ELECTROLYTES: TRANSPORT PHENOMENA
CALCULATION OF MULTICOMPONENT SYSTEMS AND EXPERIMENTAL DATA ON ELECTRICAL CONDUCTIVITY

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Calculation of Multicomponent Systems and Experimental Data on Electrical Conductivity

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The main purpose of this book is to represent and describe in some detail methods for calculating (with minimal errors) specific and molar conductivities of multicomponent electrolyte solutions. The book also considers equations for calculating densities of multi-component solutions of electrolytes, densities and viscosities of water at the saturation line at temperatures of 0–350°C, specific volumes at temperatures of 0–500°C and pressures of 1–1000 MPa, and dielectric constants at temperatures of 0–500°C and pressures of 1–500 MPa. The related calculation coefficients obtained by a mathematical treatment using methods of regression analysis of experimental data both available from the literature and obtained in our own experimental work are given for a large number of electrolytes. The account is illustrated by numerous examples.

Tables of experimental data on the specific and molar electrical conductivity for wide ranges of temperatures, pressures, and concentrations of electrolytes in aqueous solutions, obtained as a result of a mathematical treatment of appropriate information available in the literature and substantially supplemented by our experimental data are given.

The edition covers a large number of electrolytes most commonly used in the modern chemical technology. The book is intended for a wide circle of research and engineering specialists of chemical industries and related fields.

CONTENTS

INTRODUCTION

The edition suggested is a continuation of a series of works of this author devoted to many-years' theoretical researches of the structure of and interparticle interactions in aqueous solutions of electrolytes, programmed and factographic representation of experimental data and recommendations related to the methods of calculations of physicochemical parameters of binary and multicomponent systems [1–24].

In this edition, information on the specific and molar conductivity of electrolyte solutions is substantially remade in comparison with [19, 21], and new experimental data are given. Coefficients for calculating electrical conductivity of a large number of electrolytes are presented, which were obtained by a mathematical treatment (using methods of regression analysis) of experimental data available in the literature. Experimental data for most widely applied electrolytes are given for a high-temperature range.

In Part I, methods for calculating electrical conductivity and related coefficients for a wide circle of electrolytes are given; these methods make it possible to calculate, with an accuracy sufficient for practical purposes, many properties of multicomponent solutions. New regression equations (necessary for determining specific and molar electrical conductivity of solutions) were suggested for calculating densities of multicomponent solutions of electrolytes, densities of water at the saturation line in a temperature range of 0–350°C and specific volumes at temperatures of 0–500°C and pressures of 0–1000 MPa, viscosities of water at the saturation line at temperatures of 0–350°C, and dielectric constants at temperatures of 0–500°C and pressures of 1–500 MPa.

In Part II, the list of electrolytes for which specific and molar conductivities were calculated is extended in comparison with [21] (see List of Tables to Part II); the existing tables were remade. All the data are given in a single system of units of measurement. In this issue, as in [21], a logical mode of representing reference data was retained; for each

electrolyte, the maximum temperature range and the maximum range of concentrations are given. A large attention is paid to high-temperature researches. For many electrolytes, additional original experimental investigations were carried out. The author hopes that all these changes will favor the readability and applicability of the material presented.

In this edition, the following system of references is used. For each property and each electrolyte, the full bibliography is given, but many data were refined by our own experimental studies, and it is by no means necessary that all information from the references mentioned have been mathematically processed; in those cases where no references are given, this means that original data of this author were used.

The author will be very grateful to readers for any remarks and wishes.

PART I

1.1 Calculation of the Electrical Conductivity of Multicomponent Solutions of Electrolytes

The electrical conductivity of a multicomponent solution of an electrolyte (Λ, $S \cdot cm^2 \cdot mol^{-1}$) can be calculated using a theoretical equation [24]

$$\Lambda = \frac{1}{c_{kg}} \sum_{i}^{k} v_i c_{ki} [\Lambda_i^0 (1 - L_i) + K_{1i}(c_{ki})^2]$$ (1.1)

where c_k is the total amount of the components of the solution in gram-equivalents; k is the number of solution components; v_i is the number of like charges of a molecule of the electrolyte; c_{ki}, the concentration of a component, in $mol \cdot dm^{-3}$; Λ_i^0, the limiting molar conductivity of each component in water, $S \cdot cm^2 \cdot mol^{-1}$; L_i, a parameter characteristic of each solution component; and K_{1i}, a correction factor for each solution component [24].

