Solvation of copper (I) perchlorate in benzonitrile + pyridine mixtures investigated by conductance studies

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Molar conductances of Bu₄NBPh₄, Bu₄NClO₄ and CuClO₄ have been measured in the concentration range (1-175)x10⁻⁴ mol dm⁻³ at 298.15, 308.15 and 318.15 K in benzonitrile + pyridine mixtures containing 0, 20, 40, 60, 80 and 100 mol% benzonitrile. The conductance data have been analyzed by the Shedlovsky equation to obtain A₀ values of the electrolytes. Limiting ion conductances (λₐ) and solvated radii (r_y) for Cu⁺ and ClO₄⁻ have been evaluated. The results show that Cu⁺ is strongly solvated both in benzonitrile and pyridine but the solvation decreases in the binary mixtures due to a strong competition between benzonitrile and pyridine molecules. ClO₄⁻ has a poor solvation in benzonitrile, pyridine as well as in benzonitrile + pyridine mixtures.

Copper (I) solvation in binary mixtures of acetonitrile with water and also with many organic solvents is now well-studied. Such investigations in binary mixtures of other nitriles with some organic solvents have been attempted only in a few cases. Binary mixtures of benzonitrile with acetonitrile have been used for the study of solvation behaviour of Cu⁺ using transport and compressibility studies. Cu NMR studies in binary mixtures of benzonitrile with acetonitrile and pyridine have also been reported. Except these investigations, no studies of copper (I) salts in nitrite solvents other than acetonitrile are available in the literature. In this note we report solvation studies of copper (I) perchlorate in binary mixtures of benzonitrile with pyridine.

Experimental

Benzonitrile (> 99%, Merck – Schuchardt) was further purified by the method reported earlier. Pyridine (BDH AnalaR) was refluxed over KOH and distilled as before. The sources, grades and methods of preparation/purification of Bu₄NBPh₄, Bu₄NClO₄ and CuClO₄·4C₆H₅CN were reported earlier.

Conductances were measured at 1000 Hz frequency with a digital conductivity meter. Details of conductance measurements were reported previously. The accuracy of conductance measurements was ± 0.2%. Viscosities were measured using an Ubbelohde suspended bulb viscometer with flow time 280 s for distilled water. The overall accuracy of viscosity measurements was better than ± 0.1%. Densities of the pure solvents, binary mixtures and of the salt solutions were measured using an Anton Paar Digital Densimeter model (60) and a calibrated cell (type 602) with a reproducibility of ± 1 x 10⁻⁵ g cm⁻³. Relative permittivities were measured using a Universal Dielectrometer type OH-301 (Radelkis, Hungary) with an accuracy of ± 0.2%.

Results and discussion

The physical parameters of benzonitrile + pyridine mixtures measured at different compositions at 298.15, 308.15 K and 318.15 K are reported in Table I. The ρ, η° and ε values at a fixed composition (Table I) decrease with rise of temperature and at a particular temperature increase with the increase of benzonitrile composition in the mixture. The μ values, on the other side, show a minimum at 20 mol% benzonitrile at all the three temperatures.

Molar conductances of Bu₄NBPh₄, Bu₄NClO₄ and CuClO₄ have been measured in the concentration range (1-175)x10⁻⁴ mol dm⁻³ in benzonitrile, pyridine and benzonitrile + pyridine mixtures containing 20, 40, 60 and 80 mol% benzonitrile at 298.15, 308.15 and 318.15 K. The limiting molar conductances (A₀) and ion-association constants (K_y) of the electrolytes (Table II) have been determined by analysing the conductivity data using the Shedlovsky equation. Since the accuracy of conductance data was not better than ± 0.2%, the use of an extended conductance equation was not meaningful.

