CROATICA CHEMICA ACTA CCACAA **66** (3-4) 489–498 (1993)

ISSN 0011-1643
CCA–2155

Original Scientific Paper

The Stability Constants of Cadmium Chloride Complexes in 2-Propanol-Water Mixtures (0, 10, 30 and 50 Mass per Cent) from Electromotive Force Measurements

*M. Višić, A. Jadrić, and I. Mekjavić**

Laboratory of Physical Chemistry, Faculty of Technology, University of Split, 58000 Split, Teslina 10, Croatia

Received December 2, 1992

Stability constants (K_n') were determined for different Cd-chloride complexes at different ionic strengths in 2-propanol-water mixtures (containing 0, 10, 30 and 50 mass percent of 2-propanol) by a potentiometric method at 288.15, 298.15 and 313.15 K. From these values, stability constants at zero ionic strength (K_n^0) for $CdCl^+$, $CdCl_2$ and $CdCl_3^-$ complexes in an aqueous solution and 10 mass per cent 2-propanol were obtained, and in other mixtures also for the $CdCl_4^{2-}$ complex. The reactions forming all these complexes are endothermic, leading to an increase in entropy. The constant K_n^0 dependencies on the dielectric constants of the solvents were determined and comparison with literature data for methanol-water and ethanol-water was carried out.

INTRODUCTION

Stability constants for Cd-chloride complexes have been determined in different solvents using different methods: in an aqueous solution by measuring the e.m.f. of the cell,[1–4] using a polarographic method,[5–7] by measuring the solubility[8] and using a distribution method.[9] In determining the constants for methanol-water,[6,7] ethanol-water,[7,10] and dioxan-water[11] mixtures a polarographic method has been applied.

In this work, the results are given of the thermodynamic investigations involving the reactions that form different Cd-chloride complexes in 2-propanol-water mixtures (0, 10, 30 and 50 mass per cent) based on e.m.f. measurements of the concentration cell. The determined stability constants for these complexes will be used in our next work in data processing of the e.m.f. of the cell: $Cd(Hg)_{satd.}|CdCl_2(m)|AgCl|Ag$ in the same mixed solvents.

* Author to whom correspondence should be addressed.

The e.m.f. measurements were carried out on the following concentration cell:

$$\mathrm{Cd(Hg)}\left|\begin{array}{l}\mathrm{Cd(ClO_4)_2}\ (x)\\ \mathrm{HClO_4}\ (y)\\ \mathrm{NaClO_4}\ (I-x-y-z)\\ \mathrm{NaCl}\ (z)\end{array}\right|\left|\begin{array}{l}\mathrm{Cd(ClO_4)_2}\ (x)\\ \mathrm{HClO_4}\ (y)\\ \mathrm{NaClO_4}(I-x-y)\end{array}\right|\mathrm{Cd(Hg)} \qquad (1)$$

at temperatures 288.15, 298.15 and 313.15 K and at ionic strengths (I) 1.0, 2.0 and 3.0 mol dm^{-3}. In all the cases, the x and y concentrations were 0.01 mol dm^{-3}, while z was in the 0.025–0.40 mol dm^{-3} interval.

Stability constants determined at different temperatures enabled evaluation of thermodynamic values involved in the reactions forming different Cd-chloride complexes.

EXPERIMENTAL

Two stock solutions (stock 1 and 2) were prepared for each solvent and ionic strength.

Stock 1 (composition: 0.01 mol dm^{-3} $Cd(ClO_4)_2$ (x), 0.01 mol dm^{-3} $HClO_4$ (y) and (I = 0.04 mol dm^{-3}) $NaClO_4$) was prepared as follows: CdO (*p.m.* purity grade, »Lafoma« Skopje, Macedonia) in small excess was dissolved by mild heating in a known volume of standardized 0.4 mol dm^{-3} $HClO_4$ solution (obtained from 70 mass per cent of $HClO_4$ *p.a.* purity grade »Merck«). The resulting $Cd(ClO_4)_2$ solution was filtered in a volumetric flask and the undissolved CdO was thoroughly rinsed. An accurately determined volume of 0.4 mol dm^{-3} $HClO_4$ was then added to obtain the concentration (y) and a calculated amount of (I = 0.04 mol dm^{-3}) $NaClO_4$ to obtain the required ionic strength ($NaClO_4 \times H_2O$ *p.m.* purity grade, »Kemika«, was used).

