Effect of hydrogen bonding of solvent on the thermodynamic stability of cadmium ethylenediamine complexes

S. F. Ledenkov,[a]★ V. A. Sharnin,[a] and G. V. Chistyakova[b]

[a]Ivanovo State Chemical Technological University,
7 prosp. F. Engel´sa, 153460 Ivanovo, Russian Federation.
E-mail: oxt@isuct.ru
[b]Institute of Solutions Chemistry, Russian Academy of Sciences,
1 ul. Akademicheskaya, 153045 Ivanovo, Russian Federation.
Fax: +7 (093 2) 37 8509

Changes in the stability of the cadmium(II) ethylenediamine complexes in mixed water—DMSO solvents were studied by pH-metry and calorimetry. Complex cations $[Cd(en)]^{2+}$, $[Cd(en)_2]^{2+}$, and $[Cd(en)_3]^{2+}$ are formed in aqueous solutions, and the $[Cd(en)_4]^{2+}$ complex with a partially dentate ligand is stable in DMSO. An increase in the DMSO content in a solvent increases the stability of the complexes. The maximum increase in log*K* is observed for coordinatively saturated compounds. The thermodynamics of complexation is discussed from the viewpoint of solvation approach. Principal differences in the influence of aqueous-alcohol and aqueous-aprotic solvents on the stability of the metal amino complexes were revealed. Protolytic solvents exert a destabilizing effect on the multiligand complexes, because the coordination sphere is involved in H bonding.

Key words: stability of complex, mixed solvents, hydrogen bonding, thermodynamics of reaction, cadmium complexes, ethylenediamine, dimethylsulfoxide.

Complexes are usually much more stable in organic solvents than in water. A typical plot of $\log K_{\text{compl}}$ *vs.* composition of a mixed solvent is a monotonically ascending function. A rather simple shape of the plot $\log K_{\text{compl}} = F(X_2)$, where X_2 is the molar fraction of a nonaqueous solvent, sometimes suggests that the stability of a complex is determined by the effect of one factor: for instance, by a change in the dielectric constant of the medium or in the concentration of a component of the solution considered as an inert diluent, or a change in the donor ability of the solvent with respect to a complexing ion. This approach provides at best a very simplified description of complexation in solution.

Solvent (S), which selectively solvates the metal ion (M), ligand (L), and complex (ML_n), acts as an equitable participant of the chemical reaction

$$MW_{m-i}S_i + n\,LW_{p-j}S_j = ML_n + (m + np - i - nj)\,W + (i + nj)\,S, \qquad (1)$$

where W and S are the molecules of water and nonaqueous solvent, respectively.

Stability of a complex in a binary solvent is determined by structural features and thermodynamic stability of each solvate involved in reaction (1). Thus, complexation in even simple solvents is controlled by several factors.

The change in the stability of a complex in an aqueous-organic solvent can be expressed[1] through the thermodynamic transfer functions for the complex $\Delta_{tr}G^\circ(ML)$, metal ion $\Delta_{tr}G^\circ(M)$, and ligand $\Delta_{tr}G^\circ(L)$.

$$-RT\ln(K^\circ_{solv}/K^\circ_{H_2O}) = \Delta_{tr}G^\circ_r = \Delta_{tr}G^\circ(ML) - \Delta_{tr}G^\circ(M) - \Delta_{tr}G^\circ(L), \qquad (2)$$

where $\Delta_{tr}G^\circ_r$ is the change in the free energy of the reaction in the transfer process from an aqueous solution to the solvent S.

It is known[2,3] that a solvent can affect the formation of complexes in a coordination polyhedron and determine the number of coordinated ligands at the same metal ion or the mode of ligand coordination upon the formation of valence bond isomers.

Considerable solvent-induced structural changes in the coordination sphere of a complex suggest a new chemical compound. One can speak about it to an extent to which these structural changes are beyond the definition of solvation.[4]

Our earlier studies of the stepwise complexation of Zn^{2+}, Cd^{2+}, and Cu^{2+} ions with ethylenediamine[5—7] and of Ni^{2+} with amine and carboxylate ligands[8,9] in binary solvents showed that the solvent has different effects on different steps of the process. In this work, we studied the influence of a water—dimethylsulfoxide solvent on

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 723—730, April, 2004.

the stepwise coordination of ethylenediamine by the Cd^{2+} ion.

