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Abstract

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The Influence of Solvent on Coordination Interaction and the Effect of "Negative Complex Formation"

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As was shown earlier (1), in the presence of small concentrations of such solvents as alcohol, acetone, and dioxane, in aqueous systems the character of complex formation remains the same as in pure aqueous solutions. A strong increase in the concentration of nonaqueous solvents, however, is capable of sharply changing the course of complex-formation reactions (2).

In order to explain the influence of large concentrations of a nonaqueous solvent on complex-formation reactions, we studied the system Cd^{2+}—CNS^-—H_2O—dioxane by the potentiometric method. Measurement of the e.m.f. was carried out in the following chains:

$$\mathrm{Cd(Hg)} \mid \mathrm{Cd(NO_3)_2},\ \mathrm{H_2O},\ \mathrm{Dy} \mid \mathrm{KNO_3} \mid \mathrm{Hg_2Cl_2},\ \mathrm{KCl_{sat.}} \mid \mathrm{Hg},$$

where Dy is dioxane, and Cd(Hg) is a cadmium amalgam serving as the indicator electrode. The concentration of cadmium salt in the mixtures studied was constant (0.01 mol.). Three series of experiments were carried out: at 2.5, 5, and 7.5 mol. of dioxane in the mixtures. The study was conducted at a temperature of 20° ± 0.05°. The results of the potentiometric measurements (see Tables 1-3 and Fig. 1) were treated as in the works cited above.

Table 1

Results of the potentiometric study of the system Cd^{2+}—CSN^-—H_2O—Dy at a dioxane concentration of 2.5 mol.

KCNS conc.	E (V)	$\lg[Cd^{2+}]$	$K_3 \cdot 10^4$	$K_4 \cdot 10^4$
–	−0.6404	−2.000	–	–
0.3657	−0.6964	−3.9310	5.26	–
0.4876	−0.7060	−4.2621	6.88	–
0.7314	−0.7187	−4.7010	7.86	–
0.9752	−0.7283	−5.0310	8.23	–
1.2190	−0.7364	−5.3103	6.20	9.46

KCNS conc.	E (V)	$\lg[Cd^{2+}]$	$K_3 \cdot 10^4$	$K_4 \cdot 10^4$
1.4628	−0.7470	−5.6759	–	8.65
1.7066	−0.7543	−5.9276	–	9.13
1.9504	−0.7606	−6.1448	–	9.53
2.1942	−0.7669	−6.6327	–	9.33
Average . . .			$6.67 \pm 0.46 \cdot 10^{-4}$	$9.26 \pm 0.15 \cdot 10^{-4}$

Before beginning the investigation of the solutions, we attempted to clarify how dioxane would behave toward cadmium salts, which in general dissociate very readily. It was found that cadmium nitrate and perchlorate dissolve well in dioxane. From saturated solutions of the aforementioned

of salts in dioxane, we isolated the molecular compounds $Cd(NO_3)_2 \cdot 2Dy$ and $Cd(ClO_4)_2 \cdot 2Dy$ in the form of colorless crystals.

On this basis, one might have expected that cadmium ions with dioxane, and in the presence of water, would be capable of combining into complexes. But since the concentration of dioxane in each series of experiments is constant, this should not introduce interference in determining the composition of cadmium rhodanide complexes.

Table 2

Results of a potentiometric study of the system Cd^{2+}–CNS^-–H_2O–Dy at a dioxane concentration of 5 mol.

KCNS concentration	E (V)	$\lg[Cd^{2+}]$	$K_3 \cdot 10^4$	$K_4 \cdot 10^4$	$K_6 \cdot 10^4$
–	−0.6399	−2.000			
0.4884	−0.7212	−4.8034	1.52		
0.7326	−0.735	−5.3034	1.73		
0.9768	−0.7470	−5.6931	1.72		
1.2210	−0.7558	−5.9966	1.70	1.96	
1.4652	−0.7648	−6.3069		2.03	
1.7094	−0.7730	−6.5847		2.02	5.27
1.9536	−0.7830	−6.9345			5.37
2.1978	−0.7907	−7.2000			6.03
Average . . .			$1.67 \pm 0.05 \cdot 10^{-4}$	$2.00 \pm 0.03 \cdot 10^{-4}$	$5.5610 \pm 0.20 \cdot 10^{-4}$

Tables 1–3 give the values of the dissociation constants of the complexes that predominate in a certain range of concentrations of the complex-forming agent. The subscript on K indicates the number of rhodanide ions entering into the composition of the corresponding complexes.

Table 3

Results of a potentiometric study of the system Cd^{2+}—CNS^{-}—H_2O—Dy at a dioxane concentration of 7.5 mol.

