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CONCENTRATION AND TEMPERATURE EMPIRICAL RELATIONSHIPS OF THE ELECTRICAL CONDUCTIVITY OF ELECTROLYTE SOLUTIONS

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We have considered the dependences of the specific (κ) and molar (Λ) electrical conductivity (EC) of aqueous electrolyte solutions on the molar concentration and temperature for sulfates of divalent metals (Mn, Co, Ni, Cu, Zn, Cd) in a wide concentration range at 5 – 35°C. To describe such systems we propose a modified cubic equation (MCE): $\kappa = C\cdot c^{3k} + Q\cdot c^{2k} + L\cdot c^{k}$, where C, Q, L, k are empirical parameters, fixed parameter $k = 0.5$ has been considered as well. From the correlation between the calculated parameters we assume that two of them are sufficient. The maximum of specific EC (κ_m) and the corresponding concentration (c_m) have been calculated. We also assume that the systems under study are isomorphic in the normalized coordinates (κ/κ_m via c/c_m). For the dependences like $\kappa = A\cdot c^{x} + B\cdot c^{y}$ it is shown that $x = 1$ is a good approximation over the generalized sample. Empirical dependences with $y = 5/4$ and $y = 4/3$ are also considered. It is shown that they give comparable results to MCE.

The proposed approach is tested on EC data of aqueous solutions of some salts. Similar two-parameter $\kappa(\kappa_m, c_m; c)$ equations of other authors have been considered. In order to describe the dependence of the specific EC on temperature and concentration we propose an equation $\kappa = (A_{25} + a\cdot\theta)\cdot c - (B_{25} + b\cdot\theta)\cdot c^{5/4}$, where θ is the reduced temperature and A_{25}, a, B_{25} and b are empirical parameters. Also a generalized equation for the molar EC of concentrated electrolyte solutions is proposed: $\Lambda(\Lambda_*, \Lambda_m, c_m; c)$, where Λ_* is the effective limiting molar EC, and Λ_m is the molar EC at $c = c_m$. It was found that Λ_* and Λ_m depend linearly on temperature. The average value of the exponent is close to 1/3, which brings the generalized molar EC equation closer to the equation derived from the quasi-lattice model of electrolyte solutions.

Keywords: specific electrical conductivity, molar electrical conductivity, electrolyte solutions, sulfates of divalent metals, empirical equations.

Introduction

One of the most important features of electrolyte solutions is electrical conductivity. Concentrated solutions deserve special attention [1,2]. At the same time for concentrated electrolyte solutions there are practically no equations, which would have a rigorous theoretical justification. More often empirical equations are used. The Casteel-Amis equation [3] is the most popular. This equation describes dependence of specific electrical conductivity on molality of electrolyte solution:

$$\frac{\kappa}{\kappa_m} = \left(\frac{m}{\mu}\right)^{a} \cdot \exp\left(b\cdot(m-\mu)^2 - a\cdot\frac{m-\mu}{\mu}\right) \tag{1}$$

where κ_m is the maximum electrical conductivity at molality μ, while a and b are fitting parameters. Thus, the Casteel-Amis equation has four parameters to describe the concentration dependence, which makes it impossible to use for treatment of small experimental data samples. Most experimental and reference data sets contain 5-7 points in the region of concentrated solutions.

Aim and objects of the study

In this paper we have tried to get some simple empirical equations for the electrical conductivity dependence on the molar concentration and temperature. Here we consider as ‘simple’ only equations that can be converted into a linear form. At the same time, the authors did not seek theoretical justification for the equations, their applicability across the entire concentration range, or universality in the selection of electrolytes and solvents.

As objects of research, we chose the experimental data sets [4] on the specific electrical conductivity of divalent metal sulphate solutions (Mn, Co, Ni, Cu, Zn, Cd) in water at 5–35°C. Our choice is based on the following facts:

- They are typical salt solution systems with a wide range of applications;
- They all (except $CuSO_4$) show a maximum in the concentration dependence of the specific electrical conductivity, which is of particular interest;
- They are similar in their physical and chemical properties.

The molar concentrations are calculated from the density data of the solutions given in the original article [4].

Calculations and discussions

Empirical equations for specific electrical conductivity. To describe the concentration dependence of specific conductivity, we propose an empirical equation as follows:

$$\kappa = C \cdot c^{3k} + Q \cdot c^{2k} + L \cdot c^{k} \tag{2}$$

where C, Q, L, k – are fitting parameters.

