A Conductivity Study of Unsymmetrical 2:1 Type "Complex Ion" Electrolyte: Cadmium Chloride in Dilute Aqueous Solutions

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ABSTRACT: Systematic and precise measurements of electrical conductivities of aqueous solutions of cadmium chloride were performed in the 2×10^{-5} - 1×10^{-2} mol·dm^{-3} concentration range, from 278.15 to 313.15 K. Determined conductances were interpreted in terms of molecular model which includes a mixture of two 1:1 and 2:1 electrolytes. The molar limiting conductances of $\lambda^0(CdCl^+, T)$ and $\lambda^0(1/2Cd^{2+}, T)$, the equilibrium constants of $CdCl^+$ formation $K(T)$ and the corresponding standard thermodynamic functions were evaluated using the Quint-Viallard conductivity equations, the Debye−Hückel equations for activity coefficients and the mass-action equation. An excellent agreement between calculated and experimental conductivities was reached.
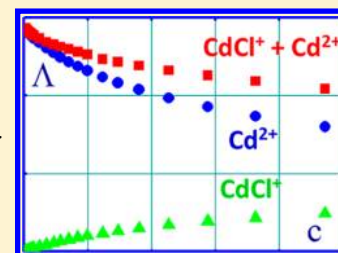
INTRODUCTION

Halides of transition-metal IIB group (Zn, Cd, and Hg), MeX$_2$, are separately treated in textbooks of electrochemistry[1−4] as the systems with "complex ions" due to the formation of series of mononuclear complexes in aqueous solutions, MeX$_n^{2−n}$, n = 1, 2, 3, and 4. Thus, the ion-pair formation is followed by further association into neutral molecules and negatively charged complex ions. Named as solutions with "complex ions", they found a special attention owing to the anomalous changes observed in colligative and dynamic properties of solutions as a function of total concentration of dissolved electrolyte (e.g., vapor pressure lowering, transference numbers, diffusion coefficients). This was clearly illustrated by difficulties to interpreted transference number determinations influenced by presence of complex and intermediate ions. Mainly in the middle of the previous century, these and other properties have been investigated by several authors using potentiometric titration, polarographic, calorimetric, solubility, liquid partition, ion-exchange, and other techniques.[5−28] Primarily, these measurements were directed to establish the distribution of metal-containing species and their corresponding formation constants. As a rule, considering the type of experimental techniques which were used, the concentrated or moderately concentrated aqueous solutions were studied, frequently with a rather large amount of added supporting electrolyte. The main conclusion reached, for example, in the case of the cadmium chloride−water system was that in very dilute solutions almost exclusively Cd^{2+} exists; that is, the electrolyte is completely dissociated. With increasing concentration, the content of the ion dipole CdCl$^+$ rises to a maximum and then decreases again and simultaneously undissociated molecules of CdCl$_2$ and negative charged complex ions CdCl$_3^-$ and CdCl$_4^{2-}$ start to appear. Besides, it should be noted that at that time, in the case of electrical conductivities, it was impossible to represent them in consistent way, because the Debye−Hückel−Onsager theory

is valid only for symmetrical electrolytes.[29−31] Only after 1978, with an appearance of the Lee−Wheaton (L-W) and the Quint−Viallard (Q-V) conductivity equations,[32−36] the conductivities of unsymmetrical electrolytes of any type can rigorously be treated. Unfortunately, the number of investigations dealing with unsymmetrical electrolytes is small and these equations continue to be rarely to be applied in the literature. Recently, Apelblat[37] discussed representation of various types of unsymmetrical electrolytes by the Q-V conductivity equation in the framework of formal association model.

As pointed out above, from the vast bulk of precise conductance investigations only small fraction has been devoted to associated unsymmetrical electrolytes, not only because the absent of suitable conductivity equations but also due to considerable mathematical difficulties arising from convergence problems in optimization procedures. From different types of unsymmetrical electrolytes, the attention was mainly directed to electrolytes of 2:1 type (alkaline earth halides). The first attempts to examine this type of electrolytes was made in pioneering works of Davies[29−31] by the modification of the Debye−Hückel−Onsager conductivity equation and before arrival of the L-W and the Q-V conductivity equations the next step was made by Fuoss and Edelson.[38] In the context of the Lee−Wheaton equation, the mathematical side of the problem was discussed by Pethybridge[39] who referred to the difficulty coming from a large number of introduced (preselected and adjustable) parameters and which is even more important that "we frequently find that a wide range of linked values of these parameters gives an equally satisfactory fit." Three groups of parameters are

involved, the closest distances of approach of ions a_i, the limiting ionic conductances and the equilibrium constants (for relations between different K_i, values see also Iwamoto et al.[40]). In the optimization procedures, the crucial part is the value of the limiting conductance of the intermediate ion $\lambda^0(MeX^+)$ which cannot be determined in an independent conductivity experiment. Historically, the ratio $r = \lambda^0(MeX^+)/\lambda^0(1/2Me^{2+})$ has been first suggested to be $r = 0.6$ by Chandler,[41] but other values from 0.5 to 0.9 were also used in the literature. Pethybridge[39] proposed the value of $r = 0.8$, "not for any theoretical reason, but rather because it seems intuitively reasonable and some of the highest precision data give a best fit in the region of this value."

