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Study to Explore Inclusion Complexes of Ionic Liquid with Cyclic Ethers in Liquid Systems

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ARTICLE DETAILS

Article history:

Received 17 January 2017

Accepted 30 January 2017

Available online 21 March 2017

Keywords:

Green Ionic Liquid

Crown Host

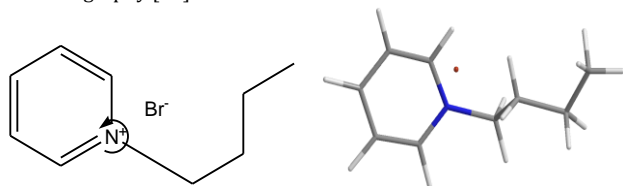
Ionic Interaction

ABSTRACT

1:1 hosts-guest inclusion complexation behavior of 1-butyl-pyridinium bromide (IL) as a guest with 18-crown-6 and dibenzo-18-crown-6 as hosts in acetonitrile media has been demonstrated here and are exceedingly suitable for diverse application in modern sciences. Conductivity and surface tension measurements show that 1:1 stoichiometric complexes are formed between IL and crown. The nature of the complexes has been established using thermodynamic parameters obtained from physicochemical studies. Enthalpy (ΔH°), entropy (ΔS°) and free energy change (ΔG°) of the complexation reaction has been evaluated from the temperature dependent formation constant data.

1. Introduction

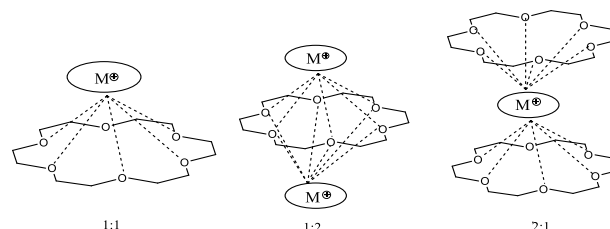
Crown ethers show a remarkable range of selectivity for binding with various cations, depending on the cavity size of the crown ethers, type of the guest donor atoms, and the polarity of the solvent molecules [1-3]. The numerous studies of 18-crown-6 (18C6) and its derivatives dibenzo-18-crown-6 (DBz-18C6) which have the highest affinity for ammonium cations, invariably showed a 1:1 stoichiometry with both NH_4^+ and RNH_3^+ guest cations in solution [4]. Due to these special properties of crowns along with Lewis basic character of oxygen atoms, they can build up stable complexes (Scheme 1) with suitable positive centre (e.g. N^+ centre containing IL) of guest molecules (Scheme 2). Because of these characteristics, there is a wide range of applications of crown complexes. They have been proposed as separation agents for removing metal ions (i.e., Cs^+ and Sr^{2+}) from mixed nuclear and chemical waste [5-7]. There is also growing interest in the use of crown ethers for radioimmuno therapy treatment of carcinomas [8] and for the development of sensors [2] ion transport of membrane interfaces [9], as solvent extraction agents [10], in the construction of ion-selective electrodes [11, 12], and in liquid chromatography [13].



Scheme 1 Molecular structures of 18-crown-6 and dibenzo-18-crown-6

Ionic liquids having non-volatility with a melting temperature below 100 °C, also known as liquid organic, molten or fused salts, they have attracted demanding scientific importance and even become a “star” material in material research. Due to their excellent capability to dissolve an huge range of organic and inorganic materials [14], high chemical and thermal stability [15], ILs have emerged as an attractive “green” alternative to traditional organic solvents in various fields of chemistry viz. synthesis [16], catalysis [15, 17], lubrication [18], and separation processes [19], etc. Most importantly, some unique and favorable properties including wide electrochemical window, high ionic conductivity and inflammability [20], ILs are playing an irreplaceable material in utilizing as highly efficient and stable electrolytes for

electrochemical and renewable energy applications [21], such as lithium batteries [22], fuel cells [23] and dye-sensitized solar cells [24].



Scheme 2 Molecular structure of 1-butyl pyridinium bromide

In vision of the above, we have tried to ascertain the nature of complex formation of 1-butyl pyridinium bromide (IL) with 18-crown-6 and dibenzo-18-crown-6 in acetonitrile media. Literature survey reveals that no work has been carried out in the present ternary systems.