For Stock 2 (composition: 0.01 mol dm^{-3} $Cd(ClO_4)_2$ (x), 0.01 mol dm^{-3} $HClO_4$ (y), 0.40 mol dm^{-3} NaCl and (I = 0.44 mol dm^{-3}) $NaClO_4$) the same procedure as for stock 1 was applied both in preparing the $Cd(ClO_4)_2$ solution and in obtaining the 0.01 mol dm^{-3} $HClO_4$ concentration. NaCl (*p.m.* purity grade, »Kemika«, Zagreb, Croatia, previously dried at 700 °C) was then added into the volumetric flask to obtain the required concentration and $NaClO_4$ to obtain the necessary ionic strength (I = 0.44 mol dm^{-3}).

To prepare these solutions in mixed solvents, the required amount of 2-propanol was added in order to obtain the specified composition of the mixed solvent, allowing for the amount of water already contained (in the $HClO_4$ solution in preparing $Cd(ClO_4)_2$, in the $HClO_4$ solution for obtaining 0.01 mol dm^{-3} $HClO_4$, and the crystallization water contained in $NaClO_4 \times H_2O$).

The saturated Cd(Hg) electrode was prepared as already described.[12]

The glass cell consisted of two parts (reference half-cell and working half-cell) interconnected by a tube fitted with a sinter glass disc (pore size 4 to 9 μm). At the bottom of the reference half-cell (capacity about 75 mL) and the working half-cell (capacity about 280 mL) a sealed-in Pt wire was placed, covered by Cd amalgam with the other end of the wire entering a narrow side tube to establish an electrical contact with a measuring instrument, across Wood alloy and wire. Both vessels were provided with silicon stoppers having openings for blowing through argon, previously purified and saturated with solvent vapours,[13] while the stopper of the working half-cell was fitted with an additioned opening for a burette from which stock 2 solution was being added on titration.

The cell temperature was maintained constant to ±0.02 °C, and the e.m.f. measurements were taken with a Feussner potentiometer.

At least two potentiometric titrations were carried out for each solvent and ionic strength at the determined temperature and always with freshly prepared amalgam and solvents. Measurements were started by transferring, with a warm dropper, a small amount of warm Cd(Hg) and 50 mL Stock 1 solution to the bottom of each half-cell. During thermostating, argon was blown through and titration was started only when the potential between the half-cells was less than 0.05 mV, the time required to reach this state depending on the working temperature and

ionic strength of the solution. A certain amount of Stock 2 solution was then added from the burette into the working half-cell and the first e.m.f. reading was taken after 10–15 minutes. A further amount of Stock 2 solution was added only after three e.m.f. readings, taken at ten-minute intervals, did not exceed 0.05 mV. During the measurements, the solution was mixed by blowing through argon.

The average deviation of each measurement from its mean value was within ±0.12 mV. In all the solvents, a decrease in deviation was observed with an increase in ionic strength of the solution.

RESULTS AND DISCUSSION

Mean values of e.m.f. of the investigated cell (1) for different additions of NaCl in 2-propanol-water at different ionic strengths and temperatures are shown in Table I.

The values from the table were used to calculate the stability constants (K_n') for the following reactions

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

and are given by the expression

$$K_n' = (c(CdCl_n^{(2-n)+})/c^\circ)/[(c(Cd^{2+})/(c^\circ)(c(Cl^-)/c^\circ)^n)] \tag{3}$$

where c(X) denotes the concentration of ion X, and $c^\circ = 1$ mol dm^{-3}.

To calculate the K_n' values, Leden's method was applied, based on the following equation[1]

$$\frac{x - c(Cd^{2+})}{c(Cd^{2+})c(Cl^-)} = \sum K_n' [c(Cl^-)]^{n-1} =$$

$$K_1' + K_2' [c(Cl^-)] + K_3' [c(Cl^-)]^2 + K_4' [c(Cl^-)]^3 \tag{4}$$

where x is the total concentration of Cd^{2+} ions (0.01 mol dm^{-3}), $c(Cd^{2+})$ is the concentration of free Cd^{2+} ions, obtained by the Nernst equation from e.m.f. of the cell, and $c(Cl^-)$ the concentration of free Cl^- ions.

The treatment consists of successive graphical extrapolations which are repeated until constant values for K_n' are obtained.

