

Thermodynamic Properties of Salophen Schiff Base + Ionic Liquid ([C_nmIm][Br]) + Dimethylformamide Ternary Mixtures at 298.15 K

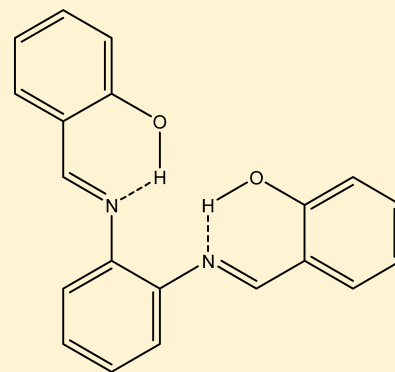
Hemayat Shekaari,^{*,†} Abolfazl Bezaatpour,[‡] and Rasoul Elhami-Kalvanagh[§]

[†]Department of Physical Chemistry, University of Tabriz, Tabriz, Iran

[‡]Department of Chemistry, Faculty of Science, University of Mohaghegh Ardabili, Ardabil, Iran

[§]Department of Chemistry, Mamaghan Branch, Islamic Azad University, Mamaghan, Iran

ABSTRACT: The densities and viscosities of ternary mixtures of *N,N'*-salicylidene-phenylenediamine Schiff base (Salophen) + ionic liquid + *N,N*-dimethylformamide (DMF) have been determined at 298.15 K and at atmospheric pressure. The ionic liquids were: 1-propyl-3-methylimidazolium bromide ([C₃mIm][Br]), 1-butyl-3-methylimidazolium bromide ([C₄mIm][Br]), 1-pentyl-3-methylimidazolium bromide ([C₅mIm][Br]), and 1-hexyl-3-methylimidazolium bromide ([C₆mIm][Br]). These data have been used to calculate the standard partial molar volumes, V_{ϕ}^0 , transfer partial molar volumes, $\Delta_{tr}V_{\phi}^0$, and viscosity *B*-coefficients for the investigated mixtures. An increase in concentration and alkyl chain length of ionic liquid results in a decreasing trend in the calculated volumetric and viscometric parameters. All of these parameters were used to interpret the effect of ionic liquids on the nonaqueous solutions of Salophen Schiff base and solute–solvent interactions occurring between the various components.



INTRODUCTION

Ionic liquids (ILs) are a new class of organic salts containing an asymmetric organic cation and noncoordinating inorganic anion. Owing to their unique chemical and physical properties, such as negligible vapor pressure ([C₄mIm][PF₆] is 10⁻¹⁰ Pa at 298 K),¹ good thermal stability, a wide liquid range, excellent solvent power for organic and inorganic and polymeric compounds, suitable viscosity, and nonflammability, easy recyclability, and reusability, they have been recognized as an alternative solvent for organic and inorganic synthesis.^{2–5}

Recently, ILs have been applied to transition metal catalysis containing Schiff base ligands with the benefit of a convenient catalyst separation, hence, an easy recovery/recycling procedure. The efficiency of such a catalyst/IL system is strongly dependent on the nature of the ILs. The presence of ILs modifies many important properties of transition metal catalysis containing a Schiff base and their derivatives related to their thermophysical properties, such as density and viscosity. The Schiff base ligand has imine groups that are produced by the condensation reactions of aldehydes, ketones, or β -ketones with primary amines and related derivatives which are used extensively, as important groups of ligands in coordination chemistry, medicine, agriculture, industry, and electronics.^{6–16} Some studies have been reported on the application of ILs in the processes containing the Schiff base ligand. A new cyanide optode was designed using a [*N,N'*-bis(salicylidene)-2,3-diaminopyridine] tributylphosphine cobalt(III) perchlorate monohydrate complex. The reduction in the absorbance value of the optode at the maximum wavelength of 380 nm was related to cyanide concentration in aqueous samples. The sensitivity of the method was improved by using an IL, 1-butyl-

3-methylimidazolium hexafluorophosphate, [C₄mIm][PF₆], introduced in constructing the optode membrane.¹⁷ A novel Schiff base extracting agent (PMBP-2-ABT) was synthesized and used for the extraction of heavy metal ions by PMBP-2-ABT/IL binary-water phase system. In IL binary-water phase system, PMBP-2-ABT was an excellent extracting agent for heavy metal ions.¹⁸

The generalized use of these new compounds needs an accurate knowledge of their thermodynamic properties both when pure and when they are mixed with compounds. The study of thermodynamic properties of Schiff base in the presence of IL mixtures is crucial from a technological point of view, but it also provides a better understanding of the mechanisms involved when using these new media. For example, their volumetric and viscometric properties of the mixtures have been used to provide information on solute–solvent interactions in mixtures. However, there are not any reports on the thermodynamic properties of Schiff base ligand in the presence of ILs according to our literature survey.

