

Measurement and correlation of excess molar volumes for mixtures of 1-propanol and aromatic hydrocarbons

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Abstract—Excess molar volumes (V_m^E) have been measured at 303.15 K for 1-propanol+benzene or toluene or o- or m- or p-xylene mixtures using V-shape dilatometer. The V_m^E values, for an equimolar composition, vary in the order: benzene>toluene~m-xylene>o-xylene>p-xylene. The V_m^E data have been used to calculate partial molar volumes, excess partial molar volumes, and apparent molar volumes of 1-propanol and aromatic hydrocarbons over the entire range of composition. The excess volume data have also been interpreted in terms of graph-theoretical approach and Prigogine-Flory-Patterson theory (PFPP). While PFPP theory fails to predict the V_m^E values for systems with s-shaped V_m^E versus x_1 graph, the V_m^E values calculated by graph theory compare reasonably well with the corresponding experimental values. This graph theory analysis has further yielded information about the state of aggregation of pure components as well as of the mixtures.

Keywords: Molar Excess Volume, Partial Molar Volume, 1-Propanol, Aromatic Hydrocarbon, Graph Theoretical Approach, Prigogine-Flory-Patterson Theory

INTRODUCTION

Increasing fuel demand, environmental concern, and occasional oil crises have been the reasons for the use of fuel additive oxygenates [1]. Oxygenates are the compounds that contain oxygen such as ethers, glycol ethers, alcohol, methylal and carbonates or biomass products such as esters of vegetable oils and used as fuel additives [2]. Methyl tertiary-butyl ether (MTBE) was used, for the first time, in 1979 to reduce air emissions/improve air quality and increase the fuel efficiency by allowing more complete combustion in internal combustion engines because/as oxygen in oxygenates readily oxidized fuel [3,4]. Oxygenate presence in fuel not only reduces the carbon monoxide emission and other toxic emissions but also increases the octane/cetane rating of fuel [5-7]. Thus the thermo-physical properties of oxygenate additive with aromatic as well as with aliphatic hydrocarbon would be of great importance in process engineering design and in formulating motor gasoline and diesel [8]. The thermo-physical properties of mixtures having oxygenate would also be of great significance to chemists in getting information about molecular structure and to understand the nature of intermolecular interactions in these binary mixtures [9-12].

This prompted us to systematically study the thermodynamics of binary mixtures of alkanol with alkane or aromatic hydrocarbon. Since a binary mixture is formed by the replacement of like contacts in the pure state by unlike contact in the mixture and as

the formations of molecular entities in the present mixtures may be visualized [13] due to the changes in the topology of 1-propanol brought on by aromatics, it appears that a recent graph theoretical approach [14,15] should provide valuable information about the state of aggregation of pure component in their binary mixture.

These considerations have led to the measurement of excess molar volume at 303.15 K of 1-propanol+aromatic hydrocarbons. The Redlich-Kister equation was used to correlate the experimental data and to obtain the partial and excess partial molar volumes along with apparent molar volume at 303.15 K and at atmospheric pressure [16]. The excess volume data have also been rationalized by graph-theoretical arguments and Prigogine-Flory-Patterson theory.

EXPERIMENTAL SECTION

Benzene, toluene, and xylenes (Merck) were shaken repeatedly with 15% (v/v) concentrated sulfuric acid in a stoppered separating funnel in order to eliminate thiophene until the acid layer was colorless [17,18]. After shaking each for a few minutes, the mixtures were allowed to settle, and the acid was drawn off. The remaining acid was neutralized by sodium bicarbonate solution, and the substance of interest was subsequently washed with distilled water and dried over fused calcium chloride for 24 h. It was then fractionally distilled and the middle fraction of the distillate was stored over sodium wire in an amber colored bottle. The 1-propanol (Merck) was dried by refluxing over fused calcium oxide for 5 h and then fractionally distilled [19]. The middle fraction of distilled 1-propanol was then dried over type 0.3 nm molecular sieves (Merck) in an amber colored bottle for several days before use. The purities of

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Table 1. Purities, measured densities (ρ) and refractive indices (n_D) of the pure components

Compound	GC results wt%	T/K	$\rho/(\text{kg m}^{-3})$		n_D	
			This work	Literature	This work	Literature
1-Propanol	99.7	298.15	799.55	799.59 [21]	1.3836	1.3833 [22]
				799.79 [17]		1.3832 [23]
				799.48 [24]		1.38370 [17]
Benzene	99.7	303.15	795.59	795.57 [21]		
		308.15	791.49	791.46 [22]	1.3795	1.3791 [23]
		298.15	873.56	873.60 [17]	1.4978	1.49792 [17]
Toluene	99.8	303.15	868.31	868.29 [17]		
		308.15	862.92	862.96 [25]	1.4914	1.4917 [26]
		298.15	862.23	862.19 [17]	1.4943	1.49413 [17]
o-Xylene	99.7	303.15	857.51	857.54 [17]		
		308.15	852.89	852.85 [27]	1.4886	1.4887 [26]
		298.15	875.90	875.94 [17]	1.5029	1.50295 [17]
m-Xylene	99.8	303.15	871.76	871.74 [17]		
		308.15	867.33	867.38 [27]	1.5028	1.50295 [17]
		298.15	860.04	860.09 [17]	1.4948	1.49464 [17]
p-Xylene	99.9	303.15	855.84	855.81 [17]		
		308.15	851.52	851.57 [27]		
		298.15	856.64	856.61 [17]	1.4935	1.49325 [17]
		303.15	852.21	852.25 [17]		
		308.15	847.89	847.87 [27]	1.4885	1.4881 [26]

the samples were checked by measuring their densities and refractive indices at 298.15 ± 0.01 K. The densities were measured with a precision of $\pm 0.05 \text{ kg m}^{-3}$ by a specially designed densimeter, consisting of a bulb of approximate volume $3.5 \times 10^{-5} \text{ m}^3$ attached to a calibrated capillary through a B-10 standard joint in the manner described by Weissenberger [20]. Air buoyancy corrections were also applied to achieve a greater accuracy. Refractive indices were measured with a thermostatically controlled Abbe refractometer (OSAW, India) using sodium D-line with an accuracy of $\pm 1 \times 10^{-4}$. Measured values of densities and refractive indices of the pure com-

pounds agree well with their respective literature values, as shown in Table 1. The purified samples were also analyzed by gas chromatography for their purity and found to have better than 99.6 wt% (Table 1). Excess molar volumes, V_m^E , for the binary mixtures were measured by V-shaped dilatometer at 303.15 K in the manner described elsewhere [14]. The temperature of the water thermostat was controlled to ± 0.01 K by a mercury-in-toluene regulator. The change in the position of the liquid level in the capillary was noted with a cathetometer (OSAW, India) that could read to ± 0.001 cm. The performance of dilatometer was checked by measuring the molar excess volume of the benzene+cyclohexane mixtures at 298.15 K over the entire composition range, and these agreed to within the experimental limit with corresponding literature [28] as shown in Fig. 1. The uncertainty in the measured V_m^E values was $\pm 1\%$.