Owing to lack of transference number data at different temperatures, precise limiting ion conductivities (λₐ) in all systems studied could not be obtained from our A₀ values by direct method. We used an indirect method based on Eqs (1) and (2) to calculate the limiting ionic conductivities (λₐ) for Bu₄N⁺ and Ph₄B⁻ in benzonitrile, pyridine and benzonitrile + pyridine mixtures at different temperatures.

\[ \lambda_{Bu_4N^+} = 5.35 - (0.0103 \varepsilon + r_y) \]  
\[ \lambda_{Ph_4B^-} = 5.00 - (0.0103 \varepsilon + r_y) \]   
... (1)
Table 1 - Density ($\rho$), viscosity ($\eta^o$), relative permittivity ($\varepsilon$) and ultrasonic velocity ($u$) for benzonitrile + pyridine mixtures at different temperatures

<table>
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<tr>
<th>Mol% benzonitrile</th>
<th>Temp. (K)</th>
<th>$\rho$ (kg m$^{-3}$)</th>
<th>$\eta^o$ (poise)</th>
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Table 2 - $\Lambda_O$ (S cm$^2$ mol$^{-1}$) and $K_A$ (dm$^3$ mol$^{-1}$) values for Bu$_4$NBPh$_4$, Bu$_4$NCIO$_4$ and CuClO$_4$ in benzonitrile + pyridine mixtures at different temperatures

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Table 3 - \( \lambda_i \) values (S cm\(^2\) mol\(^{-1}\)) and solvated radii (\( r_i \) in Å) for some ions in benzonitrile + pyridine mixtures at different temperatures

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From the \( \lambda_i \) values for \( \text{Bu}_4 \text{N}^+ \) and \( \Lambda_0 \) values of all other salts from Table 2, \( \lambda_i \) values for \( \text{Cu}^+ \) and \( \text{ClO}_4^- \) were determined using ionic additivity. The \( \lambda_i \) values for various ions at different temperatures are reported in Table 3.

The solvated radii \( (r_i) \) for \( \text{Cu}^+ \) and \( \text{ClO}_4^- \) were evaluated using the equation

\[
r_i = \frac{|Z|F^2}{6\pi\eta r_i} + 0.0103 \varepsilon + r_y \quad \ldots (3)
\]

where \( F \) is Faraday constant, \( N \) is Avogadro number, \( \eta \) and \( \varepsilon \) are the solvent viscosity and permittivity respectively and \( r_y \) is an adjustable parameter taken as 0.85 Å for all solvent systems used in this work. The solvated radii for \( \text{Cu}^+ \) and \( \text{ClO}_4^- \) so obtained are also reported in Table 3.

A perusal of the \( r_i \) values in Table 3 shows that the solvated radius for \( \text{Cu}^+ \) decreases in benzonitrile and benzonitrile + pyridine mixtures with the rise in temperature while it remains almost constant at all the three temperatures in pure pyridine. At any specific temperature \( \text{Cu}^+ \) has very large \( r_i \) value both in pure benzonitrile (6 Å at 298.15 K) and in pure pyridine (5.9 Å at 298.15 K) which shows that \( \text{Cu}^+ \) is highly solvated in both of these solvents. In benzonitrile + pyridine mixtures with 20 and 40 mol% benzonitrile the \( r_i \) value for \( \text{Cu}^+ \) drops to a minimum (5.1 Å at 298.15 K). In benzonitrile + pyridine mixture with 60 mol% benzonitrile, the \( r_i \) value for \( \text{Cu}^+ \) again rises to a value of 5.3 Å and with 80 mol% benzonitrile to a value 5.6 Å which is still less than that in pure benzonitrile or pure pyridine. \( \text{Cu}^+ \) is thus less solvated in benzonitrile +pyridine mixtures. Both these solvents have great competition for solvation of \( \text{Cu}^+ \), therefore, due to formation of mixed complexes, the solvation decreases in benzonitrile + pyridine mixtures, \( \text{ClO}_4^- \) has solvated radius 3.5 Å in pure benzonitrile and 3.4 Å in pure pyridine at 298.15 K. This value is not very large compared to the crystallographic radius of \( \text{ClO}_4^- \) (2.64 Å) which indicates that \( \text{ClO}_4^- \) is very poorly solvated in benzonitrile + pyridine mixtures. The
ri value for $\text{ClO}_4^-$ though increases up to $3.8 \, \text{Å}$ at 60 mol% benzonitrile, this does not show a very significant change in the solvation behaviour of $\text{ClO}_4^-$.  

Acknowledgement

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References