CROATICA CHEMICA ACTA CCACAA **72** (1) 55–70 (1999)

ISSN-0011-1643
CCA-2560 *Original Scientific Paper*

Stability Constants of Chlorocadmium Complexes in *t*-Butanol + Water Mixtures ($w_{t\text{-BuOH}}$ = 10%, 30%, and 50%) from Electromotive Force Measurements

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Received October 26, 1998; revised January 21, 1999; accepted January 28, 1999

Potentiometric method was applied in determining the stability constants (K_n') of cadmium chloride complexes at different ionic strengths in *t*-butanol + water mixtures ($w_{t\text{-BuOH}}$ = 10%, 30%, and 50%) at 288.15, 298.15 and 313.15 K, respectively. Calculation of the constants was performed by graphical Leden's method and by numerical methods: orthogonal polynomials, and nonlinear regression without and with scaling (weighting). The values obtained by the method of orthogonal polynomials were used to establish thermodynamic stability constants (K_n°) of $CdCl^+$, $CdCl_2$ and $CdCl_3^-$ complexes in 10 mass per cent *t*-butanol and 30 mass per cent at 288.15 and 298.15 K, and also at 313.15 K and in 50 mass per cent for $CdCl_4^{2-}$ complex. Based on temperature dependence for K_n°, the thermodynamic quantities were calculated for reactions forming complexes, which are endothermic and result in increased entropy. Dependences for K_n° and for thermodynamic quantities ΔH° and ΔS° on the solvent dielectric constant are presented and were compared with analogous literature data in 2-propanol + water and acetone + water mixtures.

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INTRODUCTION

In previous works[1,2] the formation reaction of cadmium chloride complexes in mixed solvents 2-propanol + water (0, 10, 30, and 50 mass per cent) and of acetone + water of identical compositions were investigated based on the measurements of e.m.f. of the concentration cell. The stability constants of the formed complexes were determined by Leden's method, modified so that we used the method of orthogonal polynomials instead of successive graphical extrapolation.[3]

In this work we determined the stability constants of cadmium chloride complexes in *t*-butanol + water mixtures (10, 30, and 50 mass per cent), where, besides the above cited method, we also used the method of nonlinear regression,[4] the method of nonlinear regression with scaling (weighting),[5,6] and the classical Leden's method. The aim of this work is to compare the applied calculating methods and to establish their respective adequacy for the investigated system. Furthermore, by comparing the values obtained in previous systems, it is possible to establish the influence of the organic component in a mixed solvent on the stability constants, and in general on the thermodynamics of the complexation reaction. The final values obtained for stability constants will be applied in our subsequent work when dealing with data processing for e.m.f. of the cell: Cd(Hg)(l, satd.) | $CdCl_2$ (m) | AgCl(s) | Ag(s) in the same mixtures.

The e.m.f. of the concentration cell:

$$\mathrm{Cd(Hg)}\;\left|\begin{array}{ll}\mathrm{Cd(ClO_4)_2} & (x)\\ \mathrm{HClO_4} & (y)\\ \mathrm{NaClO_4} & (I-3x-y-z)\\ \mathrm{NaCl} & (z)\end{array}\right\|\left.\begin{array}{ll}\mathrm{Cd(ClO_4)_2} & (x)\\ \mathrm{HClO_4} & (y)\\ \mathrm{NaClO_4} & (I-3x-y)\\ & \end{array}\right|\;\mathrm{Cd(Hg)} \qquad (1)$$

was measured at 288.15, 298.15 and 313.15 K at ionic strength (I) 1.0, 2.0 and 3.0 mol dm^{-3} for 10 mass per cent *t*-butanol, 1.0, 2.0 and 2.5 mol dm^{-3} for 30 mass per cent, and 1.0, 1.5 and 2.0 mol dm^{-3} for 50 mass per cent. In all these cases x and y amounted to 0.01 mol dm^{-3}, while z was in the interval of 0.025–0.50 mol dm^{-3} for 10 mass per cent *t*-butanol, 0.02–0.40 mol dm^{-3} for 30 mass per cent, and for 50 mass per cent 0.01–0.35 mol dm^{-3} for I = 1.0 mol dm^{-3}, 0.01–0.30 mol dm^{-3} for I = 1.5 mol dm^{-3}, and 0.01–0.15 mol dm^{-3} for I = 2.0 mol dm^{-3}, respectively.

EXPERIMENTAL

Two stock solutions: stock 1 and stock 2, were prepared for each series of measurements in a particular solvent and ionic strength. Stock 1 solution contained 0.01

mol dm^{-3} $Cd(ClO_4)_2$, 0.01 mol dm^{-3} $HClO_4$ and $(I-0.04)$ mol dm^{-3} $NaClO_4$. Stock 2 solution was composed of 0.01 mol dm^{-3} $Cd(ClO_4)_2$, 0.01 mol dm^{-3} $HClO_4$, 0.50 mol dm^{-3} NaCl and $(I - 0.54)$ mol dm^{-3} $NaClO_4$ for 10 and 30 mass per cent *t*-butanol. In 50 mass per cent, the NaCl concentration was 0.45, 0.40 and 0.20 mol dm^{-3} depending, on the ionic strenght of the solution, *i.e.* $(I - 0.49)$, $(I - 0.44)$ and $(I - 0.24)$ mol dm^{-3} $NaClO_4$. The procedure used in preparing these solutions has already been described in detail.[1]

The applied saturated Cd(Hg) electrodes were prepared as described earlier,[7] also the cell description and the procedure in e.m.f. measurements of the cell.[1]

At least two potentiometric titrations were carried out for each t-butanol content and for each ionic strength at a determined temperature, always using freshly prepared amalgams and solutions. The average deviation of individual measurements from their mean value was from 0.02 to 0.10 mV.