RESULTS

The excess molar volume is defined by

$$V_m^E = V_m - x_1 V_1^o - x_2 V_2^o \quad (1)$$

where V_m represents the volume of a mixture containing one mole of (1-propanol (1)+aromatic hydrocarbons (2)), x_1 , x_2 and V_1^o and V_2^o are the mole fraction and the molar volume of the pure components, respectively.

The measured V_m^E data at 303.15 K, recorded in Table 2, were fitted to the following Redlich and Kister equation:

$$V_m^E (\text{cm}^3 \text{mol}^{-1}) = x_1(1-x_1) \left[\sum_{j=0}^n A_j (1-2x_1)^j \right] \quad (2)$$

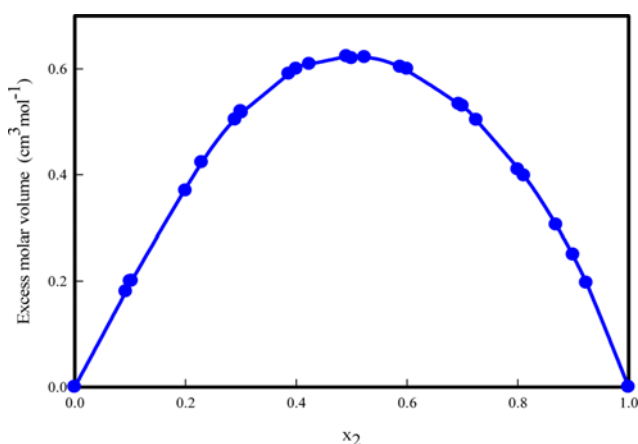


Fig. 1. Excess molar volume for benzene (1)+cyclohexane (2) at 298.15 K; line represents literature value [28] and symbols represent experimental value.

Table 2. Experimental excess volume, partial molar volumes, excess partial molar volumes and apparent molar volumes (cm³ mol⁻¹) of binary liquid mixtures of 1-propanol (1)+aromatic hydrocarbon (2) at 303.15 K

x_1	V_m^E	\bar{V}_1	\bar{V}_2	\bar{V}_1^E	\bar{V}_2^E	$V_{\phi 1}$	$V_{\phi 2}$
1-Propanol (1)+benzene (2)							
0.0540	0.053	75.911	89.948	0.408	0.001	76.484	90.00
0.1220	0.115	75.833	89.951	0.330	0.004	76.446	90.08
0.1850	0.155	75.763	89.952	0.260	0.005	76.341	90.14
0.2365	0.175	75.71	89.950	0.207	0.003	76.243	90.18
0.2990	0.197	75.654	89.94	0.151	0.001	76.162	90.23
0.3412	0.196	75.623	89.948	0.120	0.001	76.077	90.24
0.3823	0.199	75.598	89.951	0.095	0.004	76.024	90.27
0.4297	0.192	75.574	89.962	0.071	0.015	75.95	90.28
0.4855	0.179	75.554	89.985	0.051	0.038	75.872	90.29
0.5241	0.17	75.544	90.011	0.041	0.064	75.827	90.30
0.5846	0.154	75.534	90.070	0.031	0.123	75.766	90.32
0.6839	0.118	75.525	90.222	0.022	0.275	75.676	90.32
0.7598	0.088	75.521	90.388	0.018	0.441	75.619	90.31
0.8252	0.068	75.516	90.560	0.013	0.613	75.585	90.34
0.8987	0.039	75.509	90.772	0.006	0.825	75.546	90.33
0.9506	0.02	75.505	90.924	0.002	0.977	75.524	90.35
1-Propanol (1)+toluene (2)							
0.0648	0.044	75.341	107.423	-0.162	-0.004	76.182	107.47
0.1245	0.075	75.348	107.412	-0.155	-0.015	76.105	107.51
0.1824	0.103	75.354	107.396	-0.149	-0.031	76.068	107.55
0.2697	0.123	75.368	107.366	-0.135	-0.061	75.959	107.60
0.3334	0.13	75.383	107.348	-0.120	-0.079	75.893	107.62
0.3949	0.123	75.402	107.340	-0.101	-0.087	75.814	107.63
0.4552	0.111	75.424	107.347	-0.079	-0.080	75.747	107.63
0.4691	0.104	75.429	107.352	-0.074	-0.075	75.725	107.62
0.5253	0.091	75.451	107.380	-0.052	-0.047	75.676	107.62
0.5922	0.062	75.475	107.441	-0.028	0.014	75.608	107.58
0.6633	0.041	75.496	107.537	-0.007	0.110	75.565	107.55
0.7351	0.016	75.509	107.665	0.006	0.238	75.525	107.49
0.7816	0.005	75.514	107.758	0.011	0.331	75.509	107.45
0.8243	-0.007	75.514	107.847	0.011	0.420	75.495	107.39
0.8866	-0.009	75.511	107.970	0.008	0.543	75.493	107.35
0.9534	-0.004	75.505	108.073	0.002	0.646	75.499	107.34

where A_j are the adjustable parameters, and x_1 is the mole fraction of 1-propanol in 1-propanol (1)+aromatic hydrocarbon mixture. These parameters were evaluated by fitting V_m^E data to Eq. (2) by the least squares method and reported in Table 3 with the standard deviations $\sigma(V_m^E)$ of V_m^E .

$$\sigma(V_m^E)(\text{cm}^3 \text{mol}^{-1}) = \{[\sum (V_{m, \text{expt.}}^E - V_{m, \text{cal.}}^E)^2] / (m - n)\}^{1/2} \quad (3)$$

where m is the number of experimental values, and n is the number of adjustable parameters in Eq. (2). The choice of n to have 1-4 values was dictated by the consideration that the maximum deviation $\sigma_{\text{max}}(V_m^E)$ of V_m^E (as calculated from Eq. (2) from the corresponding experimental V_m^E values satisfied the relation $\sigma_{\text{max}}(V_m^E) \leq 2\sigma(V_m^E)$.

