Conductivity of N-ethylpyridinium iodide in water-dioxan mixtures

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The conductivity data of N-ethylpyridinium iodide in water-dioxan mixture are analysed by Onsager's limiting law to get both \( \Lambda_0 \) and association constant \( K_A \). Activity coefficient data obey Guntelberg's equation. \( \Lambda_0 \) decreases and \( K_A \) increases with increase in viscosity of the solvent system. The results are discussed in terms of ion-ion and ion-solvent interactions.

Conductivity studies on N-methylpyridinium iodide and its methyl substituted derivatives in 90 and 100% acetone and ethanol solvent mixtures, water-methanol, water-ethanol and water-dioxan mixtures in the entire solvent composition range indicate ionic association and hydrophobic hydration of the pyridinium ion.

In this note we report the conductance studies of N-ethylpyridinium iodide (NEPI) in water-dioxan mixture at 25°C.

Experimental

Preparation of the salt, its purification, gravimetric estimation of iodide as silver iodide, purification and preparation of water-dioxan mixtures and conductivity measurements of the salt solutions in its concentration range of \( 10^{-2} \) to \( 10^{-3} \) M at 25°C were carried out as described earlier. Maximum concentration of dioxan in the mixture was limited to 50% because of solubility of the salt.

Results and discussion

The values of the physical constants of water-dioxan solvent systems at 25°C are reported earlier. N-ethylpyridinium iodide ionizes in solution as

\[
\text{C}_2\text{H}_5\text{Py}^+ + \text{C}_2\text{H}_5\text{Py}^- + \text{I}^- \quad \text{(1)}
\]

and the ionization constant \( K_a \) is given by

\[
K_a = \frac{\alpha}{1 - \alpha} f^2 = K' f^2 
\quad \text{(2)}
\]

or \( pK' = pK_a - 2 \log f \).

The conductance data were analysed by Onsager's limiting law

\[
\Lambda = \Lambda_0 - (B_1 \Lambda_0 + B_2) \sqrt{\alpha C} \quad \text{(4)}
\]

where the degree of ionization \( \alpha \) and the constants \( B_1 \) and \( B_2 \) are taken as

\[
\alpha = \frac{\Lambda}{\Lambda_0}, \quad B_1 = \frac{8.20 \times 10^5}{(\varepsilon T)^{1/2}}, \quad B_2 = \frac{82.4}{(\varepsilon T)^{1/2} \eta} \quad \text{(5)}
\]

![Fig. 1-Variation of \( K_a, \Lambda_0, \eta \) with \( x_2 \)](image)

![Fig. 2-Variation of \( \log f \) with \( t^{1/2} \)](image)
The activity coefficient $f_\pm$, was calculated using Guntelberg\cite{8} equation,

$$-\log f_\pm = \frac{A \sqrt{C}}{1 + \sqrt{C}} \quad \ldots (6)$$

The symbols used in the equations have their usual meaning. Equations (3) and (4) were solved by the method of least squares since the plots of $\Lambda_0$ versus $\sqrt{C}$ are linear in the concentration ranges studied for the salt. The values of the derived parameters are included in Table 1.

The $\Lambda_0$, $K_A = 1/K_a$, the association constant and the viscosity of the solvent system $\eta$, are plotted against the mole fraction, $x_2$, of dioxan in Fig. 1. Examination of the Table and the Fig. 1 reveals that the $\Lambda_0$ values decrease and $K_A$ values increase with increase in $x_2$ and $\eta$ of the solvent system. This shows that the viscosity of the medium plays an important role on the mobility of the ions NEP\(^+\) and $I^-$ in solution.

The activity coefficients calculated using Eq. (6) are plotted in Fig. 2 which reveals that $-\log f_\pm$ bears a linear relationship with $I^{1/2}$. The values of $A$ both calculated and experimentally obtained from Fig. 2 for the solvent systems are in good agreement (Table 1). This shows that the use of Guntelberg's equation for the calculation of $f_\pm$ in the determination of $K_A$ is suitable for the present system.

Interactions of the type ion-ion (NEP\(^+\) $-$ $I^-$) and ion-solvent (NEP\(^+\)-solvent; $I^-$-solvent) occur both in water-rich and dioxan-rich regions in the solvent system. This has been conclusively proved in the case of NMPI from the studies of viscosity and apparent molar volumes in aqueous solutions. It may be presumed that NEP\(^+\) ion gets solvated in water-rich region and $I^-$ ion interacts with dioxan in the form of charge transfer complex in the dioxan-rich region of the solvent system.

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**References**