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Effect of ionic liquid on the solvation behavior of nonaqueous *N*,*N*′-salicylidenephenylediamine Schiff base (Salophen) solutions at 298.15 K

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ABSTRACT

Thermodynamic properties of *N*,*N*′-salicylidenephenylediamine Schiff base (Salophen) in the solutions of ionic liquid, 1-butyl-3-methylimidazolium bromide ([BMIm]Br) + organic solvents (*N*,*N*-dimethylacetamide DMA, and dimethylsulfoxide DMSO) have been measured at 298.15 K. The measured density and viscosity values have been used to calculate apparent molar volumes, V_ϕ, standard partial molar volumes, V_ϕ^0, standard partial molar volumes of transfer, $\Delta_{tr}V_\phi^0$, viscosity *B*-coefficients, and solvation numbers, B/V_ϕ^0, for the solutions being studied. All of these parameters were used to interpret the solute–solvent interactions and solvation process occurring between ionic liquid and Salophen.

1. Introduction

Schiff bases or imines, $R_2C=NR$, are the condensation products of aldehydes, ketones, and β-diketones reacting with primary amines and related derivatives. These compounds are considered as an important class of ligands in coordination chemistry and have extensive applications in different fields [1]. Schiff bases derived from aldehydes and diamines constitute one of the most relevant synthetic ligand systems with importance in asymmetric catalysis and they have preferred stock in broad range of transition-metal catalyzed reactions including lactide polymerization, epoxidation of olefins, hydroxylation, and asymmetric ring opening of epoxides [2–8]. Schiff bases containing amphiphiles in polymeric films exhibit interesting optical and electronic properties [9,10]. They have other features, such as catalytic, antimicrobial, antifungal, antiviral applications, and also synergistic effect on insecticides, plant growth regulation, anti tumoring, and dying applications [11].

It is very well known that medium plays a dramatic role on the outcome of chemical reactions. Ionic liquids, as organic electrolytes and neoteric green solvents containing the bulky cations and anions, are used in many fields, such as catalysis, chemical reactions, separations, electrochemistry, and nanoscience applications [12]. Recently, a series works have been reported on the Schiff base and its metal complexes in the presence of some ionic liquids. A new cyanide optode was designed using Schiff base complex, [*N*,*N*′-bis(salicyliden)-2,3-diaminopyridine]tributylphosphine cobalt(III) percholorate monohydrate complex, which was coated on transparent triacetylcellulose film as membrane. The sensitivity of the method was improved by using ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF_6], introduced in constructing the optode membrane. The optode was successfully applied for the determination of cyanide in drinking water [13]. In a new method, Schiff base extracting agent (PMBP-2-ABT) was established for the extraction of heavy ions, by PMBP-2-ABT/ionic liquid binary-water phase system [14]. A series of square planar nickel (II) complexes containing N,O donor Schiff base ligand have catalytic activities for the oxidation of alcohols in ionic liquid media [15]. The asymmetric epoxidation of limonene has been performed using manganese (III) Schiff base complex dissolved in 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ([BMIm]BF_4) ionic liquid and hydrogen peroxide as oxidant. The manganese (III) chiral Schiff base complex in ionic liquid was found to be stable and efficient for the epoxidation of limonene with hydrogen peroxide as oxidant [16].

Because of the importance and extensive applications of Schiff bases and ionic liquids as mentioned above, it is necessary to study the thermodynamic properties of Schiff base in the presence of

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ionic liquids for clarifying molecular interactions between Schiff base and ionic liquid.

Hence, in this work, we report the density d and viscosity η data of Salophen Schiff base in the solutions of (1-buthyl-3-methyl imidazolium bromide + DMA, DMSO) at several concentrations of ionic liquid. Apparent molar volumes V_ϕ, of Salophen Schiff base were calculated at $T = 298.15$ K using density data and used to calculate the standard partial molar volumes, V_ϕ^0 and standard partial molar volumes of transfer, $\Delta_{tr}V_\phi^0$. The viscosity B-coefficients were estimated using the Jones–Dole equation. All of these parameters were used to interpret the solute–solvent interactions and effect of ionic liquids on the solvation properties of Salophen Schiff base in the presence of ionic liquid.

2. Experimental

2.1. Materials

Reagents used in this work are *N*-methylimidazole, 1-bromobutane, Benzene-1,2-diamine, Salicylaldehyde, *N,N*-dimethylacetamide, and dimethylsulfoxide that were given in table 1. These reagents were used without further purification. The density, viscosity, and refraction index values of the pure solvents are given in table 2 and compared those with the literature values.

2.2. Synthesis of 1-butyl-3-methylimidazolium bromide [BMIm]Br

The ionic liquid, 1-butyl-3-methylimidazolium bromide [BMIm]Br, was prepared and purified by using the procedure described in the literature [17,18]. Briefly, [BMIm]Br was synthesized by direct alkylation of *N*-methylimidazole with an excess of 1-bromobutane in a round-bottom flask at $T = 353$ K for 48 h under a nitrogen atmosphere.

