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Densities and Excess Volumes for PEG 200 and PEG 400 with Nitrobenzene at Different Temperatures

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Densities, excess volumes for PEG 200 + nitrobenzene and PEG 400 + nitrobenzene at three different temperatures have been studied. Excess volumes (V^E) are calculated over entire range of compositions at three different temperatures using the standard equation. The data are fitted in to empirical equation

$V^E/X_1X_2 = [a + b(2X_1 - 1) + c(2X_1 - 1)^2]$ and constants 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 solvents is discussed in the light of hydrogen bonding.

INTRODUCTION

Many researchers[1–6] have studied physical properties of binary mixtures to understand the interaction between the two components. The present work is part of investigation of specific interactions between components of binary solution of PEG 200 and PEG 400 with polar and nonpolar solvents[7,8]. Earlier the authors[7,8] have studied densities and excess volumes of PEG 200 and PEG 400 with ethyl acetate. In this communication, densities and excess volumes for binary mixtures PEG 200 and PEG 400 with nitrobenzene at 303K, 308K and 313K are being reported.

EXPERIMENTAL

Nitrobenzene (E. Merck, analytical grade), PEG 200, PEG 400 were further purified by conventional methods[9,10] and used, the purity being checked by comparing the physical constants with literature values[11]. The measured values

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of boiling point, refractive index and density are in close agreement with the literature values[11]. The apparatus and procedure for the measurement of density with the help of Gay-Lussac pycnometer (Weld specific gravity bottle) are described elsewhere[7]. The density data are corrected to ± 0.0001 units. Mixtures were prepared by weighing the liquids in ground stoppered weighing flasks on a balance accurate to 1/10th of milligram taking due precautions to minimise evaporation. Weighings were carried out 2–3 times for reproducibility of results.

RESULTS AND DISCUSSION

The measurements of density were made at 303 K, 308 K and 313 K over the entire range of composition for both the binary systems. The excess values (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 data are given in Tables 1 and 2. Excess volume V^E against mole fraction X_1 have been plotted and the diagrams are reported in Figs. Nos. 1 and 2. The excess volumes V^E are fitted to the empirical equation

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

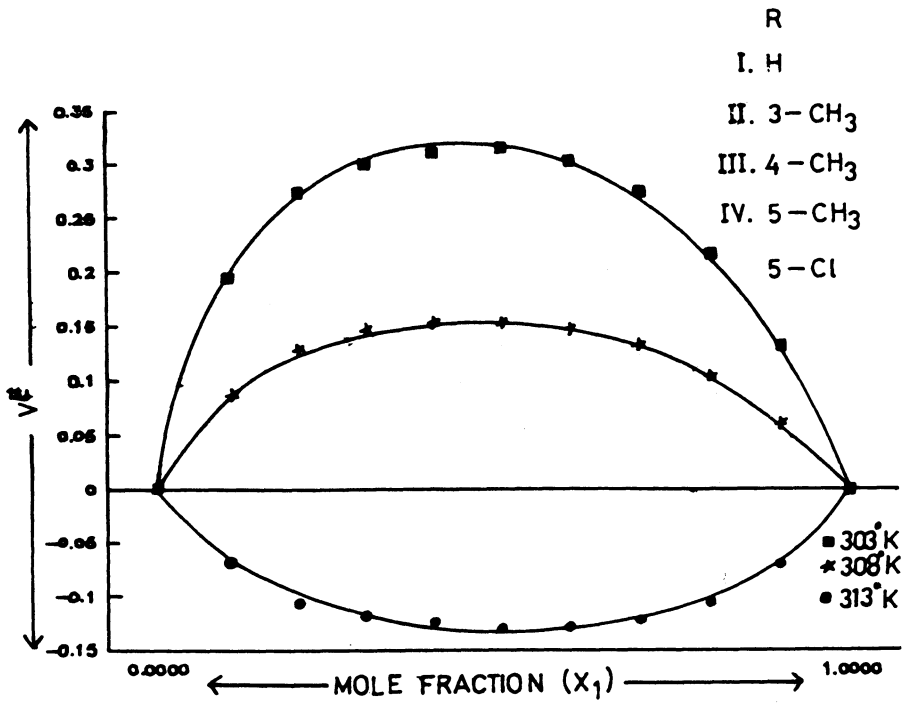

Fig. 1. Excess volume (V^E) against mole-fraction (X_1) of PEG 200 + nitrobenzene.