2. Experimental Methods

2.1 Materials

The 1-butyl pyridinium bromide (IL), 18-crown-6 (18C6) and dibenzo-18-crown-6 (DBz-18C6) of puriss grade were bought from Sigma-Aldrich, Germany and used as purchased. The mass fraction purity of IL, 18C6 and DBz-18C6 were 0.99, 0.99 and 0.98 respectively.

2.2 Apparatus and Procedure

Solubility of the chosen IL and crown ethers in acetonitrile solution have been checked and observed that the IL molecule freely soluble in 0.0012 (m)-0.0052 (m) concentration of 18C6+acetonitrile and DBz-18C6+acetonitrile binary mixtures. All the stock solutions of the investigated molecule were prepared by mass (weighed by Mettler Toledo AG-285 with uncertainty 0.0003 g), and then the working solutions were obtained by mass dilution at 298.15 K.

The conductance measurements were carried out in a Systronics-308 conductivity bridge of accuracy $\pm 1\%$, using a dip-type immersion conductivity cell, CD-10 having a cell constant of approximately $(0.1 \pm 0.001) \text{ cm}^{-1}$ [25]. Conductivity experiment was performed in an alternating current having 1 kHz working frequency. Measurements were completed in a water bath maintained temperatures at $293.15 \pm 0.01 \text{ K}$, $298.15 \pm 0.01 \text{ K}$ and $303.15 \pm 0.01 \text{ K}$.

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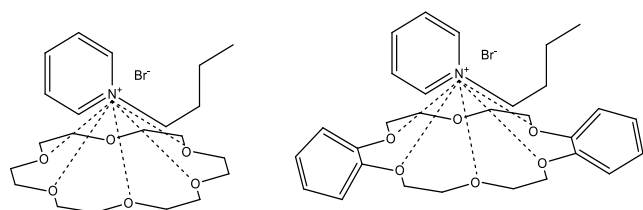
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The surface tension experiments were done by platinum ring detachment method using a Tensiometer (K9, KRÜSS; Germany) at the experimental temperature. The accuracy of the measurement was within $\pm 0.1 \text{ mNm}^{-1}$. Temperature of the system has been maintained by circulating auto-thermostated water through a double-wall glass vessel containing the solution at $298.15 \pm 0.1 \text{ K}$.

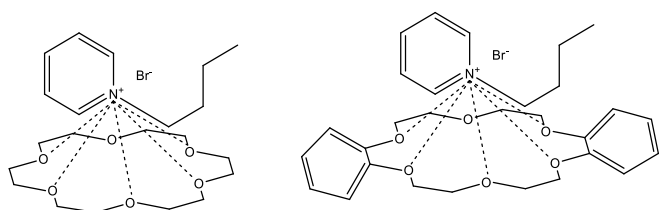
The densities (ρ) of the solvents and solution were measured by means of vibrating *U*-tube Anton Paar digital density meter (DMA 4500M) with a precision of $\pm 0.01 \text{ gcm}^{-3}$ maintained at $\pm 0.01 \text{ K}$ of the desired temperature. It was calibrated by passing triply distilled, degassed water and dry air.

The viscosities (η) of experimental mixture were measured using a Brookfield DV-III Ultra Programmable Rheometer with spindle size-42 fitted to a Brookfield digital bath TC-500.

Refractive indexes of the solution were measured with the help of a Digital Refractometer Mettler Toledo. The light source was LED, $\lambda = 589.3 \text{ nm}$. The refractometer was calibrated twice using distilled water and calibration was checked after every few measurements. The uncertainty of refractive index measurement was ± 0.0002 units.



Scheme 3 Plausible stoichiometric complexation of macrocyclic crowns with suitable positive centre



Scheme 4 Plausible mechanism of 1:1 stoichiometric complex of a guest IL with 18C6 and DBz-18C6 molecules

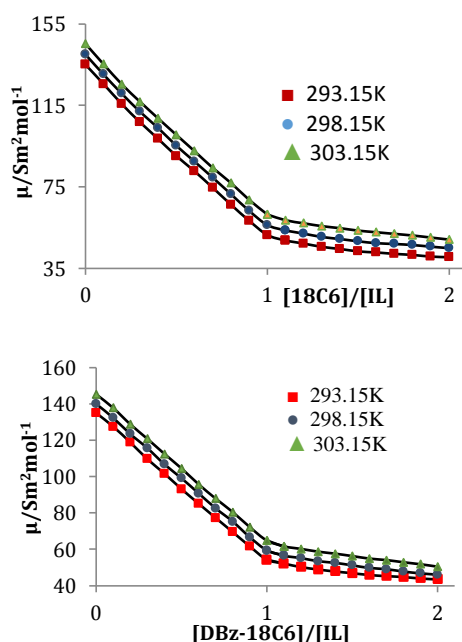


Fig. 1 Plots of molar conductivity Vs mole ratio of IL-crown complex at 293.15 K, 298.15 K and 303.15 K respectively

