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Conductance Measurements of Mixed Electrolytes

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In the present article, the application of conductance measurements of mixed electrolytes has been discussed.

Conductance measurements have been credited as one of the most appreciated technique to study various types of interaction occurring in solutions. These measurements have also been utilized to know the behaviour of ionic liquids[1-4]. The study of the variation of conductance with concentration and viscosity provides satisfactory informations about the behaviour of solutions. Formation of ion pairs and complexes in solution of electrolytes has been widely studied by such conductance data. As the review of the works carried out in the solution of single electrolyte has been presented time to time, we wish to present the studies of conductance measurements of mixed electrolytes. Such studies will provide informations regarding to ionic association and the effect on the conductance value of an electrolyte due to the presence of other electrolyte.

Perhaps it was Bray and Hunt[5] who first of all reported the conductance data of a mixture of HCl and NaCl. They reported that the conductance of this mixture was not additive in the contributions of the two electrolytes, i.e. if λ_1 and λ_2 were the equivalent conductances of the single electrolytes in solution at the same ionic strength J as obtained in the mixture, the equivalent conductance of the mixture was less than $(C_1\lambda_1 + C_2\lambda_2)/J$; where C_1 and C_2 are the concentrations of HCl and NaCl respectively, and $\lambda = \frac{1000K}{J}$, K is the specific conductance of the mixture and $J = C_1 + C_2$.

Bennewilz, Wagner and Kuchler[6] and Longsworth[7] took the mixture of HCl and KCl as electrolytes and found that the conductance of the faster cation was decreased and of the slower cation increased and the common anion was relatively unaffected. The conductance of the mixture was found to be less than that predicted by the additivity rule in conformity with Bray and Hunt's findings[5].

Kell and Gordon[8] formulated a series of equations for the equivalent and ionic conductance in mixture based on Onsagar Fuoss* theory. One of these equations is

$$\lambda_i = \lambda_i^0 + \nu_i\lambda_i^0 J^{1/2} - \sigma J^{1/2}. \tag{1}$$

This equation is used to evaluate the conductance of a solution containing three univalent ions. The co-efficients ν_i and σ in the equation (1) are defined as

$$\nu_i = 1.98 \times 10^6 (2^{1/2}) Z_i (1 - H^{1/2})_{is} \gamma_s / (DT)^{3/2} \quad (2)$$

$$\sigma = 29.15 (2^{1/2}) / (DT)^{1/2} \eta \quad (3)$$

where D is the dielectric constant, n the viscosity of the solvent at temperature T and Z_i is the sign of the charge of the ion. The subscript *i* indicates summation over the three ions and vectors r are +1 for cation and −1 for the anion.

The matrix product $Z_i(1 - H^{1/2})_{is} r_s$ is equal to 0.29289. The change of conductance of the ion in mixed electrolyte solution as compared with its conductance in binary solution is ascribed to the change in the time of relaxation co-efficient ν_i. To compute the matrix elements h_{ji} for a given μ (ion fraction of K in the mixture of KCl and LiCl), nine quantities $W_{ji} = \lambda_j^0 / (\lambda_j^0 + \lambda_{i,}^0)$ are required. Here λ_k^0, λ_{Li}^0 and λ_{Cl}^0 are known. From these matrix product is computed and written as

$$Z_i(1 - H^{1/2})_{is} r_s = Z_i(a r_i + b h_{is} r_s) \quad (4)$$

The difference between this quantity and 0.29289 on multiplication with $(0.2289/0.2929)\lambda_i^0 J^{1/2}$ provides the value of change in ionic conductance in the mixture as compared with that in binary solution at the same total ionic strength J. $\Delta \Lambda$ may be calculated from the resulting ionic quantities. It has been found that for cations the difference between the calculated and observed values of $\Delta\lambda_i$ are greater than the experimental error. And for the chloride ion the discrepancy is slightly greater than the apparent precision of the chloride data.

Further the observed values of $\Delta\lambda_i$ are numerically greater than the estimated values. The limiting law overestimates the effect of ionic interaction for the alkate chlorides at these concentrations, whereas the assumptions in the theory of mixture effect are certainly those inherent in the limiting law for binary electrolytes. It has assumed that the higher order terms are the same in the mixture as in binary solution. It is certainly an assumption with error. No theory explaining the mixture effect for the higher order terms is known.

