SHORT PAPER

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Prediction of density of liquid mixtures using Flory's statistical theory[†]

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Density of various binary and multicomponent liquid mixtures have been calculated with the help of Flory's statistical theory at different temperatures. Computed values of densities have been compared with the experimental values. Excellent agreement has been found.

Keywords: density of liquid mixtures, Flory's statistical theory

Introduction

In recent years Flory's statistical theory[1–4] has been successfully applied to binary and multicomponent liquid mixtures for estimating various thermodynamic and transport properties. For such application the necessary data required are the thermal expansivity (α), isothermal compressinility (β_T) and molar volume of pure components. Some workers used experimental properties of mixture at middle composition of binary mixture to find out the interaction parameter. The success of Flory's theory for various binary and multicomponent liquid mixtures inspired the present workers to estimate the molar volume or density of the liquid mixtures. In the present paper we report the method and the results of calculation for few binary and ternary liquid mixtures. The experimental density values of various mixtures undertaken in the present investigation were taken from the literature.[7–13]

As far as we know, the present approach is entirely new, and nobody has succeeded in estimating the densities of liquid mixtures using the most popular Flory's theory. The density of any type of liquid mixture can be predicted with excellent accuracy.

Theory

Starting with the reduced equation of state.[1–4]

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{\tilde{V}^{1/3}}{\tilde{V}^{1/3}-1} - \frac{1}{\tilde{V}\tilde{T}} \tag{1}$$

and

$$\tilde{V} = V/V^* \tag{2}$$

$$\tilde{T} = T/T^* \tag{3}$$

$$P^* = \left(\frac{\alpha}{\beta_T}\right)T\tilde{V}^2 \tag{4}$$

$$\tilde{V} = \left[1+\left(\frac{\alpha T}{3(1+\alpha T)}\right)\right] \tag{5}$$

$$\tilde{T} = \frac{\tilde{V}^{1/3}-1}{\tilde{V}^{4/3}} \tag{6}$$

and from the knowledge of thermal expansivity (α), isothermal compressibility (β_T) and molar volume (V) of pure components, the values of $\tilde{V}$, V^*, P^*, $\tilde{T}$ and T^* for pure components can be obtained. Segment fraction (ψ) and site fraction (θ) of liquid mixtures have been computed by the method suggested earlier[5] according to which

$$\psi_i = \frac{x_i V_i^*}{\sum x_i V_i^*} \tag{7}$$

$$\theta_i = \frac{\psi_i}{\psi_i + \sum_{k\neq i} \psi_k \left(\frac{V_i^*}{V_k^*}\right)^{1/3}} \tag{8}$$

The interaction parameter X_{ij} is defined as[6]

$$X_{ij} = P_i^*\left[1-\left(P_j^*/P_i^*\right)^{1/2}\left(V_j^*/V_i^*\right)^{1/6}\right]^2 \tag{9}$$

The characteristic pressure P^* for the mixture is calculated with the help of the following equation[5]:

$$P^* = \left[\left(\Sigma_i\, \psi_i P_i^*\right) - \left(\sum_{j\neq i} \psi_i \theta_j X_{ij}\right)\right] \tag{10}$$

The characteristic temperature T^* and the reduced temperature $\tilde{T}^*$ of the mixture are given by[5,6]

$$T^* = P^*/\left\{\Sigma\left(\psi_i P_i/T_i^*\right)\right\} \tag{11}$$

$$\tilde{T} = T/T^* \tag{12}$$

The ideal reduced volume $\tilde{V}^0$ is obtained from the relation

$$\tilde{V}^0 = \Sigma x_i \tilde{V}_i \tag{13}$$

The ideal reduced temperature $\tilde{T}^0$ is defined as[4]

$$\tilde{T}^0 = \frac{\tilde{V}^{0\,1/3}-1}{\tilde{V}^{0\,4/3}} \tag{14}$$

The excess reduced volume $\tilde{V}^E$ and the reduced volume $\tilde{V}^O$ for the mixture are given by[4,6]

$$\tilde{V}^E = \tilde{V}^{0\,7/3}\left(4/3-\tilde{V}^{-1}\right)^{0\,1/3}\left(\tilde{T}-\tilde{T}^0\right) \tag{15}$$

$$\tilde{V} = \tilde{V}^E + \tilde{V}^0 \tag{16}$$

The molar volume (V) of the mixture is related with the characteristic volume (V*) and reduced volume ($\tilde{V}$) of the mixture as

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Average percentage deviations (APD) of computed values of density of liquid mixtures

	Systems	Temperature (°K)	APD
1.	Chlorobenzene + cyclohexane + *n*-heptane	298.15	
	X_2 (cyclohexane) = 0.1883		0.12
	X_2 (cyclohexane) = 0.3138		0.13
2.	Benzene + chloroform + cyclohexane	303.15	0.49
3.	Toluene + chloroform + cyclohexane	303.15	0.37
4.	Chlorobenzene + chloroform + cyclohexane	303.15	0.46
5.	Dioxan + chloroform + cyclohexane	303.15	0.39
1.	Acetone + methyliodide	253.2	0.70
		263.2	0.73
		273.2	0.76
		283.2	0.77
		293.2	0.79
		303.2	0.80
		308.2	0.81
2.	Benzene + *p* - xylene	298.15	0.10
		313.15	0.09
3.	Benzene + *p* - dioxan	298.15	0.05
		313.15	0.07
4.	Cyclohexanol + cyclohexane	298.15	0.31
		313.15	0.32
		323.15	0.36
5.	Acetonitrile + benzene	298.15	0.09
6.	Benzene + DMF	298.15	0.83
7.	Acetonitrile + DMF	298.15	0.61

$$V = V^{*}\tilde{V} \quad (17)$$

where
$$V^{*} = \sum x_i V_i^{*} \quad (18)$$

The density (ρ_m) of the mixture is given by

$$\rho_m = M_m / V \quad (19)$$

where M_m is molar mass of the mixture expressed as

$$M_m = \sum x_i M_i \quad (20)$$

where x_i is mole fraction M_i is molar mass of the ith pure component.

Equation (19) in conjunction with eqns (17) can be used to compute ρ_m of the liquid mixture. Except for the mole fraction no other properties of liquid mixtures are needed to obtain the theoretical density of liquid mixtures.

Results and discussion

For testing out theoretical procedure of estimation the density of liquid mixtures from Flory's statistical theory using only the experimental values of density and ultrasonic velocity of pure components, we have selected seven binary and five ternary liquid mixtures. The experimental values of density (ρ) and ultrasonic velocity (u) of various pure liquid components comprising the mixtures are taken from the literature.[7-13] Similarly, for the comparision of theoretically computed values of mixture densities with observed densities of various liquid mixtures under the present consideration, the experimental values are taken from different source.[7-13] All the reported values of density are highly accurate and precise. Using eqns (15) – (20), the values ρ_m of for seven binary and five ternary liquid mixtures are calculated. The average percentage deviations (APD) of computed values of ρ_m from the observed values over the entire compositions range of various mixtures are calculated and reported in Table 1. Surprisingly the agreement is extremely good. APD values in case of all the binary mixtures do not exceed 0.83%, where as in the case of ternary mixtures it is only 0.49%. The excellent agreement between the observed and theoretical values for all the systems using Flory's theory demonstrates the validity of present approach.

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