A certain modification of this method was made in this work, namely, the right side of equation (4) was solved as a polynomial using the (IBM 4143) computer. In fact, a detailed programme was prepared for the whole method, and the polynomial itself was solved with ORTHLS and COEFS subroutines added.

The procedure was as follows: the concentrations of free cadmium and chloride ions in equation (4) were calculated according to the original Leden's method, with the results obtained on the computer representing the K_n' values. These K_n' values were used in calculating more accurate concentrations of free chloride and the treatment was repeated until constant K_n' values were reached. The number of repetitions depended on the composition of the mixed solvent, so that an aqueous solution and 10 mass per cent 2-propanol required 4–5 titrations while it amounted to 20 iterations with 50 mass percent.

The obtained K_n' values were not final since the e.m.f. used in computing them included also the liquid junction potential. Therefore, using the Henderson equation, the

TABLE I

Electromotive force (mV) of the cell (1) for different additions of chloride ions in 2-propanol-water at different ionic strengths and temperatures; w *is the mass per cent 2-propanol in the mixed solvent*

c(NaCl) / mol dm^{-3}	I = 1.0 mol dm^{-3}			I = 2.0 mol dm^{-3}			I = 3.0 mol dm^{-3}		
	T/K			T/K			T/K		
	288.15	298.15	313.15	288.15	298.15	313.15	288.15	298.15	313.15
					w = 0				
0.025	5.14	5.17	5.67	5.82	6.29	6.29	7.14	7.27	7.53
0.050	9.24	9.77	10.14	10.49	11.03	11.40	12.73	13.08	13.70
0.075	12.48	13.19	13.95	14.21	15.05	15.71	17.33	17.92	18.75
0.100	15.33	16.65	17.17	17.39	18.55	19.42	21.18	21.96	23.11
0.150	20.22	21.55	22.67	23.12	24.29	25.74	27.56	28.65	30.28
0.200	23.94	25.89	27.20	27.77	29.07	30.98	32.81	34.11	36.19
0.250	27.22	28.96	30.74	31.72	33.18	35.46	37.29	38.83	40.90
0.300	30.74	32.28	34.56	35.24	36.76	39.50	41.24	43.00	45.47
0.350	33.75	35.33	37.75	38.31	39.98	43.06	44.79	46.73	49.63
0.400	36.42	38.13	40.56	41.07	42.89	46.36	47.98	50.08	53.37
					w = 10%				
0.025	6.05	6.14	6.71	7.28	7.27	7.76	8.68	8.93	9.12
0.050	10.61	10.95	11.88	12.75	12.71	13.68	15.30	15.58	16.45
0.075	14.36	14.79	16.20	17.09	17.19	18.48	20.60	21.08	22.40
0.100	17.39	18.09	19.81	20.81	20.99	22.56	24.99	25.65	27.34
0.150	22.76	24.02	25.87	26.76	27.28	29.19	32.18	33.22	35.49
0.200	27.11	28.54	31.00	31.49	32.42	34.63	38.07	39.44	42.18
0.250	31.34	32.69	35.44	35.68	36.75	39.33	43.04	44.77	48.00
0.300	34.85	36.34	39.45	39.46	40.66	43.54	47.53	49.53	53.21
0.350	38.08	39.68	43.20	42.88	44.18	47.29	51.58	53.85	57.93
0.400	41.09	42.41	46.61	45.99	47.42	50.85	55.22	57.77	62.22
					w = 30%				
0.025	8.62	9.64	9.74	8.81	10.03	10.62	11.90	12.01	12.70
0.050	15.50	16.66	17.42	15.78	16.72	18.71	20.31	20.91	22.30
0.075	20.16	22.03	22.63	20.87	23.18	25.02	27.04	27.90	29.68
0.100	24.36	26.57	27.46	25.46	28.15	30.43	32.81	34.04	36.25
0.150	31.14	34.06	35.30	33.11	36.67	39.71	42.45	44.18	47.34
0.200	37.27	40.28	42.04	39.54	44.03	47.61	50.38	52.62	56.70
0.250	42.39	45.80	47.96	45.64	50.07	54.33	57.29	60.80	64.82
0.300	47.03	50.78	53.52	50.33	55.71	60.46	63.39	66.57	72.01
0.350	51.24	55.14	58.46	54.98	60.72	66.06	68.85	72.32	78.52
0.400	54.88	59.37	63.10	61.18	65.33	71.16	73.76	77.58	84.33
					w = 50%				
0.025	12.26	12.45	14.60	12.95	13.11	14.83	15.41	15.99	17.66
0.050	20.84	21.50	25.34	22.22	22.94	26.09	27.02	28.30	31.45
0.075	27.66	28.85	33.78	29.94	30.13	35.14	36.93	38.72	43.29
0.100	33.39	34.90	40.87	36.44	36.92	43.32	45.64	47.72	53.39
0.150	42.94	45.34	52.41	47.97	48.98	57.34	60.02	62.95	70.27
0.200	51.08	54.82	62.62	57.73	59.05	69.06	71.68	75.50	83.94
0.250	58.33	62.79	71.38	66.71	67.92	79.18	81.73	86.15	95.37
0.300	64.88	70.10	79.21	74.02	75.93	88.09	90.29	95.17	104.97
0.350	70.94	76.90	86.43	80.79	82.99	95.51	98.20	103.20	112.10
0.400	76.28	84.13	92.84	86.31	89.72	102.15	104.49	109.75	118.94

