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Investigation of the Complex Forming Reactions of Cd^{2+} and Cl^{-} Ions in 2-Butanone + Water Mixtures by Direct Potentiometry

Renato Tomaš,[a],* Ivo Tominić,[a] Vesna Sokol,[a] and Marija Višić[b]

[a]*Department of Physical Chemistry, Faculty of Chemical Technology, University of Split, Teslina 10, 21000 Split, Croatia*

[b]*Department of Chemistry, Faculty of Natural Sciences, Mathematics and Education, University of Split, Teslina 12, 21000 Split, Croatia*

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The complex forming reactions of cadmium and chloride ions in 2-butanone + water mixtures (with mass fraction of the organic component 0.05, 0.10 and 0.15) at three ionic strengths and three temperatures were investigated by the method of direct potentiometry by means of calibration straight lines. As that experimental technique has not yet been tested in mixed solvents, first, measurements in 10 % (mass fraction) *t*-butanol at ionic strength of 1 mol dm^{-3} and temperatures 288.15, 298.15 and 313.15 K were performed and stability constants of chlorocadmium complexes were redetermined. Comparing these values with those obtained by measuring the e.m.f. of the concentration cell with transference, reproducibility and applicability of direct potentiometry in that mixed solvent were proven. According to statistical parameters, direct potentiometry retains the precision of the potentiometry of the concentration cell with transference, but, due to the absence of junction potential, it is undoubtedly more accurate. In the mixtures of water and 2-butanone, $CdCl^{+}$, $CdCl_2$ and $CdCl_3^{-}$ complexes were found as well as their concentration stability constants (K'_n) by the method of orthogonal polynomials for each ionic strength and temperature. By the extrapolation of semiempirical straight lines to zero ionic strength, thermodynamic stability constants (K^{o}_n) were obtained. It was found that the K^{o}_n values increase with the increase of temperature and with the decrease of relative permittivity of the solvent. From the temperature dependence of K^{o}_n, thermodynamic quantities for the complex forming reactions were calculated; all the reactions are spontaneous, endothermic and lead to an increase in entropy.

Key words
2-butanone + water mixtures
chlorocadmium complexes
direct potentiometry
stability constants
thermodynamic quantities

INTRODUCTION

By measuring the e.m.f. of the chemical cell without transference, the thermodynamics of HBr electrolyte in 2-butanone + water mixtures (mass fraction, $w_{\text{2-butanone}} = 5$, 10 and 15 %) was investigated.[1] The obtained thermodynamic quantities for the transfer of that electrolyte from water into the investigated mixtures indicate changes in the solvent structure as well as in the ion-solvent interaction. Potentiometric study of $CdCl_2$ in the same mixtures could show how the change of the electrolyte type is reflected on the thermodynamic quantities of transfer.

As the Cd^{2+} ion tends to complexation, processing of the existing potentiometric data of the chemical cell with $CdCl_2$ is not possible without knowing the stability

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* Author to whom correspondence should be addressed. (E-mail: rtomas@ktf-split.hr)

constants of chlorocadmium complexes. Among the numerous methods for the determination of these constants, the most common ones in literature are the potentiometric methods. Thus, the complexation of Cd^{2+} ion with orthophosphate,[2] with polymethacrylic acid[3] and taurine[4] in water, with CN^- ion in the mixtures of acetonitrile + water[5] and also with Cl^- ion in water[6,7] and in the mixtures of 2-propanol + water,[7] acetone + water[8] and *t*-butanol + water,[9] was observed.

Whereas all the mentioned works use cells where different solutions are in contact, with direct potentiometry both electrodes are in the same solution and therefore there is no problematic junction potential. The method of direct potentiometry was investigated with $CdCl_2$ in water at 298.15 K.[10] In this work, its applicability to mixed solvents with a lower content of organic component in water was proven. For that purpose, first, the concentration stability constants (K'_n) of chlorocadmium complexes in 10 % (*w*) *t*-butanol at unit ionic strength and at temperatures of 288.15, 298.15 and 313.15 K were redetermined and compared to those obtained by measuring the e.m.f. of the concentration cell with transference.[9] Compared to that work, here the concentration of total cadmium was increased five times in order to get a faster response and more stable potential of the amalgam electrode.

Then, stability constants in 2-butanone + water mixtures were determined in the same way. Their values at three temperatures were used to determine the standard thermodynamic quantities for the formation reactions of chlorocadmium complexes.

EXPERIMENTAL

Four stock solutions, labeled A_1, A_2, B and C, had to be prepared for each solvent and each ionic strength. All solutions were prepared at 20 °C. Thus, the composition of solutions for 5 % 2-butanone was:

A_1: $x = 0.0503$ mol dm^{-3} in $Cd(ClO_4)_2$
$e = 0.0100$ mol dm^{-3} in $HClO_4$
$I - 3x - e$ in $NaClO_4$,

A_2: $y = 0.50$ mol dm^{-3} in NaCl
$e = 0.0100$ mol dm^{-3} in $HClO_4$
$I - y - e$ in $NaClO_4$,

B: $e = 0.0100$ mol dm^{-3} in $HClO_4$
$I - e$ in $NaClO_4$,

C: $x = 0.0503$ mol dm^{-3} in $Cd(ClO_4)_2$
$y = 0.50$ mol dm^{-3} in NaCl
$e = 0.0100$ mol dm^{-3} in $HClO_4$
$I - 3x - y - e$ in $NaClO_4$.

