Conductance study of electrolyte solutions in binary mixtures of dimethylformamide and dimethylsulphoxide at different temperatures

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Limiting molar conductances \( \langle \lambda \rangle \) of Ph₃PPh₃, Bu₄NBPh₄, Bu₄NNO₃, Bu₄NCIO₄, Bu₄NBr, Bu₄NI, Ph₄PBr, NaBPh₄, AgClO₄, AgNO₃, LiNO₃, NaNO₃, KNO₃ and NaBr have been determined in DMF-DMSO mixtures at 25, 35 and 45°C using Shedlovsky conductance equation. Limiting molar ionic conductances \( \langle \lambda^i \rangle \) have been calculated from \( \lambda \langle \phi_i \rangle \) assuming. Discussion of effective ionic radii \( \langle r_i \rangle \) calculated from \( \lambda^i \) values is based on ion-solvent interactions. The results indicate the existence of electrostatic ion-solvent interactions in the case of alkali metal cations via O atom of both the solvents and specific interactions between Ag⁺ ion and DMSO via S atom of S=O group of DMSO molecule. The latter is found to be in agreement with the concept of soft acid-base type of interactions. Association constants \( (K_A) \), however, yield no significant contribution.

**Study of electrolyte solutions in dimethylformamide (DMF) and dimethylsulphoxide (DMSO)** are of interest in high energy density batteries, photochemical cells, electrodeposition, wet electrolytic capacitors and electroorganic synthesis. A systematic investigation of electrolytic solutions in such solvent systems especially in their binary mixtures is, however, lacking. In the present paper we report conductance studies of some alkali metal and silver salts in complete solvent composition range of DMF-DMSO mixtures at 25, 35 and 45°C. This work is intended to show the existence of specific ion-solvent interactions in the case of Ag⁺ ion.

**Material and Methods**

Solvents, DMSO and DMF of AR grade, were purified and dried\(^ {5,6} \). Salts, Bu₄NBr, Bu₄NI, Ph₄PBr, NaBPh₄, AgClO₄, LiNO₃, NaNO₃, KNO₃ and NaBr of AR grade, were dried at \( \approx 80-100°C \) in vacuum oven for two days before use. However, Ph₄PPh₃, Bu₄NBPh₄, Bu₄NNO₃, Bu₄NCIO₄ and AgClO₄ were synthesized, purified and dried in vacuum for few days before use as described earlier\(^ {5,7} \) and the purity was determined by checking their m.p.t. Moreover, the comparison of \( \lambda_n \) value of these salts in DMF and DMSO reported in literature\(^ {5,3,8,9} \) was in excellent agreement.

Solvent mixtures were prepared by weight precise to \( \pm 0.03% \). Conductance measurements were made at 1 KHz using a digital conductivity meter and a Shedlovsky type conductance cell. Determination of cell constant was based on aqueous KCl solution. Molar conductances were calculated after the correction of solvent conductance \( \approx 2\times10^{-7} \) ohm\(^{-1} \). The temperature control of water thermostat in which measurements were carried out was \( \pm 0.05°C \). Accuracy of conductance measurement was better than 0.2%.

Analysis of the conductance data was based on Shedlovsky conductance equation for the reasons best described earlier\(^ {10} \). The solvent properties, such as viscosity \( (\eta) \), dielectric constant \( (\varepsilon) \) and Bjerrum’s critical distance \( (q) \) required for the analysis of the conductance data were taken from Table 1. Details on Shedlovsky conductance equation are given in our earlier paper\(^ {11} \). \( \varepsilon \) values for the mixtures were calculated: \( \varepsilon_{\text{mix}} = \varepsilon_{\text{DMF}}x_{\text{DMF}} + \varepsilon_{\text{DMSO}}x_{\text{DMSO}} \) where \( \varepsilon_{\text{mix}} \) refers to the dielectric constant of the mixtures of corresponding mole fraction, \( x_{\text{DMF}} \) and \( x_{\text{DMSO}} \) and \( \varepsilon_{\text{DMF}} \) and \( \varepsilon_{\text{DMSO}} \) are the dielectric constants of the pure solvent components. However, it is important to mention that the use of this relation is permissible to ideal systems. The mixtures of DMF and DMSO, however, being of dipolar aprotic solvents, are assumed to be ideal because the differences between the observed and calculated values of \( \varepsilon \) for such solvent systems are practically negligible\(^ {11,12} \). The above consideration, therefore, suggests that \( \varepsilon \) values obtained from this relation cannot be ambiguous.
The results, $\Lambda_0$ and $K_A$ from the analysis are reported in Tables 2-4. Internal consistency of the data was checked by comparing $\Lambda_0$ values of $\text{Ph}_4\text{PBPh}_4$, $\text{Bu}_4\text{NBPh}_4$, $\text{Ph}_4\text{PBr}$, $\text{NaBPh}_4$, $\text{AgClO}_4$ and $\text{NaNO}_3$ reported in Tables 2-4 with those obtained from the additivity relation as described earlier\(^1\) using $\Lambda_0$ values from Tables 2-4. An agreement within ±1 conductance unit is observed over the entire solvent composition range between 25-45°C.