Comparison of V_m^E experimental for the studied system together with smoothing curves using Eq. (2) is shown in Fig. 2.

We have also calculated the excess partial molar volumes, $\bar{V}_1^E =$

$(\bar{V}_1 - \bar{V}_1^o)$ and $\bar{V}_2^E = (\bar{V}_2 - \bar{V}_2^o)$, from V_m^E . The excess partial molar volumes, \bar{V}_1^E and \bar{V}_2^E , were evaluated using the following equations:

$$\bar{V}_1 = \bar{V}_m^E + \bar{V}_1^o + (1 - x_1) \left(\frac{\partial \bar{V}_m^E}{\partial x_1} \right)_{p,T} \quad (4)$$

$$\bar{V}_2 = \bar{V}_m^E + \bar{V}_2^o - x_1 \left(\frac{\partial \bar{V}_m^E}{\partial x_1} \right)_{p,T} \quad (5)$$

Differentiation of Eq. (2) with respect to and combination of the results of Eq. (4) and Eq. (5) leads to the following equation for the partial molar volumes of 1-propanol (\bar{V}_1) and aromatic hydrocarbon (\bar{V}_2)

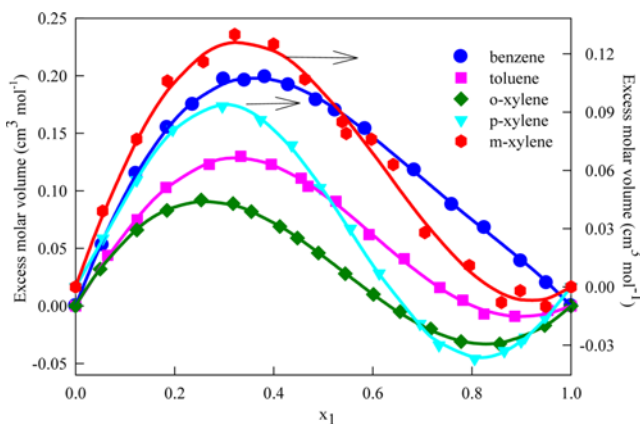
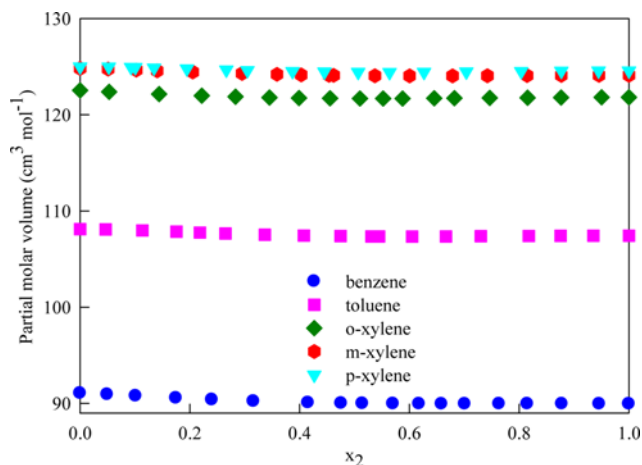
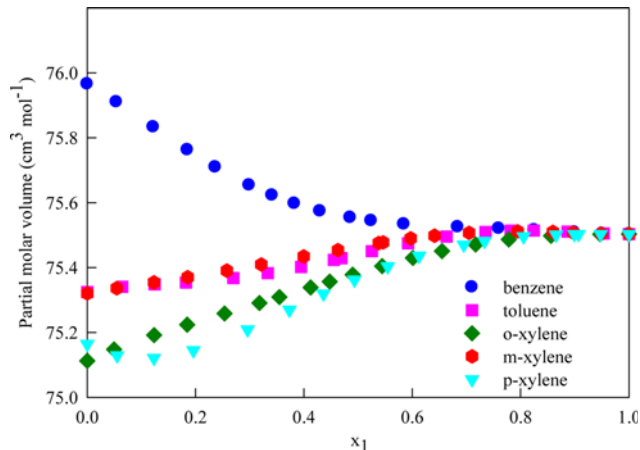
$$\bar{V}_1 = V_1^o + (1 - x_1)^2 \sum_{j=0}^n A_j (1 - 2x_1)^j + 2x_1 (1 - x_1)^2 \sum_{j=0}^n A_j (j) (1 - 2x_1)^{j-1} \quad (6)$$