For 10 % *t*-butanol, the concentrations of $Cd(ClO_4)_2$ and $HClO_4$ were $x = 0.0508$ mol dm^{-3}, and $e = 0.0103$ mol dm^{-3}, respectively, while they were the same as above in 10 % 2-butanone. Ionic strengths (I) in 5 % 2-butanone amounted to 1.0, 2.0 and 3.0 mol dm^{-3}; in 10 % 2-butanone to 1.0, 1.5 and 2.0 mol dm^{-3}; and in 15 % 2-butanone to 0.6, 1.0 and 1.5 mol dm^{-3}. In 10 and 15 % 2-butanone, ionic strength had to be decreased gradually to avoid the division of solutions in two layers in the temperature range 288.15–313.15 K. Consequently, total cadmium was reduced to $x = 0.0296$ mol dm^{-3} in 15 % 2-butanone, and total chloride to $y = 0.40$ mol dm^{-3} in 10 % 2-butanone at all ionic strengths, as well as to $y = 0.20$ mol dm^{-3} ($I = 0.6$ and 1.0 mol dm^{-3}), and $y = 0.15$ mol dm^{-3} ($I = 1.5$ mol dm^{-3}) in 15 % 2-butanone, respectively.

2-butanone (Merck, *p.a.*) and *t*-butanol (Riedel-deHaën, *p.a.*) were fractionally distilled before use. The purity of other chemicals as well as the preparation of stock solutions were described earlier.[7,10] In this work, in order to speed up the procedure, an accurate concentration of $Cd(ClO_4)_2$ in solutions A_1 and C was achieved by pipetting from the previously prepared more concentrated water solution of the same electrolyte. All stock solutions have to be of the same concentration in $HClO_4$, so its preparation was accomplished with special care. Additional pH checks, occasionally made by a combined glass electrode (In-Lab 412, Mettler Toledo), differed only by a few thousandths of a unit.

As indicator electrodes, saturated Cd(Hg) with 11 % (*w*) cadmium and AgCl/Ag electrodes were used. The amalgam electrode preparation procedure was described earlier,[11] except that here mercury of 99.9999 % purity (Merck, *suprapur*) was used, while cadmium granules (Merck, *p.a.*) were previously shortly treated with concentrated HNO_3 (Kemika, *p.a.*) to speed up amalgamation. The interpotential of amalgam electrodes, controlled in an adequate water solution (0.05 mol dm^{-3} in $Cd(ClO_4)_2$, 0.01 mol dm^{-3} in $HClO_4$, and 0.84 mol dm^{-3} in $NaClO_4$), was under 0.1 mV (usually 0.05 mV), and the electrodes retained stability and reproducibility for a long time. The preparation and requirements for the AgCl/Ag electrode were described earlier.[12] In both cases, a Feussner potentiometer was used to control the potential difference between the indicator electrodes.

A glass electrode (In-Lab 201, Mettler Toledo), of the glass membrane resistance lower than 500 MΩ, was used in this work as a reference electrode. The way of checking the stability of the glass electrode potential, as well as the composition of the solution for stability checking, was given earlier.[10] It was thus found that the same electrode retains stability of ±0.3 mV within a month. The glass electrode was kept in a solution of KCl (3 mol dm^{-3}) between measurements.

The experimental procedure for obtaining the stability constants by direct potentiometry consisted of three steps: in steps 1 and 2 data were gathered for the construction of calibration diagrams for cadmium and chloride ions, respectively, while in step 3 (or the so-called »working« measurement) the complex forming reactions were investigated potentiometrically in a three-electrode cell.

Calibration diagram for Cd^{2+} was obtained from the e.m.f. data (E_1) of the cell:

$$(-)\mathrm{Cd(Hg)}\,|\,\text{test solution}\,|\,\text{glass electrode}(+) \qquad \text{(cell 1)}$$

The cell was filled with the stock solution B (50 cm^3) and placed in a thermostated water bath at a constant temperature, with a slow stream of nitrogen passing through. Composition of test solution in Cd^{2+} was changed stepwise by adding stock solution A_1 from a burette according to Schelbach into cell 1. Each increment of A_1 was followed by the e.m.f. readings, repeated at five-minute intervals until constant.

The e.m.f. (E_2) of the cell:

$$(-)\text{Ag}\,|\,\text{AgCl}\,|\,\text{test solution}\,|\,\text{glass electrode}(+) \quad \text{(cell 2)}$$

depends on the chloride ion concentration. During calibration the $[Cl^-]$ was varied by pouring known volume portions of stock solution A_2 into cell 2, already filled with a definite volume of B.

For the »working« measurement (step 3), both cells share a common test solution which, at the beginning, was represented by a definite volume of A_1. In accordance with the desired total chloride concentration ($c_{tot}(Cl^-)$), calculated doses of stock solution C were added to A_1 and the e.m.f. of cells 1 and 2 was recorded. Equilibrium concentrations of the Cd^{2+} and Cl^- ions could be derived from the previously constructed calibration diagrams.

A digital pH-meter (MP 230, Mettler Toledo), relative accuracy ±0.1 mV, was used in all e.m.f. measurements. Each measuring step was performed simultaneously in triplicate cells at different ionic strengths and at a defined constant temperature ($T \pm 0.02$ K).

More detailed description of the procedure and cells was presented earlier.[10]

RESULTS AND DISCUSSION

Formation of chlorocadmium complexes can be shown by the following equilibrium reaction:

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

assuming the absence of polynuclear species.

The concentration stability constant (K'_n) for the above reaction is given by the equation:

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

where the expressions in square brackets denote the equilibrium concentration of the reaction participants, while $c^\circ = 1$ mol dm^{-3}.