Such an equation (2) form is chosen due to the simplicity of finding the concentration of maximum conductivity:

$$c_{\mathrm{m}} = \sqrt[k]{-\frac{Q + \sqrt{Q^2 - 3CL}}{3C}}\,, \tag{3}$$

maximum conductivity value:

$$\kappa_{\mathrm{m}} = C \cdot c_{\mathrm{m}}^{3k} + Q \cdot c_{\mathrm{m}}^{2k} + L \cdot c_{\mathrm{m}}^{k}\,, \tag{4}$$

and the inflection point c_{inf} on the concentration dependence of the conductivity $\kappa(c^k)$:

$$c_{\mathrm{inf}} = \sqrt[k]{-\frac{Q}{3C}} \tag{5}$$

The optimisation with the least-squares method has been performed in Statistica software using the Newton-Gauss algorithm. We used the data for the whole concentration range. The results of the calculations are presented in table 1. Equation (2) describes the experimental data well enough. For all systems considered, the coefficient of determination R^2 is greater than 0.999. For $CuSO_4$, values of extreme parameters are outside of the experimental data range. The maximum conductivity practically coincides with the values calculated using the Casteel-Amis equation given in the original paper [4].

Table 1 The parameters of equation (2) and the maximum specific conductivity κ_{m} (S/m) for the concentration c_{m} (mol/dm^3) at 25°C

Salt	$-C$	Q	L	k	c_{m}	$c_{\mathrm{m}[4]}$	c_{inf}	κ_{m}	$\kappa_{\mathrm{m}[4]}$
$MnSO_4$	4.55	9.03	-0.18	0.440	1.86	1.80	0.40	5.03	5.064
$CoSO_4$	3.97	7.86	0.66	0.488	1.89	1.89	0.43	5.50	5.488
$NiSO_4$	3.74	7.40	0.88	0.501	1.89	1.88	0.44	5.48	5.474
$CuSO_4$	3.12	6.51	1.31	0.532	2.11	1.99	0.53	6.10	5.998
$ZnSO_4$	3.66	7.31	1.00	0.509	1.93	1.91	0.45	5.68	5.670
$CdSO_4$	3.39	6.99	0.53	0.480	2.05	2.02	0.46	5.14	5.134

The proximity of the values of the parameter k for the systems under study should be pointed out. One can assume that this parameter depends on the system and fix it at a close to average level of 0.5. Then equation (2) acquires three parameters. The results of the three-parameter approximation are practically the same as those of the four-parameter one (except for $CuSO_4$).

Choice of parameters. For equation (2) there is a correlation between the optimal parameters C, Q, L, and k for the dependencies considered. The principal components analysis has been used to process the array of optimal parameters C, Q, L, and k. It is shown that the magnitude of the explained variance is distributed over the components as follows: first principal component (PC) 93.17%, second PC 6.69%, third PC 0.13%, fourth PC 0.003%. It can be assumed that the presence of four parameters is excessive. Thus, two parameters are sufficient to describe the systems under study with practical accuracy.

As these parameters, it is convenient to choose the maximum electric conductivity κ_m and the concentration c_m corresponding to it. For systems with maximum conductivity, κ_m and c_m are objectively observable phenomena and their values do not depend on the choice of $\kappa(c)$ dependence. At the same time, for systems where solubility does not allow for maximum conductivity, κ_m and c_m are fitting parameters of the functional dependence $\kappa(c)$.

As a solution to the problem, it is proposed to find equations of the form:

$$\kappa = Ac^x + Bc^y \tag{6}$$

where A and B are model parameters, and the exponents of powers x, y are rational numbers.

If κ_m and c_m, are defined as parameters, equation (6) is transformed to:

$$\frac{\kappa}{\kappa_m} = \frac{y}{y-x} \cdot \left(\frac{c}{c_m}\right)^x + \frac{x}{x-y} \cdot \left(\frac{c}{c_m}\right)^y \tag{7}$$

Thus, the solution to this problem comes down to determining the parameters κ_m and c_m, and selecting satisfactory values of x and y.

Choice of two-parameter models. A direct four-parameter optimization is inefficient, given the small number of experimental points and the symmetry of x and y.

Two parameters, x and y, remain when equation (7) is considered in coordinates normalised at the extrema.

Figure 1 shows the specific conductivity concentration dependences, normalised to optimum values (Table 1).