RESULTS AND DISCUSSION

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

The cited values were applied in calculating the concentration stability constants (K'_n) for the following reactions:

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

Stability constants are expressed by equation:

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

where [X] is the concentration of ion X, and $c^o = 1$ mol dm^{-3}.

Considering the balance for cadmium and chloride ions, and relation (3), we obtain the expression:

$$\frac{x-[Cd^{2+}]}{[Cd^{2+}]} = F([Cl^-]) =$$

$$= K'_1[Cl^-] + K'_2[Cl^-]^2 + K'_3[Cl^-]^3 + K'_4[Cl^-]^4, \tag{4}$$

where x denotes the total concentration of Cd^{2+} ions (0.01 mol dm^{-3}), $[Cd^{2+}]$ is the concentration of free Cd^{2+} ions, and $[Cl^-]$ the concentration of free Cl^- ions.

TABLE I

Electromotive force (e.m.f./mV) of the cell (1) for different additions of chloride ions in *t*-butanol + water mixture at different ionic strengths and temperatures

[NaCl]	T / K			T / K			T / K		
mol dm^{-3}	288.15	298.15	313.15	288.15	298.15	313.15	288.15	298.15	313.15
	$w_{t\text{-BuOH}}$ = 10%								
	I = 1.0 mol dm^{-3}			I = 2.0 mol dm^{-3}			I = 3.0 mol dm^{-3}		
0.025	6.10	6.87	6.99	7.10	7.33	7.54	8.50	8.83	9.07
0.050	11.22	11.43	12.10	12.44	12.84	13.32	14.79	15.37	15.80
0.075	14.99	15.74	16.27	16.77	17.38	18.14	19.93	20.59	21.25
0.100	18.24	18.82	19.86	20.55	21.17	22.10	24.15	25.00	26.05
0.150	23.58	24.55	26.04	26.71	27.56	29.07	30.98	32.39	34.04
0.200	28.03	29.24	31.58	31.99	32.83	34.24	37.86	38.73	40.73
0.250	32.02	33.29	35.96	36.34	37.36	39.21	42.86	43.98	47.27
0.300	35.51	36.76	39.80	40.03	41.40	43.60	47.26	48.73	52.28
0.350	38.43	39.92	43.27	43.21	45.06	47.69	51.23	52.98	56.72
0.400	41.03	42.74	46.41	46.21	48.32	51.62	54.79	56.82	60.91
0.500	45.76	47.94	52.16	51.77	54.08	58.00	61.02	63.49	67.91
	$w_{t\text{-BuOH}}$ = 30%								
	I = 1.0 mol dm^{-3}			I = 2.0 mol dm^{-3}			I = 2.5 mol dm^{-3}		
0.02	7.10	7.34	7.53	7.55	7.90	8.00	8.19	8.59	9.41
0.04	12.36	12.87	13.59	13.87	14.30	15.14	14.73	15.39	16.08
0.06	16.77	17.28	18.66	18.82	19.56	20.61	20.00	21.21	22.06
0.08	20.67	21.28	23.02	22.94	23.97	25.44	24.62	25.81	27.65
0.10	23.81	24.61	26.67	26.63	27.85	29.99	28.57	29.97	32.24
0.15	30.83	32.11	34.45	34.66	36.23	39.17	37.02	38.86	43.83
0.20	36.66	38.02	41.04	41.07	43.11	46.77	44.03	46.27	52.31
0.25	41.24	43.34	47.09	46.65	49.03	53.35	50.56	52.69	59.53
0.30	45.77	47.95	52.19	51.62	54.29	59.23	55.53	58.44	65.97
0.35	49.49	51.96	56.90	56.14	59.02	64.38	60.48	63.62	71.79
0.40	52.96	55.56	61.18	60.27	63.37	69.30	64.89	68.30	77.03
	$w_{t\text{-BuOH}}$ = 50%								
	I = 1.0 mol dm^{-3}			I = 1.5 mol dm^{-3}			I = 2.0 mol dm^{-3}		
0.01(0.01)	5.18	5.57	5.21	5.46	5.85	5.95	5.65	6.20	6.58
0.02(0.02)	9.70	10.31	10.77	10.06	10.80	10.95	10.70	11.53	11.80
0.04(0.03)	16.85	18.68	19.59	17.82	19.38	20.18	15.13	15.98	16.99
0.06(0.04)	22.96	25.09	26.54	24.14	26.16	27.94	19.01	20.29	21.60
0.08(0.05)	28.08	29.86	32.32	29.44	32.05	33.49	22.61	23.92	26.22
0.10(0.06)	32.46	34.54	37.16	34.36	37.14	39.99	25.97	27.62	29.77
0.15(0.07)	42.41	45.66	48.89	44.67	48.28	52.33	28.90	30.96	33.36
0.20(0.08)	49.88	53.74	58.32	53.39	57.56	62.75	32.00	33.57	36.73
0.25(0.09)	56.71	61.21	66.53	60.73	65.57	71.40	34.77	36.46	40.17
0.30(0.10)	62.67	67.80	73.49	67.22	72.40	79.16	37.23	39.17	42.91
0.35(0.15)	68.06	73.43	79.73	–	–	–	48.82	51.43	56.84

Concentrations enclosed in brackets refer to I = 2.0 mol dm^{-3}.

