

## Excess Free Volume and Intermolecular Interaction in Binary Liquid Mixtures of *o*-Xylene with 1-Alkanols

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The free volume for the three binary liquid systems, *o*-xylene + 1-propanol, *o*-xylene + 1-butanol and *o*-xylene + 1-pentanol, have been studied using density and sound velocity data at 303.15 K. In the present study, a new approach is applied in the computation of internal pressure ( $P_i$ ), which in turn has been used to calculate free volume. The intermolecular interaction in the binary liquid mixtures under consideration has been discussed in the light of excess free volume. The results are consistent with the theories.

**Key Words:** *o*-Xylene, 1-Propanol, 1-Butanol, 1-Pentanol, Binary mixtures.

### INTRODUCTION

Free volume has been found to be a very important property of liquid state and has been extensively applied to liquids and liquid mixtures for the study of intermolecular interaction by many workers<sup>1-10</sup>. The free volume is related to other properties such as viscosity, internal pressure, entropy and sound velocity. The present paper deals with the evaluation of free volume and excess free volume in case of three binary liquid systems namely *o*-xylene + 1-propanol, *o*-xylene + 1-butanol and *o*-xylene + 1-pentanol. The intermolecular interaction in these liquid mixtures has been discussed in the light of excess free volume.

#### Theoretical

The free volume is related to the internal pressure according to the equation<sup>11</sup>

$$V_f = \left( \frac{bRT}{P_i} \right) \frac{1}{v^2} \quad (1)$$

Here  $b$  is proportionality factor and its value is 2 for liquids and liquid mixtures. Pandey *et al.*<sup>12</sup> gave a relation for the calculation of internal pressure ( $P_i$ ) in liquids and liquid mixtures. Their relation is

$$P_i = 44.2T^{4/3}U^{3/2} \cdot \rho \quad (2)$$

where  $T$ ,  $U$  and  $\rho$  are temperature, sound velocity and density respectively.

In the present study internal pressure has been evaluated by eqn. (2) and (1) has been used to calculate free volume of liquids and liquid mixtures.

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The excess free volume ( $V_f^E$ ) is given by the relation

$$V_f^E = (V_f)_{\text{mix}} - (V_f)_{\text{idl.}} \quad (3)$$

$$(V_f)_{\text{idl.}} = X_1 V_{f_1} + X_2 V_{f_2} \quad (4)$$

where  $X_1$  and  $X_2$  are mole fraction of components 1 and 2 and  $V_{f_1}$  and  $V_{f_2}$  are free volumes of components 1 and 2 respectively.

## RESULTS AND DISCUSSION

The free volume for the binary liquid mixtures namely *o*-xylene + 1-propanol, *o*-xylene + 1-butanol and *o*-xylene + 1-pentanol has been computed using eqn. (1) and the calculated values are recorded in Table-1. The excess free volume ( $V^E$ ) has been calculated through eqn. (3) and the calculated values are also presented in Table-1. The necessary data required for the calculation have been taken from literature<sup>13</sup>. A perusal of Table-1 shows that the value of free volume decreases as the mole fraction of first named component  $x_1$  increases in all the three mixtures under consideration. It is observed that the magnitude of free volume is higher in case of *o*-xylene + 1-propanol system and decreases continuously as the chain length of alcohol increases

TABLE-1  
FREE VOLUME AND EXCESS FREE VOLUME OF BINARY LIQUID MIXTURES  
AT 303.15 K (SYSTEM (I): *o*-XYLENE + 1-PROPANOL)

Mole fraction (X) of <i>o</i> -xylene	$\rho$ (g/mL)	U (cc/s)	$V_f$ (mL/mol)	$V_f^E$ (mL/mol)
0.0000	0.7943	119200	0.8755	—
0.0684	0.8050	121100	0.7690	-0.0580
0.1120	0.8070	121800	0.7066	-0.0894
0.2106	0.8168	122700	0.5904	-0.1357
0.3175	0.8264	123400	0.4964	-0.1540
0.5010	0.8410	125100	0.3701	-0.1502
0.7217	0.8560	128100	0.2594	-0.1044
0.8029	0.8606	129200	0.2296	-0.0767
0.8719	0.8643	130900	0.2021	-0.0553
0.9329	0.8672	131900	0.1842	-0.0300
0.9511	0.8681	132200	0.1791	-0.2213
1.0000	0.8702	133000	0.1666	—

The excess free volume values are negative for all the three mixtures under consideration at all mole fractions. The negative values of excess free volume in these systems indicate the possibility of strong intermolecular interaction in these systems. The results of the excess free volume also suggest the formation of OH- $\pi$  electron hydrogen bonded complex in the mixtures.

