Conductometric investigations of rubidium soaps in water and alkanols

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The critical micelle concentration (CMC), limiting equivalent conductance and dissociation constant of the dilute solutions of rubidium soaps (caprylate, caprate, laurate and stearate) in water and alkanols (methanol, 1-butanol, 1-pentanol, 1-hexanol and 1-octanol) have been determined by conductivity measurements at 35 ± 0.05°C. The dissociation constant increases with the dielectric constant of the solvent. The limiting equivalent conductance obtained from Debye-Huckel-Onsagar equation, Onsagar-Fuoss equation and Otswald law are found to be in close agreement. The CMC values decrease with the increasing chainlength of fatty acid constituent of soap molecule but are found to be almost independent of the dielectric constant of the solvent.

While major developments have taken place in the study of sodium and potassium soaps, the study on rubidium soaps has been very limited. Trzebowski et al.1-2 and Mehrotra et al.3-5 studied the structure of rubidium soaps using infrared spectra and thermal analysis techniques. Mehrotra et al. determined the CMC of rubidium soaps by conductometric and pH-metric6, viscometric6 and ultrasonic7 measurements and also determined the molecular weight and aggregation number in aqueous solutions by light-scattering measurements8.

The present note deals with the study of rubidium soaps (caprylate, caprate, laurate and stearate) in water and alkanols (methanol, 1-butanol, 1-pentanol, 1-hexanol and 1-octanol).

Experimental

Rubidium soaps (caprylate, caprate, laurate and stearate) were prepared by the reaction of aqueous solution of rubidium carbonate with requisite amount of melted fatty acid at ~ 50-60°C. The soaps were digested on a water bath till the evolution of carbon dioxide ceased. The excess acid was removed by washing with benzene and the soaps were purified by recrystallisation with methanol. The purity of the soaps was checked by the determination of their m.p. and elemental analysis. Caprylate, m.p. 210°, Found, C = 42.6; H = 6.8; Calc. C = 42.8; H = 6.5; Caprate, m.p. 215°, Found, C = 46.3; H = 7.2; Calc., C = 46.7; H = 7.4; Laurate, m.p. 210°, Found, C = 50.9; H = 8.1; Calc., C = 50.8; H = 8.1; Stearate, m.p. 205°, Found, C = 58.3; H = 9.6; Calc, C = 58.1; H = 9.4.

The alkanols used were of AR grade. Toshniwal CL 01.10A digital conductivity meter and a dipping type conductivity cell with platinised electrodes were used for measuring the conductance of the solutions at a constant temperature (35 ± 0.05°C). The accuracy of the results was determined to be 0.5%.

Results and discussion

The equivalent conductance, \( \Lambda \) of the dilute solutions (<0.01 equiv. m\(^{-3}\)) in water and alkanols (methanol, 1-butanol, 1-pentanol, 1-hexanol, 1-octanol) of soaps varies linearly with the square root of soap concentration, \( C^{1/2} \). The limiting equivalent conductances \( \Lambda_0 \) were determined by the usual extrapolation method and are recorded in Table 1. The experimental slopes of the lines for solutions in solvents of high dielectric constant (water:methanol as 70:30) are in agreement with the theoretical slopes calculated from the values of limiting equivalent conductance, \( \Lambda_0 \) on the basis of Onsagar’s equation9 for uni-univalent electrolytes,

\[
\Lambda = \Lambda_0 - \left[ \frac{82.4}{(DT)^{1/2}} + \frac{8.20 \times 10^5}{(DT)^{3/2}} \Lambda_0 \right] C^{1/2}
\]

where \( D \), \( \eta \), \( T \) and \( C \) are dielectric constant of the solvent, coefficient of viscosity, temperature on absolute scale and concentration (equiv. m\(^{-3}\)) of the solution, respectively. A and B are constants for a given solvent at constant temperature.

The agreement between the theoretical and experimental slopes (Table 2) indicates that the Debye-Huckel-Onsagar’s theory9-13 of electrolytic conductance is applicable to these soap solutions. The results indicate that the soaps behave like ordinary uni-univalent electrolyte in dilute solutions and are ionised into metal cation, Rb\(^+\) and fatty acid anion, (RCOO\(^-\)) in solution of this concen-
The plot of \((\Lambda + \frac{SC^{1/2} - \Lambda_0}{C})\) versus \(\log C\) yields a linear curve of slope \(A'\) and intercept \(B'\) only, if the correct value of \(\Lambda_0\) has been used by trial method. The value of \(\Lambda_0\) showing exactly a linear curve was determined and the values for different soaps are recorded in Table 2 along with the values of \(\Lambda_0\) obtained from the extrapolation of \(\Lambda\) versus \(C^{1/2}\) plots. The values of \(\Lambda_0\) obtained from both the methods are in complete agreement. It is found that the values of \(\Lambda_0\) increase with the increase in the chain length of anion (from caprylate to stearate) indicating that the effect of viscosity predominates over the loss in ionic mobilities. The values of \(\Lambda_0\) increase with the increase in the dielectric constant of the sol-
vent but the difference in the values for soap solutions in water and methanol are small although there is large difference in the dielectric constant of these solvents. It is an interesting fact that the slopes of the plots of \((\frac{\Lambda + SC^{1/2} - \Lambda_0}{C}) \) versus \(\log C\) i.e. \(\Lambda'\) have values not far from the experimental Onsagar's slopes of the plots of \(\Lambda\) versus \(C^{1/2}\).

The dissociation of rubidium soaps may be represented as \(RCOORb = Rb^+ + RCOO^-\) where \(R\) is \(C_7H_{15},C_9H_{19},C_{11}H_{23}\) and \(C_{17}H_{35}\) for caprylate, caprate, laurate and stearate, respectively.

The values of dissociation constant, \(K\) were determined by the usual Ostwald's dilution law plot for uni-univalent weak electrolytes, viz.,

\[
\Lambda C = \frac{K\Lambda_0^2}{\Lambda} - K\Lambda_0.
\]

The values of the dissociation constant, \(K\) increases with the dielectric constant of the solvent (Table 3). The values of the limiting equivalent conductance \(\Lambda_0\) obtained from these plots are in agreement with those obtained from Debye-Huckel-Onsagar and Onsagar-Fuoss plots (Table 2).

The specific conductance, \(k\) of the soap solutions were plotted against the soap concentration, \(C\) in order to determine the CMC. The plots of \(k\) versus \(C\) were characterised by an intersection of two straight lines at the soap concentrations 0.045, 0.043, 0.042 and 0.025 equiv. m\(^{-3}\) for solutions of rubidium caprylate, caprate, laurate and stearate, respectively indicating the start of the formation of ionic micelles. The increase in specific conductance below the CMC is due to the ionisation of soaps in to metal cations, \(Rb^+\) and fatty acid anions \(RCOO^-\), but further increase above the CMC may be due to the formation of ionic micelles. The values of the CMC are dependent of the chain-length of the anion in the soap but are almost independent of the chain-length in alkanol used as solvent. The values of the CMC are the same as those obtained from density, viscosity, surface tension and colorimetric determinations.

References
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