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LETTERS TO EDITOR

Specific Conductivity of Electrolyte Solutions as a Function of Concentration

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It is well-known that at low concentrations of electrolyte solutions their molar (equivalent) conductivity obeys the Kohlrausch formula $\Lambda = \Lambda_0 - kC^{1/2}$ theoretically substantiated by Onsager. For the specific conductivity κ, this formula takes the form $\kappa = \Lambda_0 C - kC^{3/2}$. This dependence of κ on C passes through the maximum κ_{max} at a certain concentration C_{max}. If this dependence is expressed in dimensionless coordinates $\kappa/\kappa_{max} = f(C/C_{max})$, then the following formula is easily obtained:

$$\underline{\kappa} = 3(\underline{C} - 2/3\underline{C}^{3/2}), \quad (1)$$

in which the normalized values are underlined $\underline{\kappa} = \kappa/\kappa_{max}$, $\underline{C} = C/C_{max}$.

This result shows that in dimensionless coordinates, all dependences of this kind should fit a single curve irrespective of k value.

Precisely this was observed in [1] where many experimental data were compared. However, it is evident that the mentioned maximum corresponds to the higher concentrations than those for which the Kohlrausch–Onsager formula is valid. This is why it is of interest to consider a similar but somewhat different relationship that can describe the data of [1].

Processing of these data has shown that they are described most accurately by the formula

$$\Lambda = \Lambda_0 - kC^{3/4}, \quad (2)$$

which leads to an analogue of formula (1), namely,

$$\underline{\kappa} = 7/3(\underline{C} - 4/7\underline{C}^{7/4}). \quad (3)$$

In the general case, when the power index in the Kohlrausch-like formula is α, we obtain the following formula in place of Eqs. (1) and (3):

$$\underline{\kappa} = [(\alpha + 1)/\alpha]\underline{C} - \underline{C}^{\alpha + 1}/\alpha. \quad (4)$$

The dependence (3) coincides with the data of [1] with the accuracy of 2–3% up to the maximum and somewhat further. However, the inflexion in the experimental curve which is observed at the higher concentrations is not described (because the second derivative is always negative); hence, at the higher concentrations, formula (3) loses its physical meaning. Moreover, it is evident that the power index above 1/2 can be considered only as empirical.

However, another approach to this problem is possible.

Insofar as the decrease in Λ with the increase in concentration is associated with the ion–ion interaction, then in the framework of approximation of pair interactions we can assume that this effect makes a contribution to the electric resistance, which is proportional to the square of concentration, namely

$$1/\Lambda = 1/\Lambda_0 + k'C^2. \quad (5)$$

Now we pass again to normalized coordinates $\underline{\kappa}$ and $\underline{C}$. Then this approach leads to the following relationship (we omit elementary transformations):

$$\underline{\kappa} = 2\underline{C}/(1 + \underline{C}^2), \quad (6)$$

which is also independent of coefficient k' and describes both the ascending part of the $\underline{\kappa}$ vs. $\underline{C}$ dependence and its descending branch including the inflexion. The coordinate of the inflexion point corresponds to $\underline{C} = \sqrt{3}$, which is close to the data of (1). Equation (6) describes less adequately the initial part of the curve ($0 < \underline{C} < 0.5$) as compared with Eq. (3) but turns out to be more accurate at $0.5 < \underline{C} < 1$. The descending part is described more accurately by the equation $\underline{\kappa} = 2\underline{C}/(1 - \underline{C}^2)^{1.1}$.

Thus, the method of presentation of data on the specific conductivity in normalized coordinates, which was proposed in [1], opens up the possibility for the theoretical interpretation.

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