

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

*Marija Višić<sup>a</sup> and Ivica Mekjavić<sup>b\*</sup>*

<sup>a</sup>*Faculty of Natural Sciences and Arts, University of Split,  
Teslina 12, 21000 Split, Croatia*

<sup>b</sup>*Laboratory of Physical Chemistry, Faculty of Technology,  
University of Split, Teslina 10, 21000 Split, Croatia*

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Stability constants ( $K'_n$ ) were determined, using the potentiometric method, of different cadmium chloride complexes at different ionic strengths in 10 mass per cent acetone-water mixture at 288.15, 298.15 and 313.15 K, and in 30 and 50 mass per cent at 288.15, 298.15 and 308.15 K, respectively. These values were used to establish the thermodynamic stability constants ( $K_n^\circ$ ) of  $[\text{CdCl}]^+$ ,  $[\text{CdCl}_2]$ , and  $[\text{CdCl}_3]^-$  complexes in 10 mass per cent mixture acetone, as well as in other mixtures also of the  $[\text{CdCl}_4]^{2-}$  complex. On the basis of the temperature dependence for  $K_n^\circ$ , thermodynamic quantities were calculated for reactions forming these complexes; the results obtained indicate that the reactions are endothermic and that they result in an increase in entropy. The values obtained for  $K_n^\circ$  and thermodynamic quantities were compared with analogous data in 2-propanol-water mixtures.

### INTRODUCTION

The stability constants of different cadmium chloride complexes are determined by using the polarographic method at 298.15 K in the mixed solvents methanol-water,<sup>1,2</sup> ethanol-water,<sup>2,3</sup> and dioxan-water,<sup>4</sup> and, in our work,<sup>5</sup> by

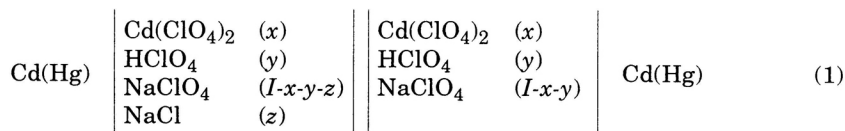
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\* Author to whom correspondence should be addressed.

means of the potentiometric method in 2-propanol-water mixtures in the temperature range of 288.15 – 313.15 K. The obtained values indicate that a decrease in the dielectric constant of the solvent results in an increase of the degree of complexation. From the temperature dependence of the stability constants in 2-propanol-water mixtures it was possible to determine the thermodynamic quantities for the reactions forming the above mentioned complexes.

In this work, the stability constants of cadmium chloride complexes were determined in acetone-water mixtures (10, 30 and 50 mass per cent acetone); the aim was to compare these values with those obtained for 2-propanol-water mixtures in order to establish a possible influence of the organic component (keto instead of alcohol group) on the stability constants and thermodynamic quantities of the reactions forming these complexes. Moreover, the obtained stability constants will be used in our next work in the processing of the measured values for the electromotive force of the cell: Cd(Hg)(l,satd.) | CdCl<sub>2</sub> (m) | AgCl(s) | Ag(s) in the same acetone-water mixtures.

The stability constants were determined on the basis of the e.m.f. measurements of the following concentration cell:



at 288.15, 298.15 and 313.15 K for the 10 mass per cent acetone at ionic strengths (*I*) 1.0, 2.0 and 3.0 mol dm<sup>-3</sup>, and at 288.15, 298.15 and 308.15 K for the 30 and 50 mass per cent acetone at the same ionic strengths. In all cases, the *x* and *y* concentrations were 0.01 mol dm<sup>-3</sup>, while the *z* value was in the 0.025–0.50 mol dm<sup>-3</sup> interval for the 10 and 30 mass per cent acetone, and in the 0.025–0.40 mol dm<sup>-3</sup> interval for the 50 mass per cent acetone-water mixture.