Equilibrium concentrations of free cadmium and chloride ions are obtained by direct potentiometry. With these concentrations, we enter the expression:

$$\frac{x-[Cd^{2+}]}{[Cd^{2+}][Cl^-]}\cdot c^\circ = F\,([Cl^-]\,/\,c^\circ) = K'_1 + K'_2([Cl^-]\,/\,c^\circ) + K'_3([Cl^-]\,/\,c^\circ)^2 + K'_4([Cl^-]\,/\,c^\circ)^3 \quad (3)$$

TABLE I. Concentration stability constants K'_n of chlorocadmium complexes in 10 % *t*-butanol + water mixture by »direct potentiometry« and »concentration cell potentiometry« (values in brackets) at different temperatures [(a)]

	288.15 K	298.15 K	313.15 K
K'_1	26.6 ± 0.4 (28.9 ± 0.5)	27.5 ± 0.4 (30.9 ± 0.7)	33.6 ± 0.2 (29.4 ± 0.6)
K'_2	131 ± 6 (86 ± 5)	145 ± 7 (67 ± 7)	147 ± 4 (88 ± 7)
K'_3	61 ± 19 (63 ± 10)	99 ± 25 (118 ± 14)	59 ± 15 (140 ± 14)
R^2	0.9997 (0.9989)	0.9994 (0.9982)	0.9977 (0.9990)

[(a)] Ionic strength $I = 1.0$ mol dm^{-3}; R is the correlation coefficient.

and then a row of the so-called simultaneous equations is obtained, where x denotes the total cadmium concentration. In this work, constants were solved by the method of orthogonal polynomials.[13] Their standard deviations, as well as the correlation coefficient (R^2), were calculated in the same way as before.[10]

Table I gives the values of K'_n, redetermined by direct potentiometry in 10 % *t*-butanol at unit ionic strength and at different temperatures. For comparison, in brackets are also the values of the constants obtained from the e.m.f. measurement of the concentration cell with transference[9] in the same system.

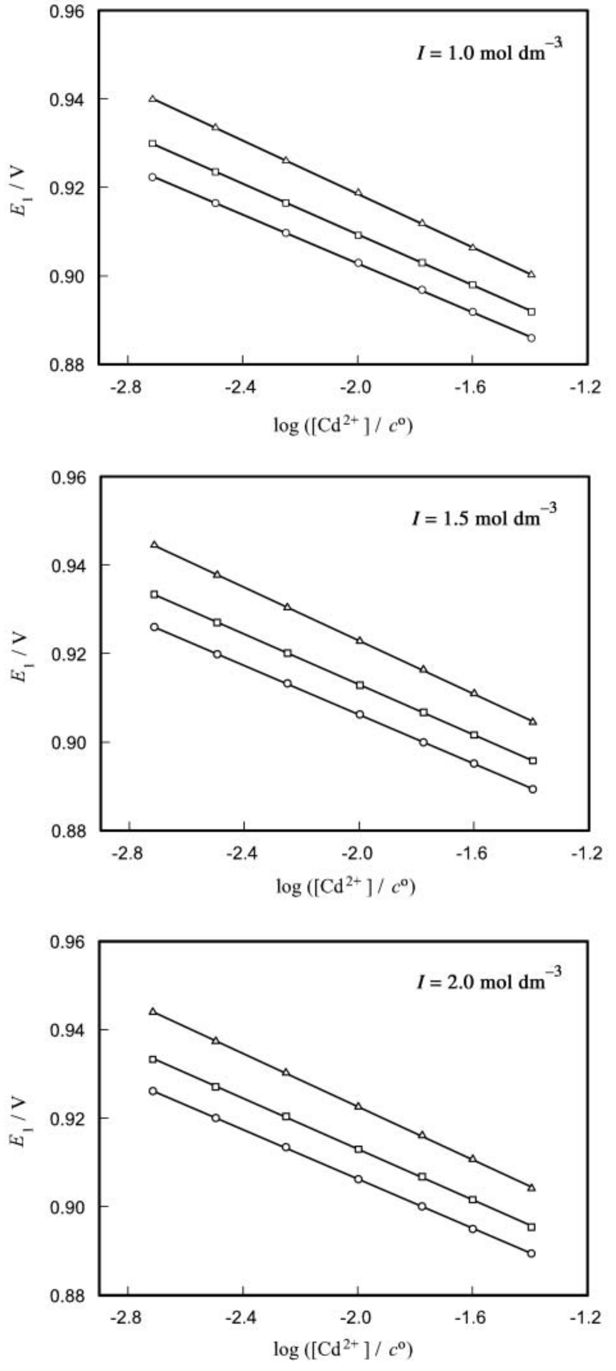
Table I indicates that, using the method of direct potentiometry, three types of chlorocadmium complexes were found: $CdCl^+$, $CdCl_2$ and $CdCl_3^-$. The agreement between the model and experiment (value R^2) is generally better in direct potentiometry. Furthermore, both experimental methods give more or less similar values of the standard deviation of constants, but direct potentiometry gives somewhat lesser deviations for K'_1. Also, our standard deviations are at the level of those of Martell and Smith, obtained for the same complexes in an aqueous medium.[14] Consequently, besides good precision, direct potentiometry has a great advantage of the absence of junction potential.

Figures 1 and 2 show the calibration diagrams for cadmium and chloride ions, respectively, obtained experimentally in 10 % (*w*) 2-butanone + water mixture, at various ionic strengths and temperatures. In the other two mixtures, the slope and interrelation of straight lines are quite similar.

Equations of calibration straight lines for cadmium and chloride ions were obtained by the method of least squares and generally are:

