Exercise 20.

The determination of the dissociation constant of a weak electrolyte by the conductometric method

Basic notions: chemical potential, electrolyte, binary electrolyte, electrolytic dissociation, degree of dissociation, molar conductivity, limiting molar conductivity, Ostwald's dilution law

Electrolytes (e.g. NaCl) are called all substances built from ions in a solid, liquid, or molten state. The role of the solvent, after introducing this type of electrolyte into the solution, is limited to solvation and separation of the ions already existing in the system. Numerous other compounds belonging to the group of potential electrolytes undergo dissociation into ions only in a solution, chemically interacting with the polar molecules of the solvent (e.g., acetic acid in water). Dissociation can be complete (strong electrolytes) or partial (weak electrolytes). In the latter case, both ions and electrically neutral molecules are present in the solution.

If an electrolyte denoted by the symbol $K_{v+}^{z+}A_{V-}^{z-}$ partially dissociates in the solution into ν_+ K^{z+} cations and ν_- A^{z-} anions:

$$(K_{v-}^{z+}A_{v-}^{z+}) \rightleftarrows v_+K^{z+} + v_-A^{z-} \tag{1}$$

the equilibrium state in this reaction (at constant pressure and temperature) reflects the thermodynamic dissociation constant (K). Assuming the molar activity system for the reactants, this constant is defined as follows:

$$K_{a,c} = \frac{\left(\frac{a_{K^{z+}}}{c^{\Theta}}\right)^{v+}\left(\frac{a_{A^{z-}}}{c^{\Theta}}\right)^{v-}}{\left(\frac{a_{K_{v+}^{z+}A_{v-}^{z-}}}{c^{\Theta}}\right)} = \left[\frac{\left(\frac{c_{K^{z+}}}{c^{\Theta}}\right)^{v+}\left(\frac{c}{c^{\Theta}}\right)^{v-}}{\left(\frac{c_{K_{v+}^{z+}A_{v-}^{z-}}}{c^{\Theta}}\right)}\right] \cdot \left[\frac{\gamma_{K^{z+}}^{v+}\gamma_{A^{z-}}^{v-}}{\gamma_{K_{v+}^{z+}A_{v-}^{z-}}}\right] = K_c \cdot \left[\frac{\left(\gamma_{K^{z+}}^{v+}\gamma_{A^{z-}}^{v-}\right)}{\left(\gamma_{K_{v+}^{z+}A_{V-}^{z+}}\right)}\right] \tag{2}$$

where a_i and c_i [mol dm^{-3}] represent the molar activity and molar concentration of individual ions and molecules in equilibrium, respectively; γ_i expresses the respective activity coefficients; c^{Θ} = 1 mol dm^{-3} – standard concentration. If molal concentrations are used to describe the dissociation constant, it is then referred to as the approximate (apparent) dissociation constant K_c:

$$K_c = \left[\frac{\left(\frac{c_{K^{z+}}}{c^{\Theta}}\right)^{v+}\left(\frac{c_{A^{z-}}}{c^{\Theta}}\right)^{v-}}{\left(\frac{c_{K_{v+}^{z+}A_{v-}^{z-}}}{c^{\Theta}}\right)}\right] \tag{3}$$

Both the constants $K_{a,c}$ and K_c are dimensionless quantities dependent on temperature. The unit value c^{Θ} is often omitted when presenting equations in simplified form, as in the case of K_c:

$$K_c = \left[\frac{\left(c_{K^{z+}}\right)^{v+}\left(c_{A^{z-}}\right)^{v-}}{\left(c_{K_{v+}^{z+}A_{v-}^{z-}}\right)}\right] \tag{3a}$$

It is important to treat concentrations and activities as dimensionless quantities, always specifying the chosen standard state.

The degree of dissociation (α), a characteristic parameter measuring the progress of electrolytic dissociation, is defined as the ratio of the concentration of dissociated molecules to the concentration of the dissolved electrolyte (c):

$$\alpha = \frac{c_{K^{z+}}}{v_+ c} = \frac{c_{A^{z-}}}{v_- c} \tag{4}$$

where v^+ and v^- are stoichiometric coefficients of cations and anions in the electrolyte. Hence, the concentrations of ions and electrically neutral molecules are described by the expressions:

$$c_{K^{z+}} = \alpha v_+ c \ , \ c_{A^{z-}} = \alpha v_- c \ \ i \ \ c_{K_{v+}^{z+} A_{v-}^{z-}} = c \cdot (1 - \alpha) \tag{5}$$