Table 2. Continued

x_1	V_m^E	\bar{V}_1	\bar{V}_2	\bar{V}_1^E	\bar{V}_2^E	$V_{\phi 1}$	$V_{\phi 2}$
1-Propanol (1)+o-xylene (2)							
0.0496	0.032	75.148	121.807	-0.355	-0.003	76.148	121.84
0.1236	0.066	75.192	121.792	-0.311	-0.018	76.037	121.89
0.1847	0.083	75.224	121.772	-0.279	-0.038	75.952	121.91
0.2535	0.092	75.258	121.744	-0.245	-0.066	75.866	121.93
0.3180	0.089	75.291	121.718	-0.212	-0.092	75.783	121.94
0.3548	0.082	75.31	121.705	-0.193	-0.105	75.734	121.94
0.4125	0.069	75.339	121.691	-0.164	-0.119	75.67	121.93
0.4478	0.059	75.357	121.687	-0.146	-0.123	75.635	121.92
0.4900	0.046	75.378	121.688	-0.125	-0.122	75.597	121.90
0.5446	0.028	75.404	121.703	-0.099	-0.107	75.554	121.87
0.6011	0.01	75.43	121.736	-0.073	-0.074	75.52	121.84
0.6549	-0.005	75.451	121.786	-0.052	-0.024	75.495	121.80
0.7168	-0.02	75.471	121.868	-0.032	0.058	75.475	121.74
0.7782	-0.031	75.486	121.975	-0.017	0.165	75.463	121.67
0.8561	-0.033	75.498	122.144	-0.005	0.334	75.464	121.58
0.9470	-0.017	75.503	122.379	0.000	0.569	75.485	121.49
1-Propanol (1)+m-xylene (2)							
0.0546	0.039	75.337	124.097	-0.166	-0.004	76.217	124.14
0.1232	0.076	75.354	124.085	-0.149	-0.016	76.120	124.19
0.1854	0.106	75.371	124.068	-0.132	-0.033	76.075	124.23
0.2578	0.116	75.391	124.048	-0.112	-0.053	75.953	124.26
0.3214	0.13	75.41	124.035	-0.093	-0.066	75.907	124.29
0.3996	0.125	75.434	124.032	-0.069	-0.069	75.816	124.31
0.4629	0.107	75.454	124.046	-0.049	-0.055	75.734	124.30
0.5381	0.085	75.476	124.087	-0.027	-0.014	75.661	124.29
0.5464	0.079	75.478	124.094	-0.025	-0.007	75.648	124.28
0.5972	0.076	75.49	124.140	-0.013	0.039	75.630	124.29
0.6412	0.063	75.499	124.192	-0.004	0.091	75.601	124.28
0.7048	0.028	75.507	124.284	0.004	0.183	75.543	124.20
0.7946	0.011	75.512	124.442	0.009	0.341	75.517	124.15
0.8595	-0.008	75.51	124.568	0.007	0.467	75.494	124.04
0.8974	-0.002	75.508	124.642	0.005	0.541	75.501	124.08
0.9488	-0.01	75.505	124.735	0.002	0.634	75.492	123.91
1-Propanol (1)+p-xylene (2)							
0.0553	0.025	75.129	124.563	-0.374	-0.006	75.955	124.60
0.1232	0.055	75.122	124.543	-0.381	-0.026	75.949	124.63
0.1962	0.081	75.145	124.509	-0.358	-0.060	75.916	124.67
0.2961	0.093	75.209	124.458	-0.294	-0.111	75.817	124.70
0.3734	0.086	75.27	124.429	-0.233	-0.140	75.733	124.71
0.4361	0.073	75.32	124.421	-0.183	-0.148	75.67	124.70
0.4933	0.051	75.362	124.431	-0.141	-0.138	75.606	124.67
0.5548	0.03	75.403	124.462	-0.100	-0.107	75.557	124.64
0.6128	0.007	75.436	124.512	-0.067	-0.057	75.514	124.59
0.6951	-0.019	75.47	124.615	-0.033	0.046	75.476	124.51
0.7335	-0.03	75.482	124.673	-0.021	0.104	75.462	124.46
0.8055	-0.037	75.496	124.790	-0.007	0.221	75.457	124.38
0.8654	-0.033	75.501	124.883	-0.002	0.314	75.465	124.32
0.8994	-0.028	75.503	124.928	0.000	0.359	75.472	124.29
0.9071	-0.026	75.503	124.937	0.000	0.368	75.474	124.29
0.9476	-0.016	75.503	124.973	0.000	0.404	75.486	124.26

Table 3. Adjustable parameters of Redlich-Kister Eq. (2) and standard deviation (σ_m) at 303.15 K

System	A_0	A_1	A_2	A_3	σ_m
1-Propanol (1)+benzene (2)	0.7119	-0.5231	0.0754	0.1987	0.002
1-Propanol (1)+toluene (2)	0.3886	-0.6366	-0.1372	0.207	0.002
1-Propanol (1)+o-xylene (2)	0.1726	-0.6525	-0.0105	0.0999	0.002
1-Propanol (1)+m-xylene (2)	0.402	-0.5535	-0.1376	0.1066	0.005
1-Propanol (1)+p-xylene (2)	0.1994	-0.7424	-0.1615	0.3658	0.001

**Fig. 2. Excess molar volume (V_m^E) of 1-propanol (1)+aromatic hydrocarbon (2) mixture as a function of mole fraction of 1-propanol (x_1) at 303.15 K; symbols represent experimental values and lines represent values calculated from Eq. (2).****Fig. 4. Partial molar volume of aromatic hydrocarbon (V_2) in a mixture of 1-propanol (1)+aromatic hydrocarbon (2) as a function of mole fraction of aromatic hydrocarbon (x_2) at 303.15 K.****Fig. 3. Partial molar volume of 1-propanol (\bar{V}_1) in a mixture of 1-propanol (1)+aromatic hydrocarbon (2) as a function of mole fraction of 1-propanol (x_1) at 303.15 K.**

$$\bar{V}_2 = V_2^o + x_1^2 \sum_{j=0}^n A_j (1-2x_1)^j + 2x_1^2 (1-x_1) \sum_{j=0}^n A_j (j)(1-2x_1)^{j-1} \quad (7)$$

The calculated results for partial molar volume are plotted in Figs. 3 and 4. The partial properties at infinite dilution are of great significance because, at the limit of infinite dilution, the solute-solute interactions disappear. The values of partial molar volume at infinite dilution provide information about solute-solvent interactions, independent of the composition effect. Therefore, by substituting $x_2=1$ and $x_1=0$ in Eq. (6), we get

$$\bar{V}_1^\infty = V_1^o + \sum_{j=0}^n A_j \quad (8)$$

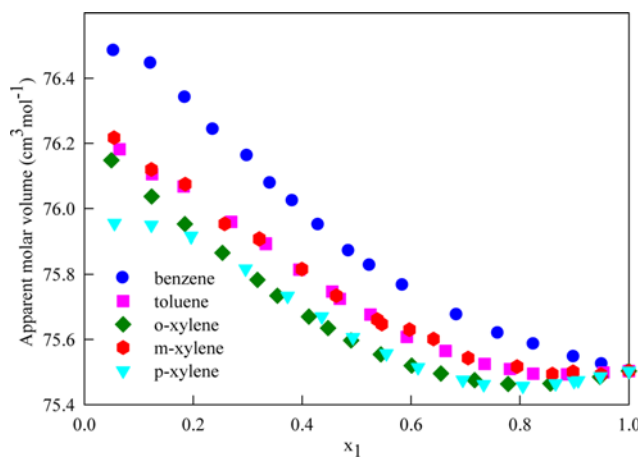
$$\bar{V}_2^\infty = V_2^o + \sum_{j=0}^n A_j (-1)^j \quad (9)$$

