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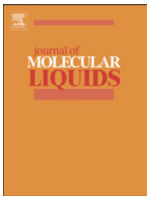

Volumetric, ultrasonic, viscometric and refractive index behaviour of binary mixtures of styrene with ethylalcohol and chlorobenzene at different temperatures (T=298.15 K to 313.15 K)

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ABSTRACT

This paper presents experimental data for densities, ρ, viscosities, η, ultrasonic speeds, u, and refractive indices, n, of pure styrene (STY), chlorobenzene (CB), ethylalcohol (EA) and of their binary liquid mixtures over the entire composition range at 298.15, 303.15, 308.15, 313.15 K. The uncertainties in density, ultrasonic speed, viscosity, and refractive index measurements are ±0.0001 g cm^{-3}, ±0.15 m s^{-1}, ±0.003 mPa s, and ±0.0002 units, respectively. From these experimental data, excess molar volume, deviations in isentropic compressibility, viscosity and in refractive index and internal pressure are calculated for all the binary mixtures, over the entire composition range. The apparent molar volume, $V_{\phi,2}$, and apparent molar compressibility, $K_{\phi,2}$, of CB and EA in styrene were also calculated. Partial molar volume,$\bar{V}^0_{\phi,2}$, and partial molar compressibility, $\bar{K}^0_{\phi,2}$, were estimated by using the values of $V_{\phi,2}$ and $K_{\phi,2}$ of CB and EA in styrene at infinite dilution. The excess and deviation functions were fitted to Redlich and Kister type polynomial equation. Moreover, theoretical predictions of refractive index of the two binary mixtures are made on the basis of empirical and semiemperical relations by using the experimental values of the pure components. The results provide information on the molecules in the pure liquids as well as in the binary mixtures.

1. Introduction

Studies of thermodynamic properties of binary mixtures are of considerable interest in the fundamental understanding of the nature of interactions between the unlike molecules. In recent years, the theoretical and experimental investigations of excess and deviation functions are taken as interaction parameters to improve the results [1–4]. Our research is concerned to the systematic study of molecular interactions in the binary mixtures, which are important in many fields of industrial and biological processes. Mixed solvents find practical applications as they provide wide range of mixtures with desired properties [5].

The present work is a continuation of our earlier studies [6–8] and deals with the qualitative and quantitative study on the binary mixtures of styrene (STY) with chlorobenzene (CB) and ethylalcohol (EA). Styrene has an oriented structure, stabilised by dipole–dipole interactions. Its molecule contains an olefinic chain attached to an aromatic ring and is an important industrial monomer used in large scale preparation of various polymers [9].

Chlorobenzene and ethylalcohol are polar molecules and are important components in synthetic chemistry (produce latex systems), in medicine and biological processes (fungicides, drugs, flavouring extracts, and antiseptics) and are widely used in preparing industrial solvents.

In view of their industrial importance, the present study reports the experimental values of densities, ρ, viscosities, η, ultrasonic speeds, u, and refractive indices, n, of pure STY, EA, CB and those of there binary mixtures over the entire composition range and at 298.15, 303.15, 308.15 and 313.15 K. The above experimental data were used to evaluate the excess molar volume, V^E, deviations in isentropic compressibility, Δk_s, deviation in viscosity, $\Delta\eta$, deviation in refractive index, Δn and deviation in internal pressure, ΔP_i at each temperature. All of these excess and deviation quantities have been fitted to Redlich and Kister type polynomial equation [10].

Partial molar volume,$\bar{V}^0_{\phi,2}$, and partial molar compressibility, $\bar{K}^0_{\phi,2}$, of CB and EA in styrene have also been calculated. Refractive indices of binary mixtures were theoretically obtained with the help of various empirical relations at each temperature. The variations of these parameters with composition offer a convenient method to study the nature and extent of interaction between the component molecules of the liquid mixtures not easily obtained by other means.

To the best of our knowledge no literature data are available for the densities, viscosities, ultrasonic speeds and refractive indices of the binary mixtures reported here and at different temperatures.

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2. Experimental

Styrene (Acros Organics, USA) of AR grade 99% chlorobenzene and ethylalcohol (S.D Fine Chem. Ltd. India) also of A.R grade 99.5% were further purified by the method given in the literature [11]. All the chemicals were stored over 0.4 nm molecular sieves to remove the traces of water, if any, and degassed just before use. The solutions were prepared by mass using a precise XB 220 (Swiss make) electronic balance with a precision of ±0.1 mg.

The densities of pure liquids and their binary mixtures were measured using a single-capillary pycnometer as described in earlier literature [7,8]. The ultrasonic speeds in liquid samples were measured by using a single crystal variable path interferometer (Mittal Enterprise, New Delhi, Model-M-82) at 3 MHz. The uncertainties in measured density and ultrasonic speed are ± 0.0001 g cm^{-3} and ± 0.15 m s^{-1}, respectively. The viscosities of pure liquids and their binary mixtures were measured using Ubbelohde-type suspended level viscometer, calibrated with triple-distilled water. The viscometer containing the test liquid was allowed to stand for about 30 min in the thermostatic water bath (Julabo, Model-MD, Germany) having a precision of ±0.02 K in order to minimize thermal fluctuations. The uncertainty in viscosity measurement is ±0.003 mPa s. The refractive indices were measured with a thermostated Abbe-refractometer (Metrix India) after calibrating it with distilled water at known temperatures. The uncertainty in the measured values of refractive indices was not more than ±0.0002 units. A minimum of three readings were taken for each sample and the average values were used in all the calculations. Reliability of the experimental data and the purity of the solvents were ascertained by comparing their densities, ultrasonic speeds, viscosities and refractive indices at different temperatures with the values reported in literature [12–21], Table 1.