$$E_1/\text{V} = L - S\,\log([Cd^{2+}]\,/\,c^\circ) \quad (4)$$

$$E_2/\text{V} = L' + S'\,\log([Cl^-]\,/\,c^\circ) \quad (5)$$



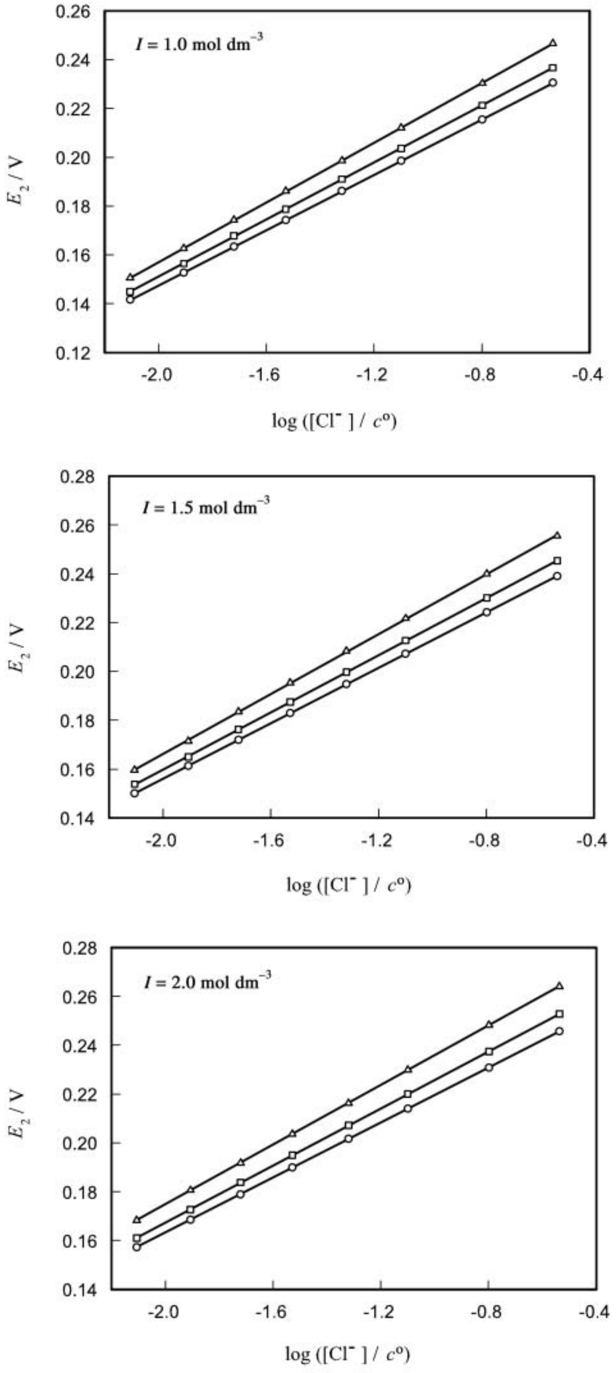


Figure 1. The e.m.f. dependence of cell 1 on the logarithm of the Cd^{2+} ion concentration ($Cd(ClO_4)_2$) in 10 % 2-butanone + water mixture at different ionic strengths and temperatures (288.15 K (○), 298.15 K (□), 313.15 K (△)).

Figure 2. The e.m.f. dependence of cell 2 on the logarithm of the Cl^- ion concentration (NaCl) in 10 % 2-butanone + water mixture at different ionic strengths and temperatures (288.15 K (○), 298.15 K (□), 313.15 K (△)).

Consequently, Eq. (4) represents the e.m.f. dependence of cell 1 on the concentration of cadmium ion, while Eq. (5) yields the e.m.f. dependence of cell 2 on known chloride ion concentrations. The values of the intercept and slope of the calibration straight line for cadmium ion (L and S) and for chloride ion (L' and S') in the investigated 2-butanone + water mixtures, at various ionic strengths and temperatures, are given in Table II.

The responses of the electrodes used in the investigated solvents (see Figures 1 and 2) are linear, the correlation coefficient values are high and, except in a few cases (marked by asterisks in Table II), amount to $R^2 = 0.9999$. Further, the average relative deviation of the experimental slope from the theoretical one is greater for the cadmium ion (about 3 %) than for the chloride ion (about 1 %). It was also found that this deviation for the cadmium ion

TABLE II. Parameters of the calibration straight lines L and S (Eq. 4) for cadmium ion and L' and S' (Eq. 5) for chloride ion in w/% 2-butanone + water mixtures at different ionic strengths (I) and temperatures[(a)]

	w = 5			w = 10			w = 15		
I / mol dm^{-3}:	1.0	2.0	3.0	1.0	1.5	2.0	0.6	1.0	1.5
					288.15 K				
L	0.8519	0.8549*	0.8532	0.8477	0.8506	0.8503	0.8447**	0.8478	0.8481*
L'	0.2589	0.2737	0.2883	0.2608	0.2695	0.2760	0.2606	0.2668	0.2727
S	0.0276	0.0273*	0.0278	0.0275	0.0278	0.0279	0.0276**	0.0276	0.0279*
S'	0.0564	0.0569	0.0565	0.0567	0.0567	0.0564	0.0565	0.0565	0.0568
					298.15 K				
L	0.8559	0.8586	0.8584	0.8520	0.8561	0.8557*	0.8485	0.8518	0.8524
L'	0.2662	0.2807	0.2966	0.2679	0.2770	0.2842	0.2676	0.2740	0.2801
S	0.0289	0.0289	0.0287	0.0287	0.0285	0.0287*	0.0287	0.0288	0.0288
S'	0.0584	0.0584	0.0583	0.0584	0.0586	0.0585	0.0586	0.0585	0.0586
					313.15 K				
L	0.8618	0.8651	0.8652	0.8582	0.8626	0.8624*	0.8528	0.8591	0.8590*
L'	0.2769	0.2939	0.3105	0.2794	0.2889	0.2969	0.2794	0.2857	0.2927
S	0.0303	0.0304	0.0304	0.0302	0.0302	0.0301*	0.0307	0.0304	0.0306*
S'	0.0611	0.0618	0.0612	0.0612	0.0613	0.0611	0.0614	0.0612	0.0615

[(a)] In cases marked by (*) and (**) R^2 amounts to 0.9998 and 0.9996, respectively; otherwise its value is 0.9999.

mainly decreases with the increase of temperature, while for the chloride ion it is greater at higher temperatures.