This work is a continuation of systematic studies on the thermodynamic properties of Schiff base ligands in the presence of ILs. In this work, we report the density, *d*, and viscosity, η , of *N,N'*-salicylidene-phenylenediamine (Salophen) Schiff base (Figure 1) + IL + *N,N*-dimethylformamide (DMF) ternary mixtures at several concentrations of ILs. The ILs were: 1-propyl-3-methylimidazolium bromide ([C₃mIm][Br]), 1-butyl-3-methylimidazolium bromide ([C₄mIm][Br]), 1-pentyl-3-

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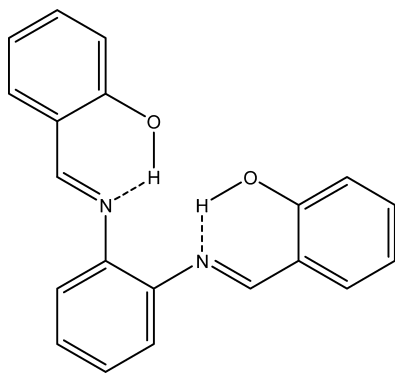


Figure 1. Structure of the N,N' -salicylidenephenylenediamine Schiff base (Salophen).

methylimidazolium bromide ($[C_5\text{mIm}][\text{Br}]$), and 1-hexyl-3-methylimidazolium bromide ($[C_6\text{mIm}][\text{Br}]$). Apparent molar volumes, V_{ϕ} , of Salophen were calculated at 298.15 K and used to calculate the standard partial molar volumes, V_{ϕ}^0 , and transfer partial molar volumes, $\Delta_{\text{tr}}V_{\phi}^0$. The viscosity B -coefficients were calculated by using the Jones–Dole equation. All of these parameters were used to investigate the effect of IL on the thermodynamic properties of Salophen Schiff base and interpret the solute–solute and solute–solvent interactions occurring between the various components in these types of ternary mixtures.

EXPERIMENTAL SECTION

Chemicals. Reagents used in this work were N -methylimidazole (>99 %, in mass fraction), 1-bromopropane (>99 %, in mass fraction), 1-bromobutane (>99 %, in mass fraction), 1-bromopentane (>99 %, in mass fraction), and 1-bromohexane (>99 %, in mass fraction) purchased from Merck, the salicylaldehyde (99 %, in mass fraction) obtained from Fluka, and N,N -dimethylformamide (99.5 %, in mass fraction) obtained from Rankem (India). These reagents were used without further purification.

Synthesis of ILs. ILs ($[C_n\text{mIm}][\text{Br}]$) were prepared and purified by using the procedure described in the literature.^{19,20} Briefly, $[C_n\text{mIm}][\text{Br}]$ was synthesized by direct alkylation of N -methylimidazole with an excess of 1-bromoalkane in a round-bottom flask at about 353 K for 48 h under a nitrogen atmosphere. The product was dried in high vacuum at 333.15 K using a rotary evaporator for at least 4 h in reduced pressure. The synthesized ILs have a purity greater than mass fraction 0.98, which was used after vacuum desiccated for at least 48 h to remove a trace amount of moisture. The water contents in the $[C_n\text{mIm}][\text{Br}]$ were found by the Karl Fischer method to be less than mass fraction 0.05 %. ILs were analyzed by ^1H NMR (Bruker Av-300) and FT-IR (Perkin Elmer, Spectrum RXI) spectra to confirm the absence of any major impurities and were found to be in agreement with those reported in the literature.²¹

Synthesis of Salophen Schiff Base. To a vigorously stirred ethanolic mixture (40 mL) of salicylaldehyde (20 mmol) was added dropwise a mixture of 1,2-diaminobenzene (10 mmol) in 40 mL of ethanol. After the addition was complete, the mixture was stirred and refluxed for 60 min. The mixture was then cooled, and the orange precipitate of the ligand was collected by filtration, then washed with ethanol and dried in a desiccator. Yield of Salophen: 2.69 g (85 %). Anal. Calcd for $\text{C}_{20}\text{H}_{16}\text{Br}_2\text{N}_2\text{O}_2$: C, 75.93; H, 5.10; N, 8.85. Found: C, 75.74;

H, 4.9; N, 8.98. IR (KBr, cm^{-1}): 1613 [ν (C=N)], 3442 [ν (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 analyses (C, H, and N) were performed using a Heraeus elemental analyzer CHN-O-Rapid (Elemental-Analyses system, GmbH).

Apparatus and Procedure. The ternary mixtures containing IL, Salophen Schiff base, and DMF were prepared by weight and filling glass vials and closing them tightly. The sample was taken from the vial with a syringe and immediately injected into the apparatus. The mass of chemicals was determined using an analytical balance (Sartorius AG TE214S) with an uncertainty of $\pm 1 \cdot 10^{-7}$ kg.

The densities of mixtures were measured using a vibrating tube densimeter (DMA 4500M, Anton Paar, 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 $\pm 1 \cdot 10^{-3}$ K using the built-in Peltier technique. The reproducibility of density measurements was better than $\pm 5 \cdot 10^{-5}$ $\text{g} \cdot \text{cm}^{-3}$. Triplicate measurements were done to obtain the average values of density.

