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Thermodynamics of the Cell: $Cd(Hg)_{satd.}|CdCl_2(m)|AgCl|Ag$ in (10, 30 and 50 Mass per Cent) 2-Propanol-Water Mixtures

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The e.m.f. of the cell: $Cd(Hg)_{satd.}|CdCl_2(m)|AgCl|Ag$ in 2-propanol-water mixtures (containing 10, 30 and 50 mass per cent 2-propanol) was measured in the temperature range 293.15 K ··· 313.15 K at 5 K intervals and in the range of molality of $CdCl_2$ $0.002 \le m/\text{mol kg}^{-1} \le 0.02$. The measured values were processed in order to obtain the standard e.m.f. of the cell for each temperature by (a) using the literature values for the stability constants of all Cd chlorido complexes and (b) assuming that only the $CdCl^+$ complex was present in the solution. The values obtained by both methods were compared and discussed. The values obtained by the first method were used to calculate the standard thermodynamic quantities for the cell reaction and the mean activity coefficients of $CdCl_2$. The standard thermodynamic quantities for $CdCl_2$ transfer from water to the investigated 2-propanol-water mixtures were also calculated. These values were compared with those obtained for the transfer of electrolytes HCl, HBr and HI to the same mixtures.

INTRODUCTION

The e.m.f. of the cell: $CdCl(Hg)_{satd.}|CdCl_2(m)|AgCl|Ag$ was investigated in aqueous solution,[1–3] then in ethanol and in ethanol-water,[3] in methanol and in methanol-water,[4] while Feakins *et al.* carried out investigations in aqueous solution and in methanol-water using unsaturated Cd-amalgam electrode. In all these works, data processing was carried out to obtain the standard e.m.f. of the cell on the assumption that only the $CdCl^+$ complex was present in the solution.

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In our work,[6] we also studied the e.m.f. of the above cell with saturated Cd-amalgam electrode in aqueous solution, but in data processing we used the values from the literature for the stability constants of all Cd-chloride complexes.[7] The data processed up to the measured molality of $CdCl_2$ $m = 0.02$ mol kg^{-1} confirmed that, the obtained standard e.m.f. values agreed well with those of other authors. However, up to this molality in aqueous solution, only 5.4 moles per cent[6] of other higher Cd-complexes were present. On the other hand, in mixed solvents, where the dielectric constant is lower, even in the range of this molality, we can expect the amount of other Cd-complexes to be larger in the solution. Therefore, it can be assumed that in data processing, it is necessary to take into account the presence of all Cd-chloride complexes.

For this reason, in processing the data for e.m.f. of the above cell in (10, 30 and 50 mass per cent) 2-propanol-water mixtures, in this work, we applied both methods in order to obtain the standard e.m.f. Based on the first method,[6] all the complexes present in the solution were taken into account, using literature data for their stability constants,[8] while with the second method[5] it was assumed that only the $CdCl^+$ complex existed in the solution. The analysis of the obtained results made it possible to establish whether the first method would be applied in dealing with the investigated mixed solvents.

The standard e.m.f. values were then used to determine the standard thermodynamic quantities for the cell reaction and in the process of transferring $CdCl_2$ from water into the mixed solvents, as well as for calculating stoichiometric activity coefficients.

The actual e.m.f. measurements were worked out in the temperature range from 293.15 to 313.15 K at 5 K intervals, at the molalities of $CdCl_2$ from 0.002 to 0.02 mol kg^{-1}.

EXPERIMENTAL

The solutions were prepared by weighing an aqueous stock solution containing 0.025 mol kg^{-1} of $CdCl_2$, redistilled water and 2-propanol, distilled before use. $CdCl_2$ and 2-propanol were *p.a.* purity (»Kemika«). The molality of the cadmium chloride in all the solutions reported was accurate to within ±0.02 per cent.

The saturated Cd(Hg) and AgCl/Ag electrode, the cell and the equipment for measuring the e.m.f., as well as the measuring method, have been described earlier.[6]

The average deviation of each measurement from their mean values (obtained as before[6]) was ±0.05 mV for 30 mass per cent of 2-propanol, and ±0.06 mV for 10 and 50 mass percent.

RESULTS AND DISCUSSION

The mean values for e.m.f. for each molality of $CdCl_2$ in mixed solvents are presented in Table I.