The left-hand side of equation (4) can be calculated by the Nernst equation from the experimental values of e.m.f. at different NaCl concentrations and represents a dependent variable. The independent variable is [Cl$^-$] and for each measured e.m.f. the value is estimated according to Leden by determination of number N, which is the average number of coordinated chloride ions per cadmium ions complexed. The first approximate N value is calculated from two adjacent e.m.f. values; the obtained value together with the total concentration of chloride ions serves to obtain the approximate concentration of free chloride ions. The approximate K_n' values are then determined using equation (4) according to the cited methods. In the next cycle, by means of K_n', a more accurate N value is calculated, and the concentration of free Cl$^-$ ions, respectively, which is used to obtain more accurate K_n' values. The procedure is repeated until there is no change in K_n' values. A description of this iterative calculating procedure will be given for each method with some comments.

I) Leden's Method

This method of successive graphical extrapolation is used for extrapolation of the left-hand side of equation (5), obtained by rearranging equation (4):

$$\frac{x-\left[\mathrm{Cd}^{2+}\right]}{\left[\mathrm{Cd}^{2+}\right]\left[\mathrm{Cl}^{-}\right]}=F^{0}([\mathrm{Cl}^{-}])=$$

$$= K_1' + K_2'[\mathrm{Cl}^-] + K_3'[\mathrm{Cl}^-]^2 + K_4'[\mathrm{Cl}^-]^3 \qquad (5)$$

shown in graph F^0([Cl$^-$]) against [Cl$^-$] to [Cl$^-$] = 0. After determining K_1' an analogous procedure is used to establish K_2' and other constants, respectively. This method, however, has all the disadvantages of graphical methods, and in addition the accumulation of errors in the higher constants, which enbody the graphically determined lower K_n'.

II) Method of Orthogonal Polynomials

Here the right-hand side of equation (5) is solved as a polynomial of the second or third degree. An already prepared computer program (ORTHLS), based on the least squares method, finds the polynomial that best approximates a series of experimental data by using orthogonal polynomials. Complete calculation is carried out on computer. The program for calculating [Cd^{2+}], [Cl$^-$] and F^0([Cl$^-$]) is written in FORTRAN, and the calculation of K_n' is preformed by interpolated subroutine ORTHLS.

III) Method of Nonlinear Regression

This method implies the application of the least squares method on nonlinear function (4). The requirement is that the best polynomial is the one having the least value of the sum of the square of residuals (difference between the measured value: left-hand side of equation (4), and the calculated value). With 11 simultaneous equations (for 11 measured values) of type (4) with unknowns from K_1' to K_n', by satisfying the requirement of the minimum, we obtain a system with 3 (respectively 4) equations having 3 (respectively 4) unknowns (depending on the number of constants), which are diagonally symmetrical, in the form:

$$K_1'\Sigma[\mathrm{Cl}^-]^2 + K_2'\Sigma[\mathrm{Cl}^-]^3 + K_3'\Sigma[\mathrm{Cl}^-]^4 + K_4'\Sigma[\mathrm{Cl}^-]^5 = \Sigma F([\mathrm{Cl}^-])[\mathrm{Cl}^-]$$

$$K_1'\Sigma[\mathrm{Cl}^-]^3 + K_2'\Sigma[\mathrm{Cl}^-]^4 + K_3'\Sigma[\mathrm{Cl}^-]^5 + K_4'\Sigma[\mathrm{Cl}^-]^6 = \Sigma F([\mathrm{Cl}^-])[\mathrm{Cl}^-]^2$$

$$K_1'\Sigma[\mathrm{Cl}^-]^4 + K_2'\Sigma[\mathrm{Cl}^-]^5 + K_3'\Sigma[\mathrm{Cl}^-]^6 + K_4'\Sigma[\mathrm{Cl}^-]^7 = \Sigma F([\mathrm{Cl}^-])[\mathrm{Cl}^-]^3$$

$$K_1'\Sigma[\mathrm{Cl}^-]^5 + K_2'\Sigma[\mathrm{Cl}^-]^6 + K_3'\Sigma[\mathrm{Cl}^-]^7 + K_4'\Sigma[\mathrm{Cl}^-]^8 = \Sigma F([\mathrm{Cl}^-])[\mathrm{Cl}^-]^4.$$

This system of equations was solved using the matrix method. It should be pointed out that in solving the system of equations (4) by this method, which have the wide range in the order of magnitude in the value of $F([\mathrm{Cl}^-])$, the solutions are consistent only for higher values of K_n'.

