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Complexation of Cd^{2+} and Cl^- Ions in Aqueous Mixtures of 2-Butanol

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Reactions of chlorocadmium complex formation have been studied in mixtures of 2-butanol + water ($w_{\text{2-BuOH}}$ = 0.05, 0.10, and 0.15) at three ionic strengths and three temperatures by means of direct potentiometry. First, calibration diagrams for cadmium and chloride ions were made, based on e.m.f. (electromotive force) measurements in solution with known concentrations of these ions, followed by e.m.f. measurements in a series of solutions with known concentrations of total cadmium and total chlorides in which complexation took place. Using the latter e.m.f. data and the respective calibration diagrams, concentrations of free cadmium and chloride ions were determined for each ionic strength and temperature. Three complexes were found in each mixed solvent: $CdCl^+$, $CdCl_2$ and $CdCl_3^-$. Their concentration stability constants (K'_n) were calculated by the method of orthogonal polynomials for each ionic strength and temperature. The thermodynamic stability constants (K°_n) were determined for each temperature in a particular mixed solvent, and were found to increase with increasing temperature, as well as with decreasing relative permittivity of the mixed solvent, for each complex species. By comparison with the K°_n constants in the 2-butanone + water solvent, the influence of the organic component was established. Thermodynamic quantities for the complex formation reactions, calculated from K°_n, have shown that complexation is spontaneous, endothermic, and accompanied by an entropy increase.

INTRODUCTION

Potentiometric investigations of complexation in aqueous cadmium chloride have developed in two distinct pathways. First, the activity coefficient is estimated by a form of the Debye–Hückel (D–H) equation, and measurements are performed on the chemical cell without liquid junction. Using this approach, Harned and Fitzgerald[1] determined the stability constant of $CdCl^+$. Reilly and Stokes[2] added NaCl to $CdCl_2$, and calculated all four constants using the extended D–H equation. Lutfullah and Paterson[3] applied the same procedure to aqueous CdI_2.

The second approach assumes a stable activity coefficient, provided the ionic strength is kept constant, and operates on a concentration cell. Besides the pioneer work by Leden,[4] one should mention the work of Vanderzee and Dawson[5] where the original cell was modified and graphical treatment was replaced by a numerical one. Following the latter scheme in our laboratory, the forma-

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tion of chlorocadmium complexes was investigated in aqueous 2-propanol,[6] acetone[7] and *t*-butanol[8] mixtures with further improvement of the computational technique.

Our recent papers report on complex formation in water[9] and 2-butanone + water mixtures[10] (with ketone mass fraction, w = 0.05, 0.10, and 0.15) determined by direct potentiometry with a reference glass electrode. This technique eliminates the greatest objection to the second approach, the junction potential. Furthermore, in contrast to the concentration cell potentiometry, here the free chloride concentration is determined experimentally.

In our laboratory, we have been determining, by means of chemical cell potentiometry, the thermodynamic quantities for electrolyte transfer from water to an alcohol (or ketone) + water mixture. These quantities were further used in an attempt to elucidate the solvent properties. The interpretation of these quantities for a 1–1 type electrolyte, such as HBr, has provided some insight into the structure and acid–base behaviour of 2-butanol + water mixtures ($w_{\text{2-BuOH}}$ = 0.05, 0.10, and 0.15).[11] The following e.m.f. measurement on the chemical cell with $CdCl_2$ in the same mixtures is expected to reveal whether the change of the electrolyte to the 2–1 type will lead to analogous conclusions about that mixed solvent. Namely, such comparison of HBr and $CdCl_2$ has already been made in 2-butanone + water mixtures ($w_{\text{2-butanone}}$ = 0.05, 0.10, and 0.15).[12]

As $CdCl_2$ forms complexes in water,[6,9] and especially in solvents of lower relative permittivity,[6–8,10] it is necessary to know their stability constants. To that purpose, this work has studied the complexation of cadmium and chloride ions in mixed 2-butanol + water solvents ($w_{\text{2-BuOH}}$ = 0.05, 0.10, and 0.15) at three different ionic strengths, and at three temperatures, using direct potentiometry. For each mixed solvent, ionic strength and temperature, the concentration stability constants have been calculated, and used to calculate the thermodynamic stability constants for each mixed solvent and temperature. Comparison of these values with analogous data obtained in 2-butanone + water[10] mixtures may indicate whether the complex stability is affected not only by the relative permittivity of the solvent, but by the nature of the organic component as well. The values of thermodynamic stability constants have made it possible to calculate and interpret the thermodynamic quantities for complexation reactions.