3. Results and discussion

The experimental densities, ρ, ultrasonic speeds, u, viscosities, η, and refractive indices, n of pure styrene, chlorobenzene, ethylalcohol and their binary mixtures are used to calculate excess thermodynamic properties of mixtures which correspond to the difference between the actual property and the property if the system behaves ideally and, thus, are useful in the study of molecular interactions and arrangements in the mixtures. In particular, they reflect the interactions that take place between solute–solute, solute–solvent and solvent–solvent species. The effects which are expected to operate between the component molecules under study are (i) structural effect which is due to the differences in shape and size of the component molecules (ii) reorientational effect between component molecules and (iii) energetic effect, i.e., molecular interaction that can be weakened or destroyed or established during the mixing process [22]. Thus, in the present study the values of excess molar volumes, V^E, deviation in isentropic compressibility, Δk_s, deviation in viscosity, $\Delta\eta$, deviation in refractive index, Δn and deviation in internal pressure ΔP_i were calculated with the help of the following standard relations:

$$V^E = V - (x_1V_1 + x_2V_2) \tag{1}$$

$$\Delta k_s = k_s - (\phi_1 k_{s1} + \phi_2 k_{s2}) \tag{2}$$

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \tag{3}$$

$$\Delta n = n - (\phi_1 n_1 + \phi_2 n_2) \tag{4}$$

$$\Delta P_i = P_i - (x_1 P_{i1} + x_2 P_{i2}) \tag{5}$$

where x and ϕ are the mole fraction and volume fraction respectively. Subscripts 1 and 2 stand for the pure components styrene and CB/EA, respectively, k_s and V are the isentropic compressibility and molar volume and can be evaluated by the following relations:

$$k_s = 1/u^2\rho \tag{6}$$

$$V = (x_1M_1 + x_2M_2)/\rho \tag{7}$$

where M is the molar mass of the pure components. The internal pressure P_i can be obtained by using the Buchler–Hirschfelder Curties equation of state [23], by applying the following relation:

$$P_i = \frac{2^{1/6}RT}{2^{1/6}V - dN^{1/3}V^{2/3}} \tag{8}$$

where N is the Avogadro number, V is the molar volume and d is the molecular diameter of the mixture or pure components, which is related to molecular polarizability, (α) as:

$$\alpha = (d/2)^3 \tag{9}$$

substituting the dependence of this parameter on the density and refractive index, mean molecular diameter of a pure component or a mixture can be expressed as a function of refractivity.

$$d = 2\left(\frac{n^2-1}{n^2+2}\cdot V \cdot \frac{3}{4}\pi N\right)^{1/3} \tag{10}$$

The values of the excess and deviation functions V^E, Δk_s, $\Delta\eta$, Δn and ΔP_i of the binary mixtures were fitted to the Redlich and Kister type equation [10].

$$Y^E = x_1x_2\sum_{i=1}^{5} A_i(1-2x_1)^{i-1} \tag{11}$$

where Y^E stands for V^E, Δk_s, $\Delta\eta$, Δn and ΔP_i. The coefficients A_i of the fitting Eq. (11), evaluated using least-squares method, and the standard deviations $\sigma(Y^E)$, calculated as,

$$\sigma(Y^E) = \left(\sum\left[(Y^E_{expt} - Y^E_{cal})^2\right]/(m-k)\right)^{1/2} \tag{12}$$

where m is the number of experimental data points and k is the number of A_i coefficients considered, have been listed in Table 2. The variations of V^E, Δk_s, $\Delta\eta$, Δn and ΔP_i with mole fraction, x_1 of styrene are shown graphically in Figs. 1–5, the first three properties are plotted at all the four studied temperatures in order to see the effect of temperature on these properties, while, the remaining two namely, Δn and ΔP_i, are plotted at 298.15 K only.

Fig. 1(a) and (b) reveals that the excess molar volume, V^E is negative over the entire composition for the two investigated mixtures at all the four temperatures. A qualitative explanation is given for the change in V^E with composition and temperature. Mixing of styrene with chlorobenzene and ethylalcohol leads to (i) structure making dipole–dipole or dipole-induced dipole (OH…π or Cl….π) type specific interactions (ii) geometrical fitting of smaller molecules into the voids created by larger molecules due to the difference in molar volumes (iii) disruption of dipolar association present in the liquid components tends to make V^E positive. The observed negative V^E values suggest that the combined effect due to (i) and (ii) dominates over that of (iii). However, out of the two effects (i) and (ii) though the interactions OH….π between H-atom of OH group of EA and π-electrons of benzene ring of STY or Cl…..π between the electronegative Cl-atom of CB and π-electrons of benzene ring of STY tend to decrease the volume of the system, the effect (ii) seems to be primarily responsible for the overall negative values of V^E for both the investigated systems. As the molar volumes of STY, CB and EA at