### Results and Discussion

There are various indirect methods in addition to direct transference data proposed for splitting $\Lambda_0$ into $\lambda^0$ values according to empirical rule i.e., nonsolvation of large tetraalkylammonium/tetraphenyl ions in organic solvents\(^1\). A comprehensive analysis of free energy of transfer, $\Delta G^B$ for $\text{Ph}_4\text{As}^+$, $\text{Ph}_4\text{B}^+$ and $\text{Ph}_4\text{P}^+$ ions, however, suggests that the sign of the overall charge of these tetrphenyl moiety still influences the behaviour of even these large ions in solution\(^1\). Table 5 presents the $\lambda^0$ values for various ions calculated on $\lambda^0(\text{Ph}_4\text{P}) \equiv \lambda^0(\text{Ph}_4\text{B})$ assumption. One of the useful applications of this assumption should be stressed: the possibility of almost identical anion-solvent and cation-solvent interactions due to similar peripheral structure.

Table 5, also summarizes effective ionic radii ($r_\text{e}$) for various ions in DMSO-DMF mixtures at different temperatures. These $r_\text{e}$ values are calculated with the help of an empirical modification of Stokes’ law proposed by Gill\(^14\) using $\lambda^0$ values from Table 3.
of temperature, and of the same order of magnitude as calculated for DMF-DMSO mixtures as suggested by Gill and Nordin. It can be seen that Li⁺, Na⁺, K⁺ and Ag⁺ ions are significantly solvated in DMF-DMSO mixtures in contrast to anions. This is justified, since the values of the cations are much larger than the crystallographic radii (r_c) of Li⁺=0.60 Å, Na⁺=0.98 Å, K⁺=1.33 Å and Ag⁺=0.126 Å whereas in the case of anions the difference is small: r_c(NO₃⁻)=0.181 Å, r_c(ClO₄⁻)=0.236 Å, r_c(I⁻)=0.216 Å and r_c(Br⁻)=0.195 Å. Moreover, the r values of the anions can be seen relatively independent of temperature, and of the same order of magnitude as reported in various other organic solvent systems.  

For further explanation of the pattern of r values of anions reference can be made to the solvent structure also. Both DMSO and DMF have large dipole moment 3.86 D (DMF) and 3.96 D (DMSO). The negative charge is localized on the oxygen atom of C=O and S=O groups of DMF and DMSO respectively, which is easily accessible for the cation solvation. In contrast, anion solvation with positive dipole charge encounters steric hindrance because the positive charge localized on the N atom of DMF and S atom of DMSO is shielded by the two methyl groups.