The viscosities were measured using an Übbelohde-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. The viscosity of mixture, η , is given by the following equation

$$\frac{\eta}{d} = Lt - \frac{K}{t} \quad (1)$$

where d is the density, t is the flow time of the mixture, and L and K are the viscometer constants. A digital stopwatch with a precision of 0.01 s has been used for the flow time measurement. The temperature was controlled using a circulating bath thermostat (Julabo NP, Germany) with a temperature stability of ± 0.01 K. The measured physical properties of DMF and their values reported in literature are given in Table 1.

Table 1. Density, d , Viscosity, η , and Refractive Index, n_D , of Pure Dimethylformamide (DMF) at $T = 298.15$ K

d $\text{g} \cdot \text{cm}^{-3}$	η $\text{mPa} \cdot \text{s}$	n_D
0.94400 (exp.)	0.805 (exp.)	1.4281 (exp.)
0.94446 ³¹	0.8605 ³³	1.4267 ²⁹
0.94380 ²⁹	0.803 ³²	1.4275 ³⁰
0.9445 ³⁰		1.4282 ³⁴

RESULTS AND DISCUSSION

Volumetric Properties. The experimental densities, d , of ternary Salophen + $[C_n\text{mIm}][\text{Br}]$ + DMF mixtures as a function of Salophen molality, m , at different molalities of ILs (m_{IL}) are reported in Table 2 at 298.15 K. The concentration range studied for both ILs and Salophen was in the dilute region, (0 to 0.2) $\text{mol} \cdot \text{kg}^{-1}$. For each concentration of IL, the densities of the mixtures increase with increasing Salophen concentration. The apparent molar volumes, V_{ϕ} , of Salophen in the DMF and reference solvent (DMF + $[C_n\text{mIm}][\text{Br}]$) were calculated from the densities of the mixtures using the following equation:²²

Table 2. Densities, d , and Apparent Molar Volumes, V_ϕ , of Salophen in the DMF + IL Mixture at 298.15 K