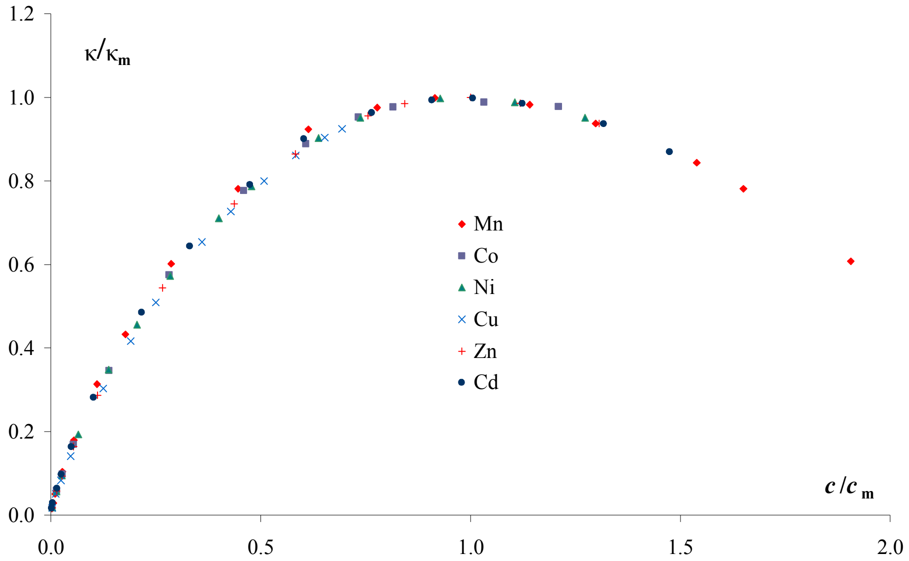

Figure 1 Concentration dependencies of specific conductivity, normalised to optimum values for divalent metal sulphate solutions at 25°C.

It can be seen that the points fit well on the same curve, indicating the isomorphism of the studied systems. Therefore, further analysis was carried out for a generalised sample of normalised specific conductivity values as a function of normalised concentration.

The optimal values of y for the generalised sample are calculated for the given values of x. A fragment of the dependence *y(x)* is shown in Figure 2.

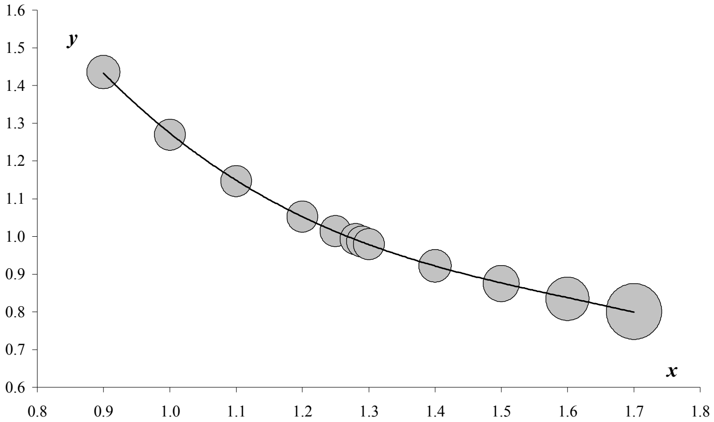

Figure 2 Dependence of the optimum values of *y(x)* (equation (7)). The diameter of the balls is proportional to the sum of squared deviations.

Figure 2 shows the relative magnitudes of the sum of squared deviations for the corresponding pairs of x and y. The optimum corresponds to the pairs $x = 1.271$ and $y = 0.998$, given the symmetry of $x = 0.998$ and $y = 1.271$. However, the sum of the squared deviations varies insignificantly over a generalised sample. If $x = 1$, then $y = 1.270 \pm 0.011$.

Approximate models of specific conductivity are proposed, where the exponent is approximated by a rational number:

$$\frac{\kappa}{\kappa_{\mathrm{m}}} = 5 \cdot \frac{c}{c_{\mathrm{m}}} - 4 \cdot \left(\frac{c}{c_{\mathrm{m}}}\right)^{\frac{5}{4}}, \tag{8}$$

$$\frac{\kappa}{\kappa_{\mathrm{m}}} = 4 \cdot \frac{c}{c_{\mathrm{m}}} - 3 \cdot \left(\frac{c}{c_{\mathrm{m}}}\right)^{\frac{4}{3}}. \tag{9}$$

The calculation result for the salts studied for the whole concentration range is shown in Table 2.

Table 2. Parameters of equations (8) and (9), maximum specific conductivity κ_{m} (S/m) at c_{m} (mol/dm^3) at 25°C (*N* is the number of experimental points).

Salt	*N*	κ_{m} (8)	c_{m} (8)	R^2 (8)	κ_{m} (9)	c_{m} (9)	R^2 (9)
$MnSO_4$	17	5.08±0.02	1.86±0.01	0.9989	5.12±0.04	1.88±0.02	0.9970
$CoSO_4$	12	5.49±0.02	1.91±0.02	0.9998	5.50±0.02	1.87±0.02	0.9996
$NiSO_4$	14	5.45±0.02	1.93±0.02	0.9997	5.47±0.02	1.89±0.01	0.9996
$CuSO_4$	13	6.38±0.08	2.45±0.06	0.9998	6.18±0.09	2.24±0.06	0.9996
$ZnSO_4$	13	5.64±0.02	1.96±0.02	0.9997	5.66±0.02	1.93±0.02	0.9997
$CdSO_4$	16	5.12±0.01	2.04±0.01	0.9997	5.16±0.02	2.03±0.02	0.9994

For all systems, models (8) and (9) give results corresponding to the four parametric models. Comparison between each other shows that equation (8) gives the best results.