IV) Method of Nonlinear Regression with Scaling

The problem of the wide range in the order of magnitudes in $F([\mathrm{Cl}^-])$ values can be reduced by scaling (weighting) the simultaneous equations (4), rearranging them in the form (6):

$$\frac{0.01}{\left[\mathrm{Cd}^{2+}\right]} - 1 = F'([\mathrm{Cl}^-]) - 1 =$$

$$= K_1'[\mathrm{Cl}^-] + K_2'[\mathrm{Cl}^-]^2 + K_3'[\mathrm{Cl}^-]^3 + K_4'[\mathrm{Cl}^-]^4 \, . \qquad (6)$$

Each simultaneous equation is multiplied by the scaling (weighting) factor $\alpha = 1 / F'([\mathrm{Cl}^-])$, which thus makes the lower values of $F([\mathrm{Cl}^-])$ comparable with the higher ones. Satisfying the required minimum of the sum of the square of residuals, we obtain the system of equations:

$$K'_1\Sigma\alpha^2[\mathrm{Cl}^-]^2 + K'_2\Sigma\alpha^2[\mathrm{Cl}^-]^3 + K'_3\Sigma\alpha^2[\mathrm{Cl}^-]^4 + K'_4\Sigma\alpha^2[\mathrm{Cl}^-]^5 = \\ = \Sigma[F'([\mathrm{Cl}^-]) - 1]\alpha^2[\mathrm{Cl}^-]$$

$$K'_1\Sigma\alpha^2[\mathrm{Cl}^-]^3 + K'_2\Sigma\alpha^2[\mathrm{Cl}^-]^4 + K'_3\Sigma\alpha^2[\mathrm{Cl}^-]^5 + K'_4\Sigma\alpha^2[\mathrm{Cl}^-]^6 = \\ = \Sigma[F'([\mathrm{Cl}^-]) - 1]\alpha^2[\mathrm{Cl}^-]^2$$

$$K'_1\Sigma\alpha^2[\mathrm{Cl}^-]^4 + K'_2\Sigma\alpha^2[\mathrm{Cl}^-]^5 + K'_3\Sigma\alpha^2[\mathrm{Cl}^-]^6 + K'_4\Sigma\alpha^2[\mathrm{Cl}^-]^7 = \\ = \Sigma[F'([\mathrm{Cl}^-]) - 1]\alpha^2[\mathrm{Cl}^-]^3$$

$$K'_1\Sigma\alpha^2[\mathrm{Cl}^-]^5 + K'_2\Sigma\alpha^2[\mathrm{Cl}^-]^6 + K'_3\Sigma\alpha^2[\mathrm{Cl}^-]^7 + K'_4\Sigma\alpha^2[\mathrm{Cl}^-]^8 = \\ = \Sigma[F'([\mathrm{Cl}^-]) - 1]\alpha^2[\mathrm{Cl}^-]^4 \ .$$

This system of equations was also solved by the cited matrix method.

The K'_n values calculated by the cited methods are not final, since they are obtained from the e.m.f. values which include the junction potential. The junction potential between the two half-cells was calculated by the Henderson equation, the e.m.f. values were corrected by that amount and the whole procedure was repeated. The final calculated K'_n values are given in Table III.

To calculate the junction potential, it is necessary to provide the data for conductivity and concentration of the particular ionic species, and they are obtained as previously described.[1] Since the conductivity is obtained by using the Walden rule, the needed data for the viscosity of the solvents are determined using the Ostwald viscosimeter (Table II), while the data for the density of solvents are taken from literature.[8]

As a rule, the junction potential increases with a higher concentration of chloride ions, it decreases with an increase in the ionic strength, while it slightly changes with an increase in *t*-butanol content; also, no temperature

TABLE II

Viscosity coefficient ($\eta \times 10^3$ / Pa s) of *t*-butanol + water mixtures at different temperatures

$w_{t\text{-BuOH}}$	T / K		
	288.15	298.15	313.15
10%	2.046	1.460	0.968
30%	5.013	3.258	1.772
50%	7.151	4.405	2.421

TABLE III

Stability constants K_n' of the cadmium chloride complexes calculated by different methods in *t*-butanol + water mixture at different ionic strengths and temperatures