## EXPERIMENTAL

Two stock solutions, stock 1 and stock 2, were prepared for each mixed solvent. Stock 1 solution contained: 0.01 mol dm<sup>-3</sup> Cd(ClO<sub>4</sub>)<sub>2</sub>, 0.01 mol dm<sup>-3</sup> HClO<sub>4</sub> and (*I*–0.04) mol dm<sup>-3</sup> NaClO<sub>4</sub>. Stock 2 solution was composed of 0.01 mol dm<sup>-3</sup> Cd(ClO<sub>4</sub>)<sub>2</sub>, 0.01 mol dm<sup>-3</sup> HClO<sub>4</sub>, 0.50 mol dm<sup>-3</sup> NaCl and (*I*–0.54) mol dm<sup>-3</sup> NaClO<sub>4</sub> for the 10 and 30 mass per cent acetone, and of 0.40 mol dm<sup>-3</sup> NaCl and (*I*–0.44) mol dm<sup>-3</sup> NaClO<sub>4</sub> for the 50 mass per cent acetone-water mixture. The procedure used in preparing these solutions was described earlier.<sup>5</sup>

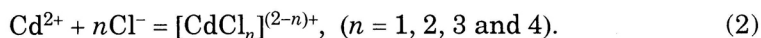
The Cd(Hg) electrode was saturated and prepared as before.<sup>6</sup> The cell description and the procedure used in the e.m.f. measurements were also previously described.<sup>5</sup>

At least two potentiometric titration were performed for each mixed solvent and ionic strength at a determined temperature, and always with a freshly prepared amalgam. The average deviation of individual measurements from their mean values was within  $\pm 0.12$  mV.

## RESULTS AND DISCUSSION

Table I presents the mean values of e.m.f. measurements of the cell (1) in the investigated solvents for different additions of NaCl at different ionic strengths and temperatures.

These values were used to calculate the stability constants ( $K'_n$ ) for the following complexation reactions



The expression for  $K'_n$  is in the form

$$K'_n = (c([\text{CdCl}_n]^{(2-n)+})/c^\circ) / [(c(\text{Cd}^{2+})/c^\circ)(c(\text{Cl}^-)/c^\circ)^n], \quad (3)$$

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

Calculation of  $K'_n$  values was carried out by Leden's method<sup>7</sup> of successive graphical extrapolations, the basis of which is the following equation

$$\frac{x - c(\text{Cd}^{2+})}{c(\text{Cd}^{2+})c(\text{Cl}^-)} = \sum K'_n [c(\text{Cl}^-)]^{n-1} = K'_1 + K'_2 [c(\text{Cl}^-)] + K'_3 [c(\text{Cl}^-)]^2 + K'_4 [c(\text{Cl}^-)]^3 \quad (4)$$

where  $x$  is the concentration of total  $\text{Cd}^{2+}$  ions ( $0.01 \text{ mol dm}^{-3}$ ),  $c(\text{Cd}^{2+})$  concentration of free  $\text{Cd}^{2+}$  ions, which is calculated by means of the Nernst equation from the measured e.m.f. of the cell, and  $c(\text{Cl}^-)$  is the concentration of free  $\text{Cl}^-$  ions. However, the original Leden's method was modified so that the right side of equation (4) was solved by computer (IBM 4143) as a polynomial by repeating the calculations until the constant  $K'_n$  values were obtained according to the procedure described in our earlier work.<sup>5</sup> The number of iterations was increased with an increase in the acetone content in the mixed solvent. This number was considerably larger than in 2-propanol-water mixtures. For example, for 50 mass per cent acetone, the number of iterations was about 30, as compared to 20 for 2-propanol.

The calculating procedure for  $K'_n$  values was repeated with the e.m.f. data corrected for the amount of the junction potential, which was calculated using the Henderson equation.