EXPERIMENTAL

Four stock solutions were prepared for each mixed solvent and ionic strength, labeled A_1, A_2, B and C. All solutions were prepared at 293.15 K. Thus, *e.g.* for 5 % 2-butanol, the composition of the solutions was:

A_1: x = 0.05081 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 = 0.5 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 = 0.05081 mol dm^{-3} in $Cd(ClO_4)_2$
y = 0.5 mol dm^{-3} in NaCl
e = 0.0100 mol dm^{-3} in $HClO_4$
$I - 3x - y - e$ in $NaClO_4$.

The ionic strengths (I) used were 1.0, 2.0, and 3.0 mol dm^{-3}. In solvents with a higher content of the organic component it was necessary to decrease I, as well as its range and, consequently, the concentration of total chlorides and cadmium. Namely, the lower solubility limit of 2-butanol in water at 298.15 K is $w_{\text{2-BuOH}}$ = 0.202 according to Otsuki *et al.*,[13] while it is even lower, $w_{\text{2-BuOH}}$ = 0.175, as read from the curve reported by Ochi *et al.*[14] Data for stock solutions in 10 % 2-butanol are: I = 1.0, 1.5, and 2.0 mol dm^{-3}, y = 0.4 mol dm^{-3}, x = 0.04954 mol dm^{-3}; for 15 % 2-butanol: I = 0.6 and 1.0 mol dm^{-3} (y = 0.2 mol dm^{-3}), and I = 1.5 mol dm^{-3} (y = 0.15 mol dm^{-3}), x = 0.02957 mol dm^{-3}.

Chemicals and the preparation of stock solutions were described earlier,[6,9,10] while 2-butanol (Merck, *p.a.*) was fractionally distilled before use. Particular attention was paid to ensuring constant pH maintenance throughout the work. These attempts were facilitated by a relatively low pH value of the solutions ($c(HClO_4)$ = 0.0100 mol dm^{-3}) and proved to be successful by occasional pH checks with a combined glass electrode (In-Lab 412, Mettler Toledo).

Saturated Cd(Hg) (11 mass percent of cadmium) and AgCl/Ag electrodes were used as indicator electrodes. Višić and Mekjavić[15] describe the method for the preparation of the amalgam electrode, while Tomaš *et al.*[10] describe improvements of the method, the chemicals used, and the means of controlling the potential difference between amalgam electrodes. The preparation and requirements for the AgCl/Ag electrode were described earlier.[12,16] In both cases, a Feussner potentiometer was used to control the potential difference between the indicator electrodes. A glass electrode was used as the reference electrode (In-Lab 201, Mettler Toledo) with a glass membrane resistance lower than 500 MΩ, suitable for application in water and in mixed solvents. Stability control and storage of the electrodes were described earlier.[9,10] Cells used in potentiometric measurements were also described in detail earlier.[9]

The measuring process consists of two phases: the potentiometric measurement in order to prepare the calibration diagrams for the cadmium and chloride ions, followed by the »working« measurement.

In order to prepare the calibration diagram for cadmium, it is necessary to perform a series of e.m.f. measurements on a cell containing Cd^{2+} ion solutions of known concentrations:

(–) Cd(Hg) | test solution | glass electrode (+) (cell 1)

These concentrations were achieved by adding calculated volumes of stock solution A_1 to solution B (50 cm^3) in cell 1. To prepare the calibration diagram for chloride ions, the e.m.f. of cell 2 was measured:

(–) Ag/AgCl | test solution | glass electrode (+) (cell 2)

for a series of solutions with known concentrations of chloride ion obtained by adding A_2 to B. Calibration diagrams derived for both ions represent the cell 1 and cell 2 e.m.f. (E_1 and E_2) dependence on the logarithm of [Cd^{2+}] and [Cl^-] (Eqs. (1) and (2)), respectively.

In the »working« experiment, specific volumes of stock solution C were added into the thermostated vessel containing stock solution A_1, as well as the amalgam, AgCl/Ag and glass electrodes. After every addition, the e.m.f. readings for both cells were started. In general, E_1 and E_2 became constant after 30 and 20 minutes, respectively. It is obvious from the composition of the stock solutions that each test solution had the same content of total cadmium (x).