Experimental

Dimethylsulfoxide (reagent grade) was purified as follows. After slow crystallization at 13—16 °C, an unfrozen portion of the solvent was removed, the crystalline mixture was heated to partial melting, and repeated crystallization and distillation *in vacuo* were carried out. Distilled DMSO was passed through a column with active carbon to obtain anhydrous, almost odorless product. The water content was determined by the Fischer method.

Ethylenediamine was synthesized by the treatment of ethylenediammonium sulfate (chemically pure grade) with alkali followed by distillation. The concentration of ethylenediamine was determined by acidometric titration. Cadmium perchlorate was synthesized by the dissolution of freshly precipitated $Cd(OH)_2$ in 70% perchloric acid (chemically pure grade), the resulting solution was concentrated on a water bath, the crystal hydrate was separated, and repeated crystallization was carried out. A concentrated aqueous solution of cadmium perchlorate was used, and its titer was determined by complexone EDTA (ethylenediaminetetraacetic acid, disodium salt (Trilon B)). The water content in solutions of ethylenediamine and cadmium perchlorate was taken into account when the solvent was composed.

A background electrolyte, $NaClO_4$ (reagent grade), was twice recrystallized as a monohydrate and dehydrated at 120—150 °C. Working solutions were prepared by the gravimetric method using distilled deaerated water.

The emf of a circuit was measured during potentiometric titration. The circuit consisted of a glass electrode and a reference electrode contacting with the solution under study through a ground-glass joint

Glass electrode|Solution under study (DMSO + H_2O),
$HClO_4$, $NH_2CH_2CH_2NH_2$, $Cd(ClO_4)_2$, $NaClO_4$||
||(DMSO + H_2O), $NaClO_4$, LiCl, $AgCl_{solid}|Ag^0$.

A measurement cell was isolated from atmosphere, and its temperature was maintained at 25±0.1 °C. The accuracy of emf measurement was at least ±0.1 mV. The ESL 63-07 glass electrode in water—DMSO mixtures gave stable and reproducible values at the slope ratio close to theoretical.

A titrant contained a solution of ethylenediamine and the background electrolyte. The initial concentrations of reactants in different series at an initial cell volume of 24 mL and a titrant volume of 20 mL are given below.

Reactant	C_0/mol L^{-1}		
$Cd(ClO_4)_2$	$6.997 \cdot 10^{-2}$	$5.077 \cdot 10^{-2}$	$5.087 \cdot 10^{-2}$
$HClO_4$	$1.437 \cdot 10^{-1}$	$1.317 \cdot 10^{-1}$	$9.977 \cdot 10^{-2}$
$NH_2CH_2CH_2NH_2$	0.632	0.315	0.477

The electrode system was calibrated before and after titration. Solutions of $HClO_4$ and buffer solutions prepared from ethylenediamine, $HClO_4$, and $NaClO_4$ were used for calibration. The $-\log[H^+]$ values for buffer solutions were calculated taking into account the $\log\beta^H$ constants (see Ref. 10). The activity coefficient of H^+ ions was accepted constant.

Calorimetric titration was carried out on an isoperibolic calorimeter with detachable cells 50 and 70 mL in volume equipped with semiconductive temperature sensors. The temperature of the outer shell was maintained constant by a PID device with an accuracy of ±0.0005 °C. The calorimeter was tested by measuring $\Delta_r H$ of water ionization and the heat of KCl dissolution. The resulting value $\Delta_{sol}H°_{298.15}(KCl, \infty H_2O) = 17.27 \pm 0.05$ kJ mol^{-1} agrees well with the known[11] value 17.243 ± 0.018 kJ mol^{-1}.

Results and Discussion

Equilibrium concentrations of H^+ ions were measured during potentiometric titration with ethylenediamine of water—dimethylsulfoxide solutions containing $Cd(ClO_4)_2$ and $HClO_4$. The constant ionic strength of solutions was maintained by sodium perchlorate.