The results of the »working« e.m.f. measurement in a three-electrode cell (E_1 and E_2), at various ionic strengths, temperatures, and NaCl concentrations, are shown in Table III for the investigated 2-butanone + water mixtures.

Equilibrium concentrations of Cd^{2+} and Cl^- ions were then obtained from calibration diagrams, *i.e.,* by the use of Eqs. (4) and (5). These data served to calculate the K'_n values by the method of orthogonal polynomials.

It was previously mentioned that the composition of stock solutions was accurately determined at 293.15 K. In this work, stability constants were calculated without taking into account the change of concentration with temperature. Since the densities of stock solutions are not the same, the concentrations at other temperatures could be only estimated. Repeated treatment with corrected concentrations in 10 % (w) 2-butanone for unit ionic strength showed that the differences in constants were negligible at 288.15 and 298.15 K, whereas at 313.15 K there was an error in K'_1, K'_2, and K'_3 of approximately 1 %, 3 %, and 6 %, respectively.

Table IV presents the K'_n values and their standard deviations for the investigated 2-butanone + water mixtures at various ionic strengths and temperatures. R is the correlation coefficient of the polynomial (Eq. (3)).

The table shows that three kinds of chlorocadmium complexes are present in the investigated mixtures: $CdCl^+$, $CdCl_2$ and $CdCl_3^-$. Comparing the K'_n values at unit ionic strength, it can be seen that the constants increase with the increase of 2-butanone content in the mixture. Consequently, the stability of the complex is greater in the solvent of lower relative permittivity. Furthermore, measurements in 15 % 2-butanone were aggravated, because, to prevent the salting-out effect, it was necessary to achieve a lower ionic strength and to narrow considerably the range of the chloride ion concentrations; as a consequence, weaker correlation arose (value R^2). The K'_n change with temperature is regular only for the first complex, *i.e.,* K'_1 increases with an increase in temperature. Standard deviations of the constants increase with increasing the degree of complexation in the investigated mixtures.

From the K'_n values listed in Table IV, the stability constants at zero ionic strength (K°_n) can be evaluated by the equation:

$$\ln K'_n - \Delta z^2 A(I/\text{mol dm}^{-3})^{1/2}/(1+B(a/\text{nm})(I/\text{mol dm}^{-3})^{1/2}) = \ln K^\circ_n + (\ln 10)\Delta C_n I/c^\circ \qquad (6)$$

from the graphical representation of its left-hand side against I. Namely, K°_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 Debye-Hückel parameters calculated by the data for relative permittivity of the solvent[15]

TABLE III. Experimental e.m.f. of cells 1 and 2 in »working« measurement for different concentrations of total chloride, $c_{tot}(Cl^-)$, in w / % 2-butanone + water mixtures at different ionic strengths and temperatures

T/K	$\frac{c_{tot}(Cl^-)}{mol\ dm^{-3}}$ (a)	E_1/V	E_2/V	E_1/V	E_2/V	E_1/V	E_2/V
		w = 5 %					
		I = 1.0 mol dm^{-3}		I = 2.0 mol dm^{-3}		I = 3.0 mol dm^{-3}	
288.15	0.025	0.8905	0.1507	0.8934	0.1623	0.8935	0.1747
	0.050	0.8941	0.1705	0.8972	0.1831	0.8978	0.1955
	0.075	0.8973	0.1823	0.9007	0.1947	0.9018	0.2075
	0.100	0.9002	0.1905	0.9042	0.2036	0.9057	0.2166
	0.150	0.9055	0.2027	0.9099	0.2159	0.9125	0.2292
	0.200	0.9100	0.2111	0.9147	0.2245	0.9182	0.2380
	0.250	0.9139	0.2176	0.9189	0.2311	0.9232	0.2446
	0.300	0.9173	0.2225	0.9226	0.2363	0.9277	0.2499
	0.350	0.9204	0.2269	0.9260	0.2409	0.9310	0.2542
298.15	0.025	0.8968	0.1540	0.8996	0.1666	0.8999	0.1790
	0.050	0.9006	0.1745	0.9035	0.1873	0.9045	0.2004
	0.075	0.9041	0.1867	0.9074	0.1994	0.9087	0.2129
	0.100	0.9073	0.1953	0.9110	0.2086	0.9128	0.2226
	0.150	0.9129	0.2079	0.9170	0.2212	0.9198	0.2355
	0.200	0.9177	0.2166	0.9221	0.2300	0.9258	0.2446
	0.250	0.9218	0.2233	0.9266	0.2368	0.9309	0.2514
	0.300	0.9253	0.2284	0.9305	0.2422	0.9354	0.2568
	0.350	0.9284	0.2328	0.9340	0.2466	0.9394	0.2613
313.15	0.025	0.9048	0.1586	0.9086	0.1727	0.9092	0.1860
	0.050	0.9089	0.1805	0.9128	0.1947	0.9142	0.2090
	0.075	0.9124	0.1930	0.9168	0.2076	0.9187	0.2220
	0.100	0.9160	0.2022	0.9204	0.2173	0.9231	0.2322
	0.150	0.9219	0.2153	0.9270	0.2304	0.9304	0.2459
	0.200	0.9269	0.2244	0.9323	0.2397	0.9369	0.2554
	0.250	0.9311	0.2313	0.9372	0.2466	0.9423	0.2624
	0.300	0.9350	0.2368	0.9413	0.2520	0.9471	0.2679
	0.350	0.9382	0.2413	0.9449	0.2565	0.9513	0.2724
		w = 10 %					
		I = 1.0 mol dm^{-3}		I = 1.5 mol dm^{-3}		I = 2.0 mol dm^{-3}	
288.15	0.010	0.8846	0.1275	0.8880	0.1353	0.8879	0.1407
	0.025	0.8869	0.1511	0.8903	0.1591	0.8903	0.1649
	0.050	0.8904	0.1708	0.8938	0.1789	0.8942	0.1846
	0.075	0.8938	0.1827	0.8974	0.1909	0.8978	0.1967
	0.100	0.8970	0.1917	0.9008	0.1999	0.9015	0.2055
	0.150	0.9024	0.2040	0.9067	0.2119	0.9074	0.2177
	0.200	0.9070	0.2122	0.9120	0.2204	0.9126	0.2263
	0.250	0.9110	0.2187	0.9158	0.2268	0.9169	0.2327
	0.300	0.9145	0.2239	0.9193	0.2321	0.9208	0.2378
298.15	0.010	0.8907	0.1305	0.8946	0.1381	0.8945	0.1439
	0.025	0.8930	0.1547	0.8969	0.1626	0.8969	0.1685
	0.050	0.8967	0.1749	0.9008	0.1831	0.9009	0.1891
	0.075	0.9002	0.1871	0.9044	0.1955	0.9047	0.2017
	0.100	0.9035	0.1962	0.9079	0.2047	0.9084	0.2109
	0.150	0.9092	0.2088	0.9138	0.2173	0.9145	0.2235
	0.200	0.9140	0.2175	0.9188	0.2260	0.9199	0.2324
	0.250	0.9182	0.2242	0.9231	0.2328	0.9244	0.2390
	0.300	0.9219	0.2295	0.9269	0.2381	0.9285	0.2443