m^a	d	V_ϕ	m	d	V_ϕ	m	d	V_ϕ	m	d	V_ϕ
mol·kg ⁻¹	g·cm ⁻³	cm ³ ·mol ⁻¹	mol·kg ⁻¹	g·cm ⁻³	cm ³ ·mol ⁻¹	mol·kg ⁻¹	g·cm ⁻³	cm ³ ·mol ⁻¹	mol·kg ⁻¹	g·cm ⁻³	cm ³ ·mol ⁻¹
Salophen + [C ₃ mIm][Br] + DMF											
$m_{IL} = 0.0000$			$m_{IL} = 0.0300$			$m_{IL} = 0.0789$			$m_{IL} = 0.1220$		
0.0000	0.94400		0.0000	0.94619		0.0000	0.94963		0.0000	0.95252	
0.0295	0.94601	258.06	0.0506	0.94965	257.05	0.0507	0.95308	256.85	0.0491	0.95585	256.56
0.0510	0.94747	257.82	0.0697	0.95094	256.95	0.0697	0.95436	256.64	0.0691	0.95719	256.45
0.0697	0.94875	257.44	0.0894	0.95228	256.68	0.0901	0.95573	256.50	0.0897	0.95856	256.32
0.0894	0.95008	257.23	0.1103	0.95368	256.50	0.1087	0.95696	256.43	0.1089	0.95983	256.20
0.1106	0.95151	256.90	0.1299	0.95499	256.36	0.1293	0.95832	256.29	0.1296	0.96119	256.08
0.1299	0.95282	256.59	0.1499	0.95631	256.26	0.1515	0.95978	256.13	0.1501	0.96252	256.03
0.1465	0.95394	256.31	0.1693	0.95758	256.14	0.1700	0.96098	256.07	0.1685	0.96372	255.91
0.1701	0.95551	256.13	0.1856	0.95864	256.10	0.1921	0.96241	255.98	0.1895	0.96506	255.86
0.1898	0.95683	255.85	0.2095	0.96019	255.95	0.2132	0.96377	255.84	0.2110	0.96642	255.82
Salophen + [C ₄ mIm][Br] + DMF											
$m_{IL} = 0.1012$			$m_{IL} = 0.1527$			$m_{IL} = 0.1970$					
0.0000	0.95101		0.0000	0.95440		0.0000	0.95720				
0.0099	0.95169	256.73	0.0097	0.95506	256.35	0.0111	0.95796	255.72			
0.0296	0.95303	256.70	0.0292	0.95639	256.28	0.0293	0.95920	255.55			
0.0502	0.95443	256.39	0.0495	0.95776	256.17	0.0497	0.96057	255.61			
0.0698	0.95576	256.17	0.0689	0.95906	255.97	0.0705	0.96196	255.58			
0.0908	0.95717	255.99	0.0865	0.96023	255.97	0.0935	0.96349	255.42			
0.1106	0.95849	255.92	0.1092	0.96174	255.75	0.1090	0.96451	255.39			
0.1300	0.95978	255.75	0.1298	0.96309	255.71	0.1285	0.96578	255.36			
0.1509	0.96117	255.52	0.1504	0.96443	255.62	0.1533	0.96738	255.36			
0.1697	0.96240	255.41	0.1702	0.96572	255.48	0.1714	0.96855	255.23			
Salophen + [C ₅ mIm][Br] + DMF											
$m_{IL} = 0.0260$			$m_{IL} = 0.0508$			$m_{IL} = 0.0747$					
0.0000	0.94747		0.0000	0.94926		0.0000	0.95079				
0.0292	0.94947	255.69	0.0282	0.95119	256.78	0.0287	0.95277	256.33			
0.0496	0.95086	255.55	0.0498	0.95267	256.40	0.0496	0.95419	256.07			
0.0698	0.95224	255.55	0.0693	0.95399	256.28	0.0702	0.95559	255.90			
0.0916	0.95372	255.39	0.0895	0.95536	256.06	0.0905	0.95695	255.79			
0.1090	0.95488	255.15	0.1094	0.95669	255.91	0.1093	0.95821	255.66			
0.1301	0.95631	255.42	0.1279	0.95793	255.75	0.1295	0.95955	255.62			
0.1499	0.95764	255.19	0.1486	0.95932	255.49	0.1516	0.96101	255.43			
0.1712	0.95906	255.13	0.1682	0.96061	255.38	0.1696	0.96220	255.30			
0.1912	0.96039	254.46	0.1917	0.96216	255.18	0.1915	0.96363	255.17			
Salophen + [C ₆ mIm][Br] + DMF											
$m_{IL} = 0.0245$			$m_{IL} = 0.0738$			$m_{IL} = 0.1205$					
0.0000	0.94576		0.0000	0.94890		0.0000	0.95172				
0.0490	0.94911	256.06	0.0523	0.95251	255.78	0.0492	0.95512	255.43			
0.0690	0.95047	256.11	0.0709	0.95378	255.69	0.0685	0.95643	255.23			
0.0924	0.95206	256.02	0.0907	0.95512	255.56	0.0903	0.95790	255.23			
0.1122	0.95340	255.83	0.1110	0.95649	255.48	0.1110	0.95929	255.11			
0.1292	0.95454	255.75	0.1285	0.95765	255.48	0.1279	0.96041	255.13			
0.1466	0.95570	255.66	0.1498	0.95907	255.32	0.1523	0.96202	255.03			
0.1716	0.95735	255.56	0.1656	0.96011	255.26	0.1714	0.96325	255.08			
0.1906	0.95863	255.29	0.1901	0.96171	255.15	0.1900	0.96446	255.01			
0.2100	0.95988	255.30	0.2122	0.96313	255.13	0.2181	0.96625	255.00			

^a m_{IL} is the molality of IL where solvent is DMF, and m is the molality of Salophen where solvent is (DMF + IL).

$$V_\phi = \frac{M}{d} - \frac{1000(d - d_0)}{mdd_0} \quad (2)$$

where M is the molar mass of the Salophen Schiff base, m is the molality of the Salophen in ternary mixtures of Salophen + [C_{*n*}mIm][Br] + DMF, d and d_0 are the densities of (Salophen + [C_{*n*}mIm][Br] + DMF) mixtures and reference solvent (desired molality of [C_{*n*}mIm][Br] in DMF), respectively. The maximum

uncertainty of calculated apparent molar volumes was less than $\pm 0.06 \text{ cm}^3 \cdot \text{mol}^{-1}$.

The variation of apparent molar volumes with respect to concentration is expressed by the following equation:²³

$$V_\phi = V_\phi^0 + S_v \cdot m \quad (3)$$

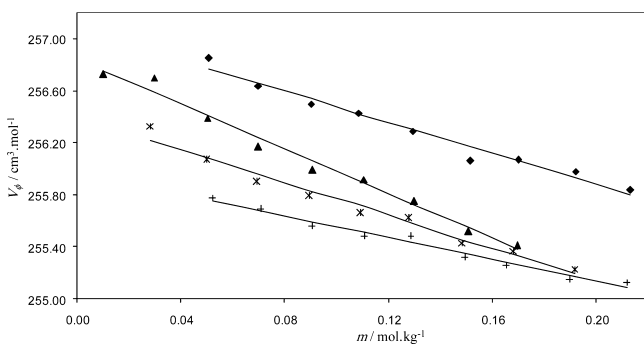
where V_ϕ^0 is the value of the limiting apparent molar volumes that equals the standard partial molar volume of the solute, and