Complexation occurs at pH 6—11, which fact is indicated by the difference of titration curves *1* and *2* (Fig. 1). The Cd^{2+} ion binds ethylenediamine to form a complex and thus shifts the acid-base equilibrium and decreases the pH of solution. Based on the differences between the neutralization curves of an $HClO_4$ solution and the same solution containing $Cd(ClO_4)_2$, one can calculate the stability constants of the $[Cd(en)_i]^{2+}$ complexes. The calculation was performed by the PHMETR algorithm[12] using the model of equilibria including three basis species (Cd^{2+}, en, H^+) and five main reactions

$$NH_2CH_2CH_2NH_2 + H^+ = (en)H^+ \qquad (\log\beta_1{}^H), \quad (3)$$

$$NH_2CH_2CH_2NH_2 + 2\,H^+ = (en)H_2{}^{2+} \qquad (\log\beta_2{}^H), \quad (4)$$

$$NH_2CH_2CH_2NH_2 + Cd^{2+} = [Cd(en)]^{2+} \qquad (\log\beta_1), \quad (5)$$

$$2\,NH_2CH_2CH_2NH_2 + Cd^{2+} = [Cd(en)_2]^{2+} \qquad (\log\beta_2), \quad (6)$$

$$3\,NH_2CH_2CH_2NH_2 + Cd^{2+} = [Cd(en)_3]^{2+} \qquad (\log\beta_3). \quad (7)$$

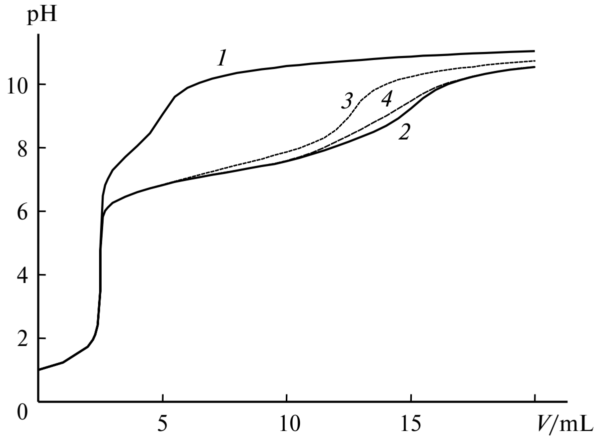


Fig. 1. Curves of pH-metric titration of $HClO_4$ (*1*) and $HClO_4$ + + $Cd(ClO_4)_2$ (*2*) solutions with ethylenediamine, the calculated curve for the model with three complexes (*3*), and the calculated curve for four complexes (*4*); *V* is the volume of ethylenediamine.

In each iteration, the required logβ values were varied to achieve a minimum of the function

$$F = \sum_{j=1}^{N}(\log[H_{exp}] - \log[H_{calc}])^2.$$

Here j and N are the number in a series and the total number of experimental points, respectively; $\log[H]_{exp}$ and $\log[H]_{calc}$ are the logarithms of equilibrium concentrations of hydrogen ions measured experimentally and calculated by the specified stoichiometric model of equilibria.

When choosing an adequate model of equilibria, the F function has a distinct minimum corresponding to the best quadratic approximation of the experimental and calculated titration curves, and the resulting constants describe the change in the properties of the system with the maximum statistical plausibility in a wide concentration region. The interval of variation of the constants was chosen rather wide to exclude F finding in a false local minimum.

The protonation constants of ethylenediamine reproducing neutralization curve *1* (see Fig. 1) were determined in special experiments (Table 1). The values of the constants agree satisfactorily with those obtained by us earlier[5] and other published data.

The model of equilibria (3)—(7) describes the change in pH during titration at the concentrations $X_{DMSO} \leq 0.1$ molar fractions with an accuracy corresponding to a real experimental error of 0.05 pH. The accepted model is adequate to experiment up to the molar ratio $C_{en}/C_{Cd} = 7$. Therefore, it can be considered that only three cadmium complexes are formed *via* reactions (5)—(7) in solutions with a low content of DMSO.

At high DMSO concentrations, the experimental titration curve *2* (see Fig. 1) cannot be reproduced by Eqs (3)—(7). Calculated curve *3* corresponding to the best description of experiment in terms of the chosen model is above the experimental curve by 0.6—0.9 pH units at the concentration ratio en/Cd = 4. This can be explained by an extremely high error in measuring the emf of the cell (30—50 mV) or by the lack of fit of the stoichiometric model considered.