Testing of the model. An approach proposed can be applied for other systems. Table 3 presents the results of the approximation of the concentration dependence of the specific conductivity for some salts in water at 25°C [5] by means of equation (8).

Table 3. Parameters of equation (8): maximum specific conductivity κ_{m} (S/m) at c_{m} value (mol/dm^3).

Salt	c_{m}	κ_{m}	R^2	Salt	c_{m}	κ_{m}	R^2
$MgCl_2$	2.47	15.88	0.9986	$NaNO_3$	6.35	19.89	0.9997
$CaCl_2$	2.74	19.93	0.9957	NaBr	*6.96*	*27.00*	0.9964
$SrCl_2$	3.20	21.06	0.9991	KNO_3	*11.5*	*37.44*	0.9999
$BaCl_2$	*4.82*	*28.65*	0.9998	KBr	*80.1*	*255.2*	0.9999
$LaCl_3$	1.61	16.99	0.9965	$Cd(NO_3)_2$	2.08	11.26	0.9894
Na_2SO_4	2.58	13.08	0.9999				

Most systems are well described by the two-parameter equation. The value of parameters outside the experimental data (italicised in Table 3) is noteworthy. In this case, such parameters should be considered effective ones.

Temperature dependence of specific electrical conductivity. The κ_m and c_m parameters calculated by means of equation (8) for divalent metal sulphate solutions at different temperatures are given in tables 4 and 5.

Table 4. Parameters of equation (8): maximum specific conductivity κ_m (S/m) at different temperatures.

Salt	5°C	10°C	15°C	20°C	30°C	35°C
$MnSO_4$	3.12	3.59	4.08	4.57	5.59	6.10
$CoSO_4$	3.23	3.76	4.31	4.89	6.10	6.72
$NiSO_4$	3.18	3.70	4.26	4.84	6.08	6.72
$CuSO_4$	3.68	4.29	4.94	5.64	7.16	7.97
$ZnSO_4$	3.31	3.85	4.41	5.02	6.28	6.94
$CdSO_4$	3.15	3.63	4.12	4.61	5.65	6.18

Table 5. Parameters of equation (8): c_m values (mol/dm^3) at maximum specific conductivity.

Salt	5°C	10°C	15°C	20°C	30°C	35°C
$MnSO_4$	1.76	1.79	1.82	1.84	1.89	1.91
$CoSO_4$	1.75	1.80	1.84	1.88	1.95	1.98
$NiSO_4$	1.76	1.80	1.85	1.89	1.97	2.02
$CuSO_4$	2.16	2.22	2.29	2.37	2.54	2.63
$ZnSO_4$	1.78	1.83	1.88	1.91	2.00	2.05
$CdSO_4$	1.89	1.93	1.96	2.00	2.08	2.12

From the analysis of κ_m and c_m temperature dependences (as well as the functions on them), we propose the following dependences:

$$5\cdot\frac{\kappa_\mathrm{m}}{c_\mathrm{m}}(\theta) = A_{25} + a\cdot\theta \tag{10}$$

$$4\cdot\frac{\kappa_\mathrm{m}}{c_\mathrm{m}^{5/4}}(\theta) = B_{25} + b\cdot\theta \tag{11}$$

on the reduced temperature

$$\theta = T - 298.15 \tag{12}$$

where A_{25}, a, B_{25}, b are empirical coefficients.

For all systems studied, the coefficient of determination of equations (10,11) exceeds 0.9997.

It should be noted that the use of Arrhenius-type equations or other similar equations to describe the temperature dependence of κ_m parameters is not correct, since not only the temperature changes but also the composition of the system.

Combining equations (8) and (10, 11, 12), we obtain an empirical dependence of the specific conductivity on the molar concentration and temperature.

$$\kappa = (A_{25} + a\cdot\theta)\cdot c - (B_{25} + b\cdot\theta)\cdot c^{5/4} \tag{13}$$

The calculated parameters A_{25}, a, B_{25}, b for the systems studied are presented in Table 6.

Table 6. Maximum absolute deviation $\Delta\kappa$ (S/m) experimental and calculated specific electrical conductivity and parameters of the equation (13): A_{25} (S/m)·(mol/dm^3)$^{-1}$, a (S/m)·(mol/dm^3)$^{-1}$·K^{-1}, B_{25} (S/m)·(mol/dm^3)$^{-5/4}$, b (S/m)·(mol/dm^3)$^{-5/4}$·K^{-1}.