Eqs. (8) and (9) represent the partial molar volume of 1-propanol \bar{V}_1^∞ and aromatics \bar{V}_2^∞ at infinite dilution, respectively. These properties are listed in Table 4. The 1-propanol in benzene displays higher value of \bar{V}_1^∞ than in toluene, indicating the stronger interaction of π -electron of toluene with hydroxyl oxygen due to the presence of an electron donating CH_3 group (Fig. 3). The \bar{V}_1^∞ values of 1-propanol in xylenes further decrease due to the presence of two CH_3 groups with the exception in o-xylene. This may be due to the steric hindrance offered by two bulky methyl groups in o-xylene (Fig. 3). Partial molar volumes calculated using the Redlich-Kister equation and its derivatives do not always provide the best representation of properties of either component at infinite dilution in the other component. Instead of using the Redlich-Kister equation, we also considered another approach, which may be more convenient and accurate, by calculating the partial molar volume at infinite dilution through apparent volumes of 1-propanol in aromatics $V_{\phi 1}$ and the apparent molar volume of aromatics in 1-propanol $V_{\phi 2}$ can be expressed as

$$V_{\phi 1} = \frac{V_m - x_2 V_2^o}{x_1} \quad (10)$$

Table 4. Partial molar volumes and excess partial molar volumes ($\text{cm}^3 \text{mol}^{-1}$) at infinite dilution at 303.15 K

System	V_1^o	V_2^o	\bar{V}_1^∞	\bar{V}_2^∞	$\bar{V}_1^{E\infty}$	$\bar{V}_2^{E\infty}$
1-Propanol (1)+benzene (2)	75.503	89.947	75.966	91.059	0.463	1.112
1-Propanol (1)+toluene (2)	75.503	107.427	75.325	108.11	-0.178	0.681
1-Propanol (1)+o-xylene (2)	75.503	121.81	75.113	122.52	-0.391	0.715
1-Propanol (1)+m-xylene (2)	75.503	124.101	75.321	199.02	-0.183	0.711
1-Propanol (1)+p-xylene (2)	75.503	124.569	75.164	124.98	-0.339	0.415

**Fig. 5. Apparent molar volume of 1-propanol ($V_{\phi 1}$) in a mixture of 1-propanol (1)+aromatic hydrocarbon (2) as a function of mole fraction of 1-propanol (x_1) at 303.15 K.**

$$V_{\phi 2} = \frac{V_m - x_1 V_1^o}{x_2} \quad (11)$$

Combination of Eqs. (1), (10) and (11) leads to

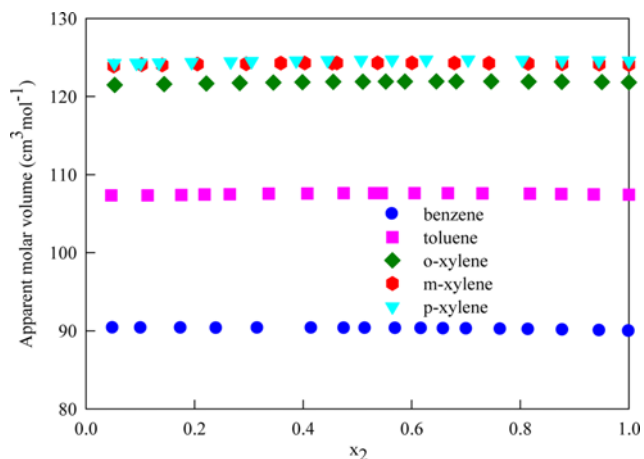
$$V_{\phi 1} = V_1^o + \frac{V_m^E}{x_1} \quad (12)$$

$$V_{\phi 2} = V_2^o + \frac{V_m^E}{x_2} \quad (13)$$

Simple graphic or analytical extrapolation of $V_{\phi 1}$ to $x_1=0$ ($x_2=1$) leads to desired value of \bar{V}_1^∞ and a simple extrapolation of $V_{\phi 2}$ to $x_2=0$ ($x_1=1$) leads to the desired value of \bar{V}_2^∞ . The \bar{V}_i^∞ results are shown in Figs. 5 and 6.

DISCUSSION

V_m^E versus x_1 plots for 1-propanol+aromatic hydrocarbon systems are s-shaped (Fig. 2) and change sign from positive to negative in the composition range $0.65 < x_1 < 0.84$, except for 1-propanol+benzene mixtures where the graph is slightly skewed toward y-axis with maxima at $x_1=0.38$ with V_m^E values are positive over the whole composition range. Similar shape and sign of the V_m^E versus x_1 curve for these systems was also reported previously, and our values were a slightly less than reported values (at the most 0.5% at $x_1=0.5$) [29]. The V_m^E values, for an equimolar composition, vary in the order: benzene>toluene~m-xylene>o-xylene>p-xylene. At the simplest qualitative level, V_m^E values may be attributed to the resul-

**Fig. 6. Apparent molar volume of aromatic hydrocarbon ($V_{\phi 2}$) in a mixture of 1-propanol (1)+aromatic hydrocarbon (2) as a function of mole fraction of aromatic hydrocarbon (x_2) at 303.15 K.**

tant of two opposing effects. The positive contribution to V_m^E values arises from the breaking of self-associated 1-propanol and dipole-dipole interactions between 1-propanol monomers and dimers and from the disruption in the favorable orientation order of the aromatic hydrocarbons. The negative contribution arises due to the presence of electron-donor-acceptor interactions between 1-propanol and aromatic hydrocarbons and change in free volume in real mixtures. In spite of this qualitative description of the present V_m^E data, the degree of association of 1-propanol and influence of aromatics on it remains to be investigated. For this purpose we analyzed the present V_m^E data in terms of an approach [14], [30] that employs [31] the graph theoretical concept of molecular connectivity parameter of the third degree, ${}^3\xi$, of the constituents of these mixtures.