The values from Table I were used to determine the standard e.m.f. (E°_m) of the cell using the equation:[6]

$$\begin{aligned} E' &= E + (RT/2F)\ln\,[(m(\mathrm{Cd}^{2+})/(m^\circ)(m(\mathrm{Cl}^-)/m^\circ)^2] - \\ &- (3RT/F)AI^{1/2}/(1 + BaI^{1/2}) - (3RT/2F)\,\ln[1 + M\sum_{\mathrm{X}} m(\mathrm{X})] = \qquad (1) \\ &= E^\circ_m - (3RT/2F)C(I/m^\circ) \end{aligned}$$

TABLE I

Electromotive force E *of the cell:* $Cd(Hg)_{satd.}/CdCl_2(m)$ *in 2-propanol-water* $/AgCl/Ag$ *from 293.15 to 313.15 K;* w *is the mass per cent of 2-propanol in the mixed solvent*

T/K	293.15	298.15	303.15	308.15	313.15
m/(mol kg^{-1})			E/V		
			w = 10%		
0.00200	0.79133	0.79375	0.79579	0.79788	0.79987
0.00300	0.77896	0.78104	0.78308	0.78494	0.78666
0.00400	0.77058	0.77245	0.77438	0.77614	0.77784
0.00501	0.76413	0.76594	0.76781	0.76937	0.77091
0.00601	0.75895	0.76076	0.76258	0.76427	0.76574
0.00701	0.75484	0.75658	0.75828	0.75980	0.76126
0.00801	0.75140	0.75309	0.75465	0.75611	0.75746
0.01001	0.74524	0.74680	0.74832	0.74981	0.75110
0.01502	0.73474	0.73623	0.73767	0.73897	0.74012
0.02002	0.72785	0.72924	0.73043	0.73147	0.73248
			w = 30%		
0.00200	0.76284	0.76538	0.76773	0.76978	0.77163
0.00300	0.75161	0.75411	0.75629	0.75818	0.76002
0.00400	0.74424	0.74666	0.74853	0.75030	0.75204
0.00500	0.73903	0.74128	0.74325	0.74502	0.74676
0.00600	0.73467	0.73672	0.73873	0.74045	0.74193
0.00700	0.73098	0.73288	0.73482	0.73653	0.73802
0.00800	0.72754	0.72952	0.73140	0.73315	0.73467
0.01000	0.72237	0.72430	0.72602	0.72762	0.72905
0.01500	0.71283	0.71463	0.71628	0.71772	0.71905
0.01860	0.70732	0.70909	0.71072	0.71213	0.71905
					0.71343
			w = 50%		
0.00233	0.73525	0.73696	0.73847	0.73989	0.74122
0.00372	0.72400	0.72583	0.72729	0.72862	0.72975
0.00465	0.71883	0.72050	0.72182	0.72308	0.72421
0.00558	0.71481	0.71630	0.71775	0.71894	0.71994
0.00651	0.71128	0.71277	0.71410	0.71522	0.71625
0.00744	0.70839	0.70996	0.71121	0.71231	0.71333
0.00930	0.70355	0.70502	0.70632	0.70740	0.70844
0.01395	0.69484	0.69629	0.69748	0.69858	0.69958
0.01860	0.68913	0.69061	0.69170	0.69272	0.69365
0.02044	0.68735	0.68873	0.68997	0.69113	0.69208

In the above equation, E is the e.m.f. of the cell for each molality of $CdCl_2$, m(X) denotes the molality of ion X, m^o = 1 mol kg^{-1}, A and B are Debye-Hückel parameters (dielectric constants required for their calculation were taken from Åkerlöf[9]), I is the ionic strength of the solution, a is the ion-size parameter (taken to be 0.45 nm), M is the molar mass of the solvent, $\sum_{X} m(X)$ is the total molality of each ionic species, and C is an empirical parameter.