In turn, Λ_i^0 is determined by the formula

$$\Lambda_i^0 = \lambda_i^0 + \lambda_j^0$$ (1.2)

where λ_i^0 and λ_j^0 are the limiting molar conductivities of a cation and an anion, respectively, in water in $S \cdot cm^2 \cdot mol^{-1}$.

The limiting molar conductivity of a cation and an anion in water can be calculated from the dependence

$$\lambda_{i,j}^0 = b_0 + b_1 t + b_2 \cdot 10^{-3} t^2 + b_3 \cdot 10^{-5} t^3 + b_4 \cdot 10^{-7} t^4$$
$$+ b_5 \cdot 10^{-9} t^5 + b_6 \cdot 10^{-12} t^6 \tag{1.3}$$

the coefficients b_i, obtained by a statistical treatment of experimental data, are given in Table 1.1.

The values of λ_i^0 and λ_j^0 in (1.2) for different pressures can also be calculated by the equation

$$\lambda_{i,j}^0 = A_0 + A_1 t + A_2 t^{0.7} + A_3 t^{0.5} \tag{1.4}$$

the coefficients A_i for a number of cations and anions, obtained by a statistical treatment of experimental data at various pressures [25], are given in Table 1.2.

Parameter L is determined by the equation

$$L_i = V_{0i} + V_{1i} t + V_{2i} c_{ki} + V_{3i} t c_{ki} + V_{4i} (t c_{ki})^2$$
$$+ V_{5i} c_{ki}^{0.7} + V_{6i} (t c_{ki})^{0.7} + V_{7i} (t c_{ki})^{0.5} \tag{1.5}$$

where V_{ji} are the coefficients obtained by a mathematical treatment of experimental data on the electrical conductivity (Table 1.3); and t is the temperature in °C.

The correction factor K_1 is determined [24] by

$$K_1 = -3.161 \cdot 10^{17} \frac{(\nu_k z_i)^2 \alpha_a}{\eta_0 \varepsilon (\varepsilon T)^3 (6 - \alpha_a^2)} \tag{1.6}$$

where ν_k the number of ions in a molecule of the electrolyte; z_i is the charge of the cation; α_a is a theoretical parameter defined in [24]; η_0, the viscosity of water; Pa·s; ε, the dielectric constant; and T, the temperature, K.

The value of α_a is equal to

$$\alpha_a = \sinh(\beta/a) \tag{1.7}$$

where β is determined by the formula [10, 14–17, 19, 20, 24]

$$\beta = \frac{1.6718 \cdot 10^{-5} |z_i z_j|}{\varepsilon T} \tag{1.8}$$

ε in (1.6) and (1.8) can be calculated (with a standard deviation of 0.33 in terms of the ε units) by the equation used in [24]:

$$\varepsilon = 1 + (a_1/T_*) \rho_* + (a_2/T_* + a_3 + a_4 T_*) \rho_*^2$$
$$+ (a_5/T_* + a_6 T_* + a_7 T_*^2) \rho_*^3 + (a_8/T_*^2 + a_9 T_* + a_{10}) \rho_*^4 \tag{1.9}$$

where

$$T_* = T/298.15 \qquad \rho_* = \rho_0/1000 \tag{1.10}$$

ρ_0 is the density of water, kg·m^{-3}; and the coefficients a_i in (1.9) have the following values:

$$a_1 = 7.62571 \quad a_2 = 244.003 \quad a_3 = -140.569 \quad a_4 = 27.7841$$

$$a_5 = -96.2805 \quad a_6 = 41.7909 \quad a_7 = -10.2099 \quad a_8 = -45.2059$$

$$a_9 = 84.6395 \quad a_{10} = -35.8644$$

Equation (1.9) is valid at temperatures of 273.15–823.15 K, densities of 0–1150 kg·m^{-3}, and pressures of 0–500 MPa.

The quantity a in (1.7) is calculated by the formula [24]

$$a = \chi_f(a_i + a_j) \tag{1.11}$$

where $\chi_f = 1$ for symmetric electrolytes and 2 for asymmetric electrolytes; the separations between the centers of an ion and the oxygen atom of a water molecule (in nm) for the ions in a solution (the effective radii [24]) and the effective radii of multiatomic ions (in nm) a_i and a_j are given in Tables 1.4 and 1.5, respectively.

The density of water in Eq. (1.10) can be calculated as follows [22].