3. Results and Discussion

3.1 Conductance

The molar conductivity (Λ) of the studied ionic liquid (IL) in acetonitrile medium is reported in our earlier investigation [26–28]. The molar conductivity of IL in acetonitrile solution was monitored as a function of

crown ethers at different temperatures. The ensuing molar conductance vs. mole ratio (crown/IL) plots at 293.15, 298.15, and 303.15 K are shown in Fig. 1. In this method stoichiometry of the complexes can be easily achieved from the breaks of the conductivity curves [29, 30]. The notable decreasing molar conductivity with increasing crown concentrations indicates the complex formation between crown and the N^+ centre of the IL one by one through ionic interaction and hence movement of the IL is restricted and the free ions per unit volume is decreased; as a result the conductivity decreases. At a particular concentration of crown, this linear decrease of molar conductivity with IL concentration arrested rather abruptly to show no or slight further decrease with increment addition of crown and which characterizes the saturation point of complex formation. A distinct break in the conductivity curve happened at a mole ratio (crown/IL) of 1:1, suggesting that the stoichiometry (Scheme 3) of the complex is equimolar and the IL is almost entirely in complexed form. From the Fig. 1, it is clear that the corresponding molar conductivity values increases rapidly with temperature due to the decrease in solute-solvent interaction and accordingly mobility of the charged complexed species are enhanced. This categorically illustrates that both the crowns forms exclusively 1:1 stoichiometric complexes (Scheme 4) with the investigated IL.

3.2 Thermodynamic Parameter Derived from Association Constant

The conductometric method has been extensively used to obtain the formation constants of host guest complexes in solution systems [31]. Therefore, 1:1 complexation of IL with crown can be expressed by the following equilibrium,



The corresponding equilibrium constant for the Eq.(1) is K_f and given by,

$$K_f = \frac{[\text{M} \cdots \text{C}^+]}{[\text{M}^+][\text{C}]} \quad (2)$$

Where, $[\text{M} \cdots \text{C}^+]$, $[\text{M}^+]$, $[\text{C}]$ and f represent the equilibrium molar concentrations of the complex, free IL, free crown and the activity coefficients of the species designated, respectively. Under this dilute condition, the activity coefficient of uncharged macrocycle, $f(\text{C})$, can be reasonably assumed as unity [32]. By using the Debye-Hückel limiting law [33] in Eq.(2) leads to the conclusion that $f(\text{M}^+) \approx f(\text{M} \cdots \text{C}^+)$ thus the activity coefficients are cancel out. Therefore the modified equation for complex formation in terms of the molar conductance (Λ), can be expressed as,

$$K_f = \frac{[\text{M} \cdots \text{C}^+]}{[\text{M}^+][\text{C}]} = \frac{(\Lambda_{\text{M}^+} - \Lambda_{\text{obs}})/(\Lambda_{\text{obs}} - \Lambda_{\text{M} \cdots \text{C}^+})[\text{C}]}{\quad} \quad (3)$$

$$\text{Where, } [\text{C}] = C_{\text{C}} - C_{\text{M}^+}(\Lambda_{\text{M}^+} - \Lambda_{\text{obs}})/(\Lambda_{\text{obs}} - \Lambda_{\text{M} \cdots \text{C}^+}) \quad (4)$$

Here, Λ_{M^+} is the molar conductivity of the IL before addition of ligand, $\Lambda_{\text{M} \cdots \text{C}^+}$ the molar conductivity of the complexed ion, Λ_{obs} the molar conductivity of the experimental solution during experiment, C_{C} the analytical concentration of the crown added and C_{M^+} the analytical concentration of the IL. The complex formation constant, K_f , and the molar conductivity of the complex, $\Lambda_{\text{M} \cdots \text{C}^+}$, were estimated by using the above equations and the values of the formation constant at different temperatures are reported in Table 1.