TABLE I

Electromotive force (e.m.f./mV) of the cell (1) for different additions of chloride ions in  $x$  mass per cent acetone-water mixture at different ionic strengths and temperatures

$c(\text{NaCl})$ mol dm <sup>-3</sup>	$I = 1.0 \text{ mol dm}^{-3}$			$I = 2.0 \text{ mol dm}^{-3}$			$I = 3.0 \text{ mol dm}^{-3}$		
	T/K			T/K			T/K		
	288.15	298.15	313.15	288.15	298.15	313.15	288.15	298.15	313.15
$x = 10$									
0.025	5.83	6.48	6.34	6.52	6.99	6.74	8.40	8.44	8.36
0.050	10.51	11.51	11.45	11.69	12.44	12.88	14.75	14.90	15.11
0.075	14.37	15.58	15.70	15.91	16.89	16.92	19.81	20.13	20.76
0.100	17.70	19.03	19.36	19.53	20.68	20.98	24.06	24.58	25.67
0.150	23.24	24.73	25.57	25.59	27.02	27.92	31.09	32.06	34.00
0.200	27.81	29.46	30.82	30.66	32.32	33.83	36.87	38.30	40.94
0.250	31.74	33.56	35.43	35.08	36.93	38.99	41.84	43.70	46.93
0.300	35.22	37.21	39.56	39.01	41.03	43.61	46.22	48.49	52.19
0.350	38.34	40.53	43.32	42.58	44.75	47.79	50.15	52.78	56.88
0.400	41.18	43.57	46.78	45.84	48.15	51.60	53.71	56.67	61.10
0.500	46.23	49.04	52.96	51.65	54.19	58.36	59.98	63.51	68.48
	T/K			T/K			T/K		
	288.15	298.15	308.15	288.15	298.15	308.15	288.15	298.15	308.15
$x = 30$									
0.025	8.44	9.88	9.97	8.46	9.94	10.32	10.87	11.33	12.14
0.050	14.55	16.94	17.16	14.78	17.42	17.90	19.24	19.72	21.65
0.075	19.36	22.40	22.78	19.95	23.42	24.03	26.12	26.37	29.31
0.100	23.46	26.99	27.54	24.48	28.56	29.32	32.10	32.11	35.88
0.150	30.60	34.75	35.74	32.39	37.35	38.57	42.31	42.15	47.13
0.200	36.91	41.42	42.97	39.35	44.89	46.73	50.92	51.10	56.83
0.250	42.66	47.38	49.59	45.62	51.60	54.10	58.41	59.22	65.42
0.300	47.99	52.82	55.73	51.33	57.65	60.80	65.02	66.60	73.12
0.350	52.93	57.81	61.45	56.55	63.16	66.91	70.93	73.29	80.07
0.400	57.51	62.43	66.77	61.34	68.22	72.51	76.27	79.37	86.35
0.500	65.73	70.71	76.34	69.83	77.20	82.39	85.57	89.98	97.28
$x = 50$									
0.025	13.33	16.04	18.07	15.89	17.65	18.20	18.45	18.85	19.58
0.050	23.52	27.70	30.32	27.56	30.07	31.60	32.20	33.27	34.67
0.075	31.97	37.33	40.36	37.42	40.68	42.61	42.96	45.06	47.93
0.100	39.48	46.14	49.77	46.63	50.61	53.21	52.36	55.50	60.03
0.150	52.87	62.00	67.04	63.27	68.39	71.72	68.66	73.39	80.53
0.200	64.46	75.49	81.70	77.10	83.10	86.96	82.07	87.84	96.54
0.250	74.42	86.79	93.84	88.44	95.09	99.37	93.15	99.58	109.22
0.300	83.00	96.33	103.97	97.88	104.92	109.56	102.44	109.33	119.60
0.350	90.45	104.49	112.59	105.90	113.47	118.45	110.20	118.50	128.42
0.400	97.01	111.60	120.07	112.84	120.71	125.89	117.27	124.79	135.88

TABLE II  
Viscosity coefficient ( $\eta \times 10^3/\text{Pa s}$ ) of  $x$  mass per cent  
acetone-water mixture at different temperatures

$x$	T/K			
	288.15	298.15	308.15	313.15
10	1.4376	1.0995	—	0.7975
30	1.8341	1.3666	1.0749	—
50	1.6545	1.2664	1.0440	—

Data required for the conductivity of particular ion species in the working and reference half-cell were obtained by using Walden's rule, as described in our previous work.<sup>5</sup> Viscosities of the mixed solvents were determined by means of Ostwald viscosimeter and are given in Table II, while the density data are taken from literature.<sup>8</sup> The final  $K'_n$  values are found in Table III.