The water density at the saturation line is calculated with a relative error of 0.0048% by the formulas

$$\rho_0 = 999.810745 + R_1 t_* + R_2 t_*^{1.5} + R_3 t_*^2 + R_4 t_*^{2.5}$$

$$+ R_5 t_*^3 + R_6 t_*^{3.5} + R_7 t_*^4 + R_8 t_*^{4.5} \tag{1.12}$$

where $R_1 = 15.910174$, $R_2 = -73.840671$, $R_3 = 141.693443$, $R_4 = -297.162815$, $R_5 = 160.758796$, $R_6 = 146.727674$, $R_7 = -194.580793$, and $R_8 = 58.847919$, between 0 and 150°C and

$$\rho_0 = 1014.554664 - R_1 t_*^{1.5} + R_2 t_*^2 + R_3 t_*^{2.5} + R_4 t_*^4 + R_5 t_*^5 + R_6 t_*^6 \tag{1.13}$$

where $R_1 = 85.134917$, $R_2 = -8.171228$, $R_3 = 51.282976$, $R_4 = -22.685588$, $R_5 = 8.114453$, and $R_6 = 0.987312$, between 150°C and 350°C ($t_* = 0.01t$).

The specific volume of water (V_0, cm^3·g^{-1}) at the saturation line in a temperature range of 0–180°C can be calculated with a relative error of 0.0026% by the equation

$$V_0 = 1.000199 + R_1 t + R_2 t^{1.5} + R_3 t^2 + R_4 t^{2.5}$$

$$+ R_5 t^3 + R_6 t^{3.5} + R_7 t^4 \tag{1.14}$$

where $R_1 = -1.5616 \cdot 10^{-4}$, $R_2 = 6.479 \cdot 10^{-5}$, $R_3 = -1.16457 \cdot 10^{-5}$, $R_4 = 3.38531 \cdot 10^{-6}$, $R_5 = -4.12981 \cdot 10^{-7}$, $R_6 = 2.36493 \cdot 10^{-8}$, and $R_7 = -5.1287 \cdot 10^{-10}$.

The specific volume of water ($V_0 \cdot 10^3$, m^3·kg^{-1}) at the saturation line in a temperature range of $0 \leq t \leq 500$°C and a pressure range of $1 \leq P \leq 1000$ MPa can be calculated as follows:

in a temperature range of $0 \leq t \leq 175$°C and a pressure range of $1 \leq P \leq 10$ MPa, or in a temperature range of $175 < t \leq 200$°C and a pressure range of $2.5 \leq P \leq 10$ MPa, or in a temperature range of $200 < t \leq 250$°C and a pressure range of $5 \leq P \leq 10$ MPa, or in a

temperature range of $250 < t \leq 300°C$ and a pressure of 10 MPa with a root-mean-square error of $0.009 \text{ m}^3\cdot\text{kg}^{-1}$ and with a relative error of 0.6% by the equation

$$V_0 \cdot 10^3 = 1.610954 + R_1(T_*/P_*) - R_2(T_*^{0.7}) + R_3(T_*^2) \tag{1.15}$$

where $T^* = T/647.27$ (T in K), $P^* = P/22.15$, $R_1 = 0.000561$, $R_2 = 1.650281$, and $R_3 = 1.627441$;

in a temperature range of $200 \leq t < 300°C$ and a pressure of 1 MPa, or in a temperature range of $250 \leq t \leq 300°C$ and a pressure range of $1 < P \leq 2.5$ MPa, or in a temperature range of $300 < t \leq 500°C$ and a pressure range of $1 \leq P \leq 10$ MPa, or at a temperature of $300°C$ in a pressure range of $2.5 < P \leq 7.5$ MPa with a root-mean-square error of 0.147 $\text{m}^3\cdot\text{kg}^{-1}$ (a relative error of 0.09%) by the equation

$$V_0 \cdot 10^3 = -133.68217 + R_1/P_* + R_2(T_*^5)/P_* + R_3/P_* + R_4/T_*^{0.7}$$

$$+ R_5 T_*/P_*^{0.5} + R_6(1/P_*^{T_*}) + R_7 T_*^{(1/P_*)} + R_8 T_* \tag{1.16}$$

where $R_1 = -9.588874$, $R_2 = 23.34165$, $R_3 = -1.178347$, $R_4 = 340.241186$, $R_5 = 1.626891$, $R_6 = 0.696686$, $R_7 = -0.014187$, and $R_8 = -213.999632$;