Table 3. Standard Partial Molar Volumes, V_{ϕ}^0 , Transfer Partial Molar Volumes, $\Delta_{tr}V_{\phi}^0$, Experimental Slopes, S_v , and Standard Deviations of Apparent Volumes, $\sigma(V_{\phi})$, of Salophen in DMF + $[C_n\text{mIm}][\text{Br}]$ Mixtures

system	m_{IL}	V_{ϕ}^0	S_v	$\Delta_{tr}V_{\phi}^0$	$\sigma(V_{\phi})$
	mol·kg ⁻¹	cm ³ ·mol ⁻¹	cm ³ ·mol ⁻² ·kg	cm ³ ·mol ⁻¹	
Salophen + DMF	0.0000	258.47 ± 0.05	-14.07 ± 0.40		0.06
Salophen + DMF + $[C_3\text{mIm}][\text{Br}]$	0.0300	257.34 ± 0.06	-6.95 ± 0.46	-1.11	0.07
Salophen + DMF + $[C_3\text{mIm}][\text{Br}]$	0.0789	257.07 ± 0.04	-5.91 ± 0.27	-1.40	0.04
Salophen + DMF + $[C_3\text{mIm}][\text{Br}]$	0.1220	256.75 ± 0.04	-4.75 ± 0.28	-1.72	0.04
Salophen + DMF + $[C_4\text{mIm}][\text{Br}]$	0.1012	256.84 ± 0.04	-8.57 ± 0.41	-1.61	0.06
Salophen + DMF + $[C_4\text{mIm}][\text{Br}]$	0.1527	256.41 ± 0.03	-5.47 ± 0.27	-2.06	0.04
Salophen + DMF + $[C_4\text{mIm}][\text{Br}]$	0.1970	255.71 ± 0.03	-2.66 ± 0.33	-2.76	0.05
Salophen + DMF + $[C_5\text{mIm}][\text{Br}]$	0.0260	257.47 ± 0.06	-12.26 ± 0.48	-1.00	0.07
Salophen + DMF + $[C_5\text{mIm}][\text{Br}]$	0.0508	256.94 ± 0.04	-9.43 ± 0.36	-1.51	0.06
Salophen + DMF + $[C_5\text{mIm}][\text{Br}]$	0.0747	256.43 ± 0.04	-6.66 ± 0.33	-2.04	0.05
Salophen + DMF + $[C_6\text{mIm}][\text{Br}]$	0.0205	256.44 ± 0.07	-5.48 ± 0.48	-2.03	0.07
Salophen + DMF + $[C_6\text{mIm}][\text{Br}]$	0.0738	255.97 ± 0.03	-4.18 ± 0.22	-2.50	0.03
Salophen + DMF + $[C_6\text{mIm}][\text{Br}]$	0.1205	255.43 ± 0.06	-2.19 ± 0.39	-3.03	0.06

S_v is the experimental slope. The sign of S_v shows the nature of the solute–solute interactions, while V_{ϕ}^0 values reflect the presence of solute–solvent interactions.^{24,25} The plots of apparent molar volumes versus m were linear, and using the least-squares treatment, the values of V_{ϕ}^0 and S_v can be obtained from the intercept and slope, respectively. The values of V_{ϕ}^0 and S_v along with their standard deviations are given in Table 3. The values of V_{ϕ}^0 shown in this table decrease with an increase in concentration of IL which indicate that the solvent molecules (DMF) are loosely attached to Salophen Schiff base, thus resulting in lower values of V_{ϕ}^0 at higher concentrations of ILs.

The S_v values as shown in Table 3 are negative and increase with an increase of IL concentration, suggesting weak solute–solute interactions, but these interactions increase with the increase in IL concentration. As can be seen, the V_{ϕ}^0 values of Salophen Schiff base are also greater than their values for Salen Schiff base reported in our previous paper due to the higher intrinsic volume of Salophen.²⁶

**Figure 2.** Comparison of apparent molar volumes of Salophen in (Salophen + DMF + $[C_n\text{mIm}][\text{Br}]$ (0.1 mol·kg⁻¹)) mixtures. ♦, $[C_3\text{mIm}][\text{Br}]$; ▲, $[C_4\text{mIm}][\text{Br}]$; ×, $[C_5\text{mIm}][\text{Br}]$; +, $[C_6\text{mIm}][\text{Br}]$ at 298.15 K.

The values of V_{ϕ} for Salophen Schiff base in ($[C_n\text{mIm}][\text{Br}]$ 0.1 mol·kg⁻¹ + DMF) mixtures have been compared together (Figure 2). The values of V_{ϕ}^0 for Salophen in the investigated mixtures have the order: $[C_3\text{mIm}][\text{Br}] > [C_4\text{mIm}][\text{Br}] > [C_5\text{mIm}][\text{Br}] > [C_6\text{mIm}][\text{Br}]$. These values are decreasing with alkyl chain length of $[C_n\text{mIm}][\text{Br}]$. It is concluded that there are weak solute–solvent interactions between DMF and

Salophen with an increasing alkyl chain length of IL and preferential solvation of Salophen with $[C_n\text{mIm}][\text{Br}]$.