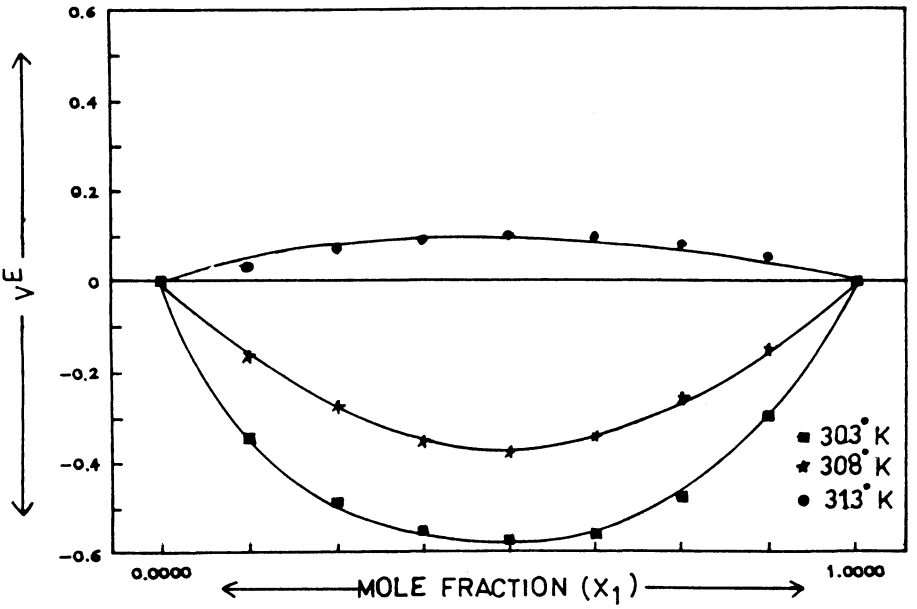

Fig. 2. Excess volume (V^E) against mole fraction (X_1) of PEG 400 + nitrobenzene.

TABLE–1
DENSITIES (d) AND EXCESS VOLUMES (V^E) FOR PEG 200 + NITROBENZENE AT 303 K, 308 K and 313 K

X_1	303 K		308 K		313 K	
	d	V^E	d	V^E	d	V^E
0.0000	1.1935	—	1.1896	—	1.1833	—
0.2557	1.1641	0.1949	1.1616	0.0854	1.1581	–0.0697
0.3338	1.1566	0.2741	1.1544	0.1302	1.1519	–0.1067
0.4142	1.1499	0.3009	1.1479	0.1474	1.1458	–0.1182
0.4626	1.1462	0.3113	1.1442	0.1527	1.1424	–0.1240
0.5148	1.1425	0.3169	1.1405	0.1529	1.1388	–0.1293
0.6237	1.1354	0.3046	1.1334	0.1480	1.1319	–0.1280
0.7169	1.1301	0.2754	1.1280	0.1333	1.1264	–0.1218
0.8170	1.1250	0.2180	1.1227	0.1058	1.1210	–0.1057
0.9170	1.1205	01340	1.1179	0.0617	1.1158	–0.0703
1.0000	1.1174	—	1.1144	—	1.1116	—

TABLE–2
DENSITIES (d) AND EXCESS VOLUME (V^E) FOR PEG 400 + NITROBENZENE AT 303 K, 308 K and 313 K

X_1	303 K		308 K		313 K	
	d	V^E	d	V^E	d	V^E
0.0000	1.1935	—	1.1896	—	1.1833	—
0.1661	1.1661	–0.3473	1.1611	–0.1677	1.1547	0.0364
0.2673	1.1553	–0.4872	1.1505	–0.2751	1.1440	0.0706
0.3639	1.1472	–0.5492	1.1428	–0.3551	1.1364	0.0910
0.4471	1.1415	–0.5707	1.1373	–0.3788	1.1312	0.1008
0.5642	1.1349	–0.5569	1.1308	–0.3415	1.1255	0.0972
0.7193	1.1280	–0.4758	1.1241	–0.2538	1.1198	0.0802
0.8131	1.1233	–0.2976	1.1198	–0.1465	1.1163	0.0531
1.0000	1.1183	—	1.1154	—	1.1128	—

TABLE–3
VALUES OF CONSTANTS a, b and c OF EQUATION (2) ALONG WITH STANDARD DEVIATION (σ)

Temp.	a	b	c	σ
		PEG 200 + Nitrobenzene		
303 K	1.1409	–0.2784	0.9354	0.0156
308 K	0.4077	0.3926	0.0615	0.0087
313 K	–0.4910	0.4986	–0.9964	0.0094
		PEG 400 + Nitrobenzene		
303 K	–2.6853	1.1113	–0.7566	0.0091
308 K	–0.8928	–2.6346	2.8801	0.0113
313 K	0.1674	0.8180	–0.6625	0.0039

The values of the constants a, b and c are evaluated by the least squares method and are reported in Table 3 along with the standard deviation (σ) defined by equation,

$$\sigma = [(V^E_{expt} - V^E_{cal})/(M - P)^{1/2}] \quad (3)$$

where M is the total number of measurements.

The excess volumes for the mixtures of PEG 200 + nitrobenzene have positive values of 303 K and 308 K and negative values at 313 K. The excess valumes for the mixture of PEG 400 + nitrobenzene have negative values at 303 K and 308 K and positive values at 313 K. The marked reduction in V^E values with the increase in C—C chain length from PEG 200 to PEG 400 suggests that formation of complex between the two unlike species due to hydrogen bond may be taking place through planes at different angles and increase in temperature may be

changing the plane of interaction between the loan pair of electrons of either oxygen or nitrogen atoms of nitrobenzene with PEG solvents.

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