Research Article

Thermo Physical Properties for Binary Mixture of Dimethylsulfoxide and Isopropylbenzene at Various Temperatures

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Density, refractive index, speed of sound, and viscosity have been measured of binary mixture dimethylsulfoxide (DMSO) + isopropylbenzene (CUMENE) over the whole composition range at 298.15, 303.15, 308.15, and 313.15 K and atmospheric pressure. From these experimental measurements the excess molar volume, deviations in viscosity, molar refractivity, speed of sound, and isentropic compressibility have been calculated. These deviations have been correlated by a polynomial Redlich-Kister equation to derive the coefficients and standard error. The viscosities have furthermore been correlated with two or three parameter models, that is, heric correlation and McAllister model, respectively.

1. Introduction

This paper contributes in part to our ongoing research on the solution properties. In the present study, data on density, viscosity, refractive index and speed of sound of binary mixture dimethylsulfoxide (DMSO) + isopropylbenzene at 298.15, 303.15, 308.15, and 313.15 K have been measured experimentally. From these results the excess molar volumes, viscosity deviations, and deviations in molar refraction and isentropic compressibility have been derived. Dimethylsulfoxide is a versatile nonaqueous dipolar aprotic solvent having wide range of applications. It is used as a solvent in many nucleophilic substitutions reactions. It has the ability to pass through membranes, an ability that has been verified by numerous subsequent researchers. It can penetrate through living tissues without damaging them. Therefore local anesthetic or penicillin can be carried through the skin without using a needle which makes it a paramount in medicinal field.

Isopropylbenzene is a naturally occurring substance present in coal tar and petroleum, insoluble in water, but is soluble in many organic solvents. It is used as a feedback for the production of Phenol and its coproduct acetone. It is also used as a solvent for fats and raisins.

The study of the thermodynamic properties of DMSO + isopropylbenzene mixtures is of interest in industrial fields where solvent mixtures could be used as selective solvents for numerous reactions.

2. Experimental Section

2.1. Materials. The chemicals used are of AR grade, dimethylsulfoxide (DMSO) and isopropylbenzene (CUMENE) are from Riedel, Germany. The chemicals are purified using standard procedure [1] and are stored over molecular sieves. The purity of the chemicals was verified by comparing viscosity, density, and refractive index with the known values reported in the literature as shown in Table 1. All the compositions are prepared by using SARTOIS balance. The possible error in the mole fraction is estimated to be less than ±1 × 10⁻⁴.

2.2. Density and Speed of Sound. Density and Speed of sound were measured by ANTON PAAR densimeter (DSA 5000) to
Table 1: Physical properties of components at 298.15 K.

<table>
<thead>
<tr>
<th>Component</th>
<th>𝑇/K</th>
<th>ρ/g cm⁻³</th>
<th>𝜂/mPa⋅s</th>
<th>𝑛_D</th>
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<td>298.15</td>
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<td>298.15</td>
<td>0.8581</td>
<td>0.7388</td>
<td>1.4298</td>
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</table>

2 Journal of Thermodynamics

2.3. Viscosity. Viscosities were measured by using calibrated modified Ubbelohde viscometer [2] as described earlier. The calibration of viscometer was done at each temperature in order to determine constants A and B of equation

\[ \eta = \frac{\eta}{\rho} = At + \frac{B}{t}. \]

Flow time was measured with an electronic stop watch with precision of ±0.01 s. For each measurement viscometer was kept vertically in water bath for half an hour at constant temperature in order to attain thermodynamic equilibrium. The temperature of the bath was maintained constant with the help of circulating type cryostat where the temperature is controlled to ±0.02 K. The efflux time was repeated at least three times for each composition. The uncertainty in the values is within ±0.003 mPa-s.

2.4. Refractive Index. Refractive indices were measured for sodium D-line by ABBE-3L refractometer having Bausch and Lomb lenses. The temperature was maintained constant with the water bath as described for the viscosity measurement. A minimum of three independent readings were taken for each composition, and the average value was considered in all the calculations. Refractive index data are accurate to ±0.0001 units.

3. Experimental Results and Correlations

At least three independent readings of all the physical property measurements on ρ, \( \eta \), \( n_D \), and \( u \) were taken for each composition and the averages of these experimental values are presented in Table 2. The experimentally determined values are used for the deviation calculations.

3.1. Excess Molar Volume. Density is used to evaluate excess molar volume calculated by the equation

\[ V^E = \frac{x_1M_1 + x_2M_2}{\rho} - \frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2}, \]

where \( \rho_1 \), \( \rho_2 \) are the densities of pure components and \( \rho \) is the density of mixture. \( M_1 \), \( M_2 \) are the molecular weight of the two components. \( x_1 \), \( x_2 \) are the mole fraction of DMSO.