1. Conceptual Aspects of Graph Theoretical Approach and Results

According to graph theory [32], if the atoms in a structural formula of a molecule are represented by vertices and bonds joining them by edges, then the resulting graph describes the totality of information contained in that molecule [31], [33-35]. Consequently, if δ_m^v , δ_n^v etc. represents the degrees of m^{th} and n^{th} vertices of the graph of a molecule, then connectivity parameters of third degree, ${}^3\xi$, is defined [36] by Eq. (15):

$${}^3\xi_i = \sum_{m < n < o < p} (\delta_m^v \delta_n^v \delta_o^v \delta_p^v)^{-0.5} \quad (14)$$

where δ_m^v etc. reflects explicitly the valency of m^{th} vertex in molec-

ular graph of i ($i=1$ or 2) and is related [35] to maximum valency, Z_m , and number of H-atoms, h_m , attached to m^{th} etc. vertex by the relation:

$$\delta_m^v = Z_m - h_m \quad (15)$$

Furthermore, Kier [31] has suggested that the information regarding effect of branching in the molecules can be obtained by evaluation of ${}^3\xi_i$ of molecules.

Since V_m^E of a (1+2) mixture reflects interactional effects on the packing of molecules and as $({}^3\xi_i)^{-1}$ of i determines [14] the effectiveness with which the molecular surface of i interacts with that of another i molecule, the interactional part of the molar volume of pure i has been taken to $({}^3\xi_i)^{-1}$. The ideal interactional molar volume of an (1+2) mixture would then be proportional to $\sum x_i ({}^3\xi_i)^{-1}$, where x_i and $({}^3\xi_i)$ denote mole fraction and connectivity parameter of third degree, respectively, of i . The interactional molar volume of a (1+2) mixture should also be proportional to $1/({}^3\xi_m)$ of the mixture. If $({}^3\xi)_m$ of the real mixture in the molecular graph is expressed by $\sum \{x_i ({}^3\xi_i)_m\}$ (where $({}^3\xi_i)_m$ denotes ${}^3\xi_i$ of i in the mixture and if the proportionality constant α_{12} is assumed to be the same for the mixture and its pure components then, V_m^E may be expressed by [14].

$$V_m^E / \text{cm}^3 \text{ mol}^{-1} = \alpha_{12} \left[\sum_{i=1}^2 \{x_i ({}^3\xi_i)_m\}^{-1} - \sum_{i=1}^2 \frac{x_i}{{}^3\xi_i} \right] \quad (16)$$

where α_{12} is the constant characteristic of the (1+2) mixture and can be evaluated using equimolar experimental V_m^E value.

As the degree of association of 1-propanol (1) and aromatic hydrocarbon (2) is not known in the mixture and pure state, we regarded $({}^3\xi_i)$ and $({}^3\xi_i)_m$ ($i=1$ or 2) as adjustable parameters and evaluated them by employing V_m^E data to Eq. (16). Only those values of $({}^3\xi_i)$ and $({}^3\xi_i)_m$ were retained that best reproduced the V_m^E data. Various $({}^3\xi_i)$ or $({}^3\xi_i)_m$ ($i=1$ or 2) parameters along with α_{12} are recorded in Table 5 and V_m^E values obtained from Eq. (16), as well as from Eq. (2) for the various binary mixtures at different mole fractions, are shown in Figs. 7 and 8. Figs. 7 and 8 reveal that V_m^E values agree reasonably well with their corresponding experimental values and thus $({}^3\xi_i)$ or $({}^3\xi_i)_m$ ($i=1$ or 2) values can be relied upon to extract information about the state of pure components as well as their mixtures.

A number of structures (I-VII) were then assumed for 1-propanol (1) and aromatics (2) and their $({}^3\xi_i)$ values were calculated from structural considerations of Eq. (14) (Fig. 9). These values were then compared with corresponding values, $({}^3\xi_i)$ obtained from Eq. (16). Any structure or combination of structures that yielded

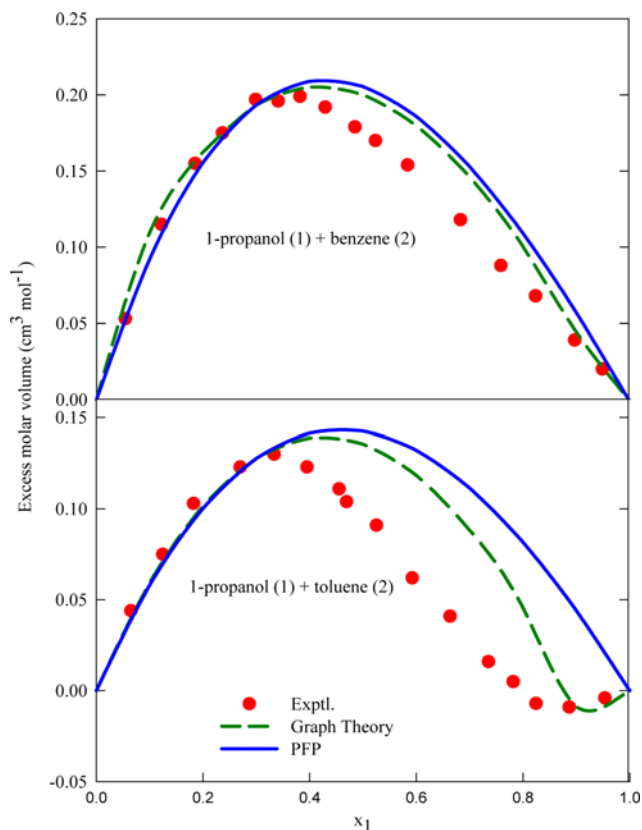


Fig. 7. Excess molar volume (V_m^E) of 1-propanol (1)+aromatic hydrocarbon (2) mixture as a function of mole fraction of 1-propanol (x_1) at 303.15 K.

$({}^3\xi_i)$ values which compared well with the corresponding $({}^3\xi_i)$ obtained from Eq. (16) were considered as representative structure of that component. It was assumed that 1-propanol exists as molecular entities I (monomer) and II (dimer). The calculated values of $({}^3\xi_i)$ for these molecular entities were 0.408 and 1.314, respectively. The $({}^3\xi_i)$ value for 1-propanol in these 1-propanol (1)+benzene or toluene or *o*- or *m*- or *p*-xylene (2) mixtures from Eq. (16) is 1.000 (Table 5). It suggests that 1-propanol exists as a mixture of monomer and dimer (average $({}^3\xi_i)$ =0.861). Further $({}^3\xi_i)$ values of 0.666, 0.940, 1.176, 1.174 and 1.218 for benzene, toluene, *o*-, *m*-, and *p*-xylene (molecular entities III-VII in Fig. 9) suggest that they exist as monomer.