Salt	A_{25}	a	B_{25}	b	$\Delta\kappa$	R^2
$MnSO_4$	13.60±0.05	0.238±0.004	9.30±0.04	0.158±0.003	0.159	0.9989
$CoSO_4$	14.34±0.05	0.258±0.004	9.74±0.04	0.167±0.004	– 0.080	0.9997
$NiSO_4$	14.11±0.04	0.255±0.004	9.56±0.04	0.164±0.003	0.095	0.9996
$CuSO_4$	12.99±0.06	0.222±0.005	8.28±0.06	0.131±0.005	0.064	0.9998
$ZnSO_4$	14.37±0.06	0.256±0.005	9.70±0.05	0.164±0.004	0.108	0.9995
$CdSO_4$	12.54±0.03	0.208±0.003	8.38±0.03	0.132±0.002	0.074	0.9997

An example of the approximation by equation (13) is shown in Fig. 3

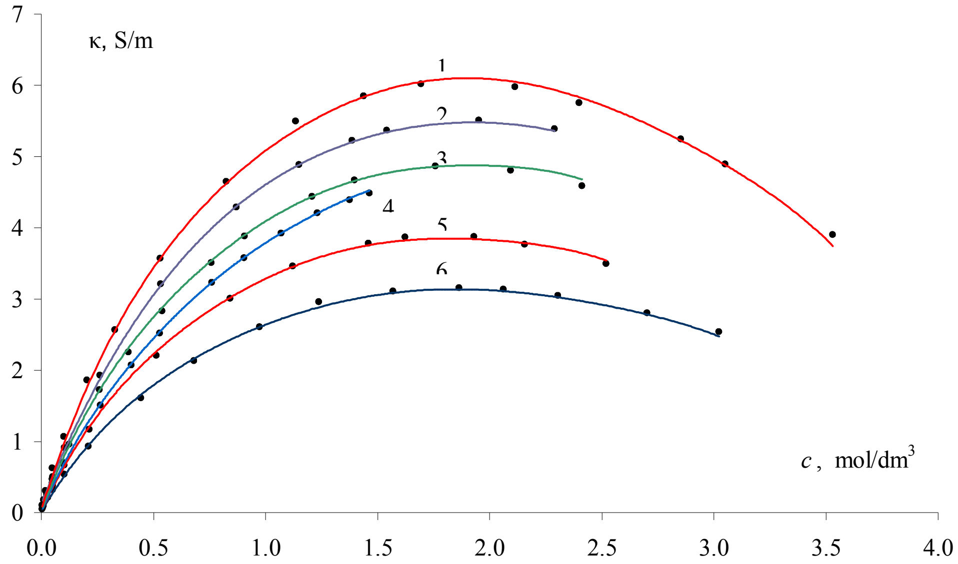

Figure. 3 The specific electrical conductivity concentration dependence for aqueous solutions: 1 – $MnSO_4$ (35°C); 2 – $CoSO_4$ (30°C); 3 – $NiSO_4$ (25°C); 4 – $CuSO_4$ (20°C); 5 – $ZnSO_4$ (15°C); 6 – $CdSO_4$ (10°C). Dots are the experimental data, while lines indicate approximation according to equation (13).

Although equation (13) describes the whole concentration range considered, it is better to use it for concentrated solutions.

Empirical equation of molar electrical conductivity of electrolyte solutions. Equation (7) can be easily linearised and takes the form of the concentration dependence of the molar conductivity at $x = 1$.

$$\frac{\kappa}{c} = \frac{y}{y-1} \cdot \frac{\kappa_\mathrm{m}}{c_\mathrm{m}} - \frac{1}{y-1} \cdot \frac{\kappa_\mathrm{m}}{c_\mathrm{m}^{y}} \cdot c^{y-1} \tag{14}$$

Equation (14) cannot adequately describe data in the whole concentration range, therefore only concentrated solutions are considered. The value of concentrations at the inflection point (Table 1) is taken conventionally as the lower limit of the region of concentrated solutions. Further calculations were performed using data for concentrations higher than c_inf.

If we consider only concentrated solutions in terms of molar conductivity, equation (14) can be written in the most general form as:

$$\Lambda = \Lambda_* - (\Lambda_* - \Lambda_\mathrm{m}) \cdot \left(\frac{c}{c_\mathrm{m}}\right)^{\frac{\Lambda_\mathrm{m}}{\Lambda_* - \Lambda_\mathrm{m}}} \tag{15}$$

where the index ‘m’ corresponds to the value at maximum specific conductivity, the asterisk indicates that this is the effective limiting conductivity. The effective limiting molar electric conductivity is a fitting parameter. The Λ_* values differ from the traditional limiting molar electric conductivity Λ_0.

By equation (15) the optimum values of parameters are calculated. For all considered systems $R^2 > 0.9995$. Figure 4 shows the temperature dependence of the effective limiting Λ_* and extreme Λ_m (according to the concentration c_m) molar conductivity. The optimum values of c_m do not differ significantly from those given above (Table 5).