T / K	288.15				298.15				313.15			
Method	I	II	III	IV	I	II	III	IV	I	II	III	IV
$w_{t\text{-BuOH}} = 10\%$												
$I = 1.0$ mol dm^{-3}												
K_1'	31	28.9	27.4	29.1	30	30.9	30.0	30.4	30	29.4	29.0	29.0
K_2'	55	86	98	82	76	67	75	70	90	88	93	91
K_3'	140	63	42	71	77	118	103	113	100	140	131	139
$I = 2.0$ mol dm^{-3}												
K_1'	34	34.2	36.3	33.9	34	34.6	33.3	34.6	33	34.8	34.2	34.9
K_2'	160	139	123	142	128	122	133	121	110	98	102	99
K_3'	70	149	174	142	185	216	198	221	285	333	327	329
$I = 3.0$ mol dm^{-3}												
K_1'	44	43.1	40.2	43.9	44	45.4	43.7	45.7	42	41.4	34.6	42.8
K_2'	265	255	281	235	220	207	221	201	270	246	304	215
K_3'	490	543	496	599	625	680	654	696	650	751	650	834
$w_{t\text{-BuOH}} = 30\%$												
$I = 1.0$ mol dm^{-3}												
K_1'	44	44.9	43.6	44.8	45	44.9	41.2	44.9	43	45.1	47.2	44.8
K_2'	220	206	222	205	200	201	242	194	210	234	186	250
K_3'	400	481	442	489	555	601	508	627	700	642	911	495
K_4'	–	–	–	–	–	–	–	–	190	630	204	938
$I = 2.0$ mol dm^{-3}												
K_1'	52	50.8	50.2	51.3	51	51.3	50.3	51.5	46	47.8	44.6	48.4
K_2'	400	362	373	347	410	362	382	354	540	476	539	457
K_3'	310	655	597	752	570	923	801	972	460	801	465	920
K_4'	1820	1250	1343	1081	1580	1103	1307	1016	2700	2403	2928	2192
$I = 2.5$ mol dm^{-3}												
K_1'	57	57.2	52.0	57.5	56	58.6	60.8	58.3	55	55.0	–	–
K_2'	440	411	517	401	520	445	397	463	490	562	–	–
K_3'	1100	1578	999	1633	900	1458	1721	1298	3400	2730	–	–
K_4'	2450	1314	2237	1231	3350	2402	1993	2750	1800	3759	–	–

TABLE III

Continued

T / K	288.15				298.15				313.15			
Method	I	II	III	IV	I	II	III	IV	I	II	III	IV
$w_{t\text{-BuOH}} = 50\%$												
$I = 1.0$ mol dm^{-3}												
K_1'	–	73.6	66.6	73.8	–	81.1	89.0	81.7	–	73.6	81.9	74.1
K_2'	–	640	833	582	–	613	415	593	–	850	608	932
K_3'	–	2993	1685	3734	–	4925	6230	5005	–	5035	6740	3650
K_4'	–	4879	7416	2911	–	5480	3035	5460	–	9565	6220	13695
$I = 1.5$ mol dm^{-3}												
K_1'	–	81.0	77.0	80.7	–	87.1	95.0	85.8	–	80.6	64.9	80.4
K_2'	–	645	764	646	–	799	565	868	–	1000	1470	982
K_3'	–	5840	4928	5910	–	7025	8865	6265	–	7525	3870	7815
K_4'	–	6782	8842	6494	–	11065	6885	13225	–	21510	29755	20730
$I = 2.0$ mol dm^{-3}												
K_1'	–	87.6	85.8	87.9	–	95.9	–	94.8	–	94.2	–	91.2
K_2'	–	932	1050	899	–	890	–	923	–	1155	–	1317
K_3'	–	9535	7495	10645	–	10410	–	10395	–	13745	–	11265
K_4'	–	14040	27090	9880	–	26100	–	22760	–	40125	–	51065

effect was observed in the investigated concentration range. Moreover, the junction potential had very little effect on K_1', averaging 0.5%, about 2% for K_2', about 7% for K_3', while the change in K_4' amounted to 10% on average. No significant difference was observed of the junction potential effect on K_n' values, depending on the calculating method applied.

From Table III it is seen that, in 10 mass per cent *t*-butanol up to ionic strength $I = 3.0$ mol dm^{-3}, complexes $CdCl^+$, $CdCl_2$ and $CdCl_3^-$ are formed, while in 30 mass per cent at $I = 1.0$ mol dm^{-3} at 313.15 K we also find complex $CdCl_4^{2-}$, which continues to be present at higher ionic strengths and with a higher content of *t*-butanol in the mixture.

Comparing all the obtained K_n' values, it can be seen that maximal deviations are found with Leden's method, especially with higher K_n' values. Also, a more reliable determination for 50 mass per cent *t*-butanol was not possible as there were only two points available for establishing K_1' values. However, it can be said that, in general, the classical Leden's method makes it possible to know the number of present complex species, and also to note the particular measurements with marked deviations.

A comparison of K'_n values obtained from the three numerical methods (II, III and IV), performed by calculating the percentage deviations in K'_n obtained by the methods II and III, II and IV, and III and IV, enables observing the following.

Deviations in all of these combinations increase from lower to higher K'_n values.

Fewest deviations were found in comparing the values obtained by the method of orthogonal polynomials (II) and the method of nonlinear regression with scaling (IV). For all mixed solvents, these deviations in K'_1 were about 1% on average, and in K'_2 up to 5%. Deviations in K'_3, and particularly in K'_4, are higher, especially with higher amounts of *t*-butanol. While K'_3 values in 10 mass per cent *t*-butanol differ by about 5% on average, they amount to about 10% with 30 and 50 mass per cent *t*-butanol, and in 50 mass per cent the average deviation for K'_4 is about 20%.

Comparing the deviations in K'_n obtained in other combinations: the method of orthogonal polynomials (II) and the method of nonlinear regression (III), and also of method (III) and method (IV) with the foregoing ones, it is observed that they are considerably higher. Thus, for instance, average deviations with 10 mass per cent *t*-butanol in K'_1 are about 6%, in K'_2 and K'_3 they amount to 12%, and 13%, respectively. In 50 mass per cent, these deviations increase up to 10% in K'_1, up to 32% in K'_2, 39% in K'_3, and about 50% in K'_4. It is also important to note that with two series of measurements in 50 mass per cent *t*-butanol (I = 2.0 mol dm^{-3} at 298.15 and 313.15 K) and with one series of measurements in 30 mass per cent (I = 2.5 mol dm^{-3} at 313.15 K), it was impossible to calculate the values by applying method (III) (one of the constants had negative value); this leads to the conclusion that the method of nonlinear regression (III) is not suitable for calculating K'_n in solvents with a higher *t*-butanol content.