The same result can also be obtained from the partial molar volume of transfer for the Salophen from DMF to DMF + IL solutions. Limiting thermodynamic properties of transfer yield qualitative and quantitative information regarding the interactions of a cosolute and a solute without having to take into account the effects of solute–solute interactions as at infinite dilution the interactions between solute molecules are negligible. The partial molar volumes of transfer, $\Delta_{tr}V_{\phi}^0$, for the Salophen from DMF to $[C_n\text{mIm}][\text{Br}]$ + DMF mixtures were calculated as follows:²³

$$\Delta_{tr}V_{\phi}^0 = V_{\phi}^0(\text{in } [C_n\text{mIm}][\text{Br}] + \text{DMF}) - V_{\phi}^0(\text{in DMF}) \quad (4)$$

The $\Delta_{tr}V_{\phi}^0$ values have negative values in this mixture and decrease with increasing concentration and alkyl chain length of $[C_n\text{mIm}][\text{Br}]$. According to the cosphere overlap model of ternary mixtures, four types of interactions may occur between the Salophen and the $[C_n\text{mIm}][\text{Br}]$ molecules in DMF: (a) the polar–ionic group interactions between the ionic centers of $[C_n\text{mIm}][\text{Br}]$ and OH groups of Salophen Schiff base, (b) polar–polar group interactions between the OH groups of Salophen Schiff base and the amine group of $[C_n\text{mIm}][\text{Br}]$ through the hydrogen bonding, (c) polar–nonpolar group interactions between the OH groups of Salophen Schiff base and alkyl group attached to the imidazolium ring of $[C_n\text{mIm}][\text{Br}]$ and amine groups of $[C_n\text{mIm}][\text{Br}]$ and nonpolar groups of Salophen, and (d) nonpolar–nonpolar group interactions between the aromatic and CH groups of Salophen and alkyl group attached to the imidazolium ring of $[C_n\text{mIm}][\text{Br}]$.²⁷ Taking the cosphere overlap model as the guideline, polar–nonpolar group interactions and nonpolar–nonpolar group interactions would lead to a negative $\Delta_{tr}V_{\phi}^0$, since the introduction of the alkyl group provides an additional tendency of polar–nonpolar and nonpolar–nonpolar groups to interact and as a result there will be a reduction in the structure of solvent formed as a result of their cospheres overlapping. In this case the c and d types of interactions are dominant between ILs and Salophen Schiff base.

Viscometric Results. The measured viscosities, η , for (Salophen Schiff base + $[C_n\text{mIm}][\text{Br}]$ + DMF) ternary

Table 4. Viscosities, η , of Salophen Schiff Base in DMF + $[C_n\text{mIm}][\text{Br}]$ Mixtures at 298.15 K

m^*	η	m	η	m	η	m	η
mol·kg ⁻¹	mPa·s	mol·kg ⁻¹	mPa·s	mol·kg ⁻¹	mPa·s	mol·kg ⁻¹	mPa·s
Salophen + $[C_3\text{mIm}][\text{Br}]$ + DMF							
$*m_{\text{IL}} = 0.0000$		$m_{\text{IL}} = 0.0300$		$m_{\text{IL}} = 0.0789$		$m_{\text{IL}} = 0.1220$	
0.0100	0.802	0.0506	0.829	0.0507	0.854	0.0491	0.877
0.0302	0.818	0.0697	0.841	0.0697	0.871	0.0691	0.892
0.0505	0.833	0.0894	0.852	0.0901	0.883	0.0897	0.908
0.0698	0.847	0.1103	0.866	0.1087	0.900	0.1089	0.922
0.0851	0.859	0.1299	0.882	0.1293	0.912	0.1296	0.939
0.1098	0.878	0.1499	0.897	0.1515	0.929	0.1501	0.951
0.1268	0.890	0.1693	0.912	0.1700	0.943	0.1685	0.964
0.1507	0.905	0.1856	0.923	0.1921	0.958	0.1895	0.977
0.1705	0.919	0.2095	0.940	0.2132	0.970	0.2110	0.993
Salophen + $[C_4\text{mIm}][\text{Br}]$ + DMF							
$m_{\text{IL}} = 0.1012$		$m_{\text{IL}} = 0.1520$		$m_{\text{IL}} = 0.1970$			
0.0100	0.872	0.0097	0.886	0.0111	0.918		
0.0296	0.887	0.0292	0.897	0.0293	0.927		
0.0502	0.903	0.0495	0.911	0.0497	0.939		
0.0698	0.919	0.0689	0.927	0.0705	0.950		
0.0908	0.932	0.0865	0.940	0.0935	0.968		
0.1106	0.947	0.1092	0.954	0.1090	0.978		
0.1300	0.958	0.1298	0.967	0.1285	0.990		
0.1509	0.970	0.1504	0.981	0.1533	1.001		
0.1697	0.983	0.1702	0.993	0.1714	1.010		
Salophen + $[C_5\text{mIm}][\text{Br}]$ + DMF							
$m_{\text{IL}} = 0.0260$		$m_{\text{IL}} = 0.0508$		$m_{\text{IL}} = 0.0747$			
0.0489	0.827	0.0282	0.836	0.0287	0.852		
0.0672	0.843	0.0498	0.855	0.0496	0.864		
0.1009	0.860	0.0693	0.871	0.0702	0.876		
0.1081	0.876	0.0895	0.885	0.0905	0.888		
0.1265	0.890	0.1094	0.898	0.1093	0.901		
0.1473	0.903	0.1279	0.910	0.1295	0.917		
0.1675	0.917	0.1486	0.924	0.1516	0.934		
0.1923	0.931	0.1682	0.938	0.1696	0.947		
0.2085	0.944	0.1917	0.953	0.1915	0.962		
Salophen + $[C_6\text{mIm}][\text{Br}]$ + DMF							
$m_{\text{IL}} = 0.0205$		$m_{\text{IL}} = 0.0738$		$m_{\text{IL}} = 0.1205$			
0.0490	0.852	0.0523	0.880	0.0492	0.939		
0.0690	0.864	0.0709	0.889	0.0685	0.950		
0.0924	0.876	0.0907	0.902	0.0903	0.964		
0.1122	0.888	0.1110	0.914	0.1110	0.977		
0.1292	0.901	0.1285	0.924	0.1279	0.989		
0.1466	0.917	0.1498	0.941	0.1523	1.001		
0.1716	0.934	0.1656	0.953	0.1714	1.018		
0.1906	0.947	0.1901	0.966	0.1900	1.031		
0.2100	0.962	0.2122	0.983	0.2181	1.042		