(cont.)

313.15	0.010	0.8993	0.1342	0.9039	0.1429	0.9037	0.1494
	0.025	0.9021	0.1602	0.9066	0.1690	0.9065	0.1755
	0.050	0.9062	0.1816	0.9108	0.1904	0.9109	0.1971
	0.075	0.9103	0.1945	0.9154	0.2035	0.9155	0.2103
	0.100	0.9139	0.2041	0.9190	0.2130	0.9193	0.2200
	0.150	0.9200	0.2173	0.9254	0.2263	0.9258	0.2334
	0.200	0.9251	0.2265	0.9305	0.2354	0.9314	0.2423
	0.250	0.9294	0.2333	0.9352	0.2425	0.9361	0.2492
	0.300	0.9333	0.2388	0.9389	0.2479	0.9404	0.2547
		w = 15 %					
		I = 0.6 mol dm^{-3}		I = 1.0 mol dm^{-3}		I = 1.5 mol dm^{-3}	
288.15	0.015 (0.02)	0.8894	0.1437	0.8928	0.1498	0.8947	0.1621
	0.030 (0.03)	0.8926	0.1625	0.8960	0.1686	0.8970	0.1733
	0.045 (0.04)	0.8954	0.1736	0.8991	0.1797	0.8987	0.1815
	0.060 (0.05)	0.8981	0.1825	0.9017	0.1884	0.9006	0.1880
	0.080 (0.06)	0.9013	0.1904	0.9051	0.1964	0.9024	0.1931
	0.100 (0.07)	0.9042	0.1968	0.9079	0.2028	0.9042	0.1977
	0.120 (0.08)	0.9072	0.2022	0.9107	0.2081	0.9059	0.2014
	0.140 (0.10)	0.9094	0.2064	0.9134	0.2123	0.9086	0.2076
	0.160 (0.12)	0.9113	0.2101	0.9157	0.2158	0.9109	0.2127
298.15	0.015 (0.02)	0.8950	0.1461	0.8988	0.1527	0.9007	0.1659
	0.030 (0.03)	0.8986	0.1654	0.9023	0.1718	0.9030	0.1774
	0.045 (0.04)	0.9016	0.1772	0.9054	0.1836	0.9050	0.1858
	0.060 (0.05)	0.9043	0.1858	0.9082	0.1921	0.9069	0.1923
	0.080 (0.06)	0.9075	0.1944	0.9117	0.2005	0.9087	0.1977
	0.100 (0.07)	0.9106	0.2010	0.9147	0.2071	0.9105	0.2025
	0.120 (0.08)	0.9136	0.2064	0.9178	0.2124	0.9121	0.2064
	0.140 (0.10)	0.9160	0.2110	0.9204	0.2169	0.9150	0.2127
	0.160 (0.12)	0.9180	0.2148	0.9229	0.2206	0.9175	0.2180
313.15	0.015 (0.02)	0.9028	0.1508	0.9089	0.1580	0.9109	0.1723
	0.030 (0.03)	0.9065	0.1713	0.9126	0.1777	0.9131	0.1844
	0.045 (0.04)	0.9098	0.1839	0.9159	0.1904	0.9156	0.1934
	0.060 (0.05)	0.9128	0.1929	0.9188	0.1993	0.9177	0.2003
	0.080 (0.06)	0.9163	0.2018	0.9224	0.2082	0.9194	0.2060
	0.100 (0.07)	0.9197	0.2090	0.9258	0.2153	0.9219	0.2109
	0.120 (0.08)	0.9227	0.2146	0.9289	0.2209	0.9237	0.2151
	0.140 (0.10)	0.9254	0.2192	0.9317	0.2255	0.9266	0.2217
	0.160 (0.12)	0.9276	0.2233	0.9345	0.2296	0.9292	0.2272

[a] Concentrations in brackets refer to I = 1.5 mol dm^{-3}.

and temperature, a is the ion-size parameter (the value of 0.45 nm was used[7–9]),

$$\Delta z^2 = z^2(\mathrm{CdCl}_n^{(2-n)+}) - z^2(\mathrm{Cd}^{2+}) - nz^2(\mathrm{Cl}^-),$$

$$-\Delta C_n = C(\mathrm{CdCl}_n^{(2-n)+}) - C(\mathrm{Cd}^{2+}) - nC(\mathrm{Cl}^-).$$

In these expressions, z and C represent the charge and the empirical constant for each ion. The standard deviation of stability constants $\sigma(K^{\mathrm{o}}_n)$ was obtained by averaging the intercept of the straight line.[7]

The obtained constants, their standard deviations and ΔC_n values at various temperatures for the investigated solvents are given in Table V.