There are only two conductivity studies dealing with dilute aqueous cadmium chloride solutions in the literature. They differ between them not only by a large distance of time but also by the behavior of $\Lambda(c) = f(c)$ curves (see Figure 1). The
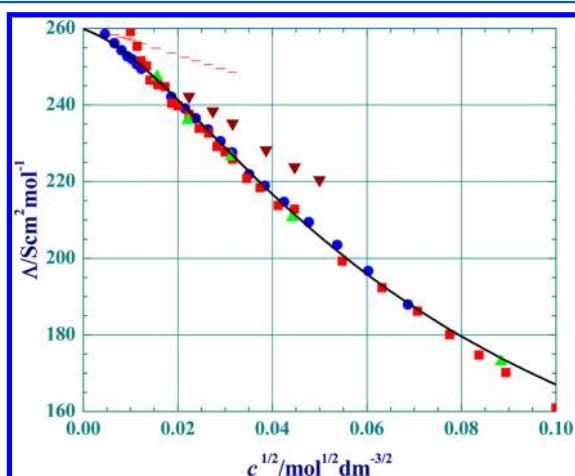

Figure 1. Experimental molar conductivities of cadmium chloride solutions at 298.15 K: (green up triangle) Jones;[42] (maroon down triangle) Fedotov;[43] (blue circle) this work set L; (red square) this work set B; (dashed red line) fully dissociated 2:1 electrolyte; (solid black line) conductivities calculated from the proposed in this work molecular model.

first set of conductances has been reported by Jones[42] in 1912 (the measurements were actually performed by A.P. West and L.G. Winston, in the 2.4×10^{-4}–0.25 mol·dm^{-3} concentration range and from 0 to 65 °C) and the second set was reported by Fedotov[43] in 1978 who determined conductivities in the 5×10^{-4}–2.5×10^{-3} mol·dm^{-3} concentration range, from 25 to 80 °C. Fedotov also, by a simple graphical extrapolation, determined values of $\lambda^0(1/2Cd^{2+})$. In both investigations, the molecular structure of solutions was ignored, thus in this "classical problem of complex ions" the speciation of aqueous solutions was never studied by electrical conductivity technique.

In order to check which set of conductances is correct, it was decided to perform new and independent measurements of cadmium chloride conductivities in dilute aqueous solutions. Measurements were carried out at two different locations using similar but not the same equipment, modern and sophisticated equipment in Ljubljana (conductivities are denoted as L-set, it covers the concentration range 2×10^{-5}–4.8×10^{-3} mol·dm^{-3} from 5 to 40 °C) and less advanced equipment in Beer Sheva (denoted as B-set, 1×10^{-4}–0.01 mol·dm^{-3} from 15 to 35 °C). Here, without going in details which will given later, it is worthwhile only to mention that both L- and B-sets of

conductivities are in an excellent agreement. They support the Jones measurements and clearly disprove the Fedotov results (Figure 1).

The analysis of determined conductances of cadmium chloride in dilute aqueous solutions permitted by using the Quint–Viallard conductivity equations to evaluate the molar limiting conductances of $\lambda^0(1/2Cd^{2+}; T)$ and $\lambda^0(CdCl^+; T)$ in the 5–40 °C temperature range. In terms of the applied molecular model, the evaluated equilibrium constants $K(T)$ served to obtain the standard thermodynamic functions of the $CdCl^+$ formation process.

■ EXPERIMENTAL SECTION

Materials. Cadmium chloride ($CdCl_2$, puriss. p.a., ≥99.0%, Fluka, Germany) was dried for 24 h at $T \approx 400$ K with a vacuum line ($p < 0.01$ Pa) and stored in a desiccator over P_2O_5 before use. Stock solution was prepared by mass from compound and demineralized distilled water.

Conductivity Measurement. Conductivity measurements in the temperature range between 288.15 and 308.15 K of aqueous solution of $CdCl_2$, from ∼1 × 10^{-4} up to ∼0.01 mol·dm^{-3} was first performed at Ben-Gurion University of Negev in Beer Sheva (B-set of data). All solutions were prepared by weight using double distilled water. Conversion from molal to molar units was performed by using densities of pure water.[2] A detailed description of the procedure and equipment has been presented elsewhere.[44]

The conductivities of the solutions at University of Ljubljana (L-set of data) in a broader temperature range (278.15–313.15 K) in diluted solutions ($0.02 \times 10^{-3} \leq c(CdCl_2)/mol·dm^{-3} \leq 4.7 \times 10^{-3}$) were determined using the system for precise measurements of electrical conductivity of solutions, described in detail.[45–47] A linear change of density with temperature, T, was observed, $d(T) = d_0(T) + bm$, where $d_0(T)$ is the density of water at given temperature, taken from the literature,[2] and m is molality of solution. From density measurements the coefficient $b = 0.159$ kg^2·dm^{-3}·mol^{-1} was determined and taken independent of temperature. Molar conductivities, $\Lambda = \kappa/c$ are given in Table 1 as a function of electrolyte molality, m, which relates to the corresponding (temperature-dependent) molar concentration $c(T)$, using the density of the solution at temperature T. Considering the sources of error (calibration, measurements, impurities), the specific conductivities are estimated to be accurate within 0.3%.