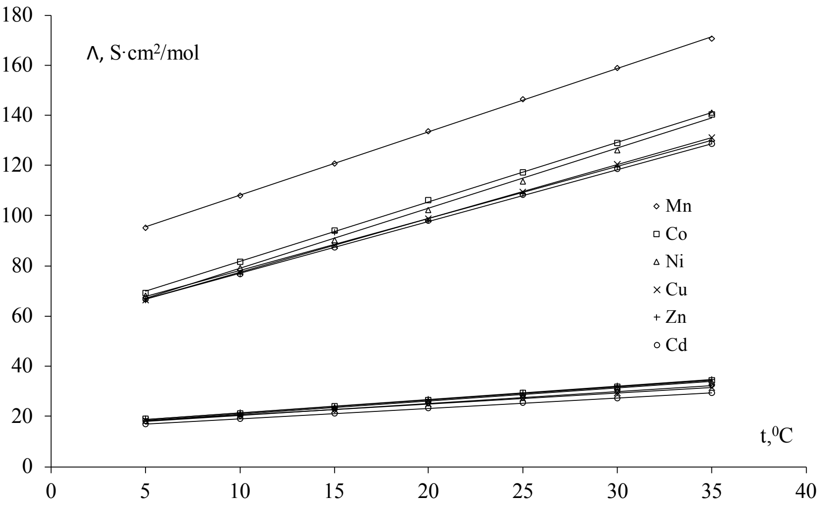

Figure 4. Temperature dependence of the effective limiting Λ_* (upper values) and extreme Λ_m (lower values) molar electrical conductivity of aqueous solutions of divalent metal sulphates.

A linear equation approximating well all the temperature dependencies considered has the form:

$$\Lambda_i = \chi_i \cdot (T - T_i) \tag{16}$$

where index i respectively '*' or 'm'. The conductivity temperature coefficient χ_i and the limiting temperature T_i are both the fitting parameters. Table 7 shows the values of parameters χ_i, T_i and functions on them. Equation (16) for the effective limiting molar electric conductivity is functionally the same as equation (10).

It is obvious that the exponent in equation (15) is a function of temperature. In the systems considered, an insignificant decrease in the exponent of equation (15) (except for $MnSO_4$) is revealed with increasing temperature. In general, for the systems studied the value of the exponent lies in the range of 0.23 – 0.39. The independence of the exponent value from the temperature is possible only if the limiting temperatures are equal ($T_* = T_m$). Table 7 presents the values of the exponent y_∞ calculated under these conditions, as the corresponding ratio of temperature coefficients and the temperature-average value of y_t. The parameter y_∞ also corresponds to the temperature limiting value of the exponent.

Table 7. Temperature coefficients of effective limiting (χ_*, $S\cdot cm^2\cdot mol^{-1}\cdot K^{-1}$) and extreme ($\chi_m$, $S\cdot cm^2\cdot mol^{-1}\cdot K^{-1}$) molar conductivity. Corresponding limiting temperatures (K). The temperature limiting value of the exponent (y_∞) and the temperature average (y_t)

Salt	χ_*	χ_m	T_*	T_m	y_∞	y_t
$MnSO_4$	2.52±0.01	0.473±0.001	240.3±0.3	240.3±0.1	0.23	0.23
$CoSO_4$	2.37±0.02	0.522±0.003	248.7±0.4	242.3±0.3	0.28	0.34
$NiSO_4$	2.40±0.05	0.513±0.004	250.2±0.9	242.2±0.4	0.27	0.34
$CuSO_4$	2.147±0.003	0.444±0.004	247.2±0.1	237.1±0.5	0.26	0.34
$ZnSO_4$	2.07±0.09	0.527±0.007	246±2	242.5±0.7	0.34	0.37
$CdSO_4$	2.07±0.01	0.415±0.002	245.9±0.2	237.3±0.3	0.25	0.31

Calculations do not give an unambiguous exponent in equations of the form (15). If we assume a close to average value of the exponent of 1/3, then equation (14) takes the form of equation (9).

Two-parameter models of specific electrical conductivity. Previously in the literature, two-parametric equations of the form (7) have been proposed. This is primarily in the work of Varela et al. [7], where a theoretical justification is given:

$$\frac{\kappa}{\kappa_m} = 2\cdot\frac{c}{c_m} - \left(\frac{c}{c_m}\right)^2 \tag{17}$$

and Gamburg's empirical equation [8]

$$\frac{\kappa}{\kappa_\mathrm{m}}=\frac{7}{3}\cdot\frac{c}{c_\mathrm{m}}-\frac{4}{3}\cdot\left(\frac{c}{c_\mathrm{m}}\right)^{7/4}. \tag{18}$$