Table 1. Equilibrium constants of protonation* of ethylenediamine (Eqs (3) and (4)) and of formation of the $[Cd(en)_i]^{2+}$ complexes (Eqs (5)—(8))

X_{DMSO} (mol. fractions)	$\log\beta_1{}^H$	$\log\beta_2{}^H$	$\log\beta_1$	$\log\beta_2$	$\log\beta_3$	$\log\beta_4$
0.0	10.10	17.56	5.48	10.16	13.12	—
0.05	9.90	17.11	5.65	10.53	13.53	—
0.1	9.80	16.92	5.63	10.41	13.37	—
0.2	9.75	16.90	5.72	10.61	13.90	14.87
0.3	9.59	16.41	5.94	11.20	14.83	16.85
0.5	9.95	17.09	6.06	11.31	15.68	18.11
0.7	10.57	18.17	6.32	11.58	16.56	19.95
0.9	10.88	18.73	6.62	12.18	17.59	21.73

* Solvent H_2O—DMSO, $\mu = 0.3$ $NaClO_4$, 298 K.

When perchloric acid is neutralized by ethylenediamine in check experiments, the titration curves are satisfactorily described using the $\log\beta_1{}^H$ and $\log\beta_2{}^H$ constants in the whole region of DMSO and ethylenediamine concentrations with the accuracy at most 0.05 pH (*i.e.*, 3 mV), which indicates that the experiment was carried out without rough errors. The complexation constants in aqueous solutions, determined using the CRYTUR Cd-selective electrode,[6] confirm that the results obtained by the pH-metric method are reliable.

Thus, the scheme of reactions (3)—(7) involving three complexes is not appropriate for the description of equilibria at $X_{DMSO} > 0.2$ molar fractions and should be supplemented by at least one reaction. Possible supplements can be (a) reactions of solvent self-protolysis and formation of cadmium hydroxo complexes, (b) formation of protonated complexes, and (c) formation of the $[Cd(en)_4]^{2+}$ complex.

The self-protolysis constant of DMSO is negligibly small:[13] the pK_s at $X_{DMSO} = 0.9$ molar fractions is 24.4. Therefore, the influence of this process on complexation can be neglected. At pH 7—10 and in the presence of excess ethylenediamine, the concentration of OH^- ions is insufficient to accumulate $[CdOH]^+$ species in any considerable amounts. Even if the stability of the hydroxo complexes in DMSO is assumed to increase by ten orders of magnitude, the concentration of uncomplexed cadmium is too low to form hydroxides. No features characteristic of formation of hydroxide complexes, such as an unstable potential of the glass electrode and turbidity of the solution, were observed during experiment. The introduction of an additional reaction of hydroxo complex formation into the scheme of equilibria (3)—(7) does not improve the stoichiometric model, because the F function does not significantly change.

The formation of protonated $[Cd(en)_iH]^{3+}$ complexes in a region of relatively high pH values also seems improbable. In the case of formation of the protonated complexes, one should expect that titration curves *1* and *2* would not coincide (see Fig. 1) at pH < 6, when the maximum accumulation of the $(en)H_2{}^{2+}$ species is observed. In addition, curves *2* and *3* should be expected to diverge considerably in a region adjacent to the titration jump, when ethylenediamine is predominantly mono- and diprotonated. It can be assumed that the Coulomb repulsion forces do not favor the stability of a complex when positively charged protonated amine enters the coordination sphere of the ion. At the same time, protonated complexes are typical of multicharged anionic ligands.[14]

The above-presented factors do not allow one to develop an adequate model of complexation in a DMSO medium on the basis of hypothesis for formation of the $[CdOH(en)]^+$ and $[Cd(en)H]^{3+}$ complexes or similar compounds.

When the model of equilibria (3)—(7) is supplemented by the reaction

$$4\ NH_2CH_2CH_2NH_2 + Cd^{2+} = [Cd(en)_4]^{2+}, \qquad (8)$$

a good agreement between experimental and calculated data (see Fig. 1, curves *2* and *4*) can be achieved for all compositions of a water—dimethylsulfoxide solvent in a rather wide interval of reactant concentrations. In this case, the divergence $\log[H]_{exp} - \log[H]_{calc}$ corresponds to the standard experimental error. Thus, the model including reactions (3)—(8) adequately describes a large body of experimental data. The equilibrium constants for reactions (3)—(8) are presented in Table 1.

The coordination of four ethylenediamine molecules by cadmium seems unusual and needs consideration in more detail.