■ DATA ANALYSIS

Conductivity Equations and Chemical Equilibria. Molar conductance of electrolyte $\Lambda(c,T)$ is the sum of ionic contributions $\lambda_j(c,T)$

$$\Lambda(c, T) = \frac{1000\kappa}{c} = \sum_j \frac{|z_j|c_j\lambda_j(c, T)}{c} \tag{1}$$

where κ is the measured specific conductance in solution of formal analytical concentration c, z_j are the corresponding charges of cations, and anions and their molar concentrations are c_j. The ionic conductances $\lambda_j(c,T)$ are represented by

Table 1. Experimental Λ$_{exp}$ and Calculated Λ$_{calc}$ Molar Conductivities of Aqueous Solutions of Cadmium Chloride as a Function of Concentration c and Temperature T^a

T/K	278.15		283.15		288.15		293.15	
$m \times 10^3$	Λ$_{exp}$	Λ$_{calc}$	Λ$_{exp}$	Λ$_{calc}$	Λ$_{exp}$	Λ$_{calc}$	Λ$_{exp}$	Λ$_{calc}$
0.02100^b	157.56	156.61	180.95	179.91	205.83	204.54	231.87	230.30
0.04370	155.90	155.72	178.98	178.88	203.83	203.35	229.54	228.93
0.06604	154.80	154.98	177.90	178.02	202.39	202.36	227.84	227.79
0.08727	154.15	154.34	177.08	177.28	201.22	201.51	226.47	226.81
0.10669	153.79	153.79	176.75	176.65	200.82	200.79	225.81	225.97
0.12842	153.11	153.22	175.91	175.98	199.51	200.03	224.65	225.08
0.15054	152.38	152.66	174.72	175.34	198.57	199.29	223.46	224.23
0.23720	150.24	150.70	172.68	173.06	196.22	196.68	220.68	221.21
0.34745	148.29	148.52	170.38	170.55	193.59	193.79	217.22	217.88
0.46166	146.50	146.52	168.11	168.25	190.89	191.16	214.66	214.84
0.56935	144.77	144.82	166.33	166.29	188.94	188.91	212.21	212.25
0.70109	142.96	142.92	164.17	164.11	186.46	186.41	209.58	209.38
0.84482	141.13	141.03	162.10	161.94	184.16	183.94	206.78	206.53
0.9955	139.47	139.22	160.05	159.87	181.89	181.57	204.23	203.81
1.2387	136.96	137.08	157.33	156.87	178.49	178.14	199.00	199.88
1.4787	134.93	134.83	154.93	154.25	174.79	175.13	196.31	196.44
1.8097	131.99	132.08	151.56	151.04	171.52	171.47	192.72	192.26
2.2781	128.83	128.73	147.87	147.14	167.72	167.01	188.18	187.18
2.8946	125.08	125.03	143.49	142.83	162.73	162.10	182.76	181.59
3.6475	121.20	121.28	138.99	138.48	157.57	157.14	176.78	175.97
4.7409	116.45	116.87	133.57	133.39	151.44	151.34	169.79	169.40
σ (Λ)	0.29		0.41		0.47		0.66	

T/K	303.15		308.15		313.15	
0.02100^b	286.41	284.77	315.14	313.24	343.02	341.95
0.04370	283.76	283.00	311.80	311.27	340.97	339.78
0.06604	281.57	281.54	309.44	309.62	337.75	337.96
0.08727	279.52	280.27	307.19	308.20	336.16	336.40
0.10669	278.87	279.19	306.50	306.99	334.45	335.06
0.12842	277.56	278.05	305.33	305.71	333.54	333.65
0.15054	276.34	276.95	303.74	304.47	331.99	332.28
0.23720	272.72	273.05	300.04	300.11	327.06	327.46
0.34745	267.98	268.76	294.78	295.30	322.42	322.15
0.46166	264.49	264.85	290.92	290.93	317.97	317.32
0.56935	261.71	261.53	287.75	287.22	314.55	313.22
0.70109	258.45	257.85	284.06	283.10	310.50	308.68
0.84482	255.05	254.21	278.54	279.05	304.51	304.21
0.9955	250.32	250.74	275.15	275.18	300.73	299.95
1.2387	245.79	245.74	270.07	269.61	295.09	293.81
1.4787	242.17	241.38	265.84	264.76	290.26	288.48
1.8097	237.37	236.08	260.48	258.88	284.36	282.02
2.2781	231.16	229.68	253.80	251.78	276.68	274.23
2.8946	224.64	222.66	246.41	244.01	268.54	265.72
3.6475	217.17	215.62	238.10	236.22	258.36	257.21
4.7409	207.43	207.42	227.40	227.17	247.69	247.33
σ (Λ)	0.87		1.01		1.01	