* m_{IL} is the molality of IL where solvent is DMF + and m is the molality of Salophen where solvent is (DMF + IL).

mixtures as a function of Salophen molality, m , at different concentrations of ILs at 298.15 K are tabulated in Table 4. The estimated uncertainty of the experimental viscosity data was ± 0.003 mPa·s. The results show an increase in the viscosity of mixtures studied with an increase in concentration of ILs, $[C_n\text{mIm}][\text{Br}]$. This is due to the fact that, with the increasing of IL concentration, the number of collision between the molecules also increases to result in a loss of kinetic energy; therefore, the molecules tend to stack together to induce the increase in the viscosity. Most studies on viscosity are confined to the description of dilute mixtures of solutes via determination of the B -coefficients in the Jones–Dole equation:²⁸

$$\frac{\eta}{\eta_0} = 1 + Ac^{1/2} + Bc \quad (5)$$

where η and η_0 are the viscosities of (Salophen Schiff base + $[C_n\text{mIm}][\text{Br}]$ + DMF) ternary mixtures and reference solvent ($[C_n\text{mIm}][\text{Br}]$ + DMF), respectively, and c is the molar concentration (calculated from molality) of Salophen Schiff base in the (Salophen Schiff base + $[C_n\text{mIm}][\text{Br}]$ + DMF) ternary mixtures. The A -coefficient is a measure of solute–solute interactions which are very small and then ignored in this equation. The viscosity B -coefficient is an empirical constant which depends on solute–solvent interactions and structural factors. The calculated B values along with their standard

deviations are given in Table 5 by fitting the experimental viscosity data to the Jones–Dole equation. The viscosity B -

Table 5. The Values of Viscosity B -Coefficients, Solvation Numbers (B/V_{ϕ}^0), and Related Standard Deviations $\sigma(\eta)$ for Salophen + DMF + $[C_n\text{mIm}][\text{Br}]$ Ternary Mixtures at 298.15 K

m_{IL} mol·kg ⁻¹	B dm ³ ·mol ⁻¹	$\sigma(\eta) \cdot 10^3$	B/V_{ϕ}^0
	DMF + Salophen		
0.0000	0.844 ± 0.99·10 ⁻³	1.49	3.27
	Salophen + $[\text{C}_3\text{mIm}][\text{Br}]$ + DMF		
0.0300	0.936 ± 3.92·10 ⁻³	2.10	3.64
0.0789	0.899 ± 4.25·10 ⁻³	2.27	3.50
0.1220	0.869 ± 3.42·10 ⁻³	1.83	3.38
	Salophen + $[\text{C}_4\text{mIm}][\text{Br}]$ + DMF		
0.1012	0.825 ± 5.41·10 ⁻³	2.90	3.21
0.1527	0.796 ± 3.46·10 ⁻³	1.85	3.10
0.1970	0.671 ± 4.51·10 ⁻³	2.41	2.62
	Salophen + $[\text{C}_5\text{mIm}][\text{Br}]$ + DMF		
0.0260	0.929 ± 4.83·10 ⁻³	2.58	3.61
0.0508	0.892 ± 5.08·10 ⁻³	2.71	3.47
0.0747	0.862 ± 4.80·10 ⁻³	2.57	3.36
	Salophen + $[\text{C}_6\text{mIm}][\text{Br}]$ + DMF		
0.0205	0.895 ± 6.45·10 ⁻³	3.45	3.49
0.0738	0.758 ± 3.52·10 ⁻³	1.88	2.96
0.1205	0.736 ± 2.02·10 ⁻³	1.08	2.88