liquid junction potential between the two half-cells was calculated and the measured e.m.f. corrected for that amount and the whole calculating procedure was repeated. The final K_n' values are given in Table III.

To calculate the liquid junction potential, experimental data were needed to ascertain the conductivity of particular ions at infinite dilution in the investigated solvents and at corresponding temperatures, which was achieved by using the Walden rule. In calculating the conductivity of individual ions in water at different temperatures use was made of literature data[15] either directly or by interpolation, while for different Cd species the average value used by Vanderzee and Dawson[2] at 298 K was taken. At other temperatures, the average value was determined on the basis of the temperature coefficient for Cd^{2+} ion.[16] The viscosity coefficients of mixed solvents at different temperatures were determined by the Ostwald viscosimeter (Table II), while those for water were taken from literature.[17] The data for solvent density were also based on literature.[18,19] The concentration of individual ions in the reference half-cell were taken from the composition of Stock 1 solution, while those from the working half-cell were taken directly from the composition of stock 2 solution (H^+, Na^+ and ClO_4^-), and the concentrations of Cl^-, Cd^{2+} and $Cd_n^{(2-n)+}$ ions were calculated by using previously obtained K_n' values.

TABLE II

Viscosity coefficient (10^3 η/Pa s) of w mass percent 2-propanol-water at different temperatures

Solvent	T/K		
	288.15	298.15	313.15
w = 0[a]	1.1374	0.8903	0.6526
w = 10%	1.9760	1.4160	0.9691
w = 30%	4.2592	2.7368	1.6199
w = 50%	4.6970	3.1132	1.8773

[a]Values from reference 17.

In general, the liquid junction potential in all the solvents increased with a higher chloride concentration in the working half-cell, while at a determined concentration it decreased with an increase in ionic strength and a decrease in temperature. The composition of mixed solvents, however, had no significant effect in this respect. For example, in the 30 mass per cent 2-propanol and at ionic strength I = 1 mol dm^{-3} at 298 K, the liquid junction potential for the maximal chloride concentration (0.4 mol dm^{-3}) was –0.50 mV and for the minimal chloride concentration (0.025 mol dm^{-3}) it was 0.03 mV. The measured e.m.f. was amounted to 59.37 mV and 9.64 mV, respectively (Table I). In all the solvents, the correction for the liquid junction potential had very little effect on K_n' (the difference in the values averaged 0.5 per cent), but its effect was somewhat greater on the other constants (2 for K_2', 7 for K_3' and 8 per cent for K_4' on the average).