The product was dried in high vacuums at about $T = 333$ K using a rotary evaporator for at least 4 h at reduced pressure. The yield of reaction is 0.99 in mass fraction. The trace amount of water in ionic liquid was removed in high vacuum for at least 48 h. Water content found by Karl Fischer method in the [BMIm]Br was less than 0.02%. This synthesized ionic liquid was analyzed by ^{1}H NMR (Bruker Av-300) and FTIR (Perkin-Elmer, Spectrum RXI) to confirm the absence of any major impurities, and they were found to be in good agreement with those reported in the literature [19,20].

2.3. Synthesis of N,N′-salicylidenephenylediamine Schiff base (Salophen)

To a vigorously stirred ethanolic solution (90 ml) of salicylaldehyde (200 mmol), a solution of benzene-1,2-diamine (100 mmol) in 100 ml of ethanol was added dropwise. After the addition, the mixture was stirred and refluxed for 1 h. The mixture was then cooled and the orange precipitate of Salophen was collected by filtration and washed with ethanol and dried in air. Yield: 22.46 g (71%). Calcd. For $C_{20}H_{16}N_2O_2$: C, 75.94; H, 5.10; N, 8.85. Found: C, 75.67; H, 4.9; N, 8.95. IR (KBr, cm^{-1}): 1613 [υ (C=N)], 3442 [υ (O–H)]. 1H NMR (500 MHz) chemical shift (δ ppm), 12.95 (s, 2H, O–H), 8.49 (s, 2H, CH=N), 6.60–7.33 (m, 12H, H-aryl). Elemental analysis (C, H, and N) were performed using a Heraeuse Elemental analyzer CHN-O-Rapid (Elemental-Analyses system, GmbH). The X-ray data for Salophen Schiff base [21] shows the presence of the intermolecular H-bonding between N atom and OH group of Salophen. The intermolecular O–H…N type H-bonding geometry is due to O–H, 0.960 Å; H…N, 1.773 Å; O…N, 2.613 Å; O–H…N, 144.4°. The structure of Salophen is shown in figure 1.

2.4. Apparatus and procedure

The solutions containing ionic liquid, organic solvent, and Salophen Schiff base were prepared by weighing Schiff base in glass vials and adding the mixtures of ionic liquid + organic solvents that previously prepared by weight. The glass vials were closed tightly. The sample was taken from the vial with a syringe and immediately used for the measurements. The mass of chemicals was determined using a digital analytical balance (Sartrious AG TE214S) with an uncertainty $\pm 1 \cdot 10^{-4}$ g.

The densities of solutions were measured using a vibrating tube densimeter (Anton Paar, DMA 4500M, Austria). The apparatus was calibrated with doubly distilled, deionized, and degassed water and dry air at atmospheric pressure. Density is extremely sensitive to temperature, so it was kept constant within ($\pm 1.0 \cdot 10^{-3}$ K) using the built-in Peltier technique. The uncertainties of density measurements was better than ($\pm 3.0 \cdot 10^{-5}$ g cm^{-3}). Duplicate measurements were done to take the average.

The viscosities were measured using an Ubbelohde-type viscometer, which has a flow time of about 230 s for water at 298.15 K. The viscometer was calibrated with doubly distilled deionized water. Viscosity of solution, η is given by the following equation

$$\frac{\eta}{d} = Lt - \frac{K}{t}, \tag{1}$$

where d is the density, t is the flow time of the solution and L and K are the viscometer constants. A digital stopwatch with a resolution of 0.01 s has been used for the measurement of flow time. The temperature was controlled using a circulating bath thermostat (Julabo NP, Germany) with a stability of ±0.01 K. The estimated uncertainly of the experimental viscosity was ±0.002 mPa s.

Refraction indices of the studied solutions were determined using a digital refractometer (ATAGO-DRA1, Japan) with an uncertainty of $\pm 1 \cdot 10^{-4}$. The instrument was calibrated with doubly distilled water before each series of measurements. A procedure

TABLE 1
Chemicals.

Chemical name	Source	Initial mass fraction purity	Purification method	Final mass fraction purity	Analysis method
DMSO	Rankem	>0.99	Non		
DMA	Rankem	>0.99	Non		
Salophen[a]	Synthetic		Recrystallization	0.9975	Elemental analysis (C, H, and N)
N-methylimidazole		>0.99	Non		
1-Bromobutane		>0.99	Non		
[BMIm]Br[b]	Synthetic		High vacuums	0.99	^{1}HNMR and FTIR
Salicylaldehyde[c]	Fluka	0.99	Non		
Benzene-1,2-diamine	Merck	>0.995	Non		

[a] *N,N′*-salicylidenephenylediamine.
[b] 1-Butyl-3-methylimidazolium bromide.
[c] 2-Hidroxybenzaldehyde.