DENSITIES (d) (g cm^{-3}) AND EXCESS VOLUMES (V^E) (cm^3 mol^{-1}) OF PEG 600 + TOLUENE AT THREE TEMPERATURES

X_1	303 K			313 K			323 K		
	d	V^E_{expt}	V^E_{cal}	d	V^E_{expt}	V^E_{cal}	d	V^E_{expt}	V^E_{cal}
0.0000	0.8577	—	—	0.8450	—	—	0.8369	—	—
0.1227	0.9652	–0.1701	–0.1823	0.9555	–0.2887	–0.3039	0.9487	–0.4377	–0.4431
0.2234	1.0125	–0.3325	–0.3225	1.0042	–0.4898	–0.4729	0.9974	–0.6199	–0.6241
0.3141	1.0406	–0.4400	–0.4266	1.0330	–0.5830	–0.5768	1.0263	–0.6953	–0.6061
0.4175	1.0632	–0.5078	–0.5075	1.0563	–0.6591	–0.6486	1.0498	–0.7805	–0.7497
0.5039	1.0775	–0.5879	–0.5373	1.0710	–0.7302	–0.6738	1.0645	–0.8327	–0.7646
0.6250	1.0922	–0.5038	–0.5150	1.0862	–0.6330	–0.6543	1.0798	–0.7467	–0.7589
0.7227	1.1013	–0.3945	–0.4413	1.0956	–0.5369	–0.5846	1.0894	–0.6589	–0.7142
0.8326	1.1096	–0.2833	–0.3025	1.1042	–0.4100	–0.4334	1.0980	–0.5436	–0.5747
0.9212	1.1151	–01690	–0.1538	1.1098	–0.2576	–0.2400	1.1036	–0.3631	–0.3430
1.0000	1.1192	—	—	1.1139	—	—	1.1075	—	—

TABLE-4

THE PARAMETERS OF Eqn. (2) AND STANDARD DEVIATION $\sigma(V^E)$ OF Eqn. (3)

SYSTEM : PEG 200 + TOLUENE

Temperature (K)	a	b	c	$\sigma(V^E)$/(cm^3 mol^{-1})
303	–1.8863	–0.3215	1.1807	0.0405
313	–2.2705	–0.1762	0.6363	0.0340
323	–2.6024	–0.2903	0.2022	0.0413

SYSTEM : PEG 400 + TOLUENE

Temperature (K)	a	b	c	$\sigma(V^E)$/(cm^3 mol^{-1})
303	–1.9790	–0.5102	0.0119	0.0305
313	–2.5221	–0.3482	–1.0025	0.0307
323	–2.8807	–0.5715	–2.0202	0.0455

SYSTEM : PEG 600 + TOLUENE

Temperature (K)	a	b	c	$\sigma(V^E)$/(cm^3 mol^{-1})
303	–2.1472	–0.3008	0.3985	0.0314
313	–2.6935	–0.2525	–0.5614	0.0352
323	–3.0570	–0.1947	–2.1179	0.0415

The excess volumes (V^E) against mole fraction (X_1) for three systems are reported in Fig. 1–3. The excess volumes (V^E) at equimolar fraction ($X_1 = X_2 = 0.5$) are reported in Table-5.

TABLE-5
EXCESS VOLUME (V^E) (cm^3 mol^{-1}) FOR BINARY SYSTEMS AT DIFFERENT TEMPERATURES AT MOLE FRACTION $X_1 = X_2 = 0.5$

Excess volume (V^E) for the system	Temperature (K)	V^E (cm^3 mol^{-1})
PEG 200 + Toluene	303	–0.4746
	313	–0.5632
	323	–0.6661
PEG 400 + Toluene	303	–0.5271
	313	–0.6665
	323	–0.7529
PEG 600 + Toluene	303	–0.5879
	313	–0.7302
	323	–0.8327