It can be seen from the values in Table III that in an aqueous solution and 10 mass per cent 2-propanol up to ionic strength I = 3 mol dm^{-3}, complexes $CdCl^+$, $CdCl_2$ and $CdCl_3^-$ are present, while in the solvents with a larger content of 2-propanol there is also the $CdCl_4^{2-}$ complex. The existence of three complexes in an aqueous solution up to the same ionic strength was also established by other authors.[1–5,8]

TABLE III

Stability constants K'_n *of the cadmium chloride complexes in 2-propanol-water at different ionic strengths and temperatures;* w *is the mass per cent 2-propanol in the mixed solvent*

I/mol dm^{-3}		T/K					
		288.15	298.15	313.15	288.15	298.15	313.15
		w = 0			w = 10%		
1.0		22.5	23.0	23.3	27.6	27.2	28.9
2.0	K'_1	26.2	27.8	26.1	37.2	34.5	35.8
3.0		35.2	34.4	34.3	47.7	46.9	46.2
1.0		43	51	48	63	73	76
2.0	K'_2	86	83	98	101	113	117
3.0		153	163	157	237	223	240
1.0		50	50	79	128	119	179
2.0	K'_3	77	92	119	204	187	230
3.0		210	225	294	612	749	919
		w = 30%			w = 50%		
1.0		48.4	53.4	51.0	74	78	90
2.0	K'_1	47.6	53.2	55.4	76	79	92
3.0		76.5	73.3	73.8	94	99	104
1.0		177	226	219	800	810	1240
2.0	K'_2	286	326	392	950	975	1250
3.0		610	640	708	2220	2535	3050
1.0		638	679	639	1700	1510	3400
2.0	K'_3	658	1365	1280	6080	5220	12030
3.0		3430	3600	3665	22115	34350	38170
1.0		436	851	1445	13860	25915	35715
2.0	K'_4	1390	1400	3015	33570	36460	66915
3.0		5000	6670	11745	172600	194500	275800

From the K'_n values listed in Table III, the stability constants at zero ionic strength (K^o_n) can be evaluated by the equation

$$\ln K'_n - \Delta z^2 A I^{1/2}/(1 + BaI^{1/2}) = \ln K^o_n + (\ln 10)\, \Delta C_n I/c^o) \qquad (5)$$

from the graphical representation of its left hand side against I. Namely, K^o_n is calculated from the intercept of the obtained straight line and ΔC_n from the slope.

In the above equation, A and B are the Debye-Hückel parameters (dielectric constants required for their calculation were taken from Åkerlöf[20]), a is the ion-size parameter, $\Delta z^2 = z^2(\mathrm{CdCl}_n^{(2-n)+}) - z^2(\mathrm{Cd}^{2+}) - nz^2(\mathrm{Cl}^-)$, and $-\Delta C_n = C(\mathrm{CdCl}_n^{(2-n)+}) - C(\mathrm{Cd}^{2+}) - nC(\mathrm{Cl}^-)$. In these expressions, z and C represent the charge and the empirical constant for each ion.

The graphical presentation of equation (5) was carried out with different values for the ion-size parameter. The best straight line was obtained with the corresponding value. This value was mainly in the 0.43 to 0.47 nm interval for all the complexes, regardless of the dielectric constant of the solvent. Therefore, the value a = 0.45 nm was chosen and it was used in calculating all the values summed up in Table IV. The uncertainties in the values of K^o_n were estimated by plotting the data several times and

averaging the intercept obtained. The established region of uncertainties correspond to the region obtained by using a in the above mentioned interval (±0.02 nm).

TABLE IV

Stability constants K_n^o *of the cadmium chloride complexes and* ΔC_n *in 2-propanol-water containing* w *mass per cent of 2-propanol at different temperatures*

T/K	288.15	298.15	313.15	288.15	298.15	313.15
		w = 0			w = 10%	
K_1^o	93 ± 2	103 ± 3	112 ± 2	138 ± 5	140 ± 4	169 ± 5
K_2^o	315 ± 15	335 ± 5	465 ± 35	490 ± 20	710 ± 20	790 ± 30
K_3^o	275 ± 15	300 ± 10	540 ± 50	830 ± 80	850 ± 90	1300 ± 150
ΔC_1	0.181	0.172	0.170	0.203	0.210	0.200
ΔC_2	0.395	0.379	0.368	0.345	0.380	0.390
ΔC_3	0.448	0.455	0.420	0.513	0.495	0.483
		w = 30%			w = 50%	
K_1^o	430 ± 20	535 ± 20	560 ± 15	2235 ± 105	2305 ± 95	3430 ± 200
K_2^o	4000 ± 100	5600 ± 200	6300 ± 500	81300 ± 4600	89200 ± 8500	150000 ± 22000
K_3^o	9400 ± 850	12100 ± 250	12900 ± 750	85300 ± 7100	103000 ± 9700	282000 ± 39000
K_4^o	1650 ± 20	4200 ± 700	5400 ± 600	116000 ± 10000	251000 ± 32000	447000 ± 51000
ΔC_1	0.200	0.185	0.194	0.190	0.195	0.175
ΔC_2	0.435	0.390	0.485	0.345	0.455	0.410
ΔC_3	0.513	0.529	0.550	0.765	0.800	0.750
ΔC_4	0.627	0.568	0.628	0.690	0.590	0.590