To reveal the most probable scheme of complexation, we carried out the calorimetric titration of dimethylsulfoxide solutions of $Cd(NO_3)_2$ with ethylenediamine.

Small portions of a titrant consisting of ethylenediamine, DMSO, and water were added to a calorimetric cell containing an aqueous solution of DMSO (X_{DMSO} = 0.7 molar fractions), $Cd(NO_3)_2$ (2.5 mmol L^{-1}), and $NaClO_4$ (0.3 mol L^{-1}) as the background electrolyte. The heat of dilution (Q_{dil}) of the same portions of the titrant but no cadmium salt was measured in a blank experiment at 25 °C. The heat of dilution of the titrant is low compared to the heat of reactant mixing (Q_{mix}) in the main experiment.

The measured enthalpy of complexation in a solution calculated to 1 mole of cadmium is the following:

$$-\Delta H = (Q_{mix} - Q_{dil})/m, \qquad (9)$$

where m is the number of moles of $Cd(NO_3)_2$ in the cell.

The observed linear increase in ΔH is proportional to the amount of added ethylenediamine up to the molar ratio en/Cd = 3 (Fig. 2). The ΔH value changes slightly with the further increase in the ligand concentration, and at en/Cd > 4 the heat effect of mixing of the solutions is equal to the heat of titrant dilution. The absence of a pronounced inflection in the titration curve is due to a low stability of the last-named complex. When a stable complex is formed, the dependence is presented by two intersecting straight lines with the intersection point corresponding to the stoichiometric en/Cd ratio in the complex, and the slope of the straight line gives the standard enthalpy of the stepwise reaction $-\Delta_r H°$.

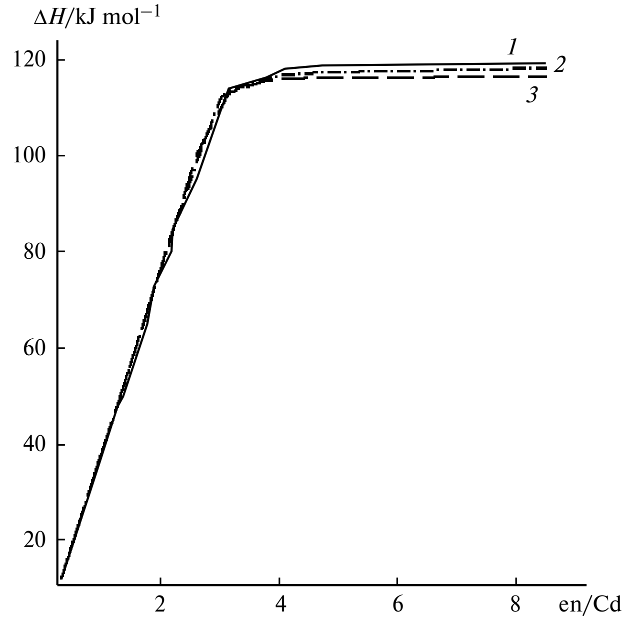


Fig. 2. Curves of calorimetric titration of $Cd(ClO_4)_2$ with ethylenediamine in the solvent with X_{DMSO} = 0.7 molar fractions: experiment (*1*), calculation by the model with three complexes (*2*), and calculation by the model involving $[Cd(en)_4]^{2+}$ (*3*); en/Cd is the ligand/metal molar ratio.

The enthalpies of coordination of the first three ethylenediamine molecules are equal to each other, because the slope of the left part of the plot is constant up to the ratio en/Cd = 3. The extensions of the linear regions of the titration curve are intersected in the point approximately corresponding to the ratio en/Cd = 3.2.

An exact method for calculation of enthalpies and stability constants has been proposed.[15] The method uses calorimetric data for complexes with arbitrary compositions and is based on the statistical principle of maximum plausibility. The latter makes it possible to check different hypotheses on the reaction scheme.

The $\Delta_r H_i°$ and $\log K_i°$ parameters of particular reactions can be found for the specified scheme of complexation by the minimization of the target function in the form

$$F = \sum_{j=1}^{N} (Q_{exp} - Q_{calc})_j^2, \qquad (10)$$

where Q_{exp} is the experimental heat release in the jth entry; Q_{calc} is the heat calculated for some set of parameters; j and N are the number in a series and total number of experimental points, respectively.

