

CALCULATION OF THERMODYNAMIC CONDUCTANCE COEFFICIENTS BASED ON THE DEBYE-HÜCKEL-ONSAGER THEORY

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Abstract

Thermodynamic conductance coefficients were calculated for HCl, LiCl, NaCl and KCl using the relationships derived in our earlier paper based on the Debye-Hückel-Onsager theory. The data calculated for dilute solutions are in good agreement with those determined by Miller.

It has been stated in the present work that the \tilde{a} values calculated by the DHO formulas depend on the concentration.

We have shown in our previous paper [1] that the relationship derived on thermodynamic basis for ionic mobilities contains two terms. The one depends on the specific properties of the ion, while the other is the same for the cation and the anion.

The relationship derived based on the Debye-Hückel-Onsager theory is similar. The ionic mobility is given by two terms: the one depends on the properties of the ion, the other is the same for the ions of the electrolyte. The thermodynamic conductance coefficients of 1—1 electrolytes can be calculated using the following relationships (based on Eqs 14, 15 and 16 in 1).

$$\frac{L_{kk}}{c_e} = \frac{l_k^0}{F^2} \left(1 - \frac{A_1 \sqrt{c_e}}{1 + B\tilde{a}\sqrt{c_e}} \right) \quad (1)$$

$$\frac{L_{aa}}{c_e} = \frac{l_a^0}{F^2} \left(1 - \frac{A_1 \sqrt{c_e}}{1 + B\tilde{a}\sqrt{c_e}} \right) \quad (2)$$

$$\frac{L_{ka}}{c_e} = \frac{A_2 \sqrt{c_e}}{1 + B\tilde{a}\sqrt{c_e}} \quad (3)$$

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The Debye-Hückel-Onsager theory can be used first of all in the case of 1—1 electrolytes, where $z_k = z_a = 1$. For electrolytes containing ions with higher valence greater deviations from experimental values may be expected, due mainly to ion-pair formation.

In the present paper we rely on data presented by Miller [2]. Miller has calculated the three thermodynamic conductance coefficients for different concentrations from the equivalent conductance, transference number of the cation and diffusion coefficient of the electrolyte (i.e. from three independent kinetic data).

We intend to determine thermodynamic conductance coefficients

$$\left(\frac{L_{kk}}{c_e}, \frac{L_{aa}}{c_e}, \frac{L_{ka}}{c_e} \right)$$

from ionic mobilities at zero concentration (l_k^0 and l_a^0), from some constants (A_1 , A_2 and B) and from the \bar{a} values of electrolytes. \bar{a} , the sum of the ionic radii of the cation and anion was intended to be determined from the concentration dependence of the equivalent conductance which is given by the Debye-Hückel-Onsager theory as follows:

$$A = A^0 - \frac{(A_1 A^0 + 2A_2)\sqrt{c_e}}{1 + B\bar{a}\sqrt{c_e}} \quad (4)$$

In the literature there appear to be few data available for \bar{a} , as stated by Erdey-Gruz [3—4], the data being between 4.0 and 4.2 Å (400—420 pm). We have attempted to calculate the sum of ionic radii from equivalent conductances given by Miller [2], using Equation 4. According to the literature, equivalent conductance calculated by Eq. 4 agree well with experimental values up to concentrations of 0.1—0.2 mol/dm³.

From the equivalent conductance at c_e concentration (A) \bar{a} can be calculated. \bar{a} values were calculated for different concentrations using equivalent conductances presented by Miller [2]. The results obtained are shown in Fig. 1 as function of the square root of the concentration.

It has been assumed previously that \bar{a} is a constant independent of the concentration at least for dilute solutions, and it depends on concentration at values exceeding 0.1—0.2 mol/dm³. As shown by Fig. 1, the curve has a maximum between 0.1 and 0.2 mol/dm³. It should be noted, however, that the equivalent conductance can be calculated with a high accuracy using Eq. 4, irrespective of the value of \bar{a} since $B\bar{a}\sqrt{c_e}$ can be neglected beside 1. The value of \bar{a} can be reliably determined from experimental data only with some arbitrary assumptions. We have assumed that best agreement between experimental and calculated data can be achieved when the maximum value of \bar{a} is used. So, in later calculations we consider \bar{a} as a constant independent

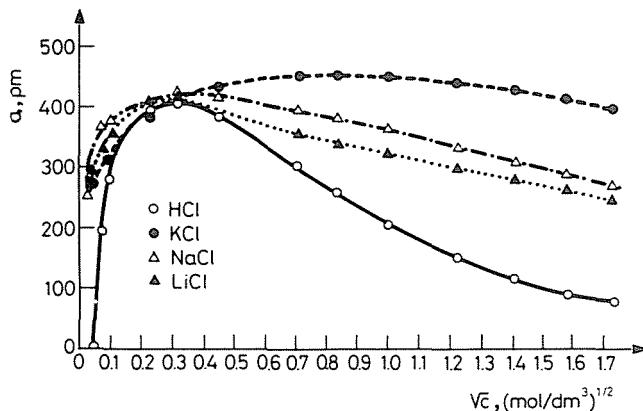


Fig. 1. \bar{a} values calculated by the DHO equation (Eq. 4) as function of the square root of the concentration (mol/dm³)

of concentration, and we use the maximum \bar{a} value for the electrolytes (see Table 1).