It can be seen that the constants increase with the increase of temperature in case of the same composition of the solvent, and with the increase of 2-butanone content at the same temperature.

Finally, the K^{o}_n values at various temperatures from Table V served to determine the standard thermodynamic quantities ΔH^{o}, ΔG^{o} and ΔS^{o} for the formation

TABLE IV. Concentration stability constants K'_n of chlorocadmium complexes in w/% 2-butanone + water mixtures at different ionic strengths and temperatures[(a)]

	288.15 K	298.15 K	313.15 K
	w = 5 %, I = 1.0 mol dm^{-3}		
K'_1	23.8 ± 0.3	26.4 ± 0.3	27.5 ± 0.4
K'_2	93 ± 5	104 ± 4	114 ± 7
K'_3	51 ± 15	38 ± 14	42 ± 25
R^2	0.9997	0.9998	0.9992
	w = 5 %, I = 2.0 mol dm^{-3}		
K'_1	28.3 ± 0.6	30.6 ± 0.3	31.3 ± 0.4
K'_2	151 ± 10	133 ± 5	147 ± 8
K'_3	59 ± 32	136 ± 15	226 ± 31
R^2	0.9994	0.9999	0.9995
	w = 5 %, I = 3.0 mol dm^{-3}		
K'_1	38.2 ± 0.9	40.1 ± 0.2	43.1 ± 0.5
K'_2	273 ± 17	251 ± 5	227 ± 10
K'_3	276 ± 64	452 ± 18	735 ± 42
R^2	0.9994	0.9999	0.9998
	w = 10 %, I = 1.0 mol dm^{-3}		
K'_1	28.0 ± 0.2	29.2 ± 0.1	36.4 ± 0.3
K'_2	109 ± 5	108 ± 3	95 ± 9
K'_3	76 ± 21	96 ± 13	202 ± 40
R^2	0.9996	0.9998	0.9984
	w = 10 %, I = 1.5 mol dm^{-3}		
K'_1	29.1 ± 0.3	30.7 ± 0.2	38.4 ± 0.5
K'_2	117 ± 9	142 ± 5	142 ± 12
K'_3	395 ± 46	92 ± 24	118 ± 50
R^2	0.9995	0.9997	0.9989
	w = 10 %, I = 2.0 mol dm^{-3}		
K'_1	32.5 ± 0.4	33.7 ± 0.2	44.2 ± 0.5
K'_2	173 ± 10	159 ± 6	127 ± 11
K'_3	153 ± 45	261 ± 27	515 ± 50
R^2	0.9993	0.9998	0.9995
	w = 15 %, I = 0.6 mol dm^{-3}		
K'_1	30.0 ± 0.7	33.6 ± 0.6	36.4 ± 0.3
K'_2	160 ± 29	135 ± 23	137 ± 10
K'_3	356 ± 259	333 ± 174	469 ± 78
R^2	0.9982	0.9978	0.9998
	w = 15 %, I = 1.0 mol dm^{-3}		
K'_1	32.8 ± 0.7	34.8 ± 0.6	38.6 ± 0.2
K'_2	151 ± 22	172 ± 20	120 ± 5
K'_3	534 ± 154	475 ± 144	840 ± 38
R^2	0.9988	0.9985	0.9999
	w = 15 %, I = 1.5 mol dm^{-3}		
K'_1	33.5 ± 0.7	36.4 ± 0.2	41.1 ± 0.7
K'_2	114 ± 38	135 ± 10	120 ± 47
K'_3	1582 ± 471	441 ± 107	1561 ± 692
R^2	0.9994	0.9996	0.9969

[(a)] R is the correlation coefficient.

TABLE V. Thermodynamic stability constants K^{o}_n of chlorocadmium complexes and ΔC_n of Eq. (6) in w/% 2-butanone + water mixtures at different temperatures

	288.15 K	298.15 K	313.15 K
	w = 5 %		
K^{o}_1	110 ± 1	129 ± 1	138 ± 2
K^{o}_2	780 ± 13	960 ± 47	1295 ± 3
K^{o}_3	220 ± 32	355 ± 58	460 ± 80
ΔC_1	0.193	0.183	0.190
ΔC_2	0.373	0.327	0.283
ΔC_3	0.523	0.613	0.597
	w = 10 %		
K^{o}_1	148 ± 1	160 ± 1	198 ± 2
K^{o}_2	1005 ± 57	1215 ± 71	1345 ± 150
K^{o}_3	500 ± 150	630 ± 127	795 ± 115
ΔC_1	0.185	0.185	0.207
ΔC_2	0.390	0.325	0.285
ΔC_3	0.650	0.520	0.635
	w = 15 %		
K^{o}_1	163 ± 7	189 ± 5	208 ± 6
K^{o}_2	1995 ± 400	2150 ± 345	2240 ± 4
K^{o}_3	1630 ± 150	2820 ± 700	3310 ± 200
ΔC_1	0.245	0.225	0.260
ΔC_2	0.295	0.300	0.237
ΔC_3	0.990	0.593	0.860

TABLE VI. Standard thermodynamic quantities for the formation reaction (1) of chlorocadmium complexes at 298.15 K in w/% 2-butanone + water mixtures