To calculate $m(Cd^{2+})$ and $m(Cl^-)$ from the molality m of $CdCl_2$ data were taken from the literature for the stability constants at zero ionic strength (K_n^o)[8] for reactions:

$$Cd^{2+} + nCl^- = CdCl_n^{(2-n)+}, \quad (n = 1, 2, 3 \text{ and } 4), \tag{2}$$

These constants are related to the concentration constants (K_n') according to the expression

$$K_n^o = K_n'[\gamma(\mathrm{CdCl}_n^{(2-n)+})]/\{[\gamma(\mathrm{Cd}^{2+})][\gamma(\mathrm{Cl}^-)]^n\}, \tag{3}$$

where γ is the activity coefficient of each ion X, and K_n' values are given by

$$K_n' = (c(\mathrm{CdCl}_n^{(2-n)+})/c^o)/[(c(\mathrm{Cd}^{2+})/c^o)(c(\mathrm{Cl}^-)/c^o)^n], \tag{4}$$

where $c(\mathrm{X})$ is the concentration of ion X, and c^o is 1 mol dm^{-3}. These constants vary with the ionic strength of the solution. Taking into account the Debye-Hückel expression for activity coefficients of each ion and using equation (3), the following dependence on ionic strength is obtained

$$\ln K_n' = \ln K_n^o + \Delta z^2 A I^{1/2}/(1 + BaI^{1/2}) + (\ln 10)\Delta C_n I/c^o, \tag{5}$$

where $\Delta z^2 = z^2(\mathrm{CdCl}_n^{(2-n)+} - z^2(\mathrm{Cd}^{2+}) - \mathrm{n}z^2(\mathrm{Cl}^-)$, and $-\Delta C_n = C(\mathrm{CdCl}_n^{(2-n)+}) - C(\mathrm{Cd}^{2+}) - \mathrm{n}C(\mathrm{Cl}^-)$. In these expressions, z and C are the charge and empirical constants for each ion, while other symbols have already been mentioned. The values for ΔC_n are also from reference 8.

The values for K_n^o and ΔC_n at 298.15 and 313.15 K were taken directly from reference 8, while at other temperatures the stability constants were obtained from the plot $\ln K_n^o$ against $1/T$, and ΔC_n by interpolation.

Calculation was carried out in the following way: for each molality of $\mathrm{CdCl_2}$, first the ionic strength of the solution was calculated using the analytical concentrations of Cd^{2+} and Cl^- ions ($I_{\mathrm{initial}} = 3md$, where d is the solvent density taken from literature[10,11]). Then, K_n' were calculated using equation (5). From these K_n' values, the concentration of free chloride ions was computed by applying the polynomial (6), which was obtained by combining the equation for the balance of Cd^{2+} and Cl^- ions [reference 6: eq. (8) and (9) enlarged by the corresponding expression for K_4'. At 10 mass per cent 2-propanol, K_4' was omitted]. From this value, the concentration of Cd^{2+} ion from the expression for the balance of Cd^{2+} ion [reference 6: eq. (8)] was then calculated, as well as the concentrations of complex ions by means of expression (4). The obtained values made it possible to calculate a new value for the ionic strength of the solution, and then new K_n' values. The treatment was repeated until constant values for K_n' were obtained.

$$K_4'\, c_{\mathrm{Cl}^-}^5 + (2K_4'\, md + K_3')c_{\mathrm{Cl}^-}^4 + (K_3'\, md + K_2')c_{\mathrm{Cl}^-}^3 + \\ K_1'\, c_{\mathrm{Cl}^-}^2 + (1 - K_1'\, md)c_{\mathrm{Cl}^-} - 2md = 0 \tag{6}$$

The polynomial (6) was calculated using the IBM 4143 computer (with ROOTCP subroutine added), the number of iterations depending on the dielectric constant (D) of the solvents and the molality of $\mathrm{CdCl_2}$. Four to five iterations were sufficient for the solvents with higher D at lower molalities; at higher ones 5–6 were required, while at lower D the number of iterations increased to 7–8.

The finally obtained equilibrium concentrations of all ionic species are expressed as molalities and using equation (1) the values for E' are calculated; then, the E_m^o value of the cell and its deviation are obtained by the least-squares method. The data are quoted in Table II. The table also contains the values for E°_m for the aqueous solution obtained from the values for E from reference 6 and constants (K°_n) from reference 8.