T/K	288.15	293.15	298.15	303.15	308.15
$c \times 10^{3c}$	Λ$_{exp}$	Λ$_{exp}$	Λ$_{exp}$	Λ$_{exp}$	Λ$_{exp}$
0.09970^d	208.59	208.59	259.18	289.97	318.32
0.12961	203.94	203.94	255.29	284.36	312.45
0.14955	200.97	200.97	251.50	278.57	308.31
0.17946	198.00	198.00	250.22	277.27	304.88
0.19940	194.70	194.70	246.45	272.09	298.79
0.24925	194.15	194.15	245.23	269.56	296.20
0.29910	193.69	193.69	244.72	268.80	295.83
0.34895	191.39	191.39	240.38	266.50	292.18
0.39879	190.86	190.86	239.75	265.81	291.72
0.49848	188.92	188.92	237.52	262.95	288.72
0.59816	186.79	186.79	233.89	259.80	285.33

Table 1. continued

T/K	288.15	293.15	298.15	303.15	308.15
$c \times 10^{3c}$	Λ_{exp}	Λ_{exp}	Λ_{exp}	Λ_{exp}	Λ_{exp}
0.69785	186.12	186.12	232.68	258.88	284.17
0.79752	182.50	182.50	229.16	253.70	278.27
0.89720	181.71	181.71	227.74	252.52	276.35
0.99687	179.98	179.98	225.86	250.38	274.90
1.1962	176.22	176.22	220.79	240.74	264.64
1.3955	174.97	174.97	218.41	238.58	261.02
1.6945	171.10	171.10	213.76	236.75	260.52
1.9934	170.16	170.16	212.76	228.94	250.83
2.9895	160.24	160.24	199.27	217.20	238.52
3.9853	154.61	154.61	192.29	209.52	229.60
4.9807	148.94	148.94	186.14	204.91	221.30
5.9757	144.60	144.60	180.05	198.77	218.09
6.9704	140.44	140.44	174.70	192.55	211.53
7.9647	136.07	136.07	170.15	187.31	205.60
9.9523	131.16	131.16	160.88	177.43	194.38

[a]Units: m, mol·kg^{-1}; c, mol·dm^{-3}; Λ, $\sigma(\Lambda)$, S·cm^2·mol^{-1}. [b]L-set, conductivities from Ljubljana. [c]c are molarities at 298.15 K. [d]B-set, conductivities from Beer Sheva.

$$\lambda_j(c, T) = \lambda_j^0(T) - S_j(T)\sqrt{I} + E_j(T)I \ln I + J_{1j}(T)I \\ - J_{2j}(T)I^{3/2}$$

$$I = \frac{1}{2}\sum_j z_j^2 c_j \tag{2}$$

where the coefficients S_j, E_j, J_{1j}, and J_{2j} are complex functions of the limiting equivalent ionic conductances λ_j^0 and distance parameters a_j and physical properties of pure water (dielectric constant $D(T)$ and viscosity $\eta(T)^2$) and these coefficients are available from the Quint−Viallard theory[34−36] (for explicit expressions of these coefficients see also ref 48).

In dilute aqueous solutions of cadmium chloride, it is assumed that only Cd^{2+} and CdCl$^+$ ions exist. Thus, the following chemical equilibria represent the molecular model of the solution.

$$CdCl_2 \rightarrow Cd^{2+} + 2Cl^-$$

$$Cd^{2+} + Cl^- \overset{K}{\rightleftharpoons} CdCl^+ \tag{3}$$

and in the term of the mass action law

$$K = \frac{[CdCl^+]}{[Cd^{2+}][Cl^-]}\frac{f_{CdCl^+}}{f_{Cd^{2+}}f_{Cl^-}} \tag{4}$$

If α denotes the fraction of CdCl$^+$ ions in the solution, from charge and material balance we have

$$[CdCl^+] = c\alpha$$

$$[Cd^{2+}] = c\beta = c(1 - \alpha)$$

$$[Cl^-] = c(2 - \alpha) \tag{5}$$

Introducing eq 5 into eq 4, the solution of so-called chemical problem (evaluation of α for a given c) comes from

$$K = \frac{\alpha}{c(1-\alpha)(2-\alpha)}F(c)$$

$$F(c) = \frac{f_{CdCl^+}}{f_{Cd^{2+}}f_{Cl^-}} \tag{6}$$

This quadratic equation with respect to the fraction of CdCl$^+$ ions has the following solution

$$\alpha = \frac{\left(3 + \frac{1}{Q(c)}\right) - \sqrt{\left(3 + \frac{1}{Q(c)}\right)^2 - 8}}{2}$$

$$Q(c) = \frac{Kc}{F(c)} \tag{7}$$

The activity coefficients in the quotient $F(c)$ can be approximated in dilute solutions by the Debye−Hückel expressions

$$\log[f_j(c, T)] = -\frac{z_j^2 A(T)\sqrt{I}}{1 + a_j B(T)\sqrt{I}}$$

$$I = c(3 - 2\alpha) \tag{8}$$

where the constants $A(T)$ and $B(T)$ depend on dielectric constant of pure water

$$A(T) = \frac{1.8246 \times 10^6}{[D(T)T]^{3/2}}$$

$$B(T) = \frac{50.29 \times 10^8}{[D(T)T]^{1/2}} \tag{9}$$

The distance parameters a_j were fixed based on the Kielland[49] recommendations, and they are as follows: $a(Cd^{2+}) = 4.5$ Å, $a(CdCl^+) = 4.0$ Å, and $a(Cl^-) = 3.0$ Å. These preselected sizes of ions are assumed to be independent of temperature T.