$({}^3\xi_i)_m$ values were next evaluated to see the postulation of 1-propanol in aromatic hydrocarbons (in Fig. 9). For this purpose it was assumed that if 1-propanol (1) in benzene or toluene or xylenes is

Table 5. Values of the various $({}^3\xi_i)$, $({}^3\xi_i)_m$ ($i=1$ or 2) and α_{12} values

System	${}^3\xi_1$	${}^3\xi_2$	$({}^3\xi_1)_m$	$({}^3\xi_2)_m$	α_{12}
1-Propanol (1)+benzene (2)	1	0.666	0.995	0.6695	-4.06738
1-Propanol (1)+toluene (2)	1	0.845	0.9968	0.845	-23.2661
1-Propanol (1)+ <i>o</i> -xylene (2)	1	1.425	0.889	1.57	-1.5084
1-Propanol (1)+ <i>m</i> -xylene (2)	1	1.174	0.9968	1.1747	-28.0647
1-Propanol (1)+ <i>p</i> -xylene (2)	1	1.249	0.972	1.274	-6.09379

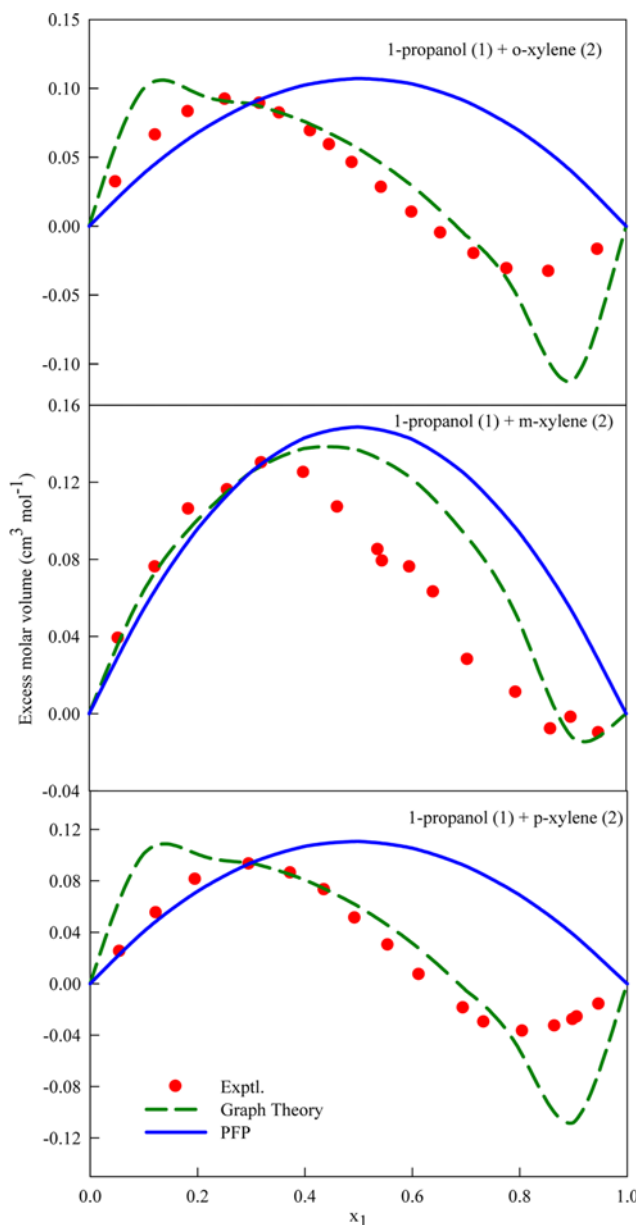


Fig. 8. Excess molar volume (V_m^E) of 1-propanol (1)+aromatic hydrocarbon (2) mixtures as a function of mole fraction of 1-propanol (x_1) at 303.15 K.

assumed to exist as molecular entity VIII (${}^3\xi=0.614$) and IX (${}^3\xi=1.364$), then $({}^3\xi)_m$ values (from Eq. (16)) of 0.995, 0.9968, 0.889, 0.9968 and 0.972, respectively (Table 5) for these mixtures suggest that 1-propanol (1)+aromatic hydrocarbons (2) mixtures contain an equilibrium mixture of molecular entity VIII and IX. For calculating $({}^3\xi)_m$ value, it is assumed that molecular entity VIII and IX is characterized by interactions between oxygen and delocalized π -electrons cloud of aromatic hydrocarbon (Fig. 9).

2. The Prigogine-Flory-Patterson (PFP) Theory

According to PFP theory [37], excess molar volume (V_m^E) is the result of three contributions due to (i) interaction between unlike molecule, (ii) the free volume change and (iii) change in internal pressure and reduced volume and expressed as

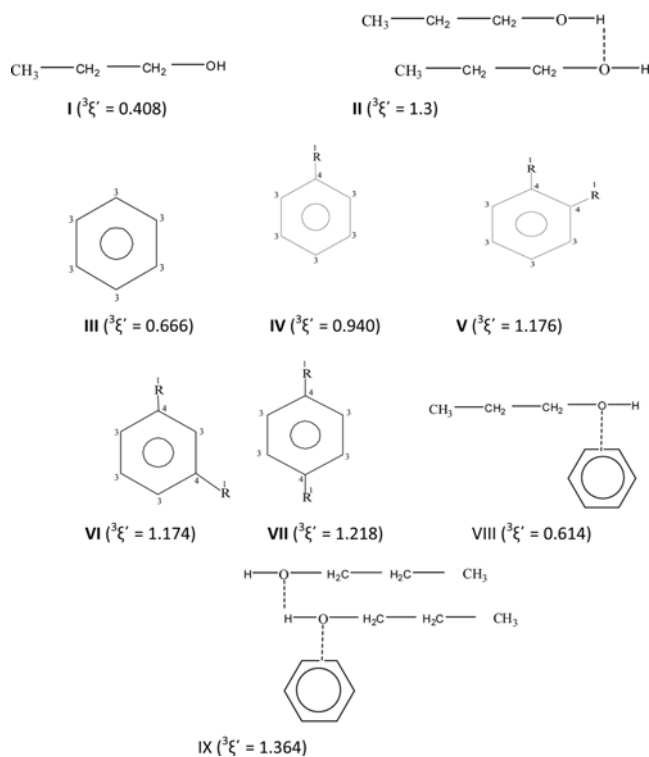


Fig. 9. Connectivity parameters of third degree (${}^3\xi'$) of molecular species I-IX.