It is seen from the values in Table IV that the K_n^o constants increase with increasing the 2-propanol content, and for the same solvent they generally increase with increasing temperature. Comparison of these values with the values in literature obtained in the same way is possible only for the aqueous solution, as shown in Table V.

TABLE V

Comparison of the stability constants (K_n^o) *for cadmium chloride complexes in aqueous solution at 298.15 K*

Reference	K_1^o	K_2^o	K_3^o
2	100 ± 3	500 ± 20	130 ± 10
4[a]	83 ± 4	339 ± 24	214 ± 15
this work	103 ± 3	335 ± 5	300 ± 10

[a] Determined at inert electrolyte $LiClO_4$.

Using K_n^o values at 298.15 K from Table IV, the amounts (in moles per cent) of Cd^{2+} ions and Cd-chloride complexes were calculated [reference 21: eqs. (4)–(6)] for different molalities of $CdCl_2$ in the range (0.002 ··· 0.02 mol kg^{-1}). Figure 1 shows the dependence of these values on the concentration of free chlorides.

It can be seen from Figure 1 that an increase in the concentration of free chlorides, or an increase in $CdCl_2$ molalities, results in a decreased amount of Cd^{2+} ions and an increase in $CdCl_n^{(2-n)+}$, the more so as the content of 2-propanol in the solvent becomes higher. On the other hand, with $CdCl^+$ complex in 50 mass per cent 2-propanol at a higher content of free chlorides, we notice a decrease in its amount but, hence the

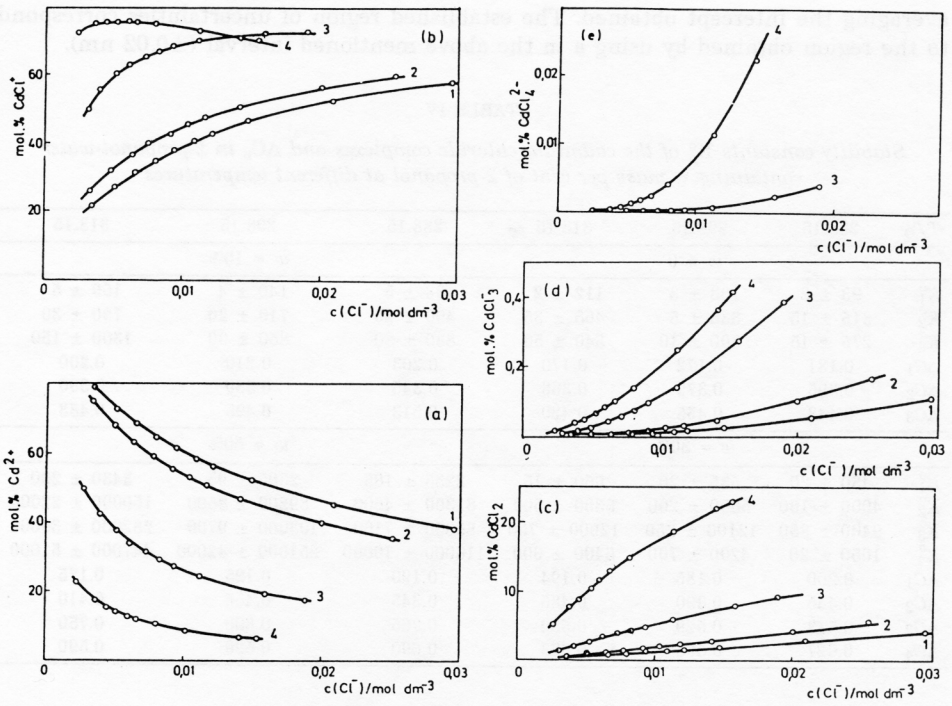

Figure 1. The dependence of the relative amounts (mole per cent) of Cd^{2+} (a), $CdCl^+$ (b), $CdCl_2$ (c), $CdCl_3^-$ (d) and $CdCl_4^{2-}$ (e) on free chloride concentration in the range of ($0.002 \leq CdCl_2$/mol $kg^{-1} < 0.02$) at 298.15 K for: aqueous solution (1), 10 mass per cent (2), 30 mass per cent (3) and 50 mass per cent 2-propanol (4).

amount of higher complexes increases more prominently. It can also be seen that the curves encircle an increasingly smaller range of free chlorides for the same range of $CdCl_2$ molalities as the 2-propanol content is increased or the dielectric constant of the solvent is decreased, which is provided by more linkages of chlorides in the complexes.