An alternative approach, using two parameters κ_m and c_m, was proposed earlier by Shestakov et al [9]:

$$\frac{\kappa}{\kappa_\mathrm{m}}=\frac{3\cdot c/c_\mathrm{m}}{1+2\cdot\left(c/c_\mathrm{m}\right)^{3/2}}. \tag{19}$$

Gamburg [8] also proposed an equation of the form:

$$\frac{\kappa}{\kappa_\mathrm{m}}=\frac{2\cdot c/c_\mathrm{m}}{1+\left(c/c_\mathrm{m}\right)^{2}} \tag{20}$$

Artemkina and Shcherbakov [10] give a generalised equation:

$$\frac{\kappa}{\kappa_\mathrm{m}}=0.3536\cdot\left(\frac{c}{c_\mathrm{m}}\right)^{3}-1.728\cdot\left(\frac{c}{c_\mathrm{m}}\right)^{2}+2.376\cdot\frac{c}{c_\mathrm{m}} \tag{21}$$

for aqueous electrolyte solutions.

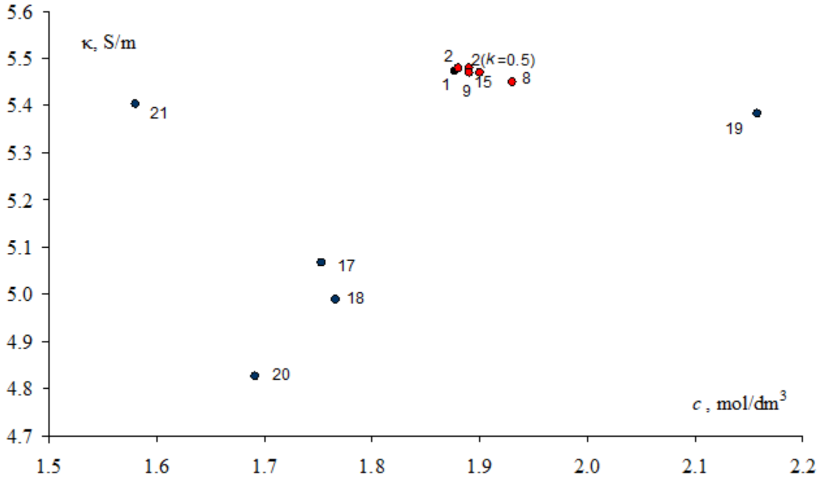

Figure 5. Maximum specific conductivity κ_m(S/m) at c_m(mol/dm^3) for $NiSO_4$ solutions at 25°C. The numbers in the figure correspond to the numbers of the equations by which the optimisation was carried out.

Figure 5 shows the optimum parameter values for all the equations considered, using $NiSO_4$ solutions at 25°C as an example. The parameters calculated by equations (17 – 21) differ considerably from each other and from Casteel-Amis equation (1). At the same time parameters by Casteel-Amis equation (1) are very close to those calculated by equations (2, 8, 9, 15) which are proposed in this work.

Thus, electrical conductivity of concentrated solutions can be characterized with practical accuracy by two parameters: κ_m and c_m.

The theoretical upper limit on the use of equations like (7) is calculated as:

$$c_\mathrm{lim}=\sqrt[y-x]{\frac{y}{x}}\cdot c_\mathrm{m}\approx 2.4\cdot c_\mathrm{m}, \tag{22}$$

but for concentrations greater than $1.5c_m$ it is not practical to use equation (7).

From the point of view of theoretical justification, equation (9) is more promising, which corresponds in form to the quasi-lattice model [11]. But this applies only to concentrated solutions.

Conclusions

New empirical equations for the concentration and temperature dependence of the specific and molar conductivity of electrolytes are proposed.

It is shown that two parameters are sufficient for the practical use of empirical equations of conductivity concentration dependence. It has been proposed to use the maximum electric conductivity and the corresponding concentration as parameters. The maximum electric conductivity and the corresponding concentration for a number of electrolyte solutions in water have been calculated. In cases where the concentration dependence of conductivity does not have a maximum, the parameters should be considered effective. For concentrated solutions, it is appropriate to use a more flexible generalized molar electric conductivity equation, where the additional parameter is the effective limiting molar electric conductivity.

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П.В. Ефимов[*], А.В. Крамаренко[†], В.А. Томак[*]. Эмпирические зависимости электрической проводимости растворов электролитов от концентрации и температуры.