in a temperature range of $0 \leq t \leq 300°C$ and a pressure range of $10 \leq P \leq 100$ MPa with a root-mean-square error of $0.010 \text{ m}^3\cdot\text{kg}^{-1}$ (a relative error of 0.09%) by the equation

$$V_0 \cdot 10^3 = 2.346719 + R_1/P_* + R_2 T_* + R_3 T_*^{0.7}$$

$$+ R_4 T_*^4 + R_5 T_*/P_*^{0.5} + R_6 T_*^5 \tag{1.17}$$

where $R_1 = -0.052553$, $R_2 = 8.547468$, $R_3 = -9.138168$, $R_4 = -2.617144$, $R_5 = 0.390176$, and $R_6 = 2.184545$;

in a temperature range of $300 < t \leq 350°C$ and a pressure range of $17.5 \leq P \leq 100$ MPa with a root-mean-square error of $0.007 \text{ m}^3\cdot\text{kg}^{-1}$ (a relative error of 0.41%) by the equation

$$V_0 \cdot 10^3 = -2.26703 + R_1 T_*^2 + R_2(1/P_*^{T_*})$$

$$+ R_3 T_*^{(1/P_*)} + R_4 \exp(T_*/P_*) \tag{1.18}$$

where $R_1 = 0.495533$, $R_2 = 0.822158$, $R_3 = 3.157102$, and $R_4 = -0.155522$;

in a temperature range of $400 \leq t \leq 500°C$ and a pressure range of $17.5 \leq P \leq 50$ MPa with a root-mean-square error of $0.137 \text{ m}^3\cdot\text{kg}^{-1}$ (a relative error of 0.85%) by the equation

$$V_0 \cdot 10^3 = -595.562918 + R_1/P_* + R_2 T_* + R_3 T_*^3 + R_4 T_*^{(1/P_*)}$$

$$+ R_5(1/P_*)^{T_*} + R_6 T_*/P_*^{0.5} + R_7 T_*/P_* + R_8 T_*^2/P_* \tag{1.19}$$

where $R_1 = 599.003573$, $R_2 = -340.295244$, $R_3 = 71.604246$, $R_4 = 894.882219$, $R_5 = -248.375903$, $R_6 = -84.650427$, $R_7 = 43.705264$, and $R_8 = -334.788341$;

in a temperature range of $350 < t \leq 500°C$ and a pressure range of $50 < P < 100$ MPa with a root-mean-square error of $0.044 \text{ m}^3\cdot\text{kg}^{-1}$ (a relative error of 1.37%) by the equation

$$V_0 \cdot 10^3 = -43.606107 + R_1/P_* + R_2 T_*^{0.7}/P_*^{0.5} + R_3/P_*^{0.5}$$

$$+ R_4 T_*/P_*^{0.5} + R_5(T_* P_*)^2 + R_6 T_*^{0.7}/P_* + R_7/(T_*^{0.5} P_*) + R_8 T_*^2 + R_9 T_* P_* \qquad (1.20)$$

where $R_1 = -2708.110299$, $R_2 = 1950.210651$, $R_3 = -366.815257$, $R_4 = -1542.862263$, $R_5 = -0.180248$, $R_6 = 1257.597823$, $R_7 = 1430.041174$, $R_8 = 22.084359$, and $R_9 = 2.658661$;

in a temperature range of $0 \le t \le 300°C$ and a pressure range of $100 \le P \le 200$ MPa with a root-mean-square error of 0.004 m^3·kg^{-1} (a relative error of 0.32%) by the equation

$$V_0 \cdot 10^3 = 0.940346 + R_1/P_* + R_2 T_*^{0.7} + R_3 T_*^4 + R_4 T_*/P_*^{0.5} \qquad (1.21)$$

where $R_1 = -0.255806$, $R_2 = -0.203399$, $R_3 = 0.255063$, and $R_4 = 0.859825$;

in a temperature range of $300 < t \le 500°C$ and a pressure range of $100 \le P \le 200$ MPa with a root-mean-square error of 0.005 m^3·kg^{-1} (a relative error of 0.29%) by the equation

$$V_0 \cdot 10^3 = 0.835756 + R_1/P_* + R_2 T_*^4 + R_3 T_*/P_* + R_4 T_*^{0.7}/P_* \qquad (1.22)$$