Thus, it is evident that the best agreements in K'_n values are shown by the method of orthogonal polynomials (II) and the method of nonlinear regression with scaling (IV). However, preference can be given to the method of orthogonal polynomials because it was applicable to the whole range, while the results obtained by the method of nonlinear regression with scaling were not satisfactory (one of the constants had negative value) in 30 mass per cent *t*-butanol for I = 2.5 mol dm^{-3} at 313.15 K.

In further processing we will use the concentration constants obtained by the method of orthogonal polynomials to calculate the thermodynamic stability constants (K°_n) by means of equation (7):

$$\log K'_n - \Delta z^2 AI^{1/2} / (1 + BaI^{1/2}) = \log K^\circ_n + \Delta C_n I/c^\circ \, . \tag{7}$$

Namely, from the graphical representation of the left-hand side of the equation against the ionic strength we obtain a straight line, so the value of K_n° is obtained from its intercept, and the value ΔC_n from its slope. In this equation, A and B are the Debye-Hückel constants, which were calculated

TABLE IV

Stability constants K_n° of the cadmium chloride complexes and ΔC_n in t-butanol + water mixtures at different temperatures

T / K	288.15	298.15	313.15
	$w_{t\text{-BuOH}}$ = 10%		
K_1°	166 ± 7	182 ± 3	200 ± 12
K_2°	794 ± 34	1000 ± 60	1260 ± 100
K_3°	400 ± 20	1200 ± 96	1590 ± 125
ΔC_1	0.177	0.173	0.157
ΔC_2	0.388	0.333	0.307
ΔC_3	0.590	0.437	0.473
	$w_{t\text{-BuOH}}$ = 30%		
K_1°	550 ± 8	630 ± 4	693 ± 24
K_2°	7945 ± 580	10000 ± 705	13180 ± 790
K_3°	10715 ± 875	18620 ± 930	25120 ± 3000
K_4°	*	*	10500 ± 1155
ΔC_1	0.196	0.196	0.192
ΔC_2	0.376	0.368	0.416
ΔC_3	0.528	0.460	0.460
ΔC_4	*	*	0.432
	$w_{t\text{-BuOH}}$ = 50%		
K_1°	4170 ± 215	5370 ± 270	6170 ± 235
K_2°	218800 ± 16190	316200 ± 28460	660700 ± 66100
K_3°	501200 ± 39600	1.32×10^6 ± 112000	1.86×10^6 ± 69000
K_4°	72450 ± 5870	93330 ± 4530	288400 ± 31700
ΔC_1	0.275	0.280	0.320
ΔC_2	0.460	0.450	0.455
ΔC_3	0.810	0.700	0.765
ΔC_4	0.770	0.855	0.800

*Not calculated – comment given in text.

by means of the dielectric constants of the solvents taken from Åkerlöf,[9] a is the ion-size parameter (taken 0.45 nm), $\Delta z^2 = z^2(\text{CdCl}_n^{(2-n)+}) - z^2(\text{Cd}^{2+}) - nz^2(\text{Cl}^-)$, and $-\Delta C_n = C(\text{CdCl}_n^{(2-n)+}) - C(\text{Cd}^{2+}) - nC(\text{Cl}^-)$. In these expressions, z and C represent the charge and the empirical constant for each ion. The values for K_n° and for ΔC_n are given in Table IV. Constant K_4° and the value ΔC_4 for 30 mass per cent *t*-butanol at 288.15 and 298.15 K were not calculated due to uncertainties, as the K_4' for only two ionic strengths were established (2.0 and 2.5 mol dm^{-3}). Deviations of K_n° values were obtained by averaging the intercept of the straight line.[1]

From Table IV, it can be seen that the thermodynamic stability constants increase with increasing the content of *t*-butanol in the mixture, and that

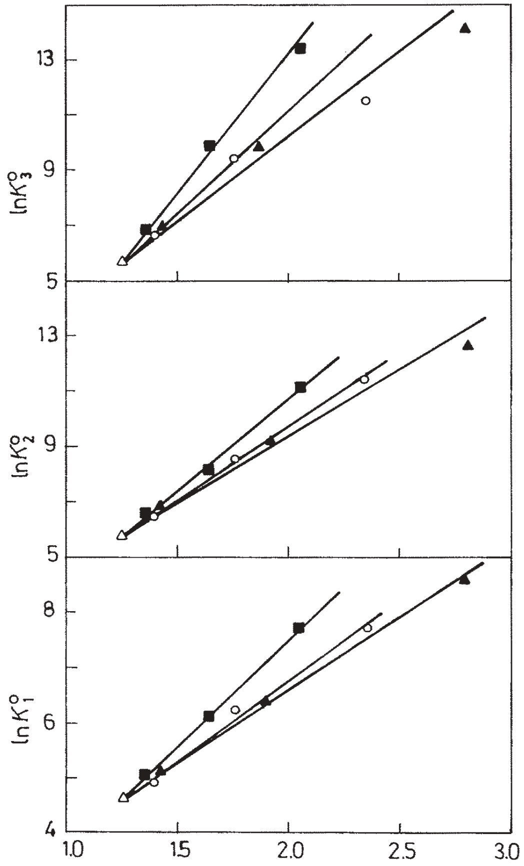

Figure 1. Variation of ln K_n° with D^{-1} at 298.15 K for: aqueous solution (Δ) (Ref. 1), *t*-butanol + water (▲), 2-propanol + water (○) (Ref. 1) and acetone + water (■) (Ref. 2) mixtures.