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Рассмотрены концентрационные (в молярной шкале) и температурные зависимости удельной κ и молярной Λ электропроводности (ЭП) водных растворов сульфатов двухвалентных металлов (Mn, Co, Ni, Cu, Zn, Cd) в широком интервале концентраций при температуре 5 – 35°C. Предложен ряд эмпирических уравнений для исследуемых зависимостей. Модифицированное кубическое уравнение (МКУ): $\kappa = C{\cdot}c^{3k} + Q{\cdot}c^{2k} + L{\cdot}c^{k}$, где C, Q, L, k эмпирические параметры. Аналогичное уравнение с фиксированным параметром $k = ½$. Проанализирована корреляция рассчитанных параметров. Сделано предположение о достаточности двух параметров. Рассчитан максимум удельной ЭП κ_m и соответствующая концентрация c_m. Сделано допущение, что в нормированных координатах κ/κ_m от c/c_m исследуемые системы изоморфны. Проанализированы зависимости вида $\kappa = A{\cdot}c^x + B{\cdot}c^y$ для обобщенной выборки. Показано, что с хорошим приближением $x = 1$. Рассмотрены эмпирические зависимости с $y = 5/4$ и $y = 4/3$. Показано, что они дают сопоставимые результаты с МКУ. Предложенный подход протестирован на данных ЭП водных растворов ряда солей. Рассмотрены аналогичные двухпараметрические $\kappa(\kappa_m,\ c_m;\ c)$ уравнения других авторов. Проанализирована температурная зависимость функций от κ_m и c_m. Предложена зависимость удельной ЭП от температуры и концентрации $\kappa = (A_{25} + a{\cdot}\theta){\cdot}c - (B_{25} + b{\cdot}\theta){\cdot}c^{5/4}$, где θ – нормированная температура, а $A_{25},\ a,\ B_{25},\ b$ эмпирические параметры. Предложено обобщенное уравнение молярной ЭП концентрированных растворов электролитов: $\Lambda(\Lambda_*,\ \Lambda_m,\ c_m;\ c)$, где Λ_* эффективная предельная молярная ЭП, а Λ_m молярная ЭП при $c = c_m$. Обнаружено, что Λ_* и Λ_m линейно зависят от температуры. Найдено, что среднее значение показателя степени близко к 1/3, что сближает обобщенное уравнение молярной ЭП с квазирешеточной моделью растворов электролитов.

Ключевые слова: удельная электрическая проводимость, молярная электрическая проводимость, растворы электролитов, сульфаты двухвалентных металлов, эмпирические уравнения.

П.В. Єфімов[*], А.В. Крамаренко[†], В.О. Томак[*]. Емпиричні залежності електричної провідності розчинів електролітів від концентрації і температури.

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Розглянуто концентраційні (у молярній шкалі) та температурні залежності питомої κ і молярної Λ електричної провідності (ЕП) водних розчинів сульфатів двовалентних металів (Mn, Co, Ni, Cu, Zn, Cd) у широкому інтервалі концентрацій, при температурі 5 – 35°C. Запропоновано ряд емпіричних рівнянь для досліджуваних залежностей. Модифіковане кубічне рівняння (МКР): $\kappa = C{\cdot}c^{3k} + Q{\cdot}c^{2k} + L{\cdot}c^{k}$, де C, Q, L, k емпіричні параметри. Аналогічне рівняння із фіксованим параметром $k = 0.5$. Проаналізовано кореляцію розрахованих параметрів. Зроблено припущення щодо достатності двох параметрів. Розрахований максимум питомої ЕП κ_m і відповідна концентрація c_m. Зроблено припущення, що у нормованих координатах, κ/κ_m від c/c_m, досліджувані системи ізоморфні. Проаналізовано залежності виду $\kappa = A{\cdot}c^x + B{\cdot}c^y$ для узагальненої вибірки. Показано, що за достатнього наближення $x = 1$. Розглянуті емпіричні залежності з $y = 5/4$ та $y = 4/3$. Показано, що вони дають зіставні результати з МКР. Запропонований підхід протестований на даних ЕП водних розчинів низки солей. Розглянуто аналогічні двопараметричні $\kappa(\kappa_m,\ c_m;\ c)$ рівняння інших авторів. Проаналізовано також температурну залежність функцій від κ_m и c_m. Запропонована залежність питомої ЕП від температури і концентрації $\kappa = (A_{25} + a{\cdot}\theta){\cdot}c - (B_{25} + b{\cdot}\theta){\cdot}c^{5/4}$, де θ – нормована температура, а $A_{25},\ a,\ B_{25},\ b$ емпіричні параметри. Запропоновано узагальнене рівняння молярної ЕП концентрованих розчинів електролітів: $\Lambda(\Lambda_*,\ \Lambda_m,\ c_m;\ c)$, де Λ_* ефективна гранична молярна ЕП, а Λ_m молярна ЕП при $c = c_m$. Виявлено, що Λ_* и Λ_m лінійно залежать від температури. Знайдено, що середнє значення показника ступеня близьке до 1/3, що зближує узагальнене рівняння молярної ЕП з квазірешітковою моделлю розчинів електролітів.

Ключові слова: питома електрична провідність, молярна електрична провідність, розчини електролітів, сульфати двовалентних металів, емпіричне рівняння.