The ΔH° and ΔS° values were calculated from the corresponding $\text{Ln}K_f$ and inverse temperature plot shown in Fig. 3 and are tabulated in Table 1 with the help of van't Hoff Eq.(5),

$$\text{Ln}K_f = -\Delta H^\circ/RT + \Delta S^\circ/RT \quad (5)$$

The negative values of enthalpy indicates that the overall energy of the system is reduced, i.e., some stabilization interaction occurs in this system, whereas negative values of entropy factor signify that there is an ordered arrangement between IL and the crown molecule for the complex formation. Further, the higher negative value of enthalpy (ΔH°) overcomes the entropic contribution for the overall process and thus the complexation process is thermodynamically feasible (ΔG°) with enthalpy driven. The data shown in Table 1 point out that formation constant $\text{Ln}K_f$ for IL with 18C6 and DBz-18C6 are higher at lower Kelvin. Also, the $\text{Ln}K_f$

values for 18C6 are comparatively higher than DBz-18C6 indicates IL form more stable complex with 18C6 with lower temperature than other one. It is obvious that the total number of donor atoms is the same for both the macrocycles. However, the macrocycles differ in: (i) the basicity of the

donor atom; (ii) the type of substituents in the macrocycle ring; and (iii) the flexibility of the macrocycle ring. Factors (i) and (iii) explain the stability order 18C6 > DBz-18C6, since the replacement of two CH₂-CH₂ units by two benzo units reduces the flexibility (unfavourable orientation of donor atoms) and reduces the electron density on the oxygen atoms of the macrocycle.

Table 1 Values of formation constant (LnK_f), enthalpy (ΔH°), entropy (ΔS°) and free energy change (ΔG°) of IL and crown complexes in acetonitrile solution at three different temperatures and at 101.325 kPa pressure^a

Guest	Host	LnK _f / M ⁻¹			ΔH° / kJmol ⁻¹	ΔS° / Jmol ⁻¹ K ⁻¹	ΔG° / kJmol ⁻¹
		293.15 K	298.15 K	303.15 K			
IL	18C6	3.73	3.66	3.58	-11.26	-6.76	-9.24
IL	DBz-18C6	3.71	3.63	3.56	-11.27	-6.97	-9.19

^a Standard uncertainties u are $u(T) = 0.01$ K, $u(\Lambda) = \pm 0.01$ Sm²mol⁻¹, $u(m) = \pm 0.0002$ molkg⁻¹ and $u(p) = \pm 10$ kPa (0.95 level of confidence)

3.3 Surface Tension

Surface tension (γ) measurement is an important tool to provide significant information about formation of exceptional complexes as well as stoichiometry of the host-guest molecules [34, 35]. IL is a surface active compound due to the unique structural features. Interaction of IL with some molecules (here, crown) affects the surface property of IL. In this study, hydrophobic alkyl group and an N⁺ group of IL interact with crown (Scheme 1) due to which γ of the IL solution shows decreasing trend. With the addition of crown in IL solution the pyridine-N⁺ group of IL binds to the oxygen atom of the crown ether through ionic interaction and the formation of complexes occurs rapidly. As a result charged portion of the IL form complex with crown and the hydrophobic portion increases i.e., surface tension of the solution again decrease slowly [36]. At a certain conc. of IL and crown ether, a single break was found in the surface tension curve (Fig. 2) which obviously implies the formation of 1:1 stoichiometric complex between IL and crown. By examining the facts of γ -values (Table 2) it is understood that 18C6 is more efficient for the formation of complexes than DBz-18C6. This is evidently due to the fact that 18C6 provides more viable features (Scheme 1) for the formation of feasible complexes than DBz-18C6.