KCNS concentration	E (V)	$\lg[Cd^{2+}]$	$K_6 \cdot 10^5$
–	−0.6308	−2.000	
1.195	−0.7772	−7.0483	1.84
1.434	−0.7882	−7.4276	2.51
1.673	−0.7941	−7.8034	2.77
1.912	−0.8080	−8.1000	3.19
Average . . .			$2.55 \pm 0.28 \cdot 10^{-5}$

Since for us the proof of the higher coordination groups is more important, for brevity the data for solutions in which the simplest complexes should form are omitted in the tables given below. As can be seen from Table 1 and Fig. 1, already at 2.5 mol. dioxane the complex $Cd(CNS)_3^-$ is detected considerably more readily (in the sense of concentration conditions) than in aqueous solution, where the formation of this complex corresponds to 1-2 mol. KCNS (^{3}) (all other conditions being equal). In addition, in the mixed solution at 2.5 mol. dioxane a more complex species is detected, namely: $Cd(CNS)_4^{2-}$.

At higher dioxane concentrations (see Tables 2 and 3) it already becomes possible to detect not only the complexes $Cd(CNS)_4^{2-}$, but also $Cd(CNS)_6^{4-}$. Thus, the introduction of dioxane, as it were, expands the coordination possibilities of cadmium, for which the coordination number 6 in anions is considered uncharacteristic. At the same time, at first glance this contradicts the fact of the formation of molecular compounds between dioxane and cadmium salts, for it is immediately difficult to imagine that in the presence of dioxane cadmium coordinates more rhodanide ions than in a purely aqueous solution. For a final resolution of this question, we also carried out potentiometric

measurements in the system Cd^{2+}—H_2O—Dy. Measurements of the emf in this case were carried out analogously to the experiments described above, at a constant concentration of $Cd(NO_3)_2$ (0.01 mol.) and an increasing concentration of dioxane (0.1-6.5 mol.). Table 4 presents the results of these measurements.

As can be seen from Table 4, instead of the expected decrease in the values of the electrode potentials, which should indicate the binding of cadmium ions into complexes, in reality a certain increase in the potentials is observed as the concentration of dioxane in the solution increases. This gives grounds for asserting that, in aqueous solutions, complex groups of cadmium with dioxane are not formed. Moreover, by following the change in electrode potentials with increasing dioxane concentration, one may speak of so-called "negative complex formation," entailing the formation of more free (in the sense of solvation) potential-determining ions. This becomes understandable if one takes into account the interaction of the nonaqueous solvent with water molecules attached to the cadmium ions through hydrogen bonding. If it is assumed that in the last mixture (Table 4) all cadmium ions are bound with dioxane, and if, from the decrease in emf from the last to the first mixture with increasing H_2O concentration in the mixtures, the concentration of "free" (with reduced hydration) and "bound" (hydrated) cadmium ions is calculated, then, by constructing the graphical dependence

Fig. 1. Dependence of $\lg \frac{[\mathrm{Cd(CNS)}_m]}{[\mathrm{Cd}^{2+}]}$ on lg[CNS]. 1 —at a dioxane concentration of 2.5 mol/l, 2 —at a dioxane concentration of 5 mol/l, 3 —at a dioxane concentration of 7.5 mol/l

Table 4

Change in the electrode potentials of cadmium for the system Cd^{2+}—H_2O—Dy

Dioxane conc.	E (V)	Dioxane conc.	E (V)
–	−0.6441	2.07	−0.6397
0.23	−0.6438	2.81	−0.6388
0.69	−0.6432	3.52	−0.6360
0.92	−0.6429	4.22	−0.6346
1.38	−0.6420	4.92	−0.6312
1.61	−0.6407	5.63	−0.6274
		6.33	−0.6223

$$\lg \frac{[\mathrm{Cd(H_2O)}_{n+x}]}{[\mathrm{Cd(H_2O)}_n]} = f(\lg[\mathrm{H_2O}])$$

it is easy to find x—the change in the number of water molecules grouped around Cd^{2+}. When the dioxane concentration is changed to 6 mol., even the most approximate calculation shows a decrease by one unit in the number of water molecules hydrating cadmium. In the presence of ions capable of forming complexes with Cd^{2+} ions, this dehydration should be still more pronounced.

Taking the latter effect into account, it is easy to explain the change in the coordination number in cadmium rhodanide complexes toward an increase as the concentration of dioxane in the solution rises, since dehydrated cadmium ions attach rhodanide addends much more readily than hydrated ones. It may therefore be assumed that, in aqueous solutions, Cd^{2+} is surrounded by six water molecules. It is known, after all, that cadmium perchlorate, even in the solid state, is formed as Cd(ClO_4)$_2 6H_2O.Inthepresenceofanexcessofrhodanideions,substitution(thoughnotcomplete)ofcoordi can be isolated. In mixed solutions, however, in which there are large concentrations of alcohol, acetone, or dioxane, which are capable of forming hydrogen bonds with water,

bonds, cadmium cations are more readily stripped of their solvation shell, and in the region of high concentrations of rhodanide ions the maximally coordinated complexes $Cd(CNS)_6^{4-}$ will be formed, which is in fact what is observed.

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