In Fig. 2 are shown the differences between the equivalent conductances calculated by Eq. 4 and those presented by Miller [2]. The data show that for dilute solutions the calculated and measured data agree well.

Table 1
 \bar{a} values applied in this paper

Name	Place of maximum c mol/dm ³	Maximum of \bar{a} pm
HCL	0.1	406
LiCl	0.1	414
NaCl	0.2	418
KCl	0.5	454

Based on the Debye-Hückel-Onsager equation for the ionic mobility, the difference between the ionic mobilities of the cation and the anion can be given as follows (see ref. [1], Eqs 11 and 12):

$$l_k - l_a = (l_k^0 - l_a^0) \left(1 - \frac{A_1 \sqrt{c_e}}{1 + B\bar{a}\sqrt{c_e}} \right) \tag{5}$$

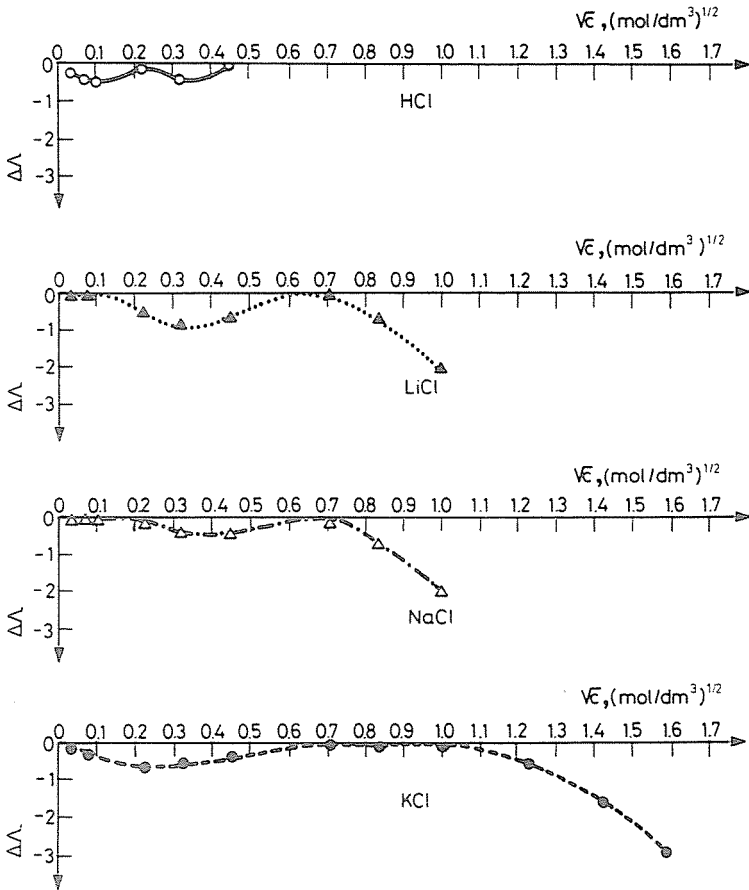


Fig. 2. Difference of the equivalent conductances presented by Miller for some electrolytes and those calculated by Eq. 4 as function of the square root of the concentration

From Eqs 11 and 12 in [1] the following relationship can also be derived:

$$l_k \cdot l_a^0 - l_a \cdot l_k^0 = (l_k^0 - l_a^0) \frac{A_2 \sqrt{c_e}}{1 + B \bar{a} \sqrt{c_e}} \quad (6)$$

\bar{a} can be calculated from Eqs 5 and 6 for different concentrations. We have first assumed that Eqs 5 and 6 provide more reliable data than Eq. 4. The data plotted against the square root of the concentration give a curve with a maximum, like those in Fig. 1. It has turned out that eventually Eqs 5 and 6 do not provide more reliable \bar{a} values than Eq. 4, so these diagrams are not included in this paper.