where $R_1 = 86.954141$, $R_2 = 1.110502$, $R_3 = 227.438491$, $R_4 = -0.862612$, and $R_5 = -313.134493$;

in a temperature range $0 \le t \le 500°C$ and a pressure range of $200 < P \le 400$ MPa with a root-mean-square error of 0.008 m^3·kg^{-1} (a relative error of 0.56%) by the equation

$$V_0 \cdot 10^3 = 0.873951 + R_1/P_* + R_2 T_*^{0.5}/P_* + R_3 T_*^{0.7} + R_4 T_*^4 \qquad (1.23)$$

where $R_1 = 9.009153$, $R_2 = -50.544371$, $R_3 = 44.292617$, and $R_4 = 0.062347$;

in a temperature range of $0 \le t \le 500°C$ and a pressure range of $400 < P \le 650$ MPa with a root-mean-square error of 0.003 m^3·kg^{-1} (a relative error of 0.31%) by the equation

$$V_0 \cdot 10^3 = 1.030222 + R_1 T_*^{0.7}/P_* + R_2 T_*/P_*^{0.5} + R_3 T_*^5 + R_4 T_*^{0.5} \qquad (1.24)$$

where $R_1 = -5.171406$, $R_2 = 4.026231$, $R_3 = 0.010345$, and $R_4 = -0.609543$;

in a temperature range of $50 \le t \le 500°C$ and a pressure range of $650 < P \le 1000$ MPa with a root-mean-square error of 0.002 m^3·kg^{-1} (a relative error of 0.16%) by the equation

$$V_0 \cdot 10^3 = 0.788527 + R_1/P_* + R_2 T_*^{0.7} + R_3 T_*/P_*^{0.5} + R_4 T_*^5 \qquad (1.25)$$

where $R_1 = -0.669328$, $R_2 = -0.221543$, $R_3 = 2.451187$, and $R_4 = 0.006543$.

The viscosity of water η_0 (Pa·s) in (1.16) in a temperature range of 0–350°C can be calculated with a root-mean-square error of 1.19 Pa·s (an average relative error of the approximation of 0.23 %) as follows:

in a temperature range of 0–200°C by the equation

$$\eta_0 = S_0 + S_1 t + S_2 t^{0.4} + S_3 t^{1.4} + S_4/(0.5 + t)$$

$$+ S_5 \exp(-0.1 t) + S_6 \ln(0.1 + t) + S_7/(1 + t^2) \qquad (1.26)$$

where $S_0 = 2628.727$, $S_1 = 49.06311$, $S_2 = -1534.221$, $S_3 = -2.47687$, $S_4 = 408.0396$, $S_5 = 166.07556$, $S_6 = 864.9666$, and $S_7 = 172.9407$, or by a more cumbersome equation with an average relative error of approximation of 0.07%

$$\eta_0 = S_0 + S_1 t + S_2/t + S_3 \exp(-0.1t) + S_4/t^2 + S_5 \sqrt{t} + S_6 \ln t \tag{1.27}$$

where $S_0 = 4496.839782$, $S_1 = -4.644252$, $S_2 = -7025.494506$, $S_3 = -159.419139$, $S_4 = 4104.442382$, $S_5 = 316.705387$, and $S_6 = -1486.934219$;

in a temperature range of 200–350°C by the equation

$$\eta_0 = S_0 + S_1 \sqrt{0.01t} + S_2 (0.01t)^{2.5} + S_3 (0.01t)^3 \tag{1.28}$$

where $S_0 = 692.164077$, $S_1 = -467.540634$, $S_2 = 40.788136$, and $S_3 = -16.011979$.

Example. Calculate the specific electrical conductivity of an $MgSO_4$–Na_2SO_4–H_2O solution at $c_{MgSO_4} = 2.57\%$ and $c_{Na_2SO_4} = 4.48\%$ at a temperature of 25°C.

The experimental value is 5.528 $S \cdot m^{-1}$ [26]. For $MgSO_4$, we have $v_i = 1$, $v_j = 1$, $z_i = 2$, $z_j = 2$, and the molar mass is $M(MgSO_4) = 120.365$; the corresponding parameters for Na_2SO_4 are $v_i = 2$, $v_j = 1$, $z_i = 1$, $z_j = 2$, and the molar mass is $M(Na_2SO_4) = 142.04$.