The values for K_n° at 298.15 K from Table IV are also presented in Figure 2 in dependence on the dielectric constant of the solvents (plot ln K_n° against D^{-1}). The dependence for K_4° is not considered because there are only two values.

Figure 2 shows that the obtained dependence in the range of dielectric constants (42.5 ··· 78.5) are straight lines. It should be noted that Turyan and Zhantalay[7] found a common straight line for methanol-water and ethanol-water mixtures for K_1° and K_2° values, respectively.

Finally, the values for K_n° constants from Table IV made it possible to determine the standard thermodynamic quantities for the reactions forming different Cd-chloride complexes. Namely, ΔH° was determined from the slope of the straight line in the plot in K_n° against T^{-1}, while ΔG° and ΔS° were calculated by applying the usual thermodynamic relations. The values at 298.15 K are given in Table VI. The uncertainties in the values of ΔG° were calculated from the uncertainties of K_n°, those for ΔH° were

estimated by plotting the data several times and averaging the slope obtained, and for ΔS° they were calculated by taking into consideration the uncertainties in the values of both ΔG° and ΔH°.

The values shown in Table VI point to the conclusion that all of the Cd-chloride complexes are formed endothermally, resulting in an increase in entropy. With several

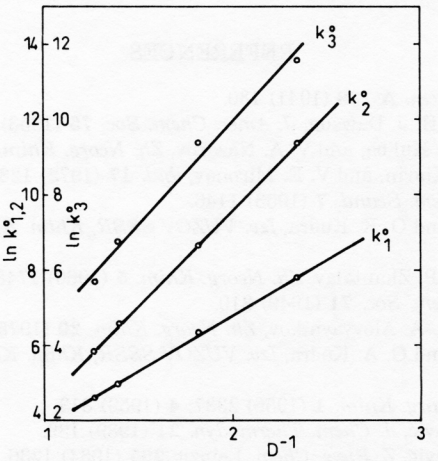

Figure 2. Variation of ln K_n° with D^{-1} at 298.15 K.

TABLE VI

Standard thermodynamic quantities for the formation reaction of the cadmium chloride complexes (2) in 2-propanol-water; w *is the mass per cent 2-propanol in the mixed solvent*

Complex	w = 0	w = 10%	w = 30%	w = 50%
		ΔH°/kJ mol^{-1}		
$CdCl^+$	5.6 ± 0.1	6.1 ± 0.1	8.2 ± 0.2	12.9 ± 0.3
$CdCl_2$	11.6 ± 0.1	14.3 ± 0.1	15.0 ± 1.1	17.9 ± 0.8
$CdCl_3^-$	19.7 ± 0.3	14.1 ± 0.6	10.8 ± 1.1	33.8 ± 1.1
$CdCl_4^{2-}$			34.7 ± 0.6	40.7 ± 1.5
		ΔG°/kJ mol^{-1}		
$CdCl^+$	−11.5 ± 0.1	−12.2 ± 0.1	−15.6 ± 0.1	−19.2 ± 0.1
$CdCl_2$	−14.4 ± 0.1	−16.3 ± 0.1	−21.4 ± 0.1	−28.3 ± 0.2
$CdCl_3^-$	−14.1 ± 0.1	−16.7 ± 0.1	−23.3 ± 0.1	−28.6 ± 0.2
$CdCl_4^{2-}$			−20.7 ± 0.4	−30.8 ± 0.3
		ΔS°/J K^{-1} mol^{-1}		
$CdCl^+$	57.4 ± 0.5	61.4 ± 0.5	79.8 ± 0.7	107.7 ± 1.1
$CdCl_2$	87.2 ± 0.5	102.6 ± 0.5	122.1 ± 3.7	155.0 ± 2.8
$CdCl_3^-$	113.4 ± 1.1	103.3 ± 2.0	114.4 ± 3.7	209.3 ± 3.7
$CdCl_4^{2-}$			185.8 ± 2.4	239.8 ± 5.1

complexes both the endothermic values and entropy exhibit a continuous rise with increasing the 2-propanol content of the solvent; however, a certain discontinuity can be observed with some of the complexes.