In terms of concentration fractions α and β, the molar conductances of cadmium chloride solutions, $\Lambda(c,T)$, from eqs 1 and 5 are

$$\Lambda(c,\,T) = 2\beta\lambda_{Cd^{2+}}(c,\,T) + \alpha\lambda_{CdCl^+}(c,\,T)$$
$$+ (2 - \alpha)\lambda_{Cl^-}(c,\,T)$$

$$= \alpha[\lambda_{CdCl^+}(c,\,T) + \lambda_{Cl^-}(c,\,T)]$$
$$+ 2\beta[\lambda_{Cd^{2+}}(c,\,T) + \lambda_{Cl^-}(c,\,T)]$$

$$= \Lambda_1(c,\,T) + \Lambda_2(c,\,T) \qquad (10)$$

At each temperature T, by combining together the chemical and conductance problems, the experimental sets of conductivities can formally be written as $(\Lambda, c) = f[K, \lambda^0(1/2Cd^{2+}), \lambda^0(CdCl^+), \lambda^0(Cl^-), a_j, D, \eta; c]$ where dielectric constants and viscosities of pure water are known,[2] the distance parameters are fixed, and the molar limiting conductance of Cl^- ion are taken from the literature.[2] They can be represented as a function of temperature by the following equation

$$\lambda^0(Cl^-;\,T)/S{\cdot}cm^2{\cdot}mol^{-1}$$
$$= 40.988 + 1.2839\theta + 5.642 \times 10^{-3}\theta^2$$
$$- 1.380 \times 10^{-5}\theta^3$$
$$\theta = T/K - 273.15 \qquad (11)$$

Thus, in the optimization procedure, three adjustable parameters $K(T)$, $\lambda^0(1/2Cd^{2+},\,T)$, and $\lambda^0(CdCl^+,\,T)$ were determined to ensure the best fitting between experimental Λ_{exp} and calculated Λ_{calc} conductivities. By changing K values, the procedure included the iterative simultaneous solution of eqs 7, 8, and 10. The interactions are stopped when the average standard deviation $\sigma(\Lambda) = \sigma(\Lambda_{exp} - \Lambda_{calc})$ is minimal.

■ RESULTS AND DISCUSSION

As pointed out above, two independent sets of cadmium chloride conductivities L and B are reported in this work (Table 1). As can be seen in Figure 1, where results at 25 °C are plotted together with the literature values, both sets are in a very nice agreement but the conductivities in B-set is slightly more scattered than in L-set, especially in most diluted solutions. These conductances confirm historical measurements performed by the Jones group[42] but not those of Fedotov.[43] Considering that L-set of conductivities is more uniform and accurate than B-set, its first 14 experimental points at lowest concentrations were included in the optimization procedure. However, the determined $K(T)$, $\lambda^0(1/2Cd^{2+})$ and $\lambda^0(CdCl^+)$ served to evaluate Λ_{calc} and the average standard deviation $\sigma(\Lambda)$ for the entire L-set which includes 21 experimental conductivities at each temperature. As can be observed, the excellent fit of measured conductivities supports the applicability of a chosen molecular model, the mixture of two 1:1 and 2:1 type electrolytes ($CdCl^+ + Cl^-$ and $Cd^{2+} + 2Cl^-$). The average standard deviation $\sigma(\Lambda)$ is lower than 1 S·cm^2·mol^{-1} in the 5−40 °C temperature range and the scattering of $\Lambda_{exp} - \Lambda_{calc}$ values is nearly random. In Table 1 are given for all investigated temperatures Λ_{exp} and Λ_{calc} conductivities of L-set with an exception of 25 °C. At this temperature, a more detailed results of calculations are presented in Table 2. They include in the addition to Λ_{exp} and Λ_{calc} values, the concentration fractions of α and β of $CdCl^+$ and Cd^{2+} ions and their contributions $\Lambda_1(c)$ and $\Lambda_2(c)$ to the calculated conductances $\Lambda_{calc}(c)$ of cadmium chloride solutions. $\Lambda_2(c)$ is the predominant term and as expected, $\Lambda_1(c)$ initially is very small but its part increases rapidly with increasing of concentration c (Figure 2). In very dilute solutions, cadmium chloride is nearly fully dissociated, but already at $c \sim 0.001$