To calculate the concentrations of the solution components (in $mol \cdot dm^{-3}$) in (1.1), we must know the density of the solution. We calculate it by the equation [22]

$$\rho = \rho_0 + \sum_{i=1}^{k} c_i (B_{1i} + B_{2i} t + B_{3i} c_i) \tag{1.29}$$

where ρ is the density of the solution in $kg \cdot m^{-3}$; ρ_0 is the density of water in $kg \cdot m^{-3}$; B_{ji} are the coefficients obtained by a mathematical treatment using regression analysis of experimental data and given in Table 1.6 [22]. From Table 1.6, we have for $MgSO_4$

$$B_1 = 9.6408 \qquad B_2 = -0.0085 \qquad B_3 = 0.0603$$

Correspondingly, for Na_2SO_4 we have

$$B_1 = 8.8058 \qquad B_2 = -0.0066 \qquad B_3 = 0.0568$$

The density of water at the saturation line can be calculated by the Eq. (1.12):

$$t_* = 0.01 \cdot 25 = 0.25$$

$$\rho_0 = 999.8100745 + 15.910174 \cdot 0.25 - 73.840671 \cdot 0.25^{1.5} + 141.693443 \cdot 0.25^2$$
$$- 297.162815 \cdot 0.25^{2.5} + 160.758796 \cdot 0.25^3 + 146.727674 \cdot 0.25^{3.5}$$
$$- 194.580793 \cdot 0.25^4 + 58.847919 \cdot 0.25^{3.5} - 194.580793 \cdot 0.25^4$$
$$+ 58.847919 \cdot 0.25^{4.5} = 997.14 \ kg \cdot m^{-3}$$

Then, the solution density calculated by (1.29) will be

$$\rho = 997.14 + 2.57(9.6408 - 0.0085 \cdot 25 + 0.0603 \cdot 2.57)$$
$$+ 4.48(8.8058 - 0.0066 \cdot 25 + 0.0568 \cdot 4.48) = 1061.62 \text{ kg·m}^{-3}$$

The concentration of the components is calculated by the formulas

$$c_{ki} = \frac{c\%\rho}{100M} \qquad (1.30)$$

$$c_k(MgSO_4) = 2.57 \cdot 1061.62/(100 \cdot 120.365) = 0.2267 \text{ mol·dm}^{-3}$$

$$c_k(Na_2SO_4) = 4.48 \cdot 1061.62/(100 \cdot 142.04) = 0.3348 \text{ mol·dm}^{-3}$$

The total amount of the components in the solution (in gram-equiv) will be

$$c_{kg} = 2 \cdot 0.2267 + 2 \cdot 0.3348 = 1.123 \text{ gram-equiv}$$

Using (1.3), we calculate the limiting molar electrical conductivity of the cations and the anions of each of the solution components. From Table 1.1, we have
for Mg^{2+}: $b_0 = 31.0311$, $b_1 = 0.2588$, $b_2 = 31.9091$, $b_3 = -28.9096$, $b_4 = 8.2089$;
for SO_4^{2-}: $b_0 = 40.6963$, $b_1 = 1.2019$, $b_2 = 14.6689$, $b_3 = -6.0308$, $b_4 = 0.8726$;
for Na^+: $b_0 = 25.7066$, $b_1 = 0.8501$, $b_2 = 5.5764$, $b_3 = -1.7986$, $b_4 = 0.2000$.
Now, we calculate the limiting molar electrical conductivity of the cations and anions:
for Mg^{2+}, we have

$$\lambda_i^0 = 31.0311 + 0.2588 \cdot 25 + 31.9091 \cdot 10^{-3} \cdot 25^2 - 28.9096 \cdot 10^{-5} \cdot 25^3$$
$$+ 8.2089 \cdot 10^{-7} \cdot 25^4 = 53.25 \text{ S·cm}^2\text{·mol}^{-1}$$

for SO_4^{2-},

$$\lambda_i^0 = 40.6963 + 1.2019 \cdot 25 + 14.6689 \cdot 10^{-3} \cdot 25^2 - 6.0308 \cdot 10^{-5} \cdot 25^3$$
$$+ 0.8726 \cdot 10^{-7} \cdot 25^4 = 79.00 \text{ S·cm}^2\text{·mol}^{-1}$$

for Na^+,

$$\lambda_i^0 = 25.7066 + 0.8501 \cdot 25 + 5.5764 \cdot 10^{-3} \cdot 25^2 - 1.7986 \cdot 10^{-5} \cdot 25^3$$
$$+ 0.2000 \cdot 10^{-7} \cdot 25^4 = 50.17 \text{ S·cm}^2\text{·mol}^{-1}$$