The Q_{calc} value for the jth entry can be calculated using the equation for a property to be measured (heat of the process), the equation of material balance with respect to reactants, and the mass action law equation.

The equation for a property to be measured determines the heat release due to complexation. This value is a function of the composition of the system

$$Q_{\text{calc}} = \sum_{i=1}^{n} \Delta_r H^\circ_i C_i, \qquad (11)$$

where C_i is the equilibrium concentration of the *i*th complex, $\Delta_r H_i^\circ$ is the molar enthalpy of formation of the *i*th complex, and *n* is the number of complexes formed. The material balance and mass action law equations are written according to the stoichiometric scheme of the reaction.

The calorimetric titration data were processed by the HEAT program.[16]

Two hypotheses based on different schemes of the reaction of cadmium with ethylenediamine were considered

(1) model based on reactions (5)—(7) assuming the formation of $[Cd(en)]^{2+}$, $[Cd(en)_2]^{2+}$, and $[Cd(en)_3]^{2+}$;

(2) model assuming the formation of the $[Cd(en)_4]^{2+}$ complex in addition to those assumed in (1).

Both the first and second schemes describe well the data of calorimetric experiment (see Fig. 2). They gave different sets of thermodynamic parameters. It was found for the first hypothesis (reactions (5)—(7)) that $\log\beta_3 = 15.78$ and $\Delta_r H_3^\circ = -116.9$ kJ mol^{-1}, while the following values were determined for the second hypothesis (reactions (5)—(8)): $\log\beta_3 = 16.88$, $\log\beta_4 = 19.96$, $\Delta_r H_3^\circ = -114.3$, $\Delta_r H_4^\circ = -118.5$ kJ mol^{-1}. The enthalpies of reactions (5) and (6) in each hypotheses are $\Delta_r H_1^\circ = -38.5$ and $\Delta_r H_2^\circ = -76.0$ kJ mol^{-1}.

One of the hypotheses can be excluded by comparison of the results obtained by the calorimetric and potentiometric methods. For this purpose, the pH-metric curves were calculated from the constants found by the first and second hypotheses under the concentration conditions corresponding to the real pH-metric experiment.

The resulting curves are shown in Fig. 1: curves *3* and *4* correspond to the first and second hypotheses, respectively. The experiment and calculation coincide rather well for the second hypothesis, while the first hypothesis does not provide appropriate results. Thus, if only the $[Cd(en)]^{2+}$, $[Cd(en)_2]^{2+}$, and $[Cd(en)_3]^{2+}$ complexes are assumed to be formed in solution, the experimental pH values at high ethylenediamine concentrations cannot be interpreted and the constants obtained by the calorimetric and pH-metric methods cannot be brought to consent.

The stoichiometric model with the $[Cd(en)_4]^{2+}$ complex provides a good agreement of the calculated and experimental pH and $\Delta_r H$ values in a wide concentration intervals of both ethylenediamine and DMSO, whereas the stability constants obtained by different methods agree satisfactorily.

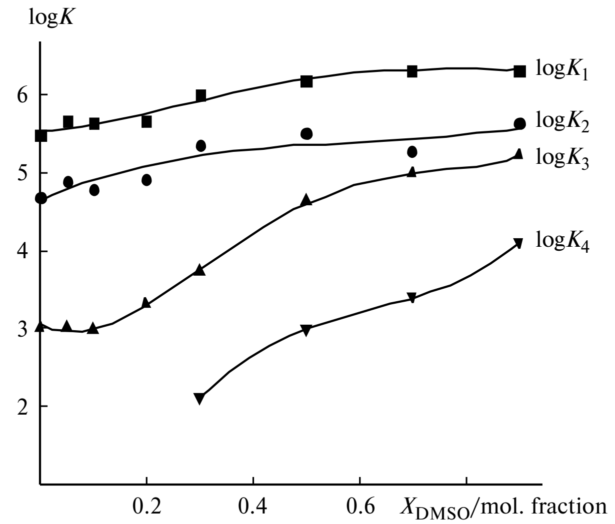


Fig. 3. Plots of the stepwise stability constants *vs.* molar fraction of DMSO in the solvent.

