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

Kanak Roy, Mahendra Nath Roy*

Department of Chemistry, University of North Bengal, Darjeeling – 734 013, West Bengal, India.

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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 dibenzo18-crown-6(DBz-18C6) which have the highest affinity for ammonium cations, invariably showed a 1:1 stoichiometry with both NH₄⁺ and RNH₂⁺ 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⁺) 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].

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 irreproachable material in utilization 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 1 Molecular structures of 18-crown-6 and dibenzo-18-crown-6

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 dibenzo18-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 dibenzo18-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 ±1%, using a dip-type immersion conductivity cell CD-10 having a cell constant of approximately 0.1±0.001 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± 0.01 K, 298.15 ± 0.01 K and 303.15±0.01 K.

*Corresponding Author
Email Address: mahendraroy2002@yahoo.co.in (Mahendra Nath Roy)

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 ±0.1 mN m⁻¹. Temperature of the system has been maintained by circulating auto-thermostatted water through a double-wall glass vessel containing the solution at 298.15 ± 0.1 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 ±0.01 g cm⁻³ maintained at ±0.01 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, λ=589.3 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.

The conductivity of IL in acetonitrile solution was monitored as a function of medium is reported in our earlier investigation [26–29].

The surface tension was measured by platinum ring driven method inside thermostated water through a double walled vessel [33]. The centre of the IL, 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,

\[ M^+\text{C} \leftrightarrow M\ldots C^+ \]

(1)

The corresponding equilibrium constant for the Eq (1) is \( K_r \) and given by,

\[ K_r = \left[ M\ldots C^+ \right] \left[ C \right] / \left[ M^+ \right] \left[ C \right] \]

(2)

Where, [M…C+], [M+], [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, \( f \), can be reasonably assumed as unity [32]. By using the Debye–Hückel limiting law [33] in Eq (2) leads to the conclusion that \( f \left( M^+ \right) = \left( f \left( M \ldots C^+ \right) \right) \) thus the activity coefficients are cancel out. Therefore the modified equation for complex formation in terms of the molar conductance (\( \Lambda \)), can be expressed as,

\[ K_r = \left[ M\ldots C^+ \right] / \left[ M^+ \right] \left[ C \right] = \Lambda_{w} \left( \Lambda_{w} \cdot \Lambda_{w,c} \right) / \left( \Lambda_{w} \cdot \Lambda_{w,c} \right) \]

(3)

Where, \( C_{\text{C}} \), \( C_{\text{c}} \), \( \Lambda_{w} \), the molar conductivity of the IL before addition of ligand, \( \Lambda_{w,c} \), the molar conductivity of the complexed ion, \( \Lambda_{w} \), the molar conductivity of the experimental solution during experiment, \( C_{\text{c}} \), the analytical concentration of the crown added and \( C_{\text{c}} \), the analytical concentration of the IL. The complex formation constant, \( K_r \), and the molar conductivity of the complex, \( \Lambda_{w,c} \), were estimated by using the above equations and the values of the formation constant at different temperatures are reported in Table 1.

The \( \Delta H^0 \) and \( \Delta S^0 \) values were calculated from the corresponding LnK, and inverse temperature plot shown in Fig. 3 and are tabulated in Table 1 in the help of van’t Hoff Eq.(5).

\[ \text{Ln}K_r = \Delta H^0 / RT + \Delta S^0 / RT \]

(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 (\( \Delta H^0 \)) overcomes the entropic contribution for the overall process and thus the complexation process is thermodynamically feasible (\( \Delta S^0 \)) with enthalpy driven. The data shown in Table 1 point out that formation constant LnK, for IL with 18C6 and DBz-18C6 are higher at lower Kelvin. Also, the \( \text{Ln} K_r \) 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 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.

3.3 Conductance

The molar conductivity (\( \Lambda \)) 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...


3.4 Apparent Molar Volume

The extent of interaction for complexation of solute (here crown solosate 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. \( \phi_s \) values have been determined from the measured density of the solutions at various temperatures (Table 3) and by using the suitable equation. \( \phi_s \) 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 (\( \phi_s^{\infty} \)) has been obtained [38].