A digital pH-meter (MP 230, Mettler Toledo), of relative accuracy ± 0.1 mV, was used in all e.m.f. measurements. Temperature was maintained within ± 0.02 K. More details on the measuring procedure were presented earlier.[10]

RESULTS AND DISCUSSION

For each mixed solvent at a definite ionic strength and temperature, the least squares method was used to obtain straight lines for cadmium and chloride ions, of the general form:

$$E_1/\mathrm{V} = L - S \log([\mathrm{Cd}^{2+}] / c^{\circ}) \qquad (1)$$

$$E_2/\mathrm{V} = L' + S' \log([\mathrm{Cl}^-] / c^{\circ}) \qquad (2)$$

together with the corresponding correlation coefficients (R^2).

The value for R^2, representing the measure of the model conformity with the experiment, was 0.9999 for all straight lines for the chloride ion. For cadmium straight lines, the R^2 value on 17 occasions was 0.9999 and 10 times 0.9998. Compared to the theoretical Nernstian slope, the slopes of the straight lines for cadmium (S) show good agreement, displaying the average deviation of – 2.5 %. In the case of chlorides, the agreement between the experimental (S') and theoretical slope is even better, with an average deviation of ± 1 %. Similar agreement was found with straight lines in mixed solvents of 2-butanone + water[10] of identical mass fractions. This all indicates a good conformity of the model with the experiment. It was also noticed that with chlorides the deviation of the slope increased with increasing temperature, while the opposite was observed with cadmium. An identical phenomenon was noticed in the 2-butanone + water solvent.[10]

In »working« measurements, the complexation reactions took place as shown by the equation:

$$\mathrm{Cd}^{2+} + n\,\mathrm{Cl}^- \rightleftharpoons \mathrm{CdCl}_n^{(2-n)+}, \ (n = 1, 2, 3, \text{ and } 4) \qquad (3)$$

For this equilibrium reaction, the expression for the concentration stability constant (K'_n) is:

$$K'_n = ([\mathrm{CdCl}_n^{(2-n)+}]/c^{\circ})/\{([\mathrm{Cd}^{2+}]/c^{\circ})([\mathrm{Cl}^-]/c^{\circ})^n\} \qquad (4)$$

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

Based on the balance for cadmium, and Eq. (4) for each species formed, the following expression was obtained:

$$\frac{x-[\mathrm{Cd}^{2+}]}{[\mathrm{Cd}^{2+}][\mathrm{Cl}^-]} \cdot c^{\circ} = F([\mathrm{Cl}^-])/c^{\circ} =$$

$$K'_1 + K'_2([\mathrm{Cl}^-]/c^{\circ}) + K'_3([\mathrm{Cl}^-]/c^{\circ})^2 + K'_4([\mathrm{Cl}^-]/c^{\circ})^3 \qquad (5)$$

where x denotes the concentration of total cadmium.

A series of nine E_1 values, measured in the »working« experiment, were used to calculate the equilibrium concentrations of the Cd^{2+} ion by means of a straight line for cadmium (Eq. (1)), while the corresponding concentrations of the chloride ion were obtained from the corresponding values of E_2 and the straight line for the chloride ion (Eq. (2)). This was done for each ionic strength and temperature.

These data were used to calculate, using Eq. (5) and applying the method of orthogonal polynomials, the values of K'_n, their standard deviations, as well as the correlation coefficient of the polynomial (5). Table I shows the results obtained.

Table I shows that three kinds of complexes were formed: $CdCl^+$, $CdCl_2$ and $CdCl_3^-$. If the K'_n values for the same ionic strength are compared, *e.g.,* at I = 1 mol dm^{-3} in different mixed solvents, it can be seen that these values increase with an increased content of the organic component. Although there are exceptions to this tendency, mainly for K'_2 in 15 % 2-butanol, one can generally conclude that the stability of the complexes is higher in solvents of lower relative permittivity. If the values of R^2 are analyzed, 15 % 2-butanol evidently displays the poorest agreement between the model and the experiment. While the average value of R^2 in 5 % solvent is 0.9998 and in 10 % solvent 0.9990, it is 0.9944 in 15 % mixed solvent. The fact is that the measurements in 15 % 2-butanol were hampered, as it was necessary, in order to prevent the »salting-out« effect, to work at lower ionic strengths and to reduce the concentration of total cadmium and chloride in stock solutions. This significantly narrowed the range of $c_{\mathrm{tot.}}(\mathrm{Cl}^-)$ in the »work-

TABLE I. Concentration stability constants (K'_n) of the chlorocadmium complexes in 2-butanol + water mixtures at different ionic strengths and temperatures[(a)]