coefficients decrease with increasing concentration, which suggest the net structural decrease. Further, the viscosity B -coefficients of Salophen in nonaqueous ILs solutions increase in the order of $[\text{C}_3\text{mIm}][\text{Br}] > [\text{C}_4\text{mIm}][\text{Br}] > [\text{C}_5\text{mIm}][\text{Br}] > [\text{C}_6\text{mIm}][\text{Br}]$. It is well-known that the size, shape, and charge of solute molecules are important in determining the viscosity B -coefficients. In the case of studied ILs, the charge of ILs are the same, hence the observed order of viscosity B -coefficients may be rationalized in terms of the alkyl chain length of ILs. Hence the higher values of the viscosity B -coefficient for the $[\text{C}_3\text{mIm}][\text{Br}]$ as compared to other studied ILs agree well with the above result. This means that, with increasing the size of alkyl chain length of ILs, the solute–solvent interactions decrease, and then interactions between Salophen and ILs increase. This trend has been shown for Salophen Schiff base + $[\text{C}_n\text{mIm}][\text{Br}]$ + DMF mixtures in 0.1 mol·kg⁻¹ of different ILs as shown in Figure 3.

A high solvation number, B/V_{ϕ}^0 value is an indication of the formation of a primary solvation shell.²³ The B/V_{ϕ}^0 ratio lies between 0 and 2.5 for unsolvated spherical species. The calculated solvation numbers, B/V_{ϕ}^0 , of Salophen Schiff base in DMF + ILs mixtures are given in Table 5. A survey of this table reveals that solvation numbers for Salophen in this mixtures decrease with the increase in concentration and alkyl chain length of ILs. It can be noted that B/V_{ϕ}^0 values are greater than 2.5 and decrease as the concentration of IL increases. It shows that the Salophen is solvated in nonaqueous IL solutions and solvation decreases at a high concentration of ILs. This trend further supports our earlier conclusions regarding the behavior of these systems from values of V_{ϕ}^0 and B .

CONCLUSIONS

The calculated standard partial molar volumes, V_{ϕ}^0 , the partial molar volumes of transfer, viscosity B -coefficients, and the

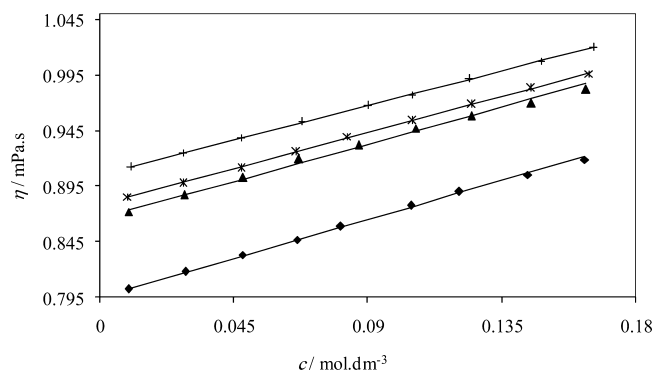


Figure 3. Viscosities of (Salophen + DMF + $[\text{C}_n\text{mIm}][\text{Br}]$ (0.1 mol·kg⁻¹)) mixtures. ♦, $[\text{C}_3\text{mIm}][\text{Br}]$; ▲, $[\text{C}_4\text{mIm}][\text{Br}]$; ×, $[\text{C}_5\text{mIm}][\text{Br}]$; +, $[\text{C}_6\text{mIm}][\text{Br}]$ at 298.15 K.

solvation number, B/V_{ϕ}^0 , for Salophen Schiff base in the presence of ILs {1-propyl-3-methylimidazolium bromide ($[\text{C}_3\text{mIm}][\text{Br}]$), 1-butyl-3-methylimidazolium bromide ($[\text{C}_4\text{mIm}][\text{Br}]$), 1-pentyl-3-methylimidazolium bromide ($[\text{C}_5\text{mIm}][\text{Br}]$), and 1-hexyl-3-methylimidazolium bromide ($[\text{C}_6\text{mIm}][\text{Br}]$)} in DMF mixtures decrease with the increasing concentration and alkyl chain length of IL. This trend suggests the dominance of nonpolar–nonpolar interactions between Salophen and ILs. Also, the calculated solvation numbers, B/V_{ϕ}^0 , for Salophen shows that its solute–solvent interactions between Salophen and DMF decrease at high concentrations of ILs and the preferential solvation of Salophen with $[\text{C}_n\text{mIm}][\text{Br}]$.

AUTHOR INFORMATION

Corresponding Author

*Tel.: 984113393139. Fax: 984113340191. E-mail address: hemayatt@yahoo.com (H. Shekaari).

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