Table 2. Experimental Λ_{exp} and Calculated Λ_{calc} Molar Conductivities of Aqueous Solutions of Cadmium Chloride at 298.15 K, Concentration Fractions α and β, and the Corresponding Contributions Λ_1 and Λ_2 to the Calculated Conductance as a Function of Concentration c^a

$c \times 10^3$	α	β	Λ_1	Λ_2	Λ_{exp}	Λ_{calc}
0.02094[b]	0.0051	0.9949	0.61	256.60	257.22	258.52
0.04357	0.0105	0.9895	1.24	254.41	255.65	256.15
0.06585	0.0155	0.9845	1.84	252.51	254.35	254.27
0.08702	0.0201	0.9799	2.39	250.83	253.22	252.72
0.10638	0.0243	0.9757	2.88	249.39	252.27	251.99
0.12804	0.0288	0.9712	3.41	247.84	251.26	250.64
0.15010	0.0333	0.9667	3.94	246.34	250.28	249.44
0.23650	0.0500	0.9500	5.89	240.93	246.82	246.25
0.34643	0.0694	0.9306	8.16	234.86	243.02	242.12
0.46029	0.0878	0.9122	10.29	229.25	239.55	239.06
0.56766	0.1038	0.8962	12.14	224.45	236.60	236.51
0.69901	0.1219	0.8781	14.23	219.09	233.32	233.63
0.84231	0.1401	0.8599	16.32	213.77	230.08	230.50
0.99253	0.1578	0.8422	18.33	208.67	227.00	227.63
1.2350	0.1836	0.8164	21.25	201.28	222.54	221.95
1.4743	0.2064	0.7936	23.83	194.81	218.64	218.89
1.8043	0.2344	0.7656	26.97	186.94	213.92	214.69
2.2713	0.2687	0.7313	30.79	177.40	208.19	209.42
2.8859	0.3067	0.6933	34.98	166.92	201.90	203.44
3.6365	0.3453	0.6547	39.19	156.40	195.59	196.69
4.7264	0.3907	0.6093	44.06	144.17	188.23	187.89
$\sigma(\Lambda)$						0.75

^{a}Units: c, mol·dm^{-3}; Λ, $\sigma(\Lambda)$, S·cm^2·mol^{-1}. ^{b}L-set, conductivities from Ljubljana.
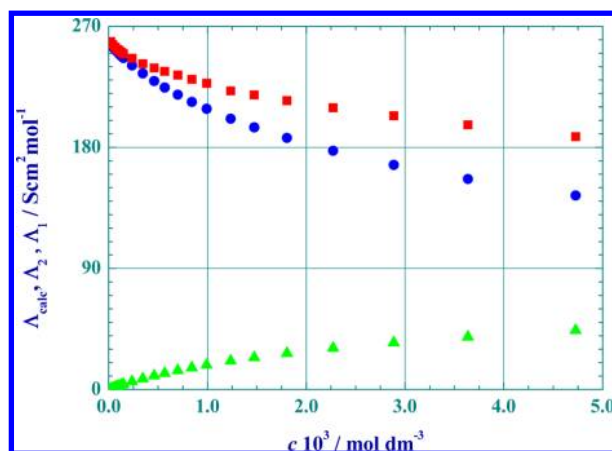

Figure 2. Contributions to calculated conductances from different cadmium ions in L-set of conductivities at 298.15 K: (red square) $\Lambda_{calc}(c)$; (green up triangle) $\Lambda_1(c)$ contribution from $CdCl^+$ ions; (blue circle) $\Lambda_2(c)$. contribution from Cd^{2+} ions.

mol·dm^{-3} nearly 20% of it is existing as $CdCl^+$ ions. This strong change in composition of cadmium chloride solutions is illustrated in Figure 3 where α and β values covering concentrations from both L- and B-sets, are plotted. It was observed in the optimization calculations that the ratio $r = \lambda^0(CdCl^+)/\lambda^0(1/2Cd^{2+})$, which gives the best fit is very close to 0.8, thus confirming the Pethybridge[39] suggestion. The only one exception was at the lowest temperature 5 °C, where r is 0.71. The Walden products weakly change with temperature and their values are $\lambda^0(CdCl^+;T)\,\eta(T) = 0.374 \pm 0.015$ S·cm^2·mol^{-1}·Pa·s, $\lambda^0(1/2Cd^{2+};T)\,\eta(T) = 0.474 \pm 0.061$
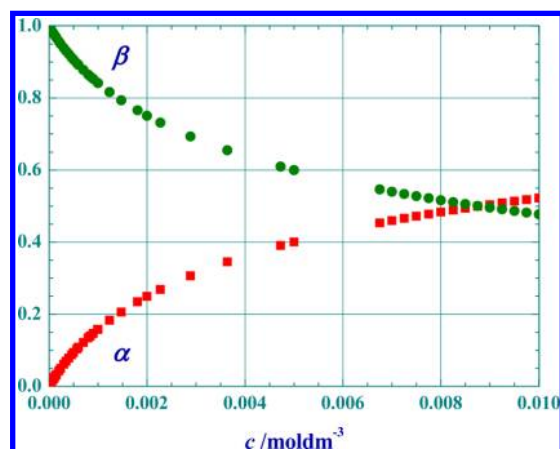
Figure 3. Concentration fractions of α(CdCl$^+$) and β(Cd^{2+}) ions in cadmium chloride solutions. L- and B-sets of conductivities at 298.15 K: (red square) α; (green circle) β.