T/K	288.15	298.15	313.15
	w = 0.05		
	I = 1.0 mol dm^{-3}		
K'_1	23.7 ± 0.2	28.0 ± 0.1	27.0 ± 0.1
K'_2	97 ± 5	98 ± 2	81 ± 2
K'_3	74 ± 17	78 ± 7	42 ± 9
R^2	0.9997	0.9996	0.9998
	I = 2.0 mol dm^{-3}		
K'_1	31.4 ± 0.3	29.8 ± 0.3	32.8 ± 0.2
K'_2	139 ± 5	158 ± 7	151 ± 4
K'_3	391 ± 21	100 ± 24	283 ± 16
R^2	0.9999	0.9998	0.9999
	I = 3.0 mol dm^{-3}		
K'_1	33.7 ± 0.3	38.0 ± 0.3	51.5 ± 0.3
K'_2	293 ± 6	289 ± 5	290 ± 7
K'_3	758 ± 24	338 ± 19	773 ± 29
R^2	0.9999	0.9997	0.9997
	w = 0.10		
	I = 1.0 mol dm^{-3}		
K'_1	27.7 ± 0.6	28.8 ± 0.5	32.7 ± 0.8
K'_2	116 ± 12	126 ± 9	115 ± 17
K'_3	188 ± 47	122 ± 37	252 ± 68
R^2	0.9994	0.9995	0.9995
	I = 1.5 mol dm^{-3}		
K'_1	33.5 ± 0.9	33.3 ± 0.7	38.4 ± 1.4
K'_2	111 ± 21	120 ± 17	122 ± 26
K'_3	315 ± 92	281 ± 74	453 ± 101
R^2	0.9985	0.9976	0.9987
	I = 2.0 mol dm^{-3}		
K'_1	34.4 ± 0.6	39.3 ± 0.2	41.6 ± 1.3
K'_2	166 ± 11	145 ± 5	116 ± 25
K'_3	266 ± 40	351 ± 20	512 ± 99
R^2	0.9987	0.9999	0.9988
	w = 0.15		
	I = 0.6 mol dm^{-3}		
K'_1	36.2 ± 1.5	36.6 ± 1.1	39.8 ± 0.4
K'_2	79 ± 43	103 ± 29	97 ± 15
K'_3	427 ± 272	265 ± 176	461 ± 106
R^2	0.9894	0.9974	0.9984
	I = 1.0 mol dm^{-3}		
K'_1	38.3 ± 0.8	40.7 ± 0.2	40.5 ± 0.9
K'_2	59 ± 26	47 ± 8	114 ± 26
K'_3	523 ± 187	639 ± 54	428 ± 177
R^2	0.9892	0.9994	0.9972
	I = 1.5 mol dm^{-3}		
K'_1	40.3 ± 0.4	41.7 ± 0.6	43.8 ± 0.2
K'_2	46 ± 20	57 ± 29	77 ± 15
K'_3	746 ± 199	770 ± 289	906 ± 230
R^2	0.9925	0.9875	0.9983

[(a)] R is the correlation coefficient; w is the mass fraction of 2-butanol.

ing« section: 0.02–0.12 mol dm^{-3} (the least), compared to 0.025–0.350 mol dm^{-3} in 5 % alcohol (the most). Consequently, the already small range of E_1 (30 to 40 mV in 5 and 10 % 2-butanol) was further reduced to only 16–23 mV in 15 % alcohol.

The values of K'_n at three ionic strengths were used to calculate the thermodynamic stability constants (K^o_n) for each mixed solvent and temperature according to the equation:

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

where A and B are Debye-Hückel constants calculated from the relative permittivity data of the solvent,[11] a is the ion-size parameter (the value of 0.45 nm was used),[6–8] $\Delta z^2 = z^2(\text{CdCl}_n^{(2-n)+}) - z^2(\text{Cd}^{2+}) - nz^2(\text{Cl}^-)$, 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, respectively, for each ion that takes part in the complex forming reactions (3).