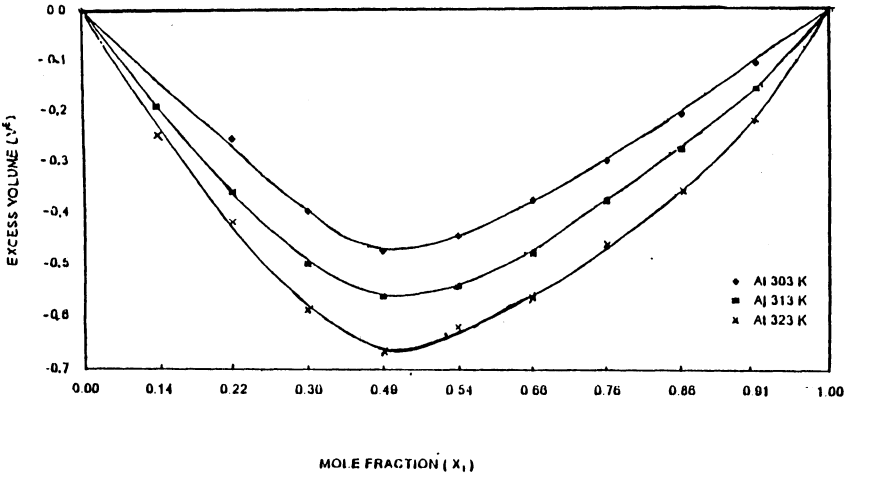

Fig. 1. PEG 200 + Toluene

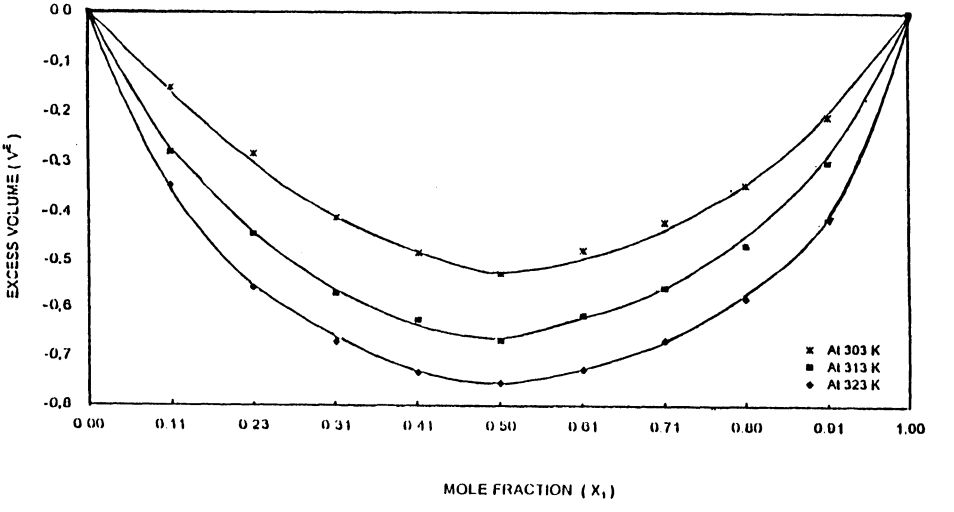

Fig. 2. PEG 400 + Toluene

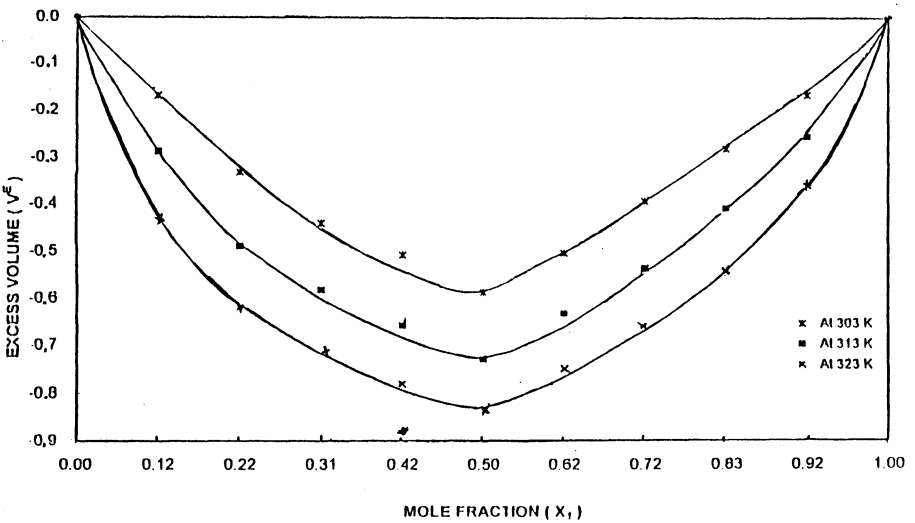

Fig. 3. PEG 600 + Toluene

The excess volume (V^E) for the system PEG 200 + toluene, PEG 400 + toluene and PEG 600 + toluene have negaitve values at all temperatures. The marked reduction in V^E with the increase in C—C chain length for PEG 200 to PEG 600 are attributed to specific interaction between two components in binary mixtures.

The negative increase in (V^E) values with increase in temperature is attributed to strong specific bond formation between the components.

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