Next the thermodynamic conductance coefficients were calculated using Eqs 13, 14 and 15 of ref. [1], for the case $z_k = z_a = 1$

$$\frac{L_{kk}}{c_e} = \frac{l_k^0}{F^2} \left(1 - \frac{A_1 \sqrt{c_e}}{1 + B \bar{a} \sqrt{c_e}} \right) \quad (7)$$

$$\frac{L_{aa}}{c_e} = \frac{l_a^0}{F^2} \left(1 - \frac{A_1 \sqrt{c_e}}{1 + B \bar{a} \sqrt{c_e}} \right) \quad (8)$$

$$\frac{L_{ka}}{c_e} = \frac{A_2 c_e}{F^2 (1 + B \bar{a} \sqrt{c_e})} \quad (9)$$

The constants in Eqs 7, 8 and 9 calculated based on refs [2] and [3] were $A_1 = 0.229$, $A_2 = 30.17$ and $B = 0.328$.

The constants refer to concentrations in mol/dm³. If the concentration is given mol/cm³, the constants should be multiplied by $\sqrt{1000}$.

In Tables 2, 3, 4 and 5 are summarised thermodynamic conductance coefficients of aqueous HCl, LiCl, NaCl and KCl solutions calculated by Eqs 7, 8 and 9 as well as data presented by Miller [2]. The data show that there is a good agreement between our calculated data and those derived by Miller

Table 2

Thermodynamic conductance coefficients of aqueous HCl solutions as function of the concentration, calculated using Eqs. 7,8 and 9, and data given by Miller

c mol/dm ³	$\frac{L_{kk}}{c_e} \cdot 10^{12}$ (calculated)	$\frac{L_{kk}}{c_e} \cdot 10^{12}$ (according to Miller)	$\frac{L_{aa}}{c_e} \cdot 10^{12}$ (calculated)	$\frac{L_{aa}}{c_e} \cdot 10^{12}$ (according to Miller)	$\frac{L_{ka}}{c_e} \cdot 10^{12}$ (calculated)	$\frac{L_{ka}}{c_e} \cdot 10^{12}$ (according to Miller)
0	37.60	37.60	8.198	8.196	0	0
0.0001	37.52	37.51	8.180	8.182	0.032	0.033
0.0005	37.41	37.41	8.157	8.162	0.070	0.077
0.001	37.34	37.34	8.141	8.148	0.098	0.109
0.005	37.04	37.03	8.076	8.094	0.210	0.234
0.01	36.84	36.83	8.032	8.056	0.287	0.317
0.05	36.10	36.11	7.871	7.886	0.564	0.565
0.1	35.66	35.62	7.775	7.766	0.730	0.680
0.2	35.15	34.95	7.663	7.596	0.923	0.787
0.5	34.40	33.40	7.500	7.235	1.205	0.940
0.7	34.11	32.46	7.438	7.038	1.312	1.006
1.0	33.81	31.10	7.372	6.781	1.424	1.096
1.5	33.48	28.92	7.300	6.418	1.550	1.230
2.0	33.25	26.85	7.251	6.108	1.635	1.355
2.5	33.08	24.91	7.231	5.835	1.699	1.476
3.0	32.95	23.09	7.184	5.573	1.750	1.564

Table 3

Thermodynamic conductance coefficients of aqueous LiCl solutions as function of the concentration, calculated using Eqs. 7,8 and 9, and data given by Miller

c mol/dm ³	$\frac{L_{kk}}{c_e} \cdot 10^{12}$ (calculated)	$\frac{L_{kk}}{c_e} \cdot 10^{12}$ (according to Miller)	$\frac{L_{aa}}{c_e} \cdot 10^{12}$ (calculated)	$\frac{L_{aa}}{c_e} \cdot 10^{12}$ (according to Miller)	$\frac{L_{ka}}{c_e} \cdot 10^{12}$ (calculated)	$\frac{L_{ka}}{c_e} \cdot 10^{12}$ (according to Miller)
0	4.154	4.153	8.198	8.197	0	0
0.0001	4.145	4.137	8.180	8.166	0.032	0.021
0.0005	4.133	4.115	8.157	8.136	0.071	0.051
0.001	4.125	4.103	8.141	8.112	0.099	0.073
0.005	4.092	4.046	8.076	8.020	0.212	0.162
0.01	4.069	4.011	8.030	7.956	0.290	0.223
0.05	3.985	3.870	7.865	7.718	0.575	0.417
0.1	3.934	3.774	7.764	7.547	0.749	0.513
0.2	3.874	3.624	7.646	7.290	0.953	0.614
0.5	3.785	3.316	7.470	6.827	1.257	0.700
0.7	3.750	3.159	7.402	6.593	1.373	0.714
1.0	3.714	2.942	7.330	6.286	1.498	0.699
1.5	3.673	2.662	7.250	5.877	1.637	0.677
2.0	3.645	2.406	7.194	5.475	1.732	0.622
2.5	3.624	2.156	7.153	5.073	1.804	0.548
3.0	3.607	1.954	7.120	4.718	1.861	0.500