It is, however, worth considering that the r values of cations are in the order: Li⁺ > Na⁺ ≈ K⁺ > Ag⁺. This is in broad agreement (with the exception of Ag⁺)
<table>
<thead>
<tr>
<th>Ions</th>
<th>$\chi^2$ (S cm$^2$ mol$^{-1}$)</th>
<th>Mole% DMSO</th>
<th>Temp. 25°C</th>
<th>Temp. 35°C</th>
<th>Temp. 45°C</th>
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<tr>
<td></td>
<td></td>
<td>0.00</td>
<td>9.99</td>
<td>20.10</td>
<td>29.90</td>
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<td>Ph$_4$B</td>
<td>24.4 0.54 24.0 0.53</td>
<td>22.5 0.53 20.8 0.53</td>
<td>19.5 0.52 17.8 0.52</td>
<td>16.3 0.53 14.9 0.43</td>
<td>13.5 0.53</td>
</tr>
<tr>
<td>Ph$_4$P$^+$</td>
<td>24.5 0.54 24.0 0.53</td>
<td>22.5 0.53 20.8 0.53</td>
<td>19.5 0.52 17.8 0.52</td>
<td>16.3 0.52 15.0 0.53</td>
<td>13.6 0.53</td>
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<td>Bu$_4$N$^+$</td>
<td>27.8 0.54 26.1 0.49</td>
<td>24.4 0.49 22.5 0.56</td>
<td>21.2 0.49 19.6 0.49</td>
<td>17.6 0.50 16.5 0.49</td>
<td>15.2 0.49</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>26.8 0.50 26.0 0.50</td>
<td>24.4 0.49 22.5 0.50</td>
<td>20.9 0.50 18.9 0.50</td>
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</tr>
<tr>
<td>Na$^+$</td>
<td>32.3 0.44 27.9 0.47</td>
<td>27.1 0.46 25.2 0.44</td>
<td>24.3 0.45 23.2 0.44</td>
<td>21.4 0.43 19.8 0.43</td>
<td>18.3 0.43</td>
</tr>
<tr>
<td>K$^+$</td>
<td>33.3 0.43 31.6 0.43</td>
<td>30.1 0.43 27.3 0.43</td>
<td>25.8 0.43 24.2 0.42</td>
<td>21.4 0.43 19.8 0.43</td>
<td>17.9 0.44</td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>36.1 0.41 35.8 0.40</td>
<td>33.7 0.39 31.1 0.40</td>
<td>29.0 0.40 26.4 0.40</td>
<td>24.4 0.40 22.6 0.40</td>
<td>20.9 0.40</td>
</tr>
<tr>
<td>CO$_3$</td>
<td>50.5 0.33 46.9 0.33</td>
<td>43.6 0.33 41.2 0.33</td>
<td>38.4 0.33 36.1 0.33</td>
<td>33.9 0.33 31.3 0.33</td>
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</tr>
<tr>
<td>NO$_3$</td>
<td>55.2 0.31 48.9 0.32</td>
<td>45.9 0.32 44.0 0.32</td>
<td>40.4 0.32 38.0 0.32</td>
<td>36.3 0.32 33.5 0.32</td>
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<tr>
<td>Br$^-$</td>
<td>52.6 0.32 48.3 0.32</td>
<td>45.4 0.33 41.8 0.33</td>
<td>39.6 0.33 36.2 0.33</td>
<td>32.8 0.33 30.6 0.33</td>
<td>28.5 0.33</td>
</tr>
<tr>
<td>T</td>
<td>52.4 0.32 48.0 0.32</td>
<td>45.4 0.33 41.8 0.33</td>
<td>39.3 0.33 36.0 0.33</td>
<td>32.5 0.33 30.2 0.33</td>
<td>28.2 0.33</td>
</tr>
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</table>

Table 5—$\chi^2$ (S cm$^2$ mol$^{-1}$) and corresponding $t_1$ (in nm) values for some ions in DMF-DMSO mixtures at 25, 35 and 45°C

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with electrostatic considerations because the data are reasonably compatible with the reverse order of $r_c$ values of the alkali metal ions; Li$^+$ < Na$^+$ < K$^+$ (Table 5). In the case of Ag$^+$ ion the $r_c$ value does not seem to be the likely factor affecting its binding with solvent molecules because $r_c$ values of Ag$^+$ ion is consistently smaller than K$^+$ ion in spite of the fact that $r_c$(Ag$^+$) < $r_c$(K$^+$).

Standard free energy of transfer (Δ$G^o_t$) from water→DMSO has been reported as -8.0 kcal/g-ion for Ag$^+$, -2.9 kcal/g-ion for K$^+$ and from water→DMF it is -4.1 kcal/g-ion for Ag$^+$ and -2.3 kcal/g-ion for K$^+$. A trend similar to that observed with Δ$G^o_t$ values is observed with free energy of solvation Δ$G^o_v$; in DMSO Δ$G^o_v$(Ag$^+$, K$^+$) is equal to -122.5 and -83.5 kcal/g-ion and in DMF it is -118.6 and -82.8 kcal/g-ion. Thus it can be concluded from these two sets of data that Ag$^+$ shows a marked specificity for DMSO. Similar conclusions can be drawn from the temperature dependence of $r_c$ data reported in Table 5 because $r_c$ values of Ag$^+$ ion in comparison to Li$^+$, Na$^+$ and K$^+$ ions, is markedly constant between 25-45°C. The probable origin of specific interaction between Ag$^+$ and DMSO must be by the sulphur atom (a soft base) of DMSO, which has a lone pair of electron, which means relatively strong 'soft acid-base' type of interactions as Ag$^+$ of d$^{10}$ electronic configuration acts as a soft acid.

Another interesting feature of Δ$G^o_t$ as well as Δ$G^o_v$, values of K$^+$ ion is that they are practically identical in DMSO and DMF. This would be expected if the coordination of DMSO and DMF to the alkali metal cations is via the oxygen atom of S=O group of DMSO and C=O group of DMF. This is indicated by infrared studies particularly by the decrease of vibrational frequency of these groups. The ability of Ag$^+$ ion to act independently of Li$^+$, Na$^+$ and K$^+$ ions thus suggests the existence of specific Ag$^+$-DMSO interactions.

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References