The E°_m values from Table II can be expressed in dependence on temperature in the range from 293.15 to 313.15 K by the following relations:

$$E^\circ_m(\mathrm{w}=0)/\mathrm{V} = 0.63577 - 1.30 \times 10^{-5}\ T/\mathrm{K} - 65.71 \times 10^{-8}\ T^2/\mathrm{K}^2, \qquad (7)$$

$$E^\circ_m(\mathrm{w}=10)/\mathrm{V} = 0.33403 + 189.21 \times 10^{-5}\ T/\mathrm{K} - 382.86 \times 10^{-8}\ T^2/\mathrm{K}^2, \qquad (8)$$

$$E^\circ_m(\mathrm{w}=30)/\mathrm{V} = 0.53945 + 30.78 \times 10^{-5}\ T/\mathrm{K} - 125.71 \times 10^{-8}\ T^2/\mathrm{K}^2, \qquad (9)$$

$$E^\circ_m(\mathrm{w}=50)/\mathrm{V} = -\,0.15830 + 500.87 \times 10^{-5}\ T/\mathrm{K} - 965.71 \times 10^{-8}\ T^2/\mathrm{K}^2. \qquad (10)$$

Data processing for the e.m.f. of the cell was also carried out according to the method by Feakins *et al.*,[5] assuming that only the $CdCl^+$ complex existed, and using the equation:

$$\begin{aligned} E' &= E + (RT/2F)\ln\alpha + (RT/\mathrm{F})\ln(1+\alpha) + (3RT/2F)\ln(m/m^\circ) - \\ &- (3RT/2F)AI^{1/2}/(1 + BaI^{1/2}) = E^\circ_m = (3RT/2F)\ b_2(I/m^\circ), \end{aligned} \qquad (11)$$

where α is the dissociation degree of $CdCl^+$, m is the molality of $CdCl_2$, b_2 is an empirical parameter, while other symbols have already been mentioned.

The dissociation degree, α, for each molality is obtained by the following equation:

$$\begin{aligned} &\lg[K_d(1-\alpha)/\alpha(m/m^\circ)(1+\alpha)] + \\ &+ 4A[(m/m^\circ)(1+2\alpha)]^{1/2}/\{1 + Ba[(m/m^\circ)(1+2\alpha)]^{1/2}\} - \\ &- b_1[(m/m^\circ)(1+2\alpha)] = 0, \end{aligned} \qquad (12)$$

where K_d is the dissociation constant of $CdCl^+$ and b_1 is an empirical parameter. This equation was obtained by combining the expression for dissociation constant [reference 5: eq. (2)] and the expression for the relation of activity coefficients [reference 5:

TABLE II

Standard e.m.f. of the cell: $Cd(Hg)_{\mathrm{satd.}}$ /$CdCl_2$ (m) in 2-propanol-water /AgCl /Ag from 293.15 to 313.15 K; w is the mass per cent 2-propanol in the mixed solvent

T/K	E°_m/V	$s(E^\circ_m)$/mV	E°_m/V	$s(E^\circ_m)$/mV	E°_m/V	$s(E^\circ_m)$/mV	E°_m/V	$s(E^\circ_m)$/mV
	w = 0[a]		w = 10%		w = 30%		w = 50%	
293.15	0.57550	0.06	0.55962	0.10	0.52177	0.23	0.47984	0.11
298.15	0.57346	0.08	0.55796	0.11	0.51915	0.17	0.47728	0.10
303.15	0.57150	0.07	0.55566	0.09	0.51747	0.20	0.47217	0.11
308.15	0.56933	0.09	0.55352	0.09	0.51493	0.22	0.46804	0.13
313.15	0.56728	0.14	0.55111	0.11	0.51252	0.22	0.46330	0.13

[a] Calculated from E values in reference 6, and constants K°_n in reference 8.

eq. (5)] with the ionic strength expressed by means of the dissociation degree [$I = (m/m^o)(1+2\alpha)$].

E_m^o was determined in the following way: for an assumed value of K_d and b_1 for each molality α is calculated by using equation (12) and from this value the ionic strength is obtained. These values for the measured molalities and the corresponding E make it possible to calculate E' by using equation (11), after which E_m^o and b_2 are obtained by the least-squares method. This treatment is repeated by means of the computer for different values of K_d and b_1 (the Newton-Raphson method of iteration) until E_m^o value is obtained for which function E' has the lowest standard deviation in relation to I.