$$\ln[\lambda^0(CdCl^+, T)\, d_0{}^{2/3}(T)] = -\frac{2226.7}{T} + 11.1966;$$
$$R^2 = 0.9812$$

$$\ln[\lambda^0(1/2Cd^{2+}, T)\, d_0{}^{2/3}(T)] = -\frac{2047.5}{T} + 10.8267;$$
$$R^2 = 0.9977$$

$$\ln[\Lambda^0(CdCl_2, T)\, d_0{}^{2/3}(T)] = -\frac{1931.2}{T} + 12.0235;$$
$$R^2 = 0.9981$$

$$(14)$$

which gives reasonable enthalpy $\Delta H_\lambda^\dagger$ values in the 16−18.5 kJ·mol^{-1} range.

Considering the molar limiting conductances of bivalent cadmium ion, its value at 25 °C as determined in this work is $\lambda^0(1/2Cd^{2+})$ = 51.56 S·cm^2·mol^{-1}. Matheson[51] measured conductivities of cadmium perchlorate and reported $\lambda^0(1/2Cd^{2+})$ = 50.0 S·cm^2·mol^{-1} by taking into account the hydrolysis and association effects. From graphical extrapolation, Fedodov[43] obtained $\lambda^0(1/2Cd^{2+})$ = 54.0 S·cm^2·mol^{-1} and the same value is given in the Millazzo book.[52] Analyzing conductivities of cadmium sulfate available in the literature, by applying the formal association model, Apelblat[53] recommended the "best" value $\lambda^0(1/2Cd^{2+})$ = 50.7 S·cm^2·mol^{-1} and suggested that all reported limiting conductances of transition-metals should be lowered at least by 1−2 S·cm^2·mol^{-1}. If all known values are taken into account, the molar limiting conductances of cadmium ion is $\lambda^0(1/2Cd^{2+})$ = 52.0 ± 1.9 S·cm^2·mol^{-1}, showing that the uncertainty continue to be too large. There is no possibility to compare the limiting conductance of CdCl$^+$ ion with those in other investigations because no attempts to obtain its value exist. Evidently, $\lambda^0(CdCl^+)$ as being the modeled quantity should only be compared within framework of the same molecular model.

The formation constants of CdX$_n^{2-n}$ n = 1, 2, 3, 4 complexes with different halides were determined in concentrated solutions by various experimental techniques and they are not always in a good agreement. This has been caused by different ionic strength of solutions, type of used supporting electrolyte,

S·cm^2·mol^{-1}·Pa·s, and $\Lambda^0(CdCl_2;T)\, \eta(T)$ = 2.324 ± 0.048 S·cm^2·mol^{-1}·Pa·s. An alternative treatment of temperature dependence of limiting conductances is based on the Eyring approach[50]

$$\left(\frac{\partial \ln[\lambda_j^0(T)\, d_0^{2/3}(T)]}{\partial T}\right)_P = \frac{\Delta H_\lambda^\dagger(T)}{RT^2}$$
$$(12)$$

where $\Delta H_\lambda^\dagger(T)$ is the partial molar enthalpy associated with the movement of ions. If it is assumed that $\Delta H_\lambda^\dagger(T)$ is independent of temperature, the integral form of eq 12 is

$$\ln[\lambda_j^0(T)\, d_0{}^{2/3}(T)] = -\frac{\Delta H_\lambda^\dagger(T)}{RT} + const$$
$$(13)$$

Using densities of pure water[2] $d_0(T)$, the limiting conductances determined in this work obey eq 13 and they can be correlated by

Table 3. Coefficients of the Quint−Viallard Conductivity Equations for $(1/2Cd^{2+} + Cl^-)$ and $(CdCl^+ + Cl^-)$ Pair Ions and the Standard Thermodynamic Function of CdCl$^+$ Formation[a]

T/K	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15
λ^0_1	22.39	29.16	33.51	38.11	41.42	47.76	52.81	57.78
λ^0_2	31.55	36.45	41.86	47.49	51.56	59.64	66.05	72.27
$\lambda^0(Cl^-)$	47.51	54.38	61.41	68.81	78.36	84.21	92.21	100.49
Λ^0	158.12	181.66	206.54	232.60	259.84	287.70	316.52	345.52
S_1	50.79	59.74	68.63	78.10	88.14	98.49	109.50	117.80
E_1	5.109	6.604	7.559	8.615	9.810	10.877	12.158	14.400
J_{11}	85.42	102.64	118.00	134.52	152.31	170.21	189.80	209.07
J_{12}	93.16	112.22	129.20	147.53	167.30	187.28	209.26	231.14
S_2	86.73	100.67	115.55	131.36	148.46	165.49	183.93	198.37
E_2	12.020	13.388	14.694	16.059	18.437	18.681	19.975	25.014
J_{21}	140.47	161.82	184.39	208.61	237.68	260.78	289.45	329.09
J_{22}	101.10	115.33	130.12	145.91	166.18	179.30	197.40	232.27
K	111.3	116.5	118.0	123.3	128.5	131.8	136.0	140.1
ΔG^0	−10.90	−11.20	−11.43	−11.74	−12.04	−12.30	−12.59	−12.87
ΔH^0	4.56	4.59	4.70	4.74	4.78	4.86	4.92	4.99
$T\Delta S^0$	15.46	15.79	16.13	16.47	16.82	17.16	17.51	17.86