A graphical representation of the left side of Eq. (6) against the ionic strength I yields a straight line. The thermodynamic stability constant of the complex (K°_n) is derived from the intercept, while ΔC_n represents the slope. Table II presents the thermodynamic stability constants for each mixed solvent at different temperatures,

TABLE II. Thermodynamic stability constants (K°_n) of the chlorocadmium complexes and ΔC_n of Eq. (6) in 2-butanol + water mixtures at different temperatures[(a)]

T/K	288.15	298.15	313.15
	w = 0.05		
K°_1	117 ± 10	126 ± 11	132 ± 13
K°_2	692 ± 38	724 ± 30	832 ± 27
K°_3	315 ± 100	445 ± 100	500 ± 150
ΔC_1	0.162	0.177	0.203
ΔC_2	0.407	0.397	0.380
ΔC_3	0.640	0.467	0.577
	w = 0.10		
K°_1	121 ± 8	135 ± 2	177 ± 6
K°_2	1175 ± 105	1720 ± 65	2060 ± 95
K°_3	1200 ± 460	1585 ± 135	2375 ± 325
ΔC_1	0.280	0.260	0.240
ΔC_2	0.355	0.240	0.185
ΔC_3	0.560	0.480	0.505
	w = 0.15		
K°_1	196 ± 6	205 ± 10	234 ± 3
K°_2	1550 ± 15	1800 ± 380	2345 ± 325
K°_3	3950 ± 55	4500 ± 500	5500 ± 560
ΔC_1	0.242	0.254	0.245
ΔC_2	0.040	0.100	0.100
ΔC_3	0.556	0.550	0.500

[(a)] w is the mass fraction of 2-butanol.

as well as their standard deviations $\sigma(K_n^\circ)$, obtained by averaging the intercept of the straight line,[6] and ΔC_n values.

It is evident that when the relative permittivity of the medium decreases, the stability of the complexes increases. Also, in each mixed solvent, the temperature raise increases the stability of each complex. Identical changes have been observed with the same complexes in aqueous 2-propanol,[6] acetone,[7] *t*-butanol[8] and 2-butanone.[10]

Figure 1 shows the dependence of K_n° on the relative permittivity of the solvent (plot $\ln K_n^\circ$ against ε_r^{-1}) together with the values for aqueous solution[6] and for 2-butanone + water mixtures.[10]

The figure shows an approximately linear dependence, as shown by Turyan and Zhantalay,[17] for K_1° and K_2° of the same complexes in methanol + water and ethanol + water, respectively, and for all three complexes, as shown by Višić and Mekjavić,[7] in 2-propanol + water and acetone + water, respectively. It can be seen that at the same relative permittivity, the values of K_1° and K_2° are somewhat higher in 2-butanone + water than in 2-butanol + water. The same relationship was found between acetone + water and 2-propanol + water mixtures for all three constants.[7] For the latter mixtures, the distance between the lines is greater, as the examined area of the solvent composition is larger (up to 50 % of the organic component). It can also be seen from Figure 1 that, relative to the first two complexes, the constants for the third complex show an inverse relation. This might easily be only an apparent discrepancy, since the constants K_3° were determined with a much higher uncertainty. Namely, in a polynomial of the Eq. (5) type, when the argument (concentration of chloride ions) is less than 1, the higher the power of the argument, the higher is the standard deviation of the parameter related to that power. Even if the inverse positioning of lines for K_3° were the actual situation, the proportion of the third complex is so small that it cannot change the ratio of complexed cadmium to total cadmium, which can be proved to be higher in 2-butanone + water mixtures. Consequently, the complex stability is not affected only by the physical properties of the mixed solvent, expressed by its relative permittivity, but also by its chemical properties, *i.e.,* the nature of the organic component in the mixed solvent (ketone, or alcohol).

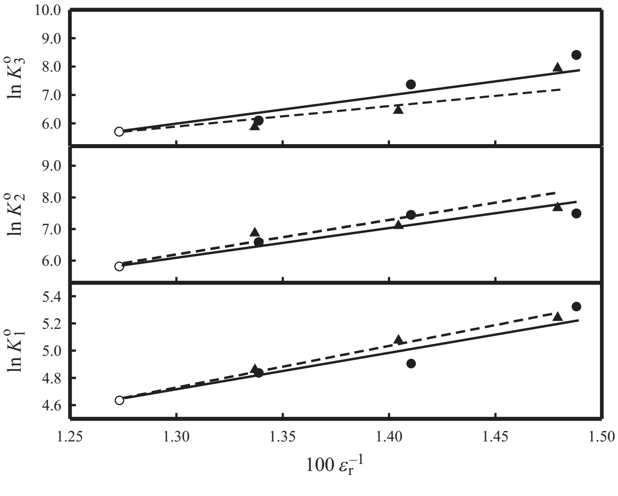

Figure 1. Plot of ln K_n° *versus* ε_r^{-1} at 298.15 K in water[6] (○), 2-butanone + water[10] (- -▲- -) and 2-butanol + water (—●—; Table II) mixtures.