Table 4

Thermodynamic conductance coefficients of aqueous NaCl solutions as functions of the concentration, calculated using Eqs.7.8 and 9 data given by Miller

c mol/dm ³	$\frac{L_{kk}}{c_e} \cdot 10^{12}$ (calculated)	$\frac{L_{kk}}{c_e} \cdot 10^{12}$ (according to Miller)	$\frac{L_{aa}}{c_e} \cdot 10^{12}$ (calculated)	$\frac{L_{aa}}{c_e} \cdot 10^{12}$ (according to Miller)	$\frac{L_{ka}}{c_e} \cdot 10^{12}$ (calculated)	$\frac{L_{ka}}{c_e} \cdot 10^{12}$ (according to Miller)
0	5.378	5.381	8.199	8.201	0	0
0.0001	5.368	5.363	8.180	8.177	0.032	0.026
0.0005	5.353	5.341	8.158	8.146	0.070	0.058
0.001	5.342	5.325	8.142	8.123	0.098	0.081
0.005	5.300	5.263	8.077	8.036	0.210	0.170
0.01	5.270	5.219	8.032	7.974	0.287	0.233
0.05	5.167	5.065	7.874	7.742	0.561	0.440
0.1	5.104	4.971	7.779	7.601	0.725	0.544
0.2	5.032	4.851	7.669	7.435	0.915	0.682
0.5	4.927	4.613	7.509	7.121	1.911	0.840
0.7	4.887	4.484	7.448	6.950	1.295	0.882
1.0	4.846	4.311	7.385	6.772	1.405	0.911
1.5	4.799	4.053	7.314	6.370	1.526	0.923
2.0	4.768	3.812	7.266	6.035	1.609	0.911
2.5	4.744	3.581	7.230	5.708	1.671	0.884
3.0	4.726	3.366	7.201	5.393	1.720	0.858

Table 5

Thermodynamic conductance coefficients of aqueous KCl solutions as function of the concentration, calculated using Eqs. 7.8 and 9 and data given by Miller

c mol/dm ³	$\frac{L_{kk}}{c_e} \cdot 10^{12}$ (calculated)	$\frac{L_{kk}}{c_e} \cdot 10^{12}$ (according to Miller)	$\frac{L_{aa}}{c_e} \cdot 10^{12}$ (calculated)	$\frac{L_{aa}}{c_e} \cdot 10^{12}$ (according to Miller)	$\frac{L_{ka}}{c_e} \cdot 10^{12}$ (calculated)	$\frac{L_{ka}}{c_e} \cdot 10^{12}$ (according to Miller)
0	7.893	7.892	8.199	8.198	0	0
0.0001	7.876	7.872	8.181	8.186	0.032	0.026
0.0005	5.854	7.844	8.159	8.148	0.0701	0.059
0.001	7.839	7.826	8.142	8.129	0.098	0.086
0.005	7.778	7.746	8.079	8.045	0.207	0.187
0.01	7.736	7.694	8.036	7.991	0.282	0.256
0.05	7.590	7.520	7.884	7.810	0.543	0.503
0.1	7.505	7.430	7.796	7.715	0.693	0.647
0.2	<u>7.408</u>	<u>7.331</u>	<u>7.695</u>	<u>7.613</u>	<u>0.870</u>	<u>0.809</u>
0.5	7.271	7.193	7.552	7.478	1.115	1.038
0.7	7.220	7.140	7.500	7.425	1.206	1.124
1.0	7.167	7.077	7.445	7.365	1.301	1.214
1.5	7.110	6.972	7.385	7.265	1.404	1.304
2.0	7.071	6.866	7.345	7.160	1.474	1.362
2.5	7.042	6.574	7.315	7.050	1.526	1.404
3.0	7.020	6.634	7.291	6.929	1.567	1.440

from experimental results. As expected, best agreement exists for dilute solutions, and the deviations become significant at medium concentrations only. Agreement of the coefficients is considered good if the ionic mobilities calculated from the coefficients differ by less than 0.4—0.5. This is a deviation of 0.5—1.0% for $\frac{L_{kk}}{c_e}$ and $\frac{L_{aa}}{c_e}$. The ionic mobilities calculated depend even less on the value of $\frac{L_{ka}}{c_e}$, so the agreement between calculated and measured data is good even at higher relative errors.

In Tables 2—5 horizontal lines mark the limit to which the agreement is acceptable; deviations become significant at higher concentrations.

For HCl and KCl solutions the agreement is acceptable up to concentrations 0.1 to 0.5 mol/dm³, however, for LiCl and NaCl the agreement is good up to 0.01 to 0.1 mol/dm³ only.

Summing up it can be stated that Eqs 7, 8 and 9 can be used for calculating thermodynamic conductance coefficients describing isothermal transport processes of binary electrolytes. The equations that we have derived based on the Debye-Hückel-Onsager equations describe the concentration dependence of the thermodynamic conductance coefficients up to concentrations up to which the Debye-Hückel-Onsager equations are valid.

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