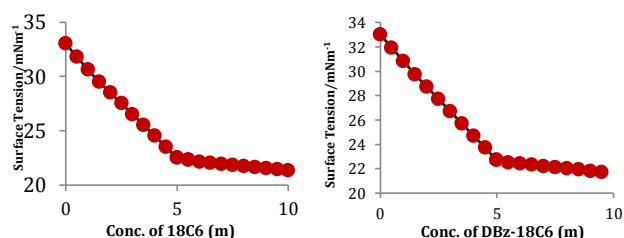


Fig. 2 Plots of surface tension Vs crown Concentration of the IL at 298.15 K

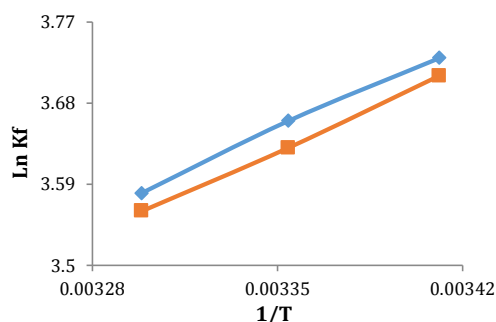


Fig. 3 Variation of LnK_f Vs 1/T of IL with 18C6 (blue line) and DBz-18C6 (brown line) at three different Kelvin

Table 2 Values of surface tension (γ) at the break point of IL (10×10^3 molkg⁻¹) with corresponding concentration of 18C6 and DBz-18C6 in acetonitrile solution at 298.15 K and 101.325 kPa pressure^a

Conc. of IL (m × 10 ³) / molkg ⁻¹	Conc. of 18C6 (m × 10 ³) / molkg ⁻¹	Surface tension (γ) / mNm ⁻¹	Conc. of DBz-18C6 (m × 10 ³) / molkg ⁻¹	Surface tension (γ) / mNm ⁻¹
5.0	5.0	22.5	5.0	22.7

^a Standard uncertainties u are $u(m) = \pm 0.0002$ molkg⁻¹, $u(\Lambda) = \pm 0.01$ Sm²mol⁻¹, $u(\gamma) = \pm 0.1$ mNm⁻¹ and $u(T) = \pm 0.01$ K, and $u(p) = \pm 10$ kPa (0.95 level of confidence)

3.4 Apparent Molar Volume

The extent of interaction for complexation of solute in solvent (here crown cosolute treated as a solvent) [37] has also been obtained from apparent molar volume measurements. The apparent molar volume is the measure of the sum of the geometric volume of the central solute molecule and changes in the solvent volume due to its interaction with the solute around the complex co-sphere. ϕ_v values have been determined from the measured density of the solutions at various temperatures (Table 3) and by using the suitable equation. ϕ_v varies linearly with the square root of molar concentration (Table 4) and is fitted to the Masson equation, from where the limiting apparent molar volume (ϕ_v^0) has been obtained [38].

The limiting molar volume (ϕ_v^0) signifies (Table 5) the solute-solvent interactions in the IL + Crown ternary solution systems. The magnitude of (ϕ_v^0) is found to be positive for all the systems under study, indicating strong solute-solvent interactions [39, 40]. The parameter S_V^* is the volumetric virial coefficient, and it characterizes the pair wise interaction of solute (here IL) species in solution. S_V^* Values (Table 5) are found to be small positive or negative under investigations, which suggest that the pair wise interaction is restricted by the interaction of the charged functional group of IL with crowns. For a constant temperature, it is observed that with increase in mass fraction ϕ_v^0 values also increases.

The increasing trends of ϕ_v^0 with the raise of mass fractions of crown indicates that the ionic interaction between N⁺ centre of IL and O-centre of crown are stronger than the ionic interaction between solute (IL) molecules. These facts also support the data and the results observed from surface tension and conductivity study discussed earlier.

Table 3 Experimental values of density (ρ), viscosity (η) and refractive index (n_D) in different concentration of 18C6 and DBz-18C6 in acetonitrile solution at three temperatures and 101.325 kPa pressure^a

Solvent conc. (m) / molkg ⁻¹	Temp / K	$\rho \cdot 10^{-3}$ / kgm ⁻³		η / mPas		n_D	
		18C6	DBz18C6	18C6	DBz18C6	18C6	DBz18C6
0.0012	293.15	0.78902	0.78914	0.39	0.40		
	298.15	0.78669	0.78712	0.38	0.39	1.3420	1.3417
	303.15	0.78501	0.78515	0.37	0.38		
0.0032	293.15	0.79453	0.79461	0.42	0.43		
	298.15	0.79264	0.79275	0.41	0.42	1.3426	1.3422
	303.15	0.79096	0.79108	0.40	0.41		
0.0052	293.15	0.79911	0.79925	0.45	0.46		
	298.15	0.79717	0.79727	0.44	0.45	1.3429	1.3427
	303.15	0.79516	0.79527	0.43	0.44		