they increase in the same solvent with a rise in temperature. Analogy was established with the mixtures 2-propanol + water,[1] and acetone + water.[2]

In order to determine the influence of the organic component in the mixed solvent on the stability constants, Figure 1 shows the dependencies of K_n° values on the solvent dielectric constant (plot ln K_n° against D^{-1}). It can be seen that straight lines are obtained (K_3° somewhat deviates with 50 mass per cent 2-propanol), and that the constants from K_1° to K_3° at the same dielectric constant are the highest in acetone + water mixtures, the least in *t*-butanol + water mixtures, while the solvents containing an alcohol component show less mutual difference. It is evident that the stability constants are influenced not only by physical properties of the mixed solvents expressed by the dielectric constant but also by the nature of the organic component, particularly by noticing the effect of the change of the alcohol into the keto group.

Since the thermodynamic stability constants were determined at different temperatures, it was possible to establish the thermodynamic quantities for the reactions forming Cd chloride complexes. Namely, ΔH° was deter-

TABLE V

Standard thermodynamic quantities for the formation reaction of the cadmium chloride complexes (2) at 298.15 K in *t*-butanol + water mixtures

Complex	$w_{t\text{-BuOH}}$ = 10%	$w_{t\text{-BuOH}}$ = 30%	$w_{t\text{-BuOH}}$ = 50%
		ΔH° / kJ mol^{-1}	
$CdCl^+$	5.7 ± 0.1	7.5 ± 0.2	11.9 ± 0.4
$CdCl_2$	13.8 ± 0.3	15.7 ± 0.1	30.5 ± 0.8
$CdCl_3^-$	19.0 ± 1.1	28.6 ± 1.4	41.6 ± 1.9
$CdCl_4^{2-}$	–	*	44.7 ± 2.1
		ΔG° / kJ mol^{-1}	
$CdCl^+$	–12.9 ± 0.0	–16.0 ± 0.0	–21.2 ± 0.1
$CdCl_2$	–17.1 ± 0.2	–22.8 ± 0.2	–31.6 ± 0.2
$CdCl_3^-$	–17.4 ± 0.2	–24.2 ± 0.2	–34.4 ± 0.2
$CdCl_4^{2-}$	–	*	–28.8 ± 0.2
		ΔS° / J K^{-1} mol^{-1}	
$CdCl^+$	62.4 ± 0.4	78.8 ± 0.7	111.0 ± 1.7
$CdCl_2$	103.6 ± 1.7	129.1 ± 1.0	208.3 ± 3.4
$CdCl_3^-$	122.1 ± 4.4	177.1 ± 5.4	254.9 ± 7.0
$CdCl_4^{2-}$	–	*	246.5 ± 7.7

*Not calculated – comment given in text.

mined from the plot ln K_n° against T^{-1}, and ΔG° and ΔS° by using the usual relations. The values at 298.15 K are given in Table V. Thermodynamic quantities for complex forming $CdCl_4^{2-}$ in 30 mass per cent *t*-butanol were not calculated because of the already mentioned uncertainty in obtaining K_4° in this mixture. Deviations of ΔG° were calculated from the deviations of K_n°, those for ΔH° were obtained by averaging the slope of the straight line, while the values for ΔS° were calculated from the deviations of ΔG° and ΔH°.

From the data shown in the table it is seen that the reactions forming Cd chloride complexes are endothermic and that they are accompanied by an increase in entropy; they also show a continuous rise as the content of t-butanol is increased in the mixture. An analogy was established with the mixtures acetone + water[2] and the mixtures 2-propanol + water.[1] However, a certain discontinuity in $CdCl_3^-$ complex in this solvent was observed.

To establish the possible influence of the organic component in the mixed solvent on the cited thermodynamic quantities, Figure 2 gives the de-