$$V_m^E = V_{inter}^E + V_{free\ vol}^E + V_{P'}^E \quad (17)$$

$$\frac{V_m^E}{x_1 V_1^* + x_2 V_2^*} = \frac{(\tilde{V}^{1/3} - 1)\tilde{V}^{2/3} \psi_1 \theta_2 (\chi_{12}^* / P_1^*)}{((4/3)\tilde{V}^{-1/3} - 1)} - \frac{(\tilde{V}_1 - \tilde{V}_2)^2 ((14/9)\tilde{V}^{-1/3} - 1) \psi_1 \psi_2 + (\tilde{V}_1 - \tilde{V}_2)(P_1^* - P_2^*) \psi_1 \psi_2}{((4/3)\tilde{V}^{-1/3} - 1)\tilde{V} P_2^* \psi_1 + P_1^* \psi_2} \quad (18)$$

The V_m^E data were calculated from Eq. (17) and using the following set of equations [38,39]:

$$\tilde{V} = \psi_1 \tilde{V}_1 + \psi_2 \tilde{V}_2 \quad (19)$$

$$\tilde{V}_i = \left(\frac{1 + (4/3)\alpha_i T}{1 + \alpha_i T} \right)^3 \quad (20)$$

$$P_i^* = \frac{T \tilde{V}_i^2 \alpha_i}{\kappa_i} \quad (21)$$

$$\psi_1 = 1 - \psi_2 = \frac{\phi_1 P_1^*}{\phi_1 P_1^* + \phi_2 P_2^*} \quad (22)$$

$$\phi_1 = 1 - \phi_2 = \frac{x_1 V_1^*}{x_1 V_1^* + x_2 V_2^*} \quad (23)$$

$$\theta_1 = 1 - \theta_2 = \frac{x_1 V_1^* (S_1/S_2)}{x_1 V_1^* (S_1/S_2) + x_2 V_2^*} \quad (24)$$

$$(S_1/S_2) = (V_1^*/V_2^*)^{-1/3} \quad (25)$$

where P_i^* and V_i^* are characteristic pressure and volume of the pure

Table 6. Molar volume (V), isobaric expansivity (α), isothermal compressibility (κ_T), characteristic pressure (P^*), characteristic molar volume (V^*) and characteristic temperature (T^*) obtained from Flory theory for the pure liquids at 303.15 K

Compound	V (cm ³ mol ⁻¹)	10 ³ α (K ⁻¹)	10 ⁶ κ_T (cm ³ J ⁻¹)	P* (J cm ⁻³)	V* (cm ³ mol ⁻¹)	T* (K)
1-Propanol	5.503	1.0344	679.79	730.272	60.01	5174.85
Benzene	89.947	1.2747	1091.1	603.59	68.9	4655.2
Toluene	107.427	1.1347	1037.93	541.63	84.03	4930.1
o-Xylene	121.81	1.003	939.63	507.04	97.31	5261.9
m-Xylene	124.101	1.034	967.71	513.05	98.64	5175.9
p-Xylene	124.569	1.0367	1017.96	489.12	98.97	5168.7

Table 7. PFP interaction parameter χ_{12}^* and values of the various contributions at ($x_1=0.4$) to excess volume (cm³ mol⁻¹) at 303.15 K

System	V_{Inter}^E	$V_{Free vol}^E$	$V_{P^*}^E$	χ_{12}^*
1-Propanol (1)+benzene (2)	0.363	0.047	-0.123	38.170
1-Propanol (1)+toluene (2)	0.227	0.010	-0.09	23.249
1-Propanol (1)+o-xylene (2)	0.053	0.00	-0.04	5.552
1-Propanol (1)+m-xylene (2)	0.125	1.719E-07	4.55E-04	12.798
1-Propanol (1)+p-xylene (2)	0.097	5.81E-06	-0.003	9.601

components obtained by dividing pressure and volume by corresponding reduced values (\tilde{P}_i, \tilde{V}_i), respectively (Table 6). In these equations ψ_b, ϕ_b, θ_b , and S_i are the molar contact energy fractions, hard core volume fraction, molecular surface fraction, contact sites per segment, for the pure components, whereas \tilde{V} is the reduced volume for the mixtures. Calculation of V_m^E from Eq. (17) needs the value of Flory interaction parameter, which was calculated using experimental data of V_m^E [15] and was used to calculate V_m^E at other mole fraction (x_1). The calculated values of various contributions to value of V_m^E for equimolar mixture along with Flory interaction parameters are recorded in Table 7. Calculated V_m^E values were found to compare well with respective experimental data for 1-propanol (1)+benzene (2), but the same cannot be said for other systems having s-shaped V_m^E versus x_1 curve as shown in Figs. 7 and 8. In these binary mixtures the PFP model was not even able to predict the sign and shape of experimental V_m^E versus x_1 curve. Similar results were also reported for binary mixtures containing self-associated component [40-46].

CONCLUSIONS

Excess molar volumes for binary mixtures of 1-propanol and aromatic hydrocarbons were measured with v-shaped dilatometer over the entire composition range at 303.15 K. The V_m^E values, for an equimolar composition, vary in the order: benzene>toluene~m-xylene>o-xylene>p-xylene. V_m^E versus x_1 plots for 1-propanol+aromatic hydrocarbon systems are s-shaped (Fig. 2) and change sign from positive to negative in the composition range $0.65 < x_1 < 0.84$, except for 1-propanol+benzene mixtures where the graph is slightly skewed toward y-axis with maxima at $x_1=0.38$ with V_m^E values are positive over the whole composition range. The volumetric properties such as excess, apparent, and partial molar volumes were also derived at infinite dilution using the present excess volume data

for the mixture. The 1-propanol in benzene shows higher value of \bar{V}_1^∞ than in toluene or m- or p-xylene, indicating the stronger interaction of π -electron of toluene/xylene with hydroxyl oxygen due to the presence of one/two electron donating CH₃ with the exception of o-xylene, which may be due to the steric hindrance due to the presence of two methyl groups. Graph-theoretical approach analysis yielded information about the state of aggregation of pure components as well as of the mixtures. PFP theory failed to predict the V_m^E values as well as sign and shape of V_m^E versus x_1 curves with the exception to benzene containing mixtures.

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