The limiting molar volume (\( \phi_s^{\infty} \)) signifies (Table 5) the solute-solvent interactions in the IL + Crown ternary solution systems. The magnitude of (\( \phi_s^{\infty} \)) is found to be positive for all the systems under study, indicating strong solute-solvent interactions [39, 40]. The parameter \( \chi^s \) is the volumetric virial coefficient, and it characterizes the pair wise interaction of solute (here IL) species in solution. \( \chi^s \) 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 \( \phi_s^{\infty} \) values also increases. The increasing trends of \( \phi_s^{\infty} \) with the raise of mass fractions of crown indicates that the iononic 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 (\( \eta \)), viscosity (\( \eta \)), and refractive index (\( n_o \)) in different concentration of 18C6 and DBz-18C6 in acetonitrile solution at three temperatures and 101.325 kPa pressure

<table>
<thead>
<tr>
<th>Solvent</th>
<th>conc(m)/molk</th>
<th>Temp /K</th>
<th>( \rho \times 10^{-3} \text{kg/m}^3 )</th>
<th>( \eta \times 10^{-3} \text{mPas} )</th>
<th>( n_o )</th>
</tr>
</thead>
<tbody>
<tr>
<td>IL + 18C6</td>
<td>293.15</td>
<td>0.000012</td>
<td>1.34223</td>
<td>1.34372</td>
<td>1.3427</td>
</tr>
<tr>
<td>IL + 18C6</td>
<td>298.15</td>
<td>0.000102</td>
<td>1.34270</td>
<td>1.34349</td>
<td>1.3427</td>
</tr>
<tr>
<td>IL + 18C6</td>
<td>293.15</td>
<td>0.00251</td>
<td>1.34270</td>
<td>1.34349</td>
<td>1.3427</td>
</tr>
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<td>1.34270</td>
<td>1.34349</td>
<td>1.3427</td>
</tr>
<tr>
<td>IL + 18C6</td>
<td>293.15</td>
<td>0.00525</td>
<td>1.34270</td>
<td>1.34349</td>
<td>1.3427</td>
</tr>
<tr>
<td>IL + 18C6</td>
<td>298.15</td>
<td>0.00525</td>
<td>1.34270</td>
<td>1.34349</td>
<td>1.3427</td>
</tr>
<tr>
<td>IL + 18C6</td>
<td>293.15</td>
<td>0.00703</td>
<td>1.34270</td>
<td>1.34349</td>
<td>1.3427</td>
</tr>
<tr>
<td>IL + 18C6</td>
<td>298.15</td>
<td>0.00703</td>
<td>1.34270</td>
<td>1.34349</td>
<td>1.3427</td>
</tr>
<tr>
<td>IL + 18C6</td>
<td>293.15</td>
<td>0.00855</td>
<td>1.34270</td>
<td>1.34349</td>
<td>1.3427</td>
</tr>
<tr>
<td>IL + 18C6</td>
<td>298.15</td>
<td>0.00855</td>
<td>1.34270</td>
<td>1.34349</td>
<td>1.3427</td>
</tr>
</tbody>
</table>

### Table 4 Experimental values of density (\( \eta \)), viscosity (\( \eta \)), and refractive index (\( n_o \)) in different concentration of 18C6 and DBz-18C6 at different temperatures and 101.325 kPa pressure

<table>
<thead>
<tr>
<th>Molarity /molk</th>
<th>( \rho \times 10^{-3} \text{kg/m}^3 )</th>
<th>( \eta \times 10^{-3} \text{mPas} )</th>
<th>( n_o )</th>
</tr>
</thead>
<tbody>
<tr>
<td>IL + 18C6</td>
<td>293.15</td>
<td>0.000012</td>
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<td>298.15</td>
<td>0.00855</td>
<td>1.34270</td>
</tr>
</tbody>
</table>

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The limiting apparent molar expansibilities, $\phi_k^0$, change in magnitude of with the change of temperature. The values of $\phi_k^0$ 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 $\phi_k^0$ 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 molar expansibilities ($\phi_k^0$) of IL in different concentration (m) of 18C6 and DBz-18C6 solution (w) at 293.15 K to 303.15 K respectively and 101.325 kPa pressure

<table>
<thead>
<tr>
<th>Solvent mixture (m)</th>
<th>IL=18C6</th>
<th>IL+DBz-18C6</th>
</tr>
</thead>
<tbody>
<tr>
<td>w (%)</td>
<td>IL=18C6</td>
<td>IL+DBz-18C6</td>
</tr>
<tr>
<td>0.0012</td>
<td>1.11</td>
<td>1.23</td>
</tr>
<tr>
<td>0.0032</td>
<td>0.66</td>
<td>0.38</td>
</tr>
<tr>
<td>0.0052</td>
<td>1.11</td>
<td>0.99</td>
</tr>
</tbody>
</table>

*Standard uncertainties $u$ are $u(T)=\pm0.01 K$, $u(m)=\pm0.0002 mol kg^{-1}$, $u(p)=\pm10 kPa$ (0.95 level of confidence). Where, $m$ and $m_0$ are mass fractions of 18C6 and DBz-18C6 in acetone 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 solution [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) 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) [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) of IL against concentration (m) of 18C6 (brown) and DBz-18C6 at 298.15 K](image-url)
References


