Volumetric and transport properties of binary liquid mixtures of sulfolane with aniline, N,N-dimethylaniline and N,N-diethylaniline at different temperatures and atmospheric pressure

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ABSTRACT

Densities and viscosities of pure sulfolane, aniline, N,N-dimethylaniline, N,N-diethylaniline and their binary mixtures with sulfolane as common component were measured over the entire composition range at $T = (303.15, 308.15,$ and $313.15)$ K and atmospheric pressure. A high precision vibrating-tube densitometer (DSA 5000, Anton-Paar, Austria) was used for the density measurements and a Cannon–Fenske routine type viscometer for the viscosity. The various thermodynamic properties such as excess molar volumes, deviation of viscosity, free energy and excess free energy of activation for viscous flow were calculated for each of the systems. The excess properties were fitted to the Redlich–Kister equation, and coefficients along with standard deviation of fit were also presented. All these properties were discussed in terms of molecular interactions. The experimental findings would be tremendous important for the accurate design of equipment, and controlling the process parameters of various chemical and industrial processes such as separation of chemicals, fluid flow, heat flow or chemical reactions.

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1. Introduction

Knowledge of thermodynamic and transport properties of pure liquids and multi-component mixtures is indispensable for various chemical and industrial processes such as separation of chemicals, fluid flow, heat flow or chemical reactions, and extremely useful in controlling the process parameters and manufacturing equipment with accurate design. Furthermore, excess thermodynamic and transport properties are useful for understanding the nature of molecular interactions [1,2] in mixtures, and helpful for developing chemical theories of solutions.

Sulfolane is an important industrial solvent having beneficial physicochemical properties that has the ability to extract monocyclic aromatic hydrocarbons from petroleum products. Sulfolane mixtures with other solvents are also of particular interest. Aromatic amines may be sulphonated with sulfuric acid in the presence of sulfolane, *e.g.*, sulphanilic acid from aniline and aromatic sulfonic acids can be made by the sulfonation of aromatic compounds. An understanding of the mixing behavior of sulfolane with esters is therefore important and has applications in many engineering areas as well as synthetic chemistry.

To the best of our knowledge, no extensive studies have been made on the mixtures of sulfolane with aniline and substituted aniline. Thus considering the industrial and scientific interests of sulfolane-aromatic amine mixtures, densities, ρ and viscosities, η of binary liquid mixtures of sulfolane with aniline, N,N-dimethylaniline and N,N-diethylaniline were measured over the entire composition range at $T = (303.15, 308.15,$ and $313.15)$ K under atmospheric pressure. Using measured density and viscosity data, excess molar volumes, V^E, deviation of viscosity, $\Delta\eta$, interaction parameter, d_{12}, free energy of activation, $\Delta G^{\ddagger}$, excess free energy of activation, $\Delta G^{\ddagger E}$ for viscous flow were computed. These results were used to gain a better understanding of the intermolecular interactions between the component molecules of the liquid mixtures.

2. Experimental section

2.1. Materials

Sulfolane (SIGMA–ALDRICH, USA, GC Grade), aniline (Thomas Baker, India, GLC grade), N,N-dimethylaniline (BDH, UK, GC grade) and N,N-diethylaniline (Merck-Schuchardt, Germany, GC grade) were used without further purification. The purity of materials was listed in table 1.

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TABLE 1
Purities and sources of the samples used in this work.

Chemical name	Source	Grade	Purification method	Mass fraction purity
Sulfolane	Sigma–Aldrich, USA	GC	No further purification	$\geqslant 0.99$
Aniline	Thomas Baker, India	GLC	No further purification	$\geqslant 0.99$
N,N-dimethylaniline	BDH, UK	GC	No further purification	$\geqslant 0.99$
N,N-diethylaniline	Merk-Schuchardt, Germany	GC	No further purification	$\geqslant 0.99$

2.2. Apparatus and procedures

Binary mixtures were prepared by mass using a balance (Mettler Toledo, B204-S, Switzerland) with a stated precision of ±0.0001 g and the masses of the components were converted to their corresponding mole fractions. From the uncertainties of masses of components derived from the accuracy of balance and purities of samples, the standard uncertainty in mole fractions was estimated to be $1 \cdot 10^{-4}$. Mixtures were allowed to stand for some time before every measurement to avoid air bubbles.