^a Standard uncertainties u are $u(T) = \pm 0.01$ K, $u(\rho) = \pm 10 \times 10^{-1}$ gcm⁻³, $u(\eta) = \pm 0.002$ mPas, $u(n_D) = \pm 0.0003$ and $u(T) = \pm 0.01$ K, $u(p) = 10$ kPa, $u(m) = \pm 0.0002$ molkg⁻¹

Table 4 Experimental values of density (ρ), viscosity (η), refractive index (n_D) of IL in different concentration of 18C6 and DBz-18C6 at different temperatures and at 101.325 kPa pressure^a

Molality /molkg ⁻¹		$\rho \times 10^{-3}$ /kgm ⁻³		η /mPas		n_D	
IL + 18C6							
T/ K ^a	293.15	298.15	303.15	293.15	298.15	303.15	298.15
m ₁ =0.0012							
0.0100	0.78919	0.78715	0.78518	0.40	0.39	0.38	1.3422
0.0251	0.78981	0.78776	0.78579	0.41	0.40	0.39	1.3427
0.0401	0.79091	0.78882	0.78681	0.42	0.41	0.40	1.343
0.0552	0.79215	0.79001	0.78801	0.43	0.42	0.41	1.3436
0.0703	0.79325	0.79095	0.78890	0.44	0.43	0.42	1.344
0.0855	0.79455	0.79195	0.78986	0.45	0.44	0.43	1.3446
m ₁ =0.0032							
0.0100	0.79463	0.79273	0.79105	0.42	0.41	0.40	1.3429
0.0251	0.79499	0.79315	0.79147	0.43	0.43	0.41	1.3434
0.0401	0.79585	0.79396	0.79212	0.44	0.43	0.42	1.3439
0.0552	0.79689	0.79496	0.79318	0.45	0.44	0.43	1.3444
0.0703	0.79792	0.79579	0.79381	0.46	0.45	0.44	1.3449
0.0855	0.79881	0.79671	0.79475	0.47	0.46	0.45	1.3454
m ₁ =0.0052							
0.0100	0.79915	0.79717	0.79520	0.45	0.44	0.43	1.3434
0.0251	0.79941	0.79743	0.79547	0.46	0.45	0.44	1.3439
0.0401	0.80011	0.79803	0.79609	0.47	0.46	0.45	1.3444
0.0552	0.80105	0.79905	0.79695	0.49	0.47	0.46	1.3449
0.0703	0.80179	0.79981	0.79781	0.50	0.49	0.47	1.3455
0.0855	0.80271	0.80051	0.79851	0.51	0.50	0.49	1.3461

IL + DBZ-18C6 m ₂ =0.0012							
0.0100	0.78932	0.78729	0.78532	0.41	0.40	0.39	1.3422
0.0251	0.78994	0.78791	0.78594	0.42	0.41	0.40	1.3425
0.0401	0.79116	0.78896	0.78691	0.43	0.42	0.41	1.3429
0.0552	0.79228	0.79015	0.78805	0.44	0.43	0.42	1.3433
0.0703	0.79347	0.79106	0.78901	0.45	0.44	0.43	1.3438
0.0855	0.79475	0.79192	0.78998	0.46	0.45	0.43	1.3443
m ₂ =0.0032							
0.0100	0.79471	0.79285	0.79118	0.44	0.43	0.42	1.3425
0.0251	0.79515	0.79327	0.79161	0.45	0.44	0.43	1.3429
0.0401	0.79606	0.79415	0.79226	0.47	0.45	0.44	1.3432
0.0552	0.79731	0.79515	0.79316	0.48	0.46	0.45	1.3437
0.0703	0.79822	0.79605	0.79418	0.49	0.48	0.46	1.3442
0.0855	0.79912	0.79695	0.79495	0.50	0.49	0.48	1.3446
m ₂ =0.0052							
0.0100	0.79930	0.79728	0.79532	0.47	0.46	0.45	1.3432
0.0251	0.79961	0.79756	0.79562	0.48	0.47	0.46	1.3435
0.0401	0.80038	0.79818	0.79625	0.50	0.48	0.47	1.3439
0.0552	0.80139	0.79918	0.79752	0.51	0.50	0.49	1.3444
0.0703	0.80202	0.79994	0.79796	0.53	0.51	0.50	1.3449
0.0855	0.80297	0.80061	0.79862	0.54	0.53	0.51	1.3454