The limiting molar electrical conductivity of the solution components can be calculated by Eq. (1.2) as follows:
for $MgSO_4$

$$\Lambda^0(MgSO_4) = 53.25 + 79.00 = 132.25 \text{ S·cm}^2\text{·mol}^{-1}$$

for Na_2SO_4

$$\Lambda^0(Na_2SO_4) = 50.17 + 79.00 = 129.17 \text{ S·cm}^2\text{·mol}^{-1}$$

Using (1.5), we calculate parameter L for each of the solution components. From Table 1.3, we have for $MgSO_4$

$$W_0 = 0.5055 \qquad W_1 = 2.7133 \cdot 10^{-4} \qquad W_2 = -1.5874 \qquad W_3 = 0.1435$$
$$W_4 = -9.3953 \cdot 10^{-4} \qquad W_5 = 1.0131 \qquad W_6 = -0.6947 \qquad W_7 = 0.7698$$

Thus, we obtain L for $MgSO_4$ to be

$$L(MgSO_4) = 0.5055 + 2.7133 \cdot 10^{-4} \cdot 25 - 1.5874 \cdot 0.2267 + 0.1435 \cdot 25 \cdot 0.2267$$
$$- 9.3953 \cdot 10^{-4}(25 \cdot 0.2267)^2 + 1.0131 \cdot 0.2267^{0.7} - 0.6947(25 \cdot 0.2267)^{0.7}$$
$$+ 0.7698(25 \cdot 0.2267)^{0.5} = 0.8408$$

for Na_2SO_4

$$W_0 = 0.2996 \qquad W_1 = 9.9530 \cdot 10^{-4} \qquad W_2 = -0.2078 \qquad W_3 = -1.5492 \cdot 10^{-2}$$
$$W_4 = 1.2170 \cdot 10^{-5} \qquad W_5 = 0.5605 \qquad W_6 = 0.1147 \qquad W_7 = -0.1534$$

$$L(Na_2SO_4) = 0.2996 + 9.9530 \cdot 10^{-4} \cdot 25 - 0.2078 \cdot 0.3348$$
$$- 1.5492 \cdot 10^{-2} \cdot 25 \cdot 0.3348 - 1.2170 \cdot 10^{-5}(25 \cdot 0.3348)^2 + 0.5605 \cdot 0.3348^{0.7}$$
$$+ 0.1147(25 \cdot 0.3348)^{0.7} - 0.1534(25 \cdot 0.3348)^{0.5} = 0.4504$$

In order to determine K_1 from (1.6), we first calculate the related terms.
The total number of ions for $MgSO_4$ is

$$v_k = 1 + 1 = 2$$

for Na_2SO_4, we have

$$v_k = 2 + 1 = 3$$

To find the theoretical parameter α_a, we take from Table 1.4 the following values of the spacings between the center of an ion and the oxygen atom of the water molecule:
for Mg^{2+}

$$a_i = 0.215 \cdot 10^{-9} \text{ nm}$$

for SO_4^{2-}

$$a_j = 0.380 \cdot 10^{-9} \text{ nm}$$

for Na^+

$$a_i = 0.235 \cdot 10^{-9} \text{ nm}$$

By Eq. (1.11), we calculate the spacing between ions as follows:
for $MgSO_4$

$$a = 0.215 \cdot 10^{-9} + 0.380 \cdot 10^{-9} = 0.595 \cdot 10^{-9} \text{ nm}$$

for Na_2SO_4

$$a = 2(0.235 \cdot 10^{-9} + 0.380 \cdot 10^{-9}) = 1.19 \cdot 10^{-9} \text{ nm}$$

From (1.9) and (1.10), we calculate the dielectric constant as follows:

$$T = 273.15 + 25 = 298.15 \qquad T_* = 298.15/298.15 = 1$$

$$\rho_* = 997.14/1000 = 0.99714$$

$$\varepsilon = 1 + (7.62571/1)0.99714 + (244.003/1 - 140.569 + 27.7841 \cdot 1) 0.99714^2$$
$$+ (-96.2805/1 + 41.7909 \cdot 1 - 10.2099 \cdot 1^2) 0.99714^3$$
$$+ (-45.2059/1^2 + 84.6395/1 - 35.8644) 0.99714^4 = 78.46$$