[a]Units: Λ^0, λ_j^0, $S_j c^{1/2}$, $E_j c$, $J_{1j} c$, $J_{2j} c^{1/2}$, j = 1, 2, S·cm^{2}mol^{-1}, 1 = CdCl$^+$, 2 = Cd^{2+}; K mol^{-1}·dm^3; ΔG^0, ΔH^0, $T\Delta S^0$ kJ·mol^{-1}.

the formulation of molecular models, applied computational procedures and other factors. In the case of CdCl⁺ formation, the values of the equilibrium constant K lie in the 20−40 mol⁻¹·dm³ range,[9,20−22,28] but when corrected to zero ionic strength[20,29,30] its value is nearly 100 mol⁻¹·dm³ which is comparable with our results (Table 3). The equilibrium constants, $K(T)$, obtained in out work, are nearly linearly dependent on temperature

$$K(T)/\text{mol}^{-1}\cdot\text{dm}^3 = -117.6 + 0.823(T/K);$$
$$R^2 = 0.9941 \tag{15}$$

Using the equilibrium constants, the standard thermodynamic functions of CdCl⁺ formation

$$\Delta G^0(T) = \Delta H^0(T) - T\Delta S^0(T)$$

$$\Delta S^0(T) = -\left(\frac{\partial \Delta G^0(T)}{\partial T}\right)_P$$

$$\Delta G^0 = -RT \ln[K(T)] \tag{16}$$

were evaluated from

$$\Delta G^0(T)/\text{kJ}\cdot\text{mol}^{-1}$$
$$= -10.624 - 5.536 \times 10^{-2}(T/K)$$
$$- 2.091 \times 10^{-5}(T/K)^2 \tag{17}$$

and they are presented in Table 3 and plotted in Figure 4. As can be observed, in the process of CdCl⁺ ion formation,
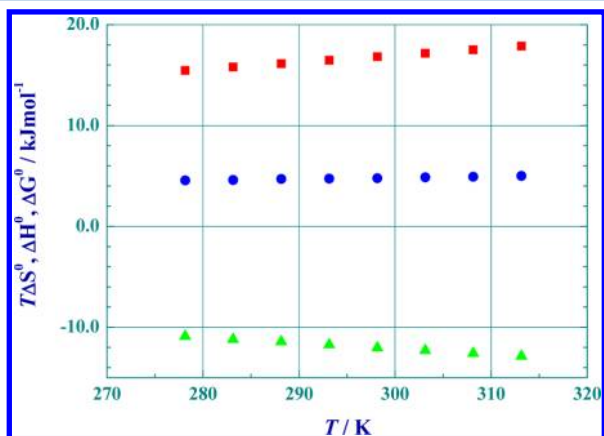

Figure 4. Standard thermodynamic function of CdCl⁺ formation. L-set of conductivitie: . (red square) $T\Delta S^0(T)$; (blue circle) $\Delta H^0(T)$; (green up triangle) $\Delta G^0(T)$.

$\Delta G^0(T) < 0$, $\Delta H^0(T) > 0$, and $T\Delta S^0(T)$, but $T\Delta S^0(T) > |\Delta G^0(T)| > \Delta H^0(T)$, thus making the entropic term dominant in the entropy−enthalpy balance. The change of thermodynamic functions with temperature is small.

CONCLUSIONS

Precise and systematic determinations of conductivities in dilute aqueous solutions of cadmium chloride were performed over a wide temperature range. Measured conductances clearly indicated a considerable deviation from fully dissociated 2:1 type unsymmetrical electrolyte. Thus, following an idea of stepwise formation of complex ions which comes from many investigations for similar systems in the literature, it was

proposed to treat dilute solutions of cadmium chloride as a mixture of two 1:1 and 2:1 type electrolytes (CdCl⁺ + Cl⁻ and Cd²⁺ + 2Cl⁻). Using the Quint−Viallard conductivity equations for representation of conductances, the Debye−Hückel equations for activity coefficients, and the mass-action equation for the formation of CdCl⁺ ions, in a suitable optimization procedure, the conductances were calculated and compared with the measured values. An excellent agreement between them was observed, and this supports the choice of molecular model. Based on this, it was possible to evaluate the molar limiting conductances of ions, the equilibrium constants, and the standard thermodynamic function of the formation process.

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Notes
The authors declare no competing financial interest.

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