Substituting these equations into equation (3):

$$K_c = v_+^{v+} v_-^{v-} \frac{\alpha^v}{1-\alpha} \cdot \left(\frac{c}{c^\Theta}\right)^{v-1} \tag{6}$$

The studied acetic acid in the experiment is a binary electrolyte (v+=v-=1) with cation concentration equal to anion concentration, i.e., $c_{K^+} = c_{A^-} = \alpha c$, and $c_{KA} = (1-\alpha)c$. Therefore, the constant is described by the formula:

$$K_c = \frac{\alpha^2}{1-\alpha} \cdot \frac{c}{c^\Theta} \tag{7}$$

In the theory of electrical conductivity of electrolytes, it is known that there is a relationship between the degree of dissociation and the molar conductivity (Λ_m) and the limiting molar conductivity (Λ^o_m) under conditions of infinite dilution:

$$\alpha = \frac{\Lambda_m}{\Lambda_m^o} \tag{8}$$

Substituting equation (7) into equation (8) results in the Ostwald dilution law:

$$K_c = \frac{{\Lambda_m}^2}{{\Lambda_m}^o({\Lambda_m}^o - \Lambda_m)} \cdot \left(\frac{c}{c^\Theta}\right) \tag{9}$$

Substituting molal concentrations for c in equation (9), the following equation is obtained:

$$K_c = \frac{{\Lambda_m}^2}{{\Lambda_m}^o({\Lambda_m}^o - \Lambda_m)} \cdot \left(\frac{10^3 c}{10^3 c^\Theta}\right) \tag{9a}$$

The molar conductivity of the electrolyte (Λm [S m2mol-1]) is defined as the ratio of the electrolytic conductivity κ to the molar concentration c. When the concentration is given in mol dm-3, this relationship can be expressed as follows:

$$\Lambda_m = \frac{\kappa}{10^3 \cdot c} \ \frac{[S \cdot m^{-1}]}{[dm^3 \cdot m^{-3}] \cdot [mol \cdot dm^{-3}]} \tag{10}$$

Equation (9a) forms the basis of the conductometric method for determining the electrolytic dissociation constant when using the concentration of acetic acid solution on a mol dm-3 scale. By transforming equation (9a), we obtain:

$$\frac{1}{\Lambda_m} = \frac{1}{{\Lambda_m}^o} + \frac{1}{(10^3 c^\Theta)\cdot({\Lambda_m}^o)\cdot K_c}\kappa \qquad (11)$$

Equation (11) is a linear equation, where the value of b = 1/ Λ^o_m [S m^2 mol^{-1}] is the point of intersection of the line with the ordinate axis. The dissociation constant Kc can be calculated from the slope coefficient of the line with respect to the abscissa axis.

Experiment section:

Solutions:

- KCl c=0.01 mol dm^{-3}
- CH_3COOH 0.01 mol dm^{-3}

Methodology:

1. Measure the conductivity of water (G_{H2O}=1/R[S]) at a temperature of 298 K.
2. Measure the conductivity of KCl (G_{KCl}) at 0.01 mol dm^{-3} where the electrolytic conductivity κ=0.1413 S m^{-1}.
3. Dilute the initial acetic acid solution to the concentrations listed in Table 1 (8 solutions).
4. Measure the conductivity for each of the solutions at 298 K. Record the results in the table.

Calculations:

1. Calculate the constant of the sensor p [m^{-1}].
2. Using the value of p and the measured conductivities for acetic acid, calculate the electrolytic conductivity κ using the formula
$$\kappa = p\ G\ [S\ m^{-1}]$$
3. Determine the values of Λ_m and $1/\Lambda_m$ for the acetic acid solutions.
4. Present experimental data on a graph using Equation (11), where $y=1/\Lambda_m$ and x=κ.
5. Determine the slope coefficient a and the value b for the line (Equation 11) using the least squares method.
6. Calculate the limiting molar conductivity from the parameter b.
7. Calculate the dissociation constant for acetic acid using the parameters a and b:
$$K_c = \frac{1}{a\cdot(10^3 c^\Theta)}\cdot b^2$$
8. Compare the experimental value with the literature value.

Table 1. Dependence of electrolytic and molar conductivity and degree of dissociation on the concentration of CH_3COOH.

G_{KCl} [S] = **p [m^{-1}] =**

c [mol dm^{-3}]	G = 1/R [S]	κ [S m^{-1}]	Λ_m [S m^2 mol^{-1}]	$1/\Lambda_m$ [$S^{-1}m^{-2}$ mol^{-1}]
0,0005				
0,001				
0,002				
0,004				
0,006				
0,008				
0,01				
0,02				