A perusal of the graph shows that for the systems *o*-xylene + 1-butanol and *o*-xylene + 1-pentanol the interaction is greater at higher alcohol concentration

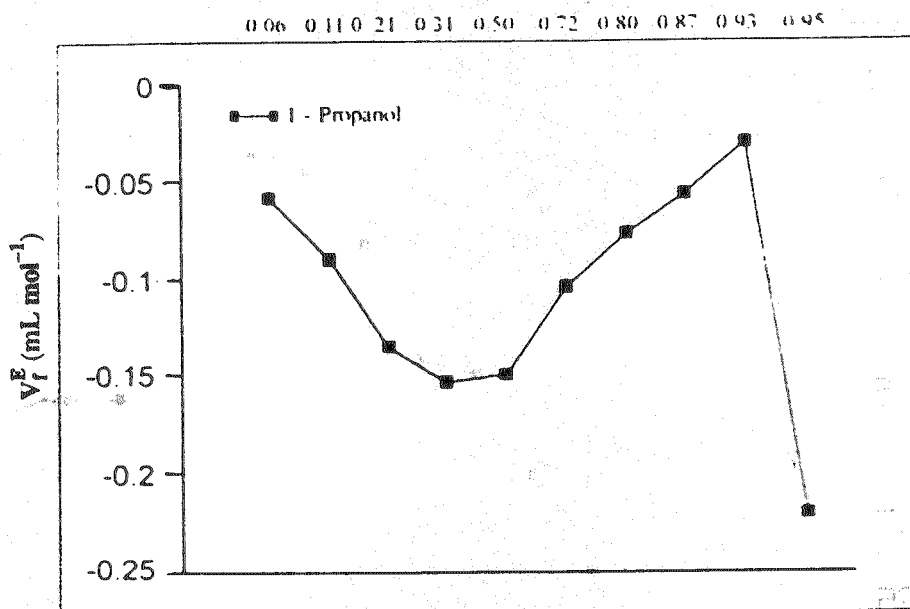


Fig. 1. Mole fraction of *o*-xylene + 1-propanol vs.  $V_f^E$  ( $\text{mL mol}^{-1}$ )

and decreases continuously as the mole fraction of alcohol decreases. However, in case of *o*-xylene + 1-propanol system the observed trend is somewhat different; here the magnitude of interaction first increases and then decreases and again finally increases. Such trends may be attributed to the formation of strong  $\pi$ -OH complex in the system.

TABLE-2  
SYSTEM (II): *o*-XYLENE + 1-PROPANOL

Mole fraction	$\rho$ (g/mL)	U (cc/s)	$V_f$ (mL/mol)	$V_f^E$ (mL/mol)
0.0000	0.8030	121300	0.8108	—
0.0525	0.8076	123500	0.4917	-0.2852
0.1029	0.8118	123700	0.4656	-0.2789
0.2001	0.8196	124400	0.4155	-0.2664
0.3561	0.8313	125600	0.3478	-0.2335
0.5045	0.8415	126500	0.2988	-0.1870
0.6566	0.8517	128400	0.2483	-0.1395
0.7284	0.8840	129100	0.2087	-0.1328
0.8168	0.8611	130200	0.2077	-0.0769
0.8979	0.8654	131200	0.1896	-0.0427
0.9206	0.8655	131700	0.1836	-0.0341
1.0000	0.8702	133000	0.1666	—