Complex	w = 5	w = 10	w = 15
		ΔH^{o}/kJ mol^{-1}	
$CdCl^+$	7.27 ± 0.10	8.31 ± 0.20	8.73 ± 0.20
$CdCl_2$	14.97 ± 0.10	9.35 ± 0.20	5.20 ± 0.10
$CdCl_3^-$	22.86 ± 0.90	12.68 ± 0.10	20.79 ± 1.30
		ΔG^{o}/kJ mol^{-1}	
$CdCl^+$	–12.05 ± 0.02	–12.64 ± 0.02	–12.89 ± 0.07
$CdCl_2$	–17.02 ± 0.12	–17.51 ± 0.14	–19.02 ± 0.40
$CdCl_3^-$	–14.38 ± 0.40	–15.98 ± 0.50	–19.28 ± 0.62
		ΔS^{o}/J K^{-1} mol^{-1}	
$CdCl^+$	64.80 ± 0.34	70.27 ± 0.67	72.51 ± 0.71
$CdCl_2$	107.29 ± 0.52	90.09 ± 0.82	81.23 ± 1.38
$CdCl_3^-$	124.90 ± 3.30	96.13 ± 1.71	134.40 ± 4.83

reactions (1) of chlorocadmium complexes in the investigated mixtures. The ΔH^{o} values were determined from the straight line slope in diagram $\ln K^{o}_n$ against T^{-1}, and their standard deviations $\sigma(\Delta H^{o})$ were determined by averaging its slope.[7] ΔS^{o} is a linear combination of the two variables, ΔH^{o} and ΔG^{o}, and $\sigma(\Delta S^{o})$ is calculated accordingly.[7] In order to determine $\sigma(\Delta G^{o})$, it was necessary to previously linearize the expression $\Delta G^{o} = -RT \ln K^{o}_{n}$. For these calculations, the K^{o}_{n} values were taken from the regression straight line $\ln K^{o}_{n}$ against T^{-1}. The values at 298.15 K are given in Table VI.

It can be seen that the complexation reactions of cadmium chloride are spontaneous, endothermic and lead to increase in entropy. It could be said that ΔG^{o} is negative, since the entropy part is dominant. The same was also found for the mixtures of 2-propanol + water,[7] acetone + water,[8] as well as for *t*-butanol + water.[9]

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REFERENCES

1. I. Tominić and I. Mekjavić, *J. Chem. Thermodyn.* **11** (1979) 167–172.
2. M. Iuliano and R. Porto, *Ann. Chim.* **84** (1994) 211–232.
3. R. Serra, F. Mas, J. M. Diaz-Cruz, C. Arino, and M. Esteban, *Electroanalysis* **12** (2000) 60–65.
4. E. Bottari and M. R. Festa, *Talanta* **46** (1998) 91–99.
5. K. Kurnia, D. E. Giles, P. M. May, P. Singh, and G. T. Hefter, *J. Coord. Chem.* **38** (1996) 183–197.
6. V. A. Prokuev, E. A. Belousov, and E. A. Karel, *Zh. Neorg. Khim.* **30** (1985) 1203–1205.
7. M. Višić, A. Jadrić, and I. Mekjavić, *Croat. Chem. Acta* **66** (1993) 489–498.
8. M. Višić and I. Mekjavić, *Croat. Chem. Acta* **69** (1996) 17–26.
9. M. Višić, R. Tomaš, and I. Mekjavić, *Croat. Chem. Acta* **72** (1999) 55–70.
10. R. Tomaš, M. Višić, I. Tominić, and V. Sokol, *Croat. Chem. Acta* **74** (2001) 91–101.
11. M. Višić and I. Mekjavić, *J. Chem. Thermodyn.* **21** (1989) 139–145.
12. D. J. G. Ives and G. J. Janz, *Reference Electrodes*, Academic Press, New York, 1961, p. 203.
13. B. Carnahan, H. A. Luther, and J. O. Wilkes, *Applied Numerical Methods*, John Wiley and Sons, New York, 1969, p. 574.
14. A. E. Martell and R. M. Smith, *Critical Stability Constants*, Vol. 4, Plenum Press, New York, 1981, p. 108.
15. G. Åkerlöf, *J. Am. Chem. Soc.* **54** (1932) 4125–4139.

SAŽETAK

Ispitivanje reakcija kompleksiranja iona Cd^{2+} i Cl^{-} u smjesama 2-butanon + voda izravnom potenciometrijom

Renato Tomaš, Ivo Tominić, Vesna Sokol i Marija Višić

Ispitane su reakcije nastajanja klorokadmijevih kompleksa u smjesama 2-butanon + voda (s masenim udjelom organskoga sastojka od 0,05, 0,10 i 0,15) pri tri ionske jakosti i tri temperature metodom izravne potenciometrije uz pomoć baždarnih pravaca. Kako ta eksperimentalna tehnika još nije bila testirana u miješanim otapalima, prvo su obavljena mjerenja u 10 %-tnom *t*-butanolu pri ionskoj jakosti od 1 mol dm^{-3} i temperaturama 288,15, 298,15 i 313,15 K i redeterminirane konstante stabilnosti klorokadmijevih kompleksa. Usporedbom tih vrijednosti s onima dobivenim mjerenjem EMS koncentracijskoga članka s prijenosom dokazana je reproducibilnost i primjenjivost izravne potenciometrije u tome miješanom otapalu. Prema statističkim parametrima izravna potenciometrija zadržava preciznost potenciometrije koncentracijskoga članka s prijenosom, ali je zbog odsustva spojnog potencijala nedvojbeno točnija. U smjesama vode i 2-butanona nađeni su kompleksi $CdCl^{+}$, $CdCl_2$ i $CdCl_3^{-}$ te određene njihove koncentracijske konstante stabilnosti (K'_{n}) metodom ortogonalnih polinoma za svaku ionsku jakost i temperaturu. Ekstrapoliranjem semiempirijskih pravaca na nultu ionsku jakost dobivene su termodinamičke konstante stabilnosti (K^{o}_{n}). Utvrđeno je da vrijednosti K^{o}_{n} rastu s porastom temperature te sa smanjenjem relativne permitivnosti otapala. Iz ovisnosti K^{o}_{n} o temperaturi izračunane su termodinamičke veličine za reakcije nastajanja spomenutih kompleksa; sve su reakcije spontane, endotermne i vode do porasta entropije.