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# Excess molar volume of binary mixtures containing an oxygenate

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## ABSTRACT

Increasing fuel demand, environmental concern, and occasional oil crises brought the use of oxygenated compounds as fuel additives to improve octane/cetane rating of fuel. These oxygenates are the oxygen containing compounds such as ethers, alcohol, and esters of vegetable oils. In order to study the interactions of oxygenate with gasoline components, excess molar volumes ( $V_m^E$ ) for 2-propanol + benzene or toluene or xylenes mixtures were reported. The  $V_m^E$  values, for an equimolar composition, follow the sequence: benzene > m-xylene > p-xylene > toluene > o-xylene. The excess volume data were interpreted in terms of a Graph-theoretical approach and the Prigogine–Flory–Patterson theory. While the Graph-theoretical approach yielded information about the state of aggregation of pure components as well as of the mixtures, the PFP theory correctly predicts the values as well as the sign and shape of curves for benzene containing mixtures but for other systems, predicted values were smaller for  $x_1 < 0.4$  and higher thereafter than the corresponding experimental values. Partial molar volumes, excess partial molar volumes, and apparent molar volumes of 2-propanol and aromatic hydrocarbons were also calculated from  $V_m^E$  data and interpreted qualitatively.

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## 1. Introduction

Oxygenates are 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 [1–3]. Increasing fuel demand, environmental concern, and occasional oil crises turn the researchers to study the use of fuel additive oxygenates [4]. These compounds improve air quality and increase the fuel efficiency by allowing more complete combustion in internal combustion engines as oxygen in oxygenates readily oxidized fuel [5,6]. The presence of oxygenates in fuel not only reduces the carbon monoxide emission and other toxic emissions but also increases the octane/cetane rating of fuel [7,8]. Thus the thermo-physical properties of oxygenate additive with aromatic as well as with aliphatic hydrocarbon would be of great importance in processing engineering design and in formulating motor gasoline and diesel [9]. 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 [10–13].

This prompted us to carry out a systemic study of the thermodynamics of binary mixtures of alkanol with alkane or aromatic hydrocarbon. Since 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 [14]

due to the changes in the topology of 2-propanol brought on by aromatics, it appears that a recent Graph theoretical approach [15,16] 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 2-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 [17]. The excess volume data have also been rationalized by Graph-theoretical arguments and the Prigogine–Flory–Patterson theory.

## 2. 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 [18,19]. After each shaking of 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 2-propanol (Merck) was dried by refluxing over fused calcium oxide for 5 h and then fractionally distilled [20]. The middle fraction of distilled 2-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 the samples were checked by measuring their densities and

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refractive indices. 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 [21]. 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 value of densities and refractive indices of the pure compounds agree well with their respective literature values as shown in Table 1 [13,18,22–28]. 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 have been measured by V-shaped dilatometer at 303.15 K in the manner described elsewhere [29]. The temperature of water thermostat was controlled to  $\pm 0.01 \text{ K}$  by a mercury-in-toluene regulator. The change in the position of the liquid level in the capillary was noted with a cathetometer (OSAW, Ambala) that could read to  $\pm 0.001 \text{ cm}$ . 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 [30]. The uncertainty in the measured  $V_m^E$  values was  $\pm 1\%$ .

### 3. Results

The excess molar volume is defined by

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

In which  $V_m$  represents the volume of a mixture containing 1 mol of (2-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 were recorded in Table 2 and were fitted to the following Redlich and Kister equation

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

**Table 1**  
Purities, measured densities ( $\rho$ ) 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	
2-Propanol	99.8	298.15	781.24	781.28 [13]	1.3753	1.3751 [22]	
				781.01 [23]		1.3765 [24]	
				781.06 [25]		1.3752 [18]	
				780.9 [28]			
Benzene	99.7	298.15	772.26	772.27 [13]	1.3714	1.3716 [24]	
				873.55	873.60 [18]	1.4977	1.49792 [18]
				873.30	868.29 [18]		
				862.93	862.96 [26]	1.4913	1.4917 [27]
Toluene	99.8	298.15	862.22	862.19 [18]	1.4944	1.49413 [18]	
				857.53	857.54 [18]		
				852.88	852.85 [26]	1.4887	1.4887 [27]
				875.91	875.94 [18]	1.5028	1.50295 [18]
o-Xylene	99.7	298.15	871.77	871.74 [18]			
				867.35	867.38 [26]	1.5027	1.50295 [18]
				860.05	860.09 [18]	1.4949	1.49464 [18]
				855.83	855.81 [18]		
m-Xylene	99.8	298.15	851.54	851.57 [26]			
				856.63	856.61 [18]	1.4934	1.49325 [18]
				852.22	852.25 [18]		
				847.88	847.87 [26]	1.4886	1.4881 [27]

where  $A_j$  are the adjustable parameters, and  $x_1$  is the mole fraction of 2-propanol in 2-propanol (1) + aromatic hydrocarbon (2) 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  $V_m^E$ .

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

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 data for the studied system together with smoothing curves using Eq. (2) is shown in Fig. 1.

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 molar volumes,  $\bar{V}_1^E$  and  $\bar{V}_2^E$ , were evaluated using 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  $x_1$  and combination of the results of Eqs. (4) and (5) leads to the following equation for the partial molar volumes of 2-propanol ( $\bar{V}_1$ ) and aromatic hydrocarbon ( $\bar{V}_2$ )

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

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

The calculated results for partial molar volume and excess partial molar volumes are plotted in Figs. 2–5. The partial and excess partial molar 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 2-propanol  $\bar{V}_1^\infty$  and aromatic hydrocarbons  $\bar{V}_2^\infty$  at infinite dilution, respectively. These properties are listed in Table 4. The 2-propanol in benzene displays a higher value of  $\bar{V}_1^\infty$  than in toluene indicating the stronger interaction of  $\pi$ -electron of toluene with hydroxyl oxygen due to the presence of

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