Excess gibb’s free energy of activation has been also calculated using the viscosity and density of the mixture by the equation

\[ \Delta G^E = RT \left[ \ln (\eta V) - \sum_{i=1}^{2} x_i \ln (\eta V_i) \right] \]

\( R \) is a universal gas constant; \( T \) is the temperature of the mixture. \( \eta_1, \eta_2 \) are the viscosity of the mixture and pure compound, respectively. \( V, V_i \) refers to the molar volume of the mixture and pure components, respectively.

3.2. Viscosity Calculations. The deviation in viscosity is obtained by equation

\[ \Delta \eta = \eta - x_1 \eta_1 - x_2 \eta_2. \]

\( \eta_1, \eta_2 \) refers to the viscosity of pure components and \( \eta \) is the viscosity of mixture. McAllister [3] model

\[ \ln n = x_1^3 \ln n_1 + x_2^3 \ln n_2 + 3x_1^2x_2 \ln n_{12} + 3x_1x_2^2 \ln n_{21} - \ln \left[ x_1 + x_2 \frac{M_2}{M_1} \right] + 3x_1x_2^2 \ln \left[ \frac{1 + (2M_2/M_1)}{3} \right] + x_2^3 \ln \left[ \frac{M_2}{M_1} \right] \]

and Herric correlation

\[ \ln n = x_1 \ln n_1 + x_2 \ln n_2 + x_1x_2 \left[ \alpha_{12} + \alpha'_{12} (x_1 - x_2) \right] - \ln M_{\text{mix}} + x_1 \ln M_1 + x_2 \ln M_2 \]

have been fitted to viscosity data and it was found that both have the same standard errors at each temperature.

3.3. Isentropic Compressibility. The experimental results for the speed of sound of binary mixture are listed in Table 2. The isentropic compressibility was evaluated by \( K_S = u^{-2} \rho^{-1} \) and the deviation in isentropic compressibility is calculated using the below equation:

\[ K_S^E = K_S - K_S^id \]

and deviation in speed of sound by

\[ \Delta u = u - x_1u_1 - x_2u_2, \]
Table 2: Density, $\rho$, viscosity, $\eta$, speed of sound, $u$, and refractive indices, $n_D$, for DMSO(1) + CUMENE(2) at different temperatures.

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<th>$x_1$</th>
<th>$\rho$ (g cm$^{-3}$)</th>
<th>$\eta$ (mPa s)</th>
<th>$u$ (m s$^{-1}$)</th>
<th>$n_D$</th>
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\[ \Delta R = R_m - \sum \Phi_i R_i, \] (11)

where \( n_r \) refers to refractive index, \( R_m \) is molar refraction of the mixture, \( R_i \) is molar refraction of the \( i \)th component, and \( \Phi \) is ideal state volume fraction.

All the deviations \( (V^E, \Delta R, \Delta \eta, \Delta u, K^E_S) \) have been fitted to Redlich-Kister [7] polynomial regression of the type

\[ \Delta Y = \sum_{i=1}^{m} A_j (1 - 2x_i)^{j-1} \] (12)

to derive the constant \( A_j \) using the method of least square. Standard deviation for each case is calculated by

\[ \sigma = \left[ \frac{\sum (\Delta Y_{\text{expt}} - \Delta Y_{\text{calc}})^2}{m-n} \right]^{0.5}, \] (13)

where \( m \) is the number of data points and \( n \) is the number of coefficients. Derived parameters of the redlich-Kister (12) equation and standard deviations (13) are presented in Table 3.
4. Discussions

The deviations in excess molar volume at 298.15 to 313.15 K versus the mole fraction of DMSO are shown in Figure 1. The molar volume of the mixture and the viscosity data have also been used for the calculation of Gibb’s free energy presented in Figure 5. The negative values of $V^E$ indicate an interaction between the molecules which decreases with an increase of temperature. The large negative $V^E$ values indicate a contraction of the volume and can be explained in terms of the heteroassociation in the mixture and suggest the strongest association occurs in this binary system [8].

The viscosity and deviations are presented in Table 2 and plotted in Figure 2, respectively. The negative values of $\Delta \eta$ obtained for the investigated mixture suggest that there may be reduction in the strength of H-bonds upon mixing. The viscosity data can be qualitatively explained by considering that the Cumene has a branching CH$_3$ group, leading to packing of molecules in the pure state and a consequent lower density and larger mobility (lower viscosity) of the structure. This may be because interaction of Cumene with DMSO is less [6].

The viscosity data is also fitted to the two- and the three-parameter model, that is, heric correlation and the McAllister model and the evaluated parameters are presented in Table 4. The deviations decrease with the increase in temperature.

The deviations in molar refraction are shown in Figure 3. The $\Delta R$ values are negative for the whole composition range which goes on decreasing as the temperature of the solution increases.

The results of derived $\kappa^E$ are also plotted in Figure 4. The deviations are negative over the whole composition range.
The $K_E^S$ is negative near the composition of $x_1 = 0.7$ and then abruptly goes to zero.

**Symbols**

$A_0, A_1, A_2, A_3$: Parameters of Redlich-Kister equation  
$A_{12}, A_{21}$: Interaction coefficient of McAllister model

**References**