^a Standard uncertainties u are: $u(\rho) = \pm 0.00005 \text{ g cm}^{-3}$, $u(\eta) = \pm 0.002 \text{ mPa s}$, $u(n_D) = \pm 0.0003$ and $u(T) = \pm 0.01 \text{ K}$, $u(p) = \pm 10 \text{ kPa}$, $u(m) = \pm 0.0002 \text{ mol kg}^{-1}$

Table 5 Limiting apparent molar volume (ϕ_V^0), experimental slope (S_V^*), viscosity B - and A - coefficient of IL in acetonitrile mixture of 18C6 and DBZ-18C6 at 293.15 K, 298.15 K and 303.15 K temperatures respectively (101.325 kPa pressure)^a

Molality of crowns in acetonitrile(m) ^b /mol kg ⁻¹	$\phi_V^0 \cdot 10^6 / \text{m}^3 \text{mol}^{-1}$	$S_V^* \cdot 10^6 / \text{m}^3 \text{mol}^{-1/2}$	$B / \text{kg} \cdot \text{mol}^{-1}$	$A / \text{kg}^{1/2} \cdot \text{mol}^{-1/2}$
IL+18C6 in acetonitrile				
293.15 K				
m ₁ =0.0012	283.41	-289.73	1.416	0.106
m ₁ =0.0032	289.51	-255.79	2.084	-0.192
m ₁ =0.0052	293.2	-236.9	2.496	-0.251
298.15 K				
m ₁ =0.0012	280.44	-260.17	1.337	0.137
m ₁ =0.0032	287.07	-237.83	1.830	-0.108
m ₁ =0.0052	292.98	-228.21	2.447	-0.250
303.15 K				
m ₁ =0.0012	278.46	-247.32	1.306	0.151
m ₁ =0.0032	284.96	-214.49	1.761	-0.096
m ₁ =0.0052	292.69	-222.25	2.300	-0.229
IL+DBZ-18C6 in acetonitrile				
293.15 K				
m ₂ =0.0012	281.93	-290.13	1.372	0.104
m ₂ =0.0032	289.51	-272.54	1.808	0.051
m ₂ =0.0052	290.81	-238.33	2.112	-0.014
298.15 K				
m ₂ =0.0012	277.03	-245.97	1.321	0.119
m ₂ =0.0032	286.73	-244.14	1.777	0.030
m ₂ =0.0052	290.58	-222.02	2.008	-0.016
303.15 K				
m ₂ =0.0012	276.98	-242.71	1.157	0.156
m ₂ =0.0032	284.62	-217.21	1.615	0.058
m ₂ =0.0052	290.48	-221.51	1.797	0.024

^a Standard uncertainties u are $u(T) = \pm 0.01 \text{ K}$, $u(m) = \pm 0.0002 \text{ mol kg}^{-1}$, $u(p) = \pm 10 \text{ kPa}$ (0.95 level of confidence); Where, ^b m₁ and ^b m₂ are molality of 18C6 and DBZ-18C6 in acetonitrile mixture respectively

3.5 Temperature Dependent Limiting Apparent Molar Volume

The variation of $\phi_V^0 = a_0 + a_1T + a_2T^2$ with the temperature of the IL in aqueous crown mixture can be expressed by the general polynomial equation as given below,

$$\phi_V^0 = a_0 + a_1T + a_2T^2 \quad (6)$$

Where, a_0 , a_1 , a_2 are the empirical coefficients depending on the solute, mass fraction (w_1) of the co-solute crown, and T is the Kelvin temperature. The limiting apparent molar expansibilities, ϕ_E^0 , can be obtained by the following equation,

$$\phi_E^0 = \left(\delta \phi_V^0 / \delta T \right)_p = a_1 + 2a_2T \quad (7)$$

The limiting apparent molar expansibilities, ϕ_E^0 , change in magnitude of with the change of temperature. The values of ϕ_E^0 for different solutions of the studied IL at 293.15 K, 298.15 K and 303.15 K are reported in Table 6. The table reveals that ϕ_E^0 is small positive in all studied temperature. This fact can attributed to the presence of small caging or packing effect [41] for IL in solutions.