The densities of the pure liquid and binary liquid mixtures were measured using a high precision vibrating tube digital density meter (model DSA 5000, Anton Paar, Austira). The density meter cell was calibrated with deionized double-distilled water and dry air at atmospheric pressure. This instrument kept the samples at working temperature with a resolution of 0.001 K. By measuring the damping of the oscillation of U-tube caused by the viscosity of filled sample, the DSA 5000 automatically corrects viscosity related errors on density. The standard uncertainty of density measurement claimed by manufacture was $1 \cdot 10^{-3}$ kg · m⁻³. Considering the contribution of sample impurity to the uncertainty [3], the standard uncertainties for measurements were estimated to be 0.01 K for temperature and 0.1 kg · m⁻³ for density.

Viscosities of samples were measured using a Cannon–Fenske routine type viscometer keeping it in a water thermostat that maintained the samples temperature with a resolution of 0.01 K. Calibration was carried out using pure n-hexane, n-heptane and n-nonane. An electronic digital stopwatch with a readability of 0.01 s was used for efflux time measurement. Triplicate measurements of efflux times were reproducible within ±0.03 s. The viscosity was calculated from the following relationship,

$$\eta = A\rho t - \frac{B\rho}{t}, \tag{1}$$

where, η is the dynamic viscosity, t is the efflux time, A and B are the calibration constants of the viscometer and B is related to kinetic energy correction factor. A and B were evaluated through the non-linear regression of η/ρ versus t data to equation (1). η and ρ of n-hexane, n-heptane and n-nonane required for the calibration were taken from the literatures [4,5]. Taking into account the purity of chemicals, the relative standard uncertainty of the viscosity measurement was within 1.0%. The comparison of experimental densities and viscosities of pure liquids was made with literature [6–11] values in table 2. The excellent agreement between experimental and literature values are found.

3. Theory and calculations

The excess volume, V^E is computed from density, ρ values through the following equation,

$$V^E = V_m - V_{id}, \tag{2}$$

where, $V_m = (x_1 M_1 + x_2 M_2)/\rho$, $V_{id} = x_1 M_1/\rho_1 + x_2 M_2/\rho_2$, ρ is the density of binary liquid mixtures, x_1, M_1 and ρ_1, and x_2, M_2 and ρ_2 are the mole fraction, molar mass and density of pure components, respectively.

The deviation of viscosity, $\Delta\eta$ can be obtained from the following equation,

$$\Delta\eta = \eta - \eta_{id}, \tag{3}$$

where, η_{id} is the viscosity of ideal mixtures. Arrhenius proposed the following relation for calculating viscosity of an ideal mixture,

$$\ln\eta_{id} = x_1 \ln\eta_1 + x_2 \ln\eta_2, \tag{4}$$

where, η_1 and η_2 are the viscosities of pure components, respectively.

On the basis of the absolute reaction rate theory of Eyring [12], Gibbs free energy, $\Delta G^{\ddagger}$ and excess Gibbs free energy, $\Delta G^{\ddagger E}$ of activation for viscous flow can be calculated from following equations,

$$\Delta G^{\ddagger} = RT\ln\left(\frac{\eta V}{Nh}\right), \tag{5}$$

$$\Delta G^{\ddagger E} = RT(\ln\eta V - x_1 \ln\eta_1 V_1 - x_2 \ln\eta_2 V_2), \tag{6}$$

TABLE 2
Comparison of experimental densities and viscosities of pure liquids with literature values.[a]

Compounds	T/K	ρ/kg · m⁻³		η/mPa · s	
		Expt.	Lit.	Expt.	Lit.
Sulfolane	303.15	1260.1	1261.8 [6], 1262.9 [7]	10.2	10.0304 [6], 10.401 [7]
	308.15	1255.7	1257.0 [6]	8.95	8.7947 [6]
	313.15	1251.3	1251.6 [6], 1254.1 [7]	7.88	7.8365 [6], 8.0712 [7]
Aniline	303.15	1013.0	1012.9 [8]	3.25	3.19 [8]
	308.15	1008.7	1008.6 [8]	2.80	2.8 [8]
	313.15	1004.4	1004.2 [8]	2.42	2.42 [8]
N,N-dimethylaniline	303.15	947.7	948.0 [9], 947.67 [10]	1.18	1.174 [9], 1.172 [10]
	308.15	943.5	943.55 [10]	1.09	1.111 [10]
	313.15	939.4	938.5 [9]	1.01	0.982 [9]
N,N-diethylaniline	303.15	925.9	926.0 [9], 925.29 [11]	1.72	1.703 [9], 1.711 [11]
	308.15	921.9	921.26 [11]	1.55	1.548 [11]
	313.15	917.9	917.7 [9]	1.40	1.402 [9]

[a] Standard combined uncertainties u_c are $u_c(\rho) = 0.1$ kg · m⁻³, $u_c(T) = 0.01$ K, and $u_c(p) = 2$ kPa. The relative standard combined uncertainty u_r in viscosity is $u_r(\eta) = 1\%$.