It is seen from the Table III that in the 10 mass per cent acetone, up to the ionic strength  $I = 3 \text{ mol dm}^{-3}$ , complexes  $[\text{CdCl}]^+$ ,  $[\text{CdCl}_2]$  and  $[\text{CdCl}_3]^-$  exist, while in the solvents with a higher content of acetone also complex  $[\text{CdCl}_4]^{2-}$  is present; the same was found in the case of 2-propanol-water solvents.<sup>5</sup>

Values of  $K'_n$  were applied in calculating the thermodynamic stability constants, *i.e.* the stability constants at zero ionic strength. For this purpose, the left-hand side of equation (5) is presented graphically against ionic strength:

$$\ln K'_n - \Delta z^2 A I^{1/2} / (1 + B a I^{1/2}) = \ln K_n^\circ + (\ln 10) \Delta C_n I / c^\circ. \quad (5)$$

From the intercept of the obtained straight line we get the  $K'_n$  values, and from its slope the values for  $\Delta C_n$ . In equation (5)  $A$  and  $B$  represent the Debye-Hückel constants which were calculated by using the dielectric constants of the solvents taken from Åkerlöf,<sup>9</sup>  $a$  is the ion-size parameter (taken as 0.45 nm),  $\Delta z^2 = z^2 ([\text{CdCl}_n]^{(2-n)+}) - z^2(\text{Cd}^{2+}) - n z^2(\text{Cl}^-)$ , and  $-\Delta C_n = C([\text{CdCl}_n]^{(2-n)+}) - C(\text{Cd}^{2+}) - n C(\text{Cl}^-)$ . In these expressions,  $z$  and  $C$  are the charge and the empirical constant of each individual ion. The value for  $a$  of 0.45 nm was chosen because, in graphical presentation, the best straight lines can be obtained for  $a$  in the interval from 0.43 to 0.47 nm; for this reason, the mean value was taken and was used in calculating the constants for all the complexes and mixed solvents. The values of  $K_n^\circ$  and  $\Delta C_n$  are given in Table IV. Deviations of  $K_n^\circ$  values were estimated by repeating graphical presentations of the values; they represent the average deviations, which are in agreement with the corresponding interval of the values for  $a$  ( $\pm 0.02 \text{ nm}$ ).



TABLE IV

Stability constants  $K_n^\circ$  of the cadmium chloride complexes and  $\Delta C_n$  in  $x$  mass per cent acetone-water mixtures at different temperatures

	288.15 K	298.15 K	313.15 K
	$x = 10$		
$K_1^\circ$	126 ± 4	153 ± 4	166 ± 6
$K_2^\circ$	690 ± 45	740 ± 10	890 ± 37
$K_3^\circ$	660 ± 25	1000 ± 33	1515 ± 43
$\Delta C_1$	0.200	0.170	0.140
$\Delta C_2$	0.367	0.347	0.357
$\Delta C_3$	0.507	0.480	0.467
	288.15 K	298.15 K	308.15 K
	$x = 30$		
$K_1^\circ$	363 ± 16	457 ± 23	490 ± 11
$K_2^\circ$	1260 ± 70	3550 ± 130	3980 ± 220
$K_3^\circ$	11220 ± 910	19950 ± 1100	26915 ± 2200
$K_4^\circ$	3900 ± 300	6310 ± 500	13490 ± 1100
$\Delta C_1$	0.180	0.160	0.163
$\Delta C_2$	0.500	0.417	0.217
$\Delta C_3$	0.483	0.350	0.333
$\Delta C_4$	0.553	0.520	0.513
	$x = 50$		
$K_1^\circ$	1445 ± 70	2290 ± 95	3550 ± 140
$K_2^\circ$	41700 ± 2800	71000 ± 6500	87100 ± 3400
$K_3^\circ$	420000 ± 30000	631000 ± 44000	980000 ± 60000
$K_4^\circ$	$1.25 \times 10^6 \pm 100000$	$4.27 \times 10^6 \pm 260000$	$5.01 \times 10^6 \pm 270000$
$\Delta C_1$	0.235	0.200	0.135
$\Delta C_2$	0.510	0.430	0.430
$\Delta C_3$	0.475	0.450	0.455
$\Delta C_4$	0.485	0.360	0.380