Table 6 Limiting apparent molal expansibilities (ϕ_E^0) of IL in different concentration (m) of 18C6 and DBZ-18C6 solution (w_1) at 293.15 K to 303.15 K respectively and 101.325 kPa pressure^a

Solvent mixture(m) ^b	$\phi_E^0 \times 10^6 / \text{m}^3 \text{mol}^{-1} \text{K}^{-1}$					
Acetonitrile + crowns	IL+18C6			IL+DBZ-18C6		
	293.15 K	298.15 K	303.15 K	293.15 K	298.15 K	303.15 K
m ₁ or m ₂ =0.0012	1.11	1.21	1.23	5.25	5.34	5.43
m ₁ or m ₂ =0.0032	0.66	0.67	0.68	0.38	0.39	0.4
m ₁ or m ₂ =0.0052	1.11	1.21	1.23	0.98	0.99	1.01

^a Standard uncertainties u are $u(T) = \pm 0.01 \text{ K}$, $u(m) = \pm 0.0002 \text{ mol kg}^{-1}$, $u(p) = \pm 10 \text{ kPa}$ (0.95 level of confidence); ^b m₁ and ^b m₂ are mass fractions of 18C6 and DBZ-18C6 in acetonitrile mixture respectively

3.6 Viscosity

Molecular interaction operating in a viscous material (IL) along with the co-solutes (crown) can be explained by the viscosity B - and A -coefficients developed by Jones-Dole [42]. In the studied ternary systems the viscosity is found to be increasing with increasing mass fraction of crowns (Table 4). The viscosity B -coefficients (Table 5) which are an indication of solute-solvent interactions, are found to be all positive, and increase with the increasing concentration of 18C6 and DBZ-18C6, which is considered to arise because of increasing IL and crown interaction as well as increase in the solvation [43-45]. These types of interactions are weakened with rise in temperature and thus the values of B -coefficient decreases with increase in temperature. These trends also supported the conductance, surface tension and density scrutiny.

3.7 Refractive Index and Limiting Molar Refraction

Compactness of the complexes can be deduced also from the refractive index measurements. The refractive index (n_D) and molar refraction (R_M) are considered as valuable tools for investigating the molecular interactions taking place in solution systems (Tables 3 and 4). As the interaction between the solute and the solvent (here formation of the complex between IL and crown) increases the medium becomes more compact, resulting in a higher value of the limiting molar refraction (R_M^0) [46, 47]. Therefore, it is distinct from Fig. 4 that the crown complexes are denser or closely packed, which may be explained as due to greater ion solvent interactions between IL and crown. With increase in temperature the compactness of the solution is to some extent reduced due to the thermal motion of liquids. Thus, the molar refraction value decreases with increase in temperature. These findings are in good agreement with the results found from all the above measurements.

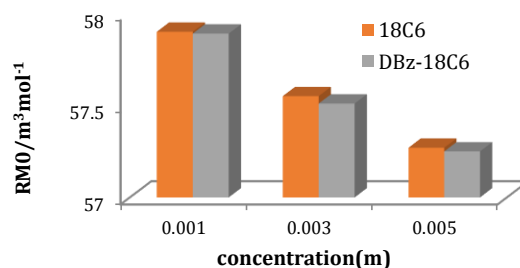


Fig. 4 Plot of limiting molar refraction (R_M^0) of IL against concentration (m) of 18C6 (brown) and DBZ-18C6 at 298.15 K

4. Conclusion

This study concludes that the selected ionic liquid forms 1:1 stoichiometric complexes with both the crown ethers through ionic-interaction. Physicochemical investigation for complex formation in ternary system by surface tension, conductometric volumetric and refractometric method is already proved the details. Thermodynamic contribution confirms the feasible mechanism of complexation. Further,

this outcome reveals that complex formation between IL and 18C6 is more efficient than IL and DBz-18C6. All the findings support the complexation process and thus the current work describes its appropriateness towards assorted applications in the field of modern biomedical as well as industrial areas.

Acknowledgements

This research work was supported by University Grants Commission, New Delhi, India (No. 540/27/DRS/2007, SAP-1) and UGC-RGNF, India (No. F.1/2012-13/RGNF-2012-13-SC-WES-17229). One of the author Prof. M.N. Roy, is grateful to the UGC, New Delhi, Govt. of India, for being awarded a one-time grant under the Basic Scientific Research via the Grant-in-Aid no. F4-10/2010 (BSR) regarding his active service for augmenting of research facilities to aid further research work.

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