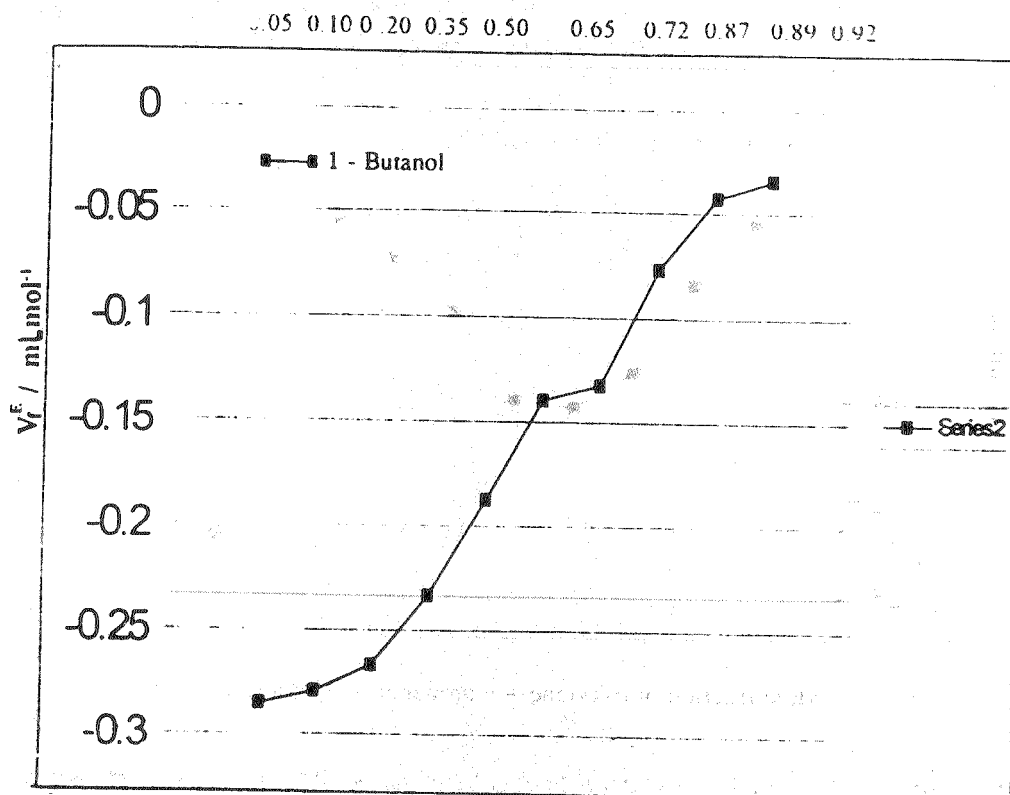


Fig. 2. Mole fraction of *o*-xylene + 1-butanol vs.  $V_r^E$  (mL mol<sup>-1</sup>)

TABLE-3  
SYSTEM (III): *o*-XYLENE + 1-PENTANOL

Mole fraction	$\rho$ (g/mL)	U (cc/s)	$V_r$ (mL/mol)	$V_r^E$ (mL/mol)
0.0000	0.8062	127000	0.4943	—
0.0626	0.8105	127100	0.3105	-0.1632
0.1286	0.8151	127000	0.3017	-0.1504
0.2229	0.8215	127300	0.2854	-0.1358
0.3307	0.8284	127500	0.2695	-0.1164
0.4999	0.8401	128100	0.2441	-0.0863
0.6329	0.8487	129100	0.2222	-0.0863
0.7082	0.8534	129700	0.2107	-0.0515
0.7857	0.8582	130700	0.1968	-0.0400
0.8122	0.8597	131000	0.1927	-0.0354
0.8839	0.8639	131700	0.1826	-0.0221
1.0000	0.8702	133000	0.1666	—

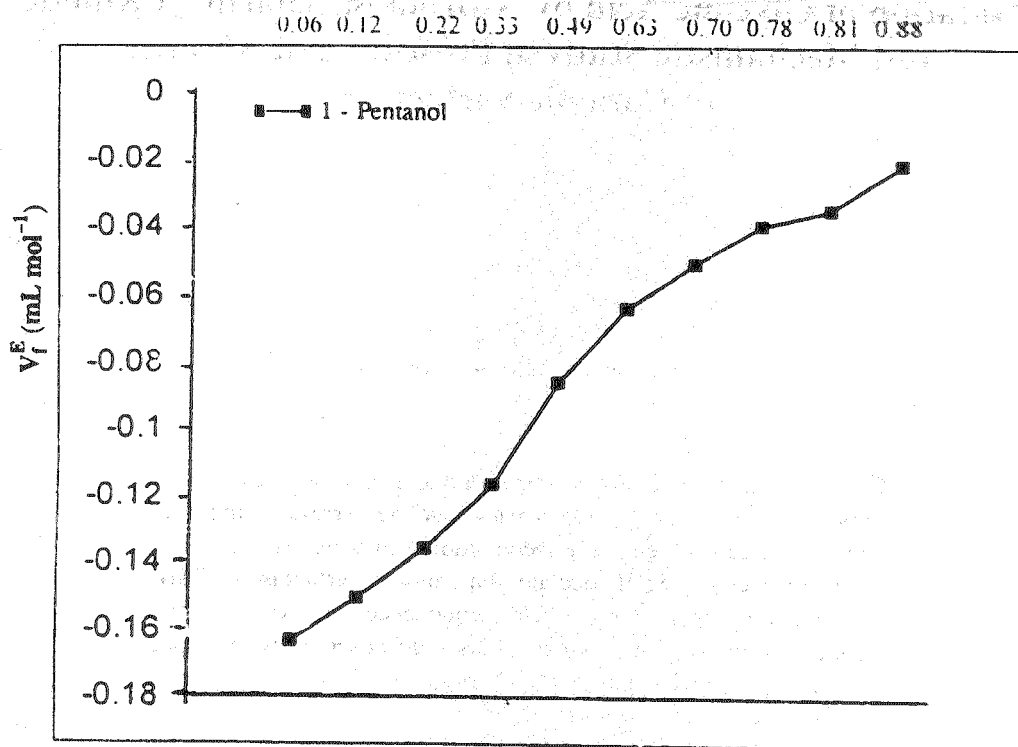


Fig. 3. Mole fraction of *o*-xylene + 1-pentanol vs.  $V_f^E$  (mL mol<sup>-1</sup>)

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