This treatment was successfully applied to aqueous solution (values for E from reference 6) and 10 mass per cent 2-propanol; certain difficulties appeared at 30 mass per cent, while for 50 mass per cent calculation was possible only when a considerable number of the measured E values were discarded. Therefore, Table III gives data only for 0, 10 and 30 mass per cent 2-propanol. With these solvents, however, it was found that, for each K_d, it was sufficient to change b_1 in the interval from –2.0 to 2.0; the influence of b_1 on E_m^o was negligible, in contrast to the influence of even very small changes in K_d. This table shows data for stability constants K_1^o (= K_d^{-1}) and E_m^o at b_1 –2.0 and 2.0 with an average standard deviation for aqueous solution of 0.13 mV, for 10 mass per cent of 2-propanol 0.12 mV, and for 30 mass per cent 0.24 mV.

TABLE III

The results of processing the e.m.f. of the cell: $Cd(Hg)_{satd.}/CdCl_2(m)$ *in 2-propanol-water /AgCl /Ag at different temperatures by means of the Feakings* et al.[5] *method;* w *is the mass per cent 2-propanol in the mixed solvent*

T/K	b_1	w = 0[a]		w = 10%		w = 30%	
		K_1^o (= K_d^{-1})	E_m^o/V	K_1^o (= K_d^{-1})	E_m^o/V	K_1^o (= K_d^{-1})	E_m^o/V
293.15	–2.0	87.5	0.57579	111.9	0.56060	775	0.51665
	2.0	88.6	0.57576	112.9	0.56058	787	0.51650
298.15	–2.0	89.8	0.57398	105.5	0.55917	730	0.51560
	2.0	90.8	0.57395	106.6	0.55913	735	0.51554
303.15	–2.0	89.4	0.57207	119.3	0.55678	741	0.51351
	2.0	90.5	0.57204	120.5	0.55675	752	0.51337
308.15	–2.0	92.6	0.56994	126.1	0.55458	833	0.51008
	2.0	93.5	0.56990	127.2	0.55455	847	0.50991
313.15	–2.0	99.7	0.56745	129.0	0.55243	909	0.50678
	2.0	100.9	0.56741	130.2	0.55239	917	0.50669

[a] Calculated from E values in reference 6.

From the above data it can be seen that the values for E_m^o from Table II, in relation to the mean values from Table III, in aqueous solution are about 0.5 mV lower, in 10 mass per cent 2-propanol about 1 mV, while in 30 mass per cent they are about 5 mV higher. Thus, as the content of 2-propanol in the solvent is increased, *i.e.* as the amount of the higher complexes of $CdCl^+$ is increased, the deviations are also increased. Namely, it is seen from Table IV, obtained by using K_n^o values from reference

TABLE IV

Mole fraction x_i of species in 2-propanol-water of $CdCl_2$ of different molalities m *at 298.15 K calculated from* K_n^o *values in reference 8;* w *is the mass per cent 2-propanol in the mixed solvent*

m/mol kg^{-1}	$10^2 x_i$				
	Cd^{2+}	$CdCl^+$	$CdCl_2$	$CdCl_3^-$	$CdCl_4^{2-}$
			$w = 0$		
0.002	78.5	21.3	0.2	–	–
0.02	39.7	56.6	3.6	0.09	–
			$w = 10\%$		
0.002	74.3	25.3	0.4	–	–
0.02	35.1	59.4	5.3	0.16	–
			$w = 30\%$		
0.002	49.7	49.2	1.2	0.01	–
0.02	16.8	72.9	9.8	0.43	0.01
			$w = 50\%$		
0.002	24.5	71.0	4.5	0.01	–
0.02	6.7	70.2	22.7	0.40	0.03

8, that at $m = 0.02$ mol kg^{-1} $CdCl_2$, the content of higher Cd-chloride complexes of $CdCl^+$ are in the 3.7 moles per cent interval in aqueous solution, up to 23.1 moles per cent in 50 mass per cent 2-propanol solution. It can, therefore, be concluded, with regard to the investigated 2-propanol-water mixtures, that in data processing of the e.m.f. of the cell it is necessary to use the method which takes into account all Cd-chloride complexes.

The standard e.m.f. of the cell and its temperature coefficient (dE_m^o/dT) derived from equations (7) – (10) were used to determine the thermodynamic quantities (ΔG^o, ΔH^o and ΔS^o) by usual relations for cell reaction:

$$Cd(s) + 2\,AgCl(s) = 2\,Ag(s) + (Cd^{2+} + 2\,Cl^-) \qquad (13)$$

The data for 298.15 K are in Table V. The uncertainties were calculated from standard errors in E_m^o.