It should be mentioned that nearly straight lines are also obtained for each ionic strength by plotting ln K_n' against T^{-1} (values taken from Table III).

Acknowledgement. — This work was financially supported by the Ministry of Science and Technology of the Republic of Croatia.

REFERENCES

1. I. Leden, *Z. Phys. Chem.* **A 188** (1941) 180.
2. C. E. Vanderzee and H. J. Dawson, *J. Amer. Chem. Soc.* **75** (1953) 5659.
3. V. E. Mironov, F. Ya. Kul'ba, and V. A. Nazarov, *Zh. Neorg. Khim.* **8** (1963) 916.
4. V. A. Fedorov, L. I. Kiprin, and V. E. Mironov, *ibid.* **17** (1972) 1233.
5. L. Eriksson, *Acta Chem. Scand.* **7** (1953) 1146.
6. O. I. Hotsyanovskii and O. K. Kudra, *Izv. VUZOV SSSR, Khim. Khim. Tekhnol.* No. 1 (1958) 43.
7. I. Ya. Turyan and B. P. Zhantalay, *Zh. Neorg. Khim.* **5** (1960) 1748.
8. E. King, *J. Amer. Chem. Soc.* **71** (1949) 319.
9. E. A. Belousov and A. A. Alovyaynikov, *Zh. Neorg. Khim.* **20** (1975) 1428.
10. O. I. Hotsyanovskii and O. A. Kudra, *Izv. VUZOV SSSR, Khim. Khim. Tekhnol.* No 2. (1958) 36.
11. I. Ya. Turyan, *Zh. Neorg. Khim.* **1** (1956) 2337; **4** (1959) 813.
12. M. Višić and I. Mekjavić, *J. Chem. Thermodyn.* **21** (1989) 139.
13. M. Višić and I. Mekjavić, *Z. Phys. Chem.* Leipzig **265** (1984) 1236.
14. S. Glasstone, *Introduction of Electrochemistry*, New York, D. van Nostrand, 1942, p. 212.
15. R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, London, Butherworths, 1959, p. 465.
16. D. Dobos, *Electrochemical Data*, Amsterdam, Elsevier, 1975, p. 88.
17. A. N. Lange, *Lange's Handbook of Chemistry*, J. A. Dean (Ed.), 13th Edition, New York, McGraw Hill, 1985, Sect. 10, p. 99.
18. R. L. Moore and W. A. Felsing, *J. Amer. Chem. Soc.* **69** (1947) 1076.
19. K. Schwabe and R. Müller, *Ber. Bunsen Phys. Chem.* **47** (1970) 1248.
20. G. Åkerlöf, *J. Amer. Chem. Soc.* **54** (1932) 4125.
21. M. Višić and I. Mekjavić, *Croat. Chem. Acta* **66** (1993) 479.

SAŽETAK

Konstante stabilnosti kadmij klorid kompleksa u smjesama 2-propanol-voda (s 0, 10, 30 i 50 masenih % alkohola) na osnovi mjerenja elektromotorne sile članka

M. Višić, A. Jadrić i I. Mekjavić

Potenciometrijskom metodom određene su konstante stabilnosti (K_n') kadmijevih kloro-kompleksa pri raznim ionskim jakostima u smjesama 2-propanol-voda (s 10, 30 i 50 masenih % alkohola) pri 288.15, 298.15 i 313.15 K. Iz tih vrijednosti dobivene su standardne konstante stabilnosti (K_n°) za komplekse $CdCl^+$, $CdCl_2$ i $CdCl_3^-$ u vodenoj otopini i u 10 %-tnom 2-propanolu, a u ostalim smjesama i za kompleks $CdCl_4^{2-}$. Reakcije nastajanja svih spomenutih kompleksa endotermne su i dovode do porasta entropije. Prikazane su ovisnosti konstanti K_n° o dielektričkoj konstanti otapala i izvršena je usporedba s literaturnim podacima za smjese metanol-voda i etanol-voda.