Data for NaCl—KCl mixture at high concentration indicates that the conductance at lower concentrations can be predicted correctly by the mixture rule.

During the recent years Lee and Wheaton[10] have also derived the conductance equations for the mixed electrolyte base on a new model for ions in solution using the concept of the Gurney Cospher. They have obtained equations applicable to solutions containing any no. of ionic species, of any valency type, by using the matrix method of Onsagar and

Kim. One of these equations is

$$\lambda_j = \lambda_j^0 + \left\{1 + Z_j \sum_{P=2}^{S} x_j^P \sum_{\nu=1}^{S} t_\nu x_\nu^P\right\}[A_\nu^P(t)(\beta K)] + \beta_2^P(t)(\beta K)^2 + C_\nu^P(t)(\beta K)^3 - \frac{|Z_i|(Kt)}{(1+t)}\{1 + v_j^{(1)}(t)(\beta K)^2\} + V_j^2(t)(\beta K)^2 + \pi_j^{(5)}t/6 \quad (5)$$

where t = XR and

$$A_\nu^p(t) = \pi_v^{(1)}C_{1P}(t)C_\nu^P(t) = \pi_\nu^{(4)}C_{7P}(t) \quad (6)$$

$$\beta_\nu^P(t) = \{\pi_v^{(1)}C_{4,P}(t) + \pi_v^{(2)}[C_{2P}(t) + C_{5P}(5)] + \pi_v^{(3)}C_{3P}(t) + G_V^P(t)\} \quad (7)$$

where the terms have the same meaning as described in their original paper[11].

Using equation (5) with the equation

$$L_{equiv} = \sum_{i=1}^{S} |Z_i| M_i \lambda_l \Big/ \sum_{n}^{K} C_n \quad (8)$$

They have provided a way to estimate the equivalent conductance of a solution containing a mixture of K salts or electrolytes at the stoichiometric equivalent concentrations $C_1, C_2, C_3, \ldots, C_K$.

Bianchi[12] have measured the conductivities of $BaCl_2$–HCl solutions at 298.15°K and used the results to test the equations developed by Lee and Wheaton commonly known as LW theory. They found less satisfactory results for mixture than for pure electrolytes. Further Korbratna Indaratna *et al.*[13] have made the same study for NaCl–$BaCl_2$–H_2O at 298.2 K at various ionic compositions. They have examined the LW treatment and found it able to deal with more concentrated solutions.

Recently Upadhyay[14] attempted to observe the variation of conductance values of mixed electrolytes with their ultrasonic velocities. It has been found that the conductance of electrolytes increases with the increase in the value of ultrasonic velocities of the solutions.

REFERENCES

1. Samuel Glasstone, An Introduction to Electrochemistry, Tenth Printing, Affiliated East West Pvt. Ltd., Madras.
2. J. O. M. Bocknis and A. K. N. Reddy, Modern Electrochemistry, Volume 1, Plenum Press, New York (1970).
3. Duncan A. MacInnes, The Principles of Electrochemistry, Dover Edition, Dover Publications, Inc., New York.
4. R. A. H. Horne, Water and Aqueous Solutions, Wiley Interscience, New York (1972).
5. Bray and Hunt, *J. Am. Chem. Soc.*, **81**, 3207 (1969).

6. Wagner and Kuchler, *J. Am. Chem. Soc.*, **81**, 3207 (1959).
7. Longsworth, *J. Am. Chem. Soc.*, **52**, 1987 (1930).
8. G. S. Kell and A. R. Gordon, *J. Am. Chem. Soc.*, **81**, 3207 (1959).
9. J. Quint and A. Viallard, *J. Solution Chem.*, **7**, 137, 525, 533 (1978).
10. W. H. Lee and R. J. Wheaton, *J. Chem. Soc., Faraday Trans. 2*, **74**, 743, 1456 (1978); **75**, 1128 (1979).
11. L. Onsagar, *J. Phyl. Chem.*, **36**, 2689 (1932).
12. H. Bianchi, *J. Faraday Trans. 1*, **83(a)**, 3027 (1987).
13. Korbratna Indaratna, *J. Faraday Trans. 1*, **82**, 1755 (1986).
14. G. S. Upadhyay, Thermodynamic, acoustical and electrical properties of some multicomponent solutions, Ph.D. Thesis, Magadh University (1989).

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