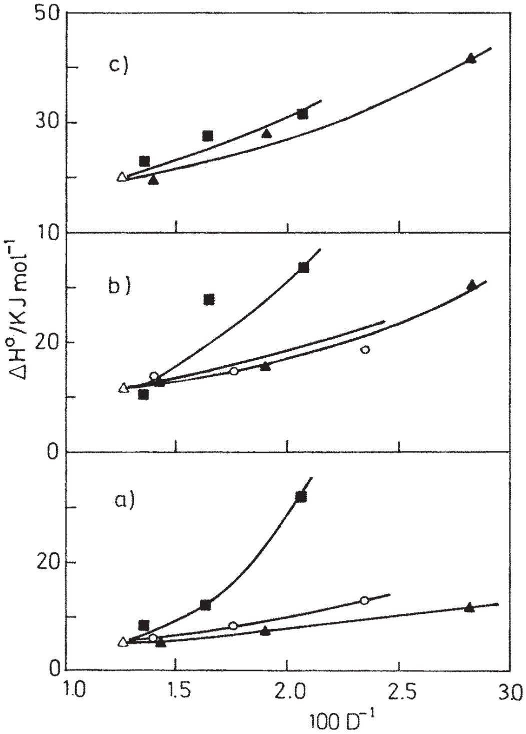

Figure 2. Variation of ΔH° with D^{-1} at 298.15 K for the formation reaction of: a) $CdCl^+$, b) $CdCl_2$ and c) $CdCl_3^-$ complexes in: aqueous solution (Δ) (Ref. 1), *t*-butanol + water (▲), 2-propanol + water (O) (Ref. 1) and acetone + water (■) (Ref. 2) mixtures.

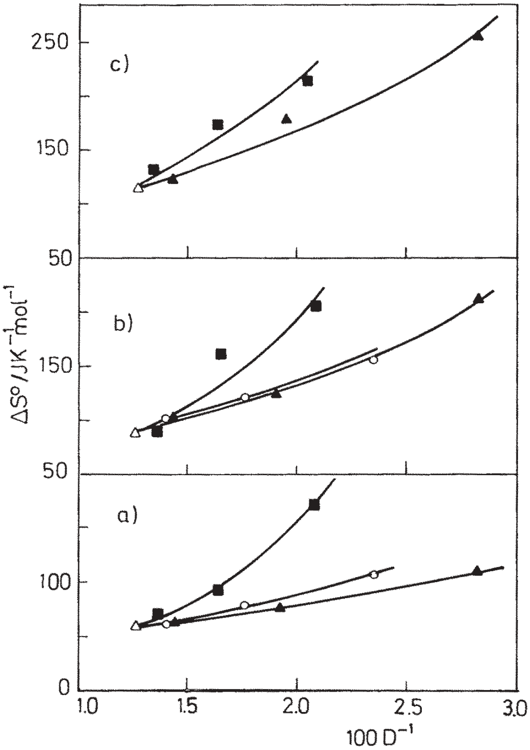

Figure 3. Variation of $\Delta S°$ with D^{-1} at 298.15 K for the formation reaction of: a) $CdCl^+$, b) $CdCl_2$ and c) $CdCl_3^-$ complexes in: aqueous solution (Δ) (Ref. 1), *t*-butanol + water (▲), 2-propanol + water (○) (Ref. 1) and acetone + water (■) (Ref. 2) mixtures.

pendence of $\Delta H°$ on the dielectric constant of the solvent (plot $\Delta H°$ against D^{-1}), and Figure 3 analogous dependence for $\Delta S°$. No data are given for $CdCl_3^-$ complex in 2-propanol + water mixtures in view of the cited discontinuity. It can also be concluded that endothermicity and increase in entropy at the same dielectric constant are most pronounced with acetone + water mixtures, and in general the least with t-butanol + water ($\Delta H°$ for complex $CdCl_2$ somewhat deviates with 50 mass per cent 2-propanol), their differences being less prominent with alcohol mixtures. Therefore, the thermodynamic quantities $\Delta H°$ and $\Delta S°$ of the complexation reactions are influenced both by physical properties of the mixed solvents expressed by the dielectric constant and also by the organic component, this effect being more prominent when there is a change of the alcohol group into the keto group.

Acknowledgement. – This work was supported by the Ministry of Science and Technology of the Republic of Croatia (Project No. 011008).

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SAŽETAK

Konstante stabilnosti kadmij klorid kompleksa u smjesama *t*-butanol + voda ($w_{t\text{-BuOH}}$ = 10%, 30% i 50%) na osnovi mjerenja elektromotorne sile članka

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Potenciometrijskom metodom određene su konstante stabilnosti (K_n') klorokadmijevih kompleksa pri raznim ionskim jakostima u smjesama *t*-butanol + voda ($w_{t\text{-BuOH}}$ = 10%, 30% i 50%), pri 288,15 K, 298,15 K i 313,15 K. Izračunavanje konstanti izvršeno je klasičnom grafičkom Ledenovom metodom, kao i numeričkim metodama (ortogonalni polinomi, nelinearna regresija bez i sa skaliranjem). Iz vrijednosti dobivenih metodom ortogonalnih polinoma dobivene su termodinamičke konstante stabilnosti (K_n°) za komplekse $CdCl^+$, $CdCl_2$ i $CdCl_3^-$ u 10%-tnom *t*-butanolu i 30%-tnom pri 288,15 i 298,15 K, a pri 313,15 K i u 50%-tnom još i za kompleks $CdCl_4^{2-}$. Na osnovi temperaturne ovisnosti K_n° izračunane su termodinamičke veličine za reakcije nastajanja spomenutih kompleksa, koje su sve endotermne i dovode do porasta entropije. Prikazane su ovisnosti K_n° i termodinamičkih veličina ΔH° i ΔS° o dielektričkoj konstanti otapala i izvršena je usporedba s analognim literaturnim podacima za smjese 2-propanol + voda i aceton + voda.