TABLE III. Standard thermodynamic quantities for the formation reaction (3) of the chlorocadmium complexes in 2-butanol + water mixtures at 298.15 K [(a)]

Complex	w = 0.05	w = 0.10	w = 0.15
		ΔH°/kJ mol^{-1}	
$CdCl^+$	3.74 ± 0.05	11.02 ± 0.10	6.03 ± 0.15
$CdCl_2$	5.40 ± 0.10	12.68 ± 0.50	12.89 ± 0.10
$CdCl_3^-$	10.81 ± 0.50	20.79 ± 0.10	40.74 ± 0.20
		ΔG°/kJ mol^{-1}	
$CdCl^+$	–11.99 ± 0.22	–12.16 ± 0.04	–13.19 ± 0.12
$CdCl_2$	–16.32 ± 0.10	–18.32 ± 0.09	–18.58 ± 0.52
$CdCl_3^-$	–14.87 ± 0.56	–18.26 ± 0.21	–20.85 ± 0.28
		ΔS°/J K^{-1} mol^{-1}	
$CdCl^+$	52.76 ± 0.76	77.75 ± 0.36	64.46 ± 0.64
$CdCl_2$	72.85 ± 0.47	103.97 ± 1.70	105.55 ± 1.78
$CdCl_3^-$	86.13 ± 2.52	130.97 ± 0.78	206.57 ± 1.15

[(a)] w is the mass fraction of 2-butanol.

The standard thermodynamic quantities for the complex forming reactions (Eq. (3)) were calculated on the basis of K_n° values at different temperatures (Table II). The value of ΔH° was determined from the slope of the straight line in the plot $\ln K_n^\circ$ against T^{-1}, and the values of ΔG° and ΔS° were established by means of the usual thermodynamic relations. Table III gives the values of standard thermodynamic quantities at 298.15 K together with their standard deviations, calculated as in Ref. 10.

The data indicate that all complexation reactions are exergonic, increasing with a higher content of the organic component in the mixture. All the reactions are endothermic and accompanied by an entropy increase. The entropy term dominates over ΔH°, and makes reactions exergonic in spite of their endothermity. This is a common phenomenon when the reaction makes the free highly-solvated ions »disappear«, leading to a significant increase of disorder in the system. The same was found for the complexation reactions of Cd^{2+} and Cl^- in aqueous mixtures of 2-propanol,[6] acetone,[7] *t*-butanol,[8] and 2-butanone.[10] Similar behavior was observed in reactions of ionic association, *e.g.,* Na^+ and Br^- in 2-butanol + water mixtures with $w_{2\text{-BuOH}}$ = 0.70, 0.80, 0.90, and 0.95.[18]

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SAŽETAK

Kompleksiranje Cd^{2+} i Cl^- iona u smjesama vode i 2-butanola

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Ispitivane su reakcije nastajanja klorokadmijevih kompleksa u smjesama 2-butanol + voda ($w_{\text{2-BuOH}}$ = 0,05, 0,10 i 0,15) pri tri ionske jakosti i tri temperature primjenom izravne potenciometrije. Najprije su na temelju EMS mjerenja otopina poznatih koncentracija kadmijevih, odnosno kloridnih iona, izrađeni baždarni dijagrami za te ione. Zatim su EMS mjerenja izvedena u nizu otopina poznate koncentracije ukupnoga kadmija i ukupnih klorida u kojima dolazi do kompleksiranja. Na temelju tih mjerenja i baždarnih pravaca, za svaku ionsku jakost i temperaturu, određene su koncentracije slobodnih kadmijevih i kloridnih iona. Za svaku ionsku jakost i temperaturu u pojedinome miješanome otapalu za nađene komplekse $CdCl^+$, $CdCl_2$ i $CdCl_3^-$ izračunane su koncentracijske konstante stabilnosti (K_n') primjenom metode ortogonalnih polinoma. Za svaku temperaturu u pojedinome miješanome otapalu određene su termodinamičke konstante stabilnosti (K_n°) koje se, za svaku kompleksnu vrstu, povećavaju porastom temperature kao i sa smanjenjem relativne permitivnosti miješanoga otapala. Usporedbom s konstantama K_n° u otapalu 2-butanon + voda utvrđen je utjecaj organske komponente. Termodinamičke veličine za reakcije nastajanja kompleksa, izračunane iz K_n°, pokazale su da je kompleksiranje spontano, endotermno te da je praćeno porastom entropije.