From (1.8), we find β;
for $MgSO_4$

$$\beta = 1.6718 \cdot 10^{-5} \cdot 2 \cdot 2/(78.46 \cdot 298.15) = 2.8588 \cdot 10^{-9}$$

for Na_2SO_4

$$\beta = 1.6718 \cdot 10^{-5} \cdot 1 \cdot 2/(78.46 \cdot 298.15) = 1.4294 \cdot 10^{-9}$$

From (1.7), we determine α_a:
for $MgSO_4$

$$\alpha_a = \sinh (2.8588 \cdot 10^{-9}/0.595 \cdot 10^{-9}) = 61.041$$

for Na_2SO_4

$$\alpha_a = \sinh (1.4294 \cdot 10^{-9}/1.19 \cdot 10^{-9}) = 1.512$$

The water viscosity at the saturation line can be calculated by Eq. (1.27) as

$$\eta_0 = 4496.839782 - 4.644252 \cdot 25 - 7025.494506/25 - 159.419139 \exp(-0.1 \cdot 25)$$
$$+ 4104.442382/25^2 + 316.705387 \cdot 25^{0.5} - 1486.934219 \ln(25) = 890.47 \text{ Pa·s}$$

From (1.6), we find K_1 as follows:
for $MgSO_4$

$$K_1 = -3.161 \cdot 10^{17} \frac{(2 \cdot 2)61.041}{890.47 \cdot 78.46(78.46 \cdot 298.15)^3(6 - 61.041^2)} = 0.0928$$

for Na_2SO_4

$$K_1 = -3.161 \cdot 10^{17} \frac{(3 \cdot 1)1.512}{890.47 \cdot 78.46(78.46 \cdot 298.15)^3(6 - 1.512^2)} = -1.2946$$

The electrical conductivity of the multicomponent solution is calculated from Eq. (1.1) as follows:

$$\Lambda = 1/1.123 \ \{2 \cdot 0.2267 \ [132.25 \ (1 - 0.8408) + 0.0928 \cdot 0.2267^2]$$
$$+ \ 2 \cdot 0.3348 \ [129.17 \ (1 - 0.4504) - 1.2946 \cdot 0.3348^2]\} = 50.75 \ \text{S·cm}^2\text{·mol}^{-1}$$

The specific conductivity is calculated by the thermodynamic equation

$$\kappa = \frac{c_{kg} \cdot \Lambda}{10} \tag{1.31}$$

i.e., $\kappa = 1.123 \cdot 50.75/10 = 5700 \ \text{S·m}^{-1}$.

Making similar calculations for $t = 50°\text{C}$, we obtain $\kappa = 8.655 \ \text{S·m}^{-1}$. The experimental value is $\kappa = 8.487 \ \text{S·m}^{-1}$ [26].

1.2 Calculation of the Electrical Conductivity of Binary Solutions of Electrolytes

The molar electrical conductivity of a binary solution of an electrolyte can be calculated by the theoretical equation derived in [24]:

$$\Lambda = \Lambda^0(1 - k_2 c_{ki} a_e) + K_1(c_{ki})^2 \tag{1.32}$$

where a_e is a theoretical coefficient, and the parameter K_2 is determined [24] as

$$K_2 = 1.372 \cdot 10^{19} \frac{v_k |z_i| q}{(\varepsilon T)^5} \tag{1.33}$$

where

$$q = \frac{|z_i z_j|}{|z_i| + |z_j|} \cdot \frac{\lambda_i^0 + \lambda_j^0}{|z_i| \lambda_i^0 + |z_j| \lambda_j^0} \tag{1.34}$$

For estimation purposes, the value of a_e can be calculated from three experimental points using the equation of a hyperbola

$$a_e \sqrt{c_k} + A a_e + B \sqrt{c_k} + D = 0 \tag{1.35}$$

First, we find the values of a_{ei} ($i = 1, 2, 3$) from (1.32):

$$a_e = \frac{\Lambda^0 - \Lambda + K_1(c_{ki}^2)}{\Lambda^0 K_2 c_k} \tag{1.36}$$

Then, from the solution of the system of equations

$$a_{e1} \sqrt{c_{k1}} + A a_{e1} + B \sqrt{c_{k1}} + D = 0$$

$$a_{e2} \sqrt{c_{k2}} + A a_{e2} + B \sqrt{c_{k2}} + D = 0$$

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