TABLE V

Standard thermodynamic quantities for the cell reaction (13) at 298.15 K; w *is the mass per cent 2-propanol in the mixed solvent*

w	ΔG^o/kJ mol^{-1}	ΔH^o/kJ mol^{-1}	ΔS^o/J K^{-1} mol^{-1}
0	–110.66 ± 0.02	–133.95 ± 0.07	–78.1 ± 0.2
10%	–107.67 ± 0.02	–130.15 ± 0.09	–75.4 ± 0.2
30%	–100.18 ± 0.04	–125.61 ± 0.18	–85.3 ± 0.5
50%	–92.10 ± 0.02	–135.24 ± 0.05	–144.7 ± 0.1

It can be seen from the table that the reaction spontaneity (ΔG^{o}) decreases continuously with an increase of the 2-propanol content in a mixed solvent, which is conditioned by the decrease of its dielectric constant. At ΔH^{o}, however, a certain discontinuity is observed; namely, the reaction exothermity decreases up to 30 mass per cent 2-propanol, after which it is increased. Finally, ΔS^{o} starting from 10 mass per cent of 2-propanol decreases progressively with an increase of its content in the solvent.

The stoichiometric activity coefficient $\gamma_{\pm}$ of cadmium chloride for each molality m can be calculated according to the Nernst equation

$$E = E_m^{o} = (RT/2F)\ln\{4[(m/m^{o})\gamma_{\pm}]^{3}\}. \qquad (14)$$

for the cell reaction (13) provided that Cd-complexes do not occur in the solution. The values of E for round molalities were calculated from the straight line equation which was obtained by the least-squares method from a plot of E (Table I) against $\lg(m/m^{o})$, while E_m^{o} was taken from Table II. Data for 298.15 K are in Table VI.

TABLE VI

Mean activity coefficients $\gamma_{\pm}$ of $CdCl_2$ in 2-propanol-water containing w *mass per cent of 2-propanol at 298.15 K*

m/mol kg^{-1}	0.002	0.005	0.007	0.01	0.015	0.02
w = 0^{a}	0.762	0.603	0.553	0.505	0.455	0.423
w = 10%	0.721	0.560	0.511	0.463	0.414	0.383
w = 30%	0.542	0.393	0.349	0.307	0.266	0.241
w = 50%	0.350	0.237	0.205	0.176	0.148	0.131

[a] Calculated from E values in reference 6.

The data from the table show that the activity coefficients decrease in each solvent with an increase of $CdCl_2$ molality, and for each molality with an increase of the 2-propanol content in the solvent, namely, with decreasing dielectric constant, which is in agreement with the Debye-Hückel theory.

However, the stoichiometric activity coefficients are involved here, as seen from Figure 1 where the dependencies of the $\lg \gamma_{\pm}$ on the ionic strength of the solution for $CdCl_2$ and $ZnCl_2$[12] are shown, that is, for the same electrolyte type, in aqueous solution and in 50 mass per cent 2-propanol together with the Debye-Hückel limiting law. Namely, $ZnCl_2$, which does not form complexes, behaves in the usual way, *i.e.* in agreement with the limiting law at a lower ionic strength, while at higher ones greater positive deviations occur the lower is the dielectric constant. On the other hand, with $CdCl_2$, the values at lower ionic strengths are considerably smaller than those expected according to the limiting law; after that, this negative deviation increases in proportion to the decrease in the dielectric constant of the solvent. Obviously, the reason for this behaviour is the greater degree of complexity both with the increasing concentration and with the decreasing dielectric constant (Table IV).

Finally, the standard thermodynamic quantities for $CdCl_2$ transfer from water to 2-propanol-water were calculated. The standard Gibbs energy of transfer is obtained by the equation

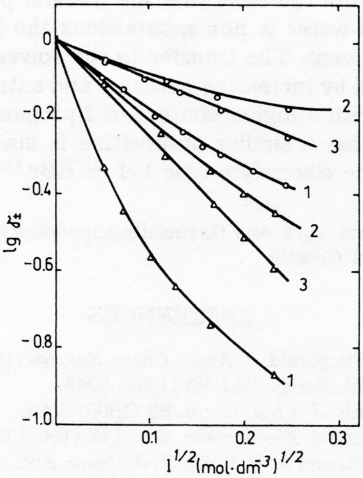

Figure 1. Variation of lg $\gamma_\pm$ with $I^{1/2}$ at 298.15 K for $CdCl_2$ (1), $ZnCl_2^{12}$ (2) and the Debye-Hückel limiting law (3) in aqueous solution (○) and in 50 mass fractions of 2-propanol (Δ).

