# Conductance of Potassium Chloride, Sodium Chloride, and Sodium Bromide in Methanol-water Mixture at 35°

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Conductances of potassium chloride, sodium chloride, and sodium bromide in methanol-water (76.24 w/w) have been measured at 35°. The equivalent conductance at zero concentration and the dissociation constants have been determined by using the methods of Fuoss and Kraus and that of Shedlovsky. The values obtained by the two methods are in good agreement. The diameters of the ion pairs have also been calculated, employing Bjerrum's and Stoke's methods.

Conductances of the solutions of potassium chloride, sodium chloride, and sodium bromide in methanol-water mixture (76.24 w/w) have been measured at 35° to determine their dissociation constants. This study has been undertaken as a part of a programme to investigate the effect of salts on the kinetics of certain nucleophilic substitutions (to be published later).

## EXPERIMENTAL

Potassium chloride, sodium chloride, sodium bromide, and methanol used were of E. Merck "extra pure" quality. The salts were recrystallised from triple distilled water and were dried and kept in a vacuum desiccator. Traces of water from methanol were removed by refluxing with magnesium methoxide and then distilling in absence of moisture. The methods of preparation of solvent and solutions and conductance measurements at 35° were the same as reported earlier[1].

TABLE I

| Conc.(equiv./litre). | KCl $\Lambda$ ohm$^{-1}$. | NaCl. $\Lambda$ ohm$^{-1}$ | NaBr. $\Lambda$ ohm$^{-1}$. |
|---|---|---|---|
| 0.010 | 108.00 | 85.34 | 70.94 |
| 0.009 | 108.71 | 86.97 | 74.18 |
| 0.008 | 109.13 | 87.04 | 75.46 |
| 0.007 | 109.56 | 87.67 | 77.21 |
| 0.006 | 111.27 | 87.98 | 77.53 |
| 0.005 | 113.50 | 80.02 | 78.27 |
| 0.004 | 113.50 | 90.08 | 78.82 |
| 0.003 | 118.23 | 90.51 | 79.15 |

1. Das et al., this Journal, 1959, 36, 410.

TABLE II

| Salts. | Equiv. cond. at zero conc. ($\Lambda_0$) by | | Diss. const. ($K \times 10^2$) by | | Radii of the ion pair. | |
|---|---|---|---|---|---|---|
| | Fuoss & Kraus' method[2]. | Shedlovsky's method[3]. | Fuoss & Kraus' method | Shedlovsky's method. | Bjerrum's method[4]. | Stoke's method[7] |
| KCl | 128.21 | 128.21 | 7.44 | 8.68 | 1.22 Å | 3.994Å |
| NaCl | 100.00 | 100.00 | 15.96 | 10.50 | 1.59 | 3.295 |
| NaBr | 87.72 | 87.72 | 15.60 | 15.20 | 1.74 | 3.580 |

DISCUSSION

The change in equivalent conductance with concentration is satisfactorily represented by the Onsager equation for a completely dissociated electrolyte. The evaluation of the equivalent conductance ($\Lambda_0$) at zero concentration can be made by plotting $\Lambda$ against $\sqrt{C}$. The above methods have been reported by various authors (cf. Harned and Owen[8]) to be unreliable in cases of a number of electrolytes involving incomplete dissociation and ion association. Fuoss and Kraus[2] and Shedlovsky[3] suggested methods for the evaluation of $\Lambda_0$ along with the dissociation constant '$K$' of the electrolyte.

We have employed both these methods for the simultaneous evaluation of $\Lambda_0$ and $K$. For this the viscosity of the solvent was measured by the method reported by Das et al[5]. The dielectric constant was obtained from the intrapolation of Åkerlof's data[6]. The methods of extrapolation of $\Lambda_0$ and '$K$' were similar to those described by Das et al.[5]

In Table I, the equivalent conductance of KCl, NaCl, and NaBr at various concentrations have been tabulated. The values of $\Lambda_0$ and $K$ for each electrolyte have been determined by the above two methods and are recorded in Table II. It is evident from these results that $\Lambda_0$ and $K$, obtained by the two methods, are in good agreement.

The distance of the closest approach of the two ions of the electrolytes has been calculated by Bjerrum's method[4]. The mean diameter of the ion pair has also been evaluated by addition of cationic and anionic radii, calculated from the limiting mobility of the ions (assuming Stoke's law). The limiting mobility of the ions, are, however, calculated on the assumption that $K^+$ and $Cl^-$ ions have the same transport numbers. The mean diameters of the ion pairs, calculated by the two methods, are recorded in Table II.

It is to be found that the mean diameter of the ion pairs calculated by these two methods differs to some extent and rather low values are obtained by Bjerrum's method.

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5. Das et al., this Journal, 1960, 37, 683.
6. J. Amer. Chem. Soc., 1936, 58, 1241.
7. Ibid., 1954, 76, 1991.
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