It is seen from the Table IV that  $K_n^\circ$  values increase with increasing the acetone content and, in the same solvent, they increase with rising temperature. Figure 1 shows the dependence of  $K_n^\circ$  on the dielectric constant of the solvent (plot  $\ln K_n^\circ$  against  $D^{-1}$ ), together with the values for aqueous solution<sup>5</sup> and for the 2-propanol-water mixtures.<sup>5</sup>

Figure 1 shows that straight lines were obtained ( $K_3^\circ$  value for 50 mass per cent acetone and 50 mass per cent 2-propanol slightly deviating) which indicate that the values from  $K_1^\circ$  to  $K_3^\circ$  with the same dielectric constant are higher in the acetone-water mixtures than in the 2-propanol-water ones. It is evident that the complexation reaction and, thus, the stability constants,

are influenced not only by the physical properties of the mixed solvents, expressed by the dielectric constant, but also by their chemical properties. *i.e.* the nature of the organic component in the solvent. No values for  $K_4^\circ$  are shown because there are only two of them; however, for the same dielectric constant, they are also higher in the acetone-water mixtures than in the 2-propanol-water ones. It should be noted that Turyan and Zhantalay<sup>2</sup> have found a common straight line for the methanol-water and ethanol-water mixtures for  $K_1^\circ$  and  $K_2^\circ$ , respectively.

The standard thermodynamic quantities for the reactions forming the complexes were calculated on the basis of  $K_n^\circ$  values at different temperatures (Table IV). From the slope of the straight line in the plot  $\ln K_n^\circ$  against  $T^{-1}$  the value of  $\Delta H^\circ$  was determined, and the values of  $\Delta G^\circ$  and  $\Delta S^\circ$  were

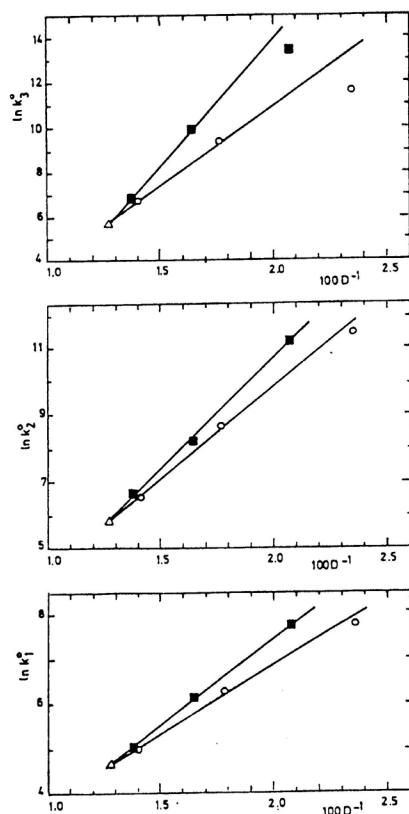


Figure 1. Variation of  $\ln K_n^\circ$  with  $D^{-1}$  at 298.15 K for: aqueous solution ( $\Delta$ ) (Ref. 5), 2-propanol-water (o) (Ref. 5) and acetone-water ( $\blacksquare$ ) mixtures.



established by means of the usual thermodynamic relations. The values at 298.15 K are given in Table V. Deviations of  $\Delta G^\circ$  were calculated from the deviations of  $K_n^\circ$ , those for  $\Delta H^\circ$  were obtained by averaging the slope of the straight line, while the values for  $\Delta S^\circ$  were calculated from the deviations of  $\Delta G^\circ$  and  $\Delta H^\circ$ .