$$\Delta G_t^o = 2F[(E_x^o)_\mathrm{w} - (E_x^o)_\mathrm{s}], \tag{15}$$

where $(E_x{}^o)_\mathrm{w}$ and $(E_x{}^o)_\mathrm{s}$ are the standard e.m.f. of the cell in aqueous solution and in a mixed solvent on a mole-fraction scale, respectively, and are calculated for E_m^o (Table II) using the known relation.[13] For the temperature range from 293.15 to 313.15 K the following dependencies for ΔG_t^o were obtained:

$$\Delta G_t^o(w=10)/\mathrm{J\ mol^{-1}} = 57698 - 366.02\ T/\mathrm{K} + 60.65 \times 10^{-2}\ T^2/\mathrm{K}^2, \tag{16}$$

$$\Delta G_t^o(w=30)/\mathrm{J\ mol^{-1}} = 17569 - 61.08\ T/\mathrm{K} + 10.48 \times 10^{-2}\ T^2/\mathrm{K}^2, \tag{17}$$

$$\Delta G_t^o(w=50)/\mathrm{J\ mol^{-1}} = 152733 - 976{,}48\ T/\mathrm{K} + 173.13 \times 10^{-2}\ T^2/\mathrm{K}^2. \tag{18}$$

The standard entropy and enthalpy of transfer (ΔS_t^o and ΔH_t^o) were then calculated from the usual relations. The values for temperature at 298.15 K are listed in Table VII. The uncertainties were calculated from the standard errors for E_m^o in mixed solvents and in water.

TABLE VII

Standard thermodynamic quantities for the transfer of $CdCl_2$ from water to 2-propanol-water containing w *mass per cent of 2-propanol at 298.15 K*

w	ΔG_t^o/kJ mol^{-1}	ΔH_t^o/kJ mol–1	ΔS_t^o/J K–1 mol^{-1}
10%	2.48 ± 0.04	3.79 ± 0.02	4.4 ± 0.1
30%	8.67 ± 0.04	8.25 ± 0.10	–1.4 ± 0.3
50%	15.50 ± 0.04	–1.17 ± 0.08	–55.9 ± 0.3

It can be concluded from the table that the transfer process of Cd^{2+} and Cl^{-} ions from water to 2-propanol-water is non-spontaneous the higher is the content of 2-propanol in the mixed solvent. The transfer to the solvents with a lower content of 2-propanol is accompanied by increasing enthalpy and entropy; on the other hand, the transfer to the solvents with a higher content of 2-propanol results in their decrease. It should be mentioned that a similar observation is made with the transfer to the same mixed solvents of the electrolyte type 1–1 as HBr,[14,15] HCl[16] and HJ.[16]

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SAŽETAK

Termodinamika članka: $Cd(Hg)_{zas.}|CdCl_2(m)|AgCl|Ag$ u 10, 30 i 50- tnoj smjesi 2-propanol-voda

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Mjerena je EMS članka: $Cd(Hg)_{zas.}|CdCl_2(m)$, smjesa 2-propanol-voda$|AgBr|Ag$ s 10, 30 i 50 masenih % alkohola u temperaturnom području 293,15 K ··· 313,15 K u intervalu po 5 K i u području molalnosti $CdCl_2$ $0{,}002 \leq m/\text{mol kg}^{-1} \leq 0{,}02$. Izmjerene vrijednosti upotrijebljene su za dobivanje standardne EMS članka za pojedine temperature, i to a) uzevši u obzir literaturne podatke za konstante stabilnosti svih Cd-kloridnih kompleksa i b) uz pretpostavku da u otopini postoji samo kompleks $CdCl^{+}$. Vrijednosti dobivene objema metodama su uspoređene i raspravljene. Vrijednosti dobivene prvom metodom upotrijebljene su za izračunavanje standardnih termodinamičkih veličina za reakciju članka i prosječnih koeficijenata aktiviteta $CdCl_2$. Također su izračunane standardne termodinamičke veličine za prijenos $CdCl_2$ iz vode i proučavana miješana otapala. Te su vrijednosti uspoređene s onima za prijenos elektrolita HBr, HCl i HI iz vode u ista miješana otapala.