TABLE V

Standard thermodynamic quantities for the formation reaction of the cadmium chloride complexes (2) at 298.15 K in  $x$  mass per cent acetone-water mixtures

Complex	$x = 10$	$x = 30$	$x = 50$
	$\Delta H^\circ/\text{kJ mol}^{-1}$		
$[\text{CdCl}]^+$	$8.6 \pm 0.1$	$12.2 \pm 0.3$	$32.2 \pm 0.3$
$[\text{CdCl}_2]$	$10.3 \pm 0.2$	$28.0 \pm 1.8$	$33.3 \pm 1.2$
$[\text{CdCl}_3]^-$	$23.0 \pm 0.2$	$27.7 \pm 1.7$	$31.3 \pm 0.8$
$[\text{CdCl}_4]^{2-}$	—	$31.3 \pm 2.0$	$44.6 \pm 2.1$
	$\Delta G^\circ/\text{kJ mol}^{-1}$		
$[\text{CdCl}]^+$	$-12.5 \pm 0.1$	$-15.2 \pm 0.1$	$-19.2 \pm 0.1$
$[\text{CdCl}_2]$	$-16.4 \pm 0.1$	$-20.3 \pm 0.1$	$-27.7 \pm 0.2$
$[\text{CdCl}_3]^-$	$-17.1 \pm 0.1$	$-24.5 \pm 0.1$	$-33.1 \pm 0.2$
$[\text{CdCl}_4]^{2-}$	—	$-21.7 \pm 0.2$	$-37.8 \pm 0.2$
	$\Delta S^\circ/\text{J K}^{-1} \text{ mol}^{-1}$		
$[\text{CdCl}]^+$	$70.8 \pm 0.4$	$91.9 \pm 1.3$	$172.4 \pm 1.4$
$[\text{CdCl}_2]$	$89.6 \pm 0.8$	$162.0 \pm 6.1$	$204.6 \pm 4.0$
$[\text{CdCl}_3]^-$	$134.5 \pm 0.9$	$175.1 \pm 6.0$	$216.0 \pm 3.2$
$[\text{CdCl}_4]^{2-}$	—	$177.8 \pm 6.7$	$276.4 \pm 7.6$

It can be seen from the Table V that all the reactions forming the cadmium chloride complexes are endothermic, and that they are accompanied by a rise in entropy which increases as the amount of acetone in the solvent becomes larger. It should be noted that reactions (2) in the 2-propanol-water mixtures<sup>5</sup> were found to be endothermic also with an increase in entropy, although in the acetone-water mixtures their endothermicity and entropy increase were more pronounced. It can, therefore, be concluded that the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  are also affected by the nature of the organic component in the mixed solvent.

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## SAŽETAK

**Konstante stabilnosti kadmij klorid kompleksa u smjesama  
acetona-voda (s 10, 30 i 50 masenih % acetona) na osnovi  
mjerjenja elektromotorne sile članka**

*Marija Višić i Ivica Mekjavić*

Potenciometrijskom metodom određene su konstante stabilnosti ( $K_n'$ ) kadmijevih kloro-kompleksa pri raznim ionskim jakostima u 10%-tnoj smjesi acetona-voda pri 288.15, 298.15 i 313.15 K i u 30 i 50%-tnoj smjesi pri 288.15, 298.15 i 308.15 K. Iz tih vrijednosti dobivene su termodinamičke konstante stabilnosti ( $K_n^\circ$ ) za komplekse  $[\text{CdCl}]^+$ ,  $[\text{CdCl}_2]$  i  $[\text{CdCl}_3]^-$  u 10%-tnom acetonu, a u ostalim smjesama i za kompleks  $[\text{CdCl}_4]^{2-}$ . Na osnovi temperaturne ovisnosti  $K_n^\circ$  izračunane su termodinamičke veličine za reakcije nastajanja spomenutih kompleksa, iz kojih vrijednosti proizlazi da su sve reakcije endotermne i da dovode do porasta entropije. Dobivene vrijednosti za  $K_n^\circ$  i termodinamičke veličine uspoređene su s analognim literaturnim podacima za smjese 2-propanol-voda.