As follows from the data in Fig. 3, an increase in the DMSO content in the solvent is accompanied by the faster increase in the stepwise constant $\log K_3$ compared to the $\log K_1$ and $\log K_2$ constants. Probably, the factors, which induce an additional stabilization of the $[Cd(en)_3]^{2+}$ complex, additionally favor the stabilization of the $[Cd(en)_4]^{2+}$ complex, which is not formed in an aqueous solution.

Similar results were obtained[17] by the polarographic studies of the stability of the Cd^{II} complexes with propylenediamine in an aqueous DMF. For at most 50 vol.% DMF in a solution, the number of the complexes is three. For a content of 75 vol.% DMF, four propylenediamine complexes were found, and the stability constant of the fourth complex was $\log K_4 = 1.35$.

In the general case, the replacement of solvent demands a detailed analysis of the stoichiometric model of the process with addition or exclusion of some species.

Let us consider the thermodynamics of complexation. Note that despite a high stability of the $[Cd(en)_4]^{2+}$ complex ($\log K_4 = 3.1$—3.4), the enthalpy of coordination of the fourth ligand is only -4.2 kJ mol^{-1}, while this value is approximately -38 kJ mol^{-1} for the first three ligands.

The entropic contributions for the first, second, third, and fourth steps of coordination calculated by the equation $T\Delta_r S = \Delta_r H - \Delta_r G$ are -2.0, -8.0, -9.5, and 13.4—15.2 kJ mol^{-1} , respectively (at $X_{\text{DMSO}} = 0.7$ molar fractions).

The monoligand complex is stabilized in solution due to high exothermicity of its formation at a low entropic contribution, which counteracts complexation. When the tetraligand complex is formed, the entropic factor is determining and the enthalpy of the reaction is low, although it favors the process.

Somewhat different ratio of the $\Delta_r H$ and $T\Delta_r S$ contributions is observed for complexation in an aqueous solution.

The $\Delta_r H$ and $T\Delta_r S$ values determined[18] for the stepwise reactions of Cd^{2+} with ethylenediamine (298 K, $\mu = 0.5$ KNO_3) are given below.

Step	$-\Delta_r H$	$T\Delta_r S$
	kJ mol^{-1}	
1	25.5	5.9
2	26.0	0
3	28.8	−17.6

The first complex is stabilized in an aqueous solution, as well as in DMSO, predominantly due to the enthalpic contribution, and the entropy of the reaction is relatively low and positive, which favors stability. The interval of changing $T\Delta_r S$ of the first three stepwise reactions for an aqueous medium is ~3-fold broader than for a water—DMSO mixture. The contribution of $T\Delta_r S$ is most significant in the third step of complexation in an aqueous medium. For comparison, at $X_{DMSO} = 0.7$ molar fractions the ratio of the reaction parameters is substantially different, namely, $\Delta_r H_3 = -38.4$ and $T\Delta_r S_3 = -9.5$ kJ mol^{-1}, *i.e.*, the role of the entropic effects in an aprotic medium is not so significant as in water.

The entropy of the reaction depends not only on a change in the number of particles during processes (5)—(7). In this case, the entropy change should be always positive (reactions in the gas phase); however, $\Delta_r S$ is determined, to a greater extent, by intermolecular bonds in solvate spheres of reactants. In other words, the entropy characteristics reflect both specific features of the structure of the complex and changes in the structure of the solvent caused by complex formation.

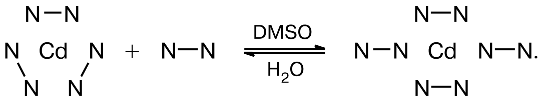
The enthalpies of the first three stepwise reactions change rather slightly with the solvent composition, and $\Delta_r H$ is almost independent of the coordination step. Therefore, it can be assumed that the unusually low heat effect of the reaction

$$[Cd(en)_3]^{2+} + NH_2CH_2CH_2NH_2 = [Cd(en)_4]^{2+} \qquad (12)$$

is related to some distinctive features of the structure of coordination sphere of the tetraligand complex.

Cadmium(II) is characterized by the octahedral configuration of complexes (often with distortions), although the coordination numbers seven and nine were found in particular cases. In some cadmium complexes, ethylenediamine can be a monodentate ligand. Unusual features of the stereochemical structure of the cadmium compounds were observed[19] in crystals of $Cd(en)(NO_2)_2$ in which ethylenediamine is not the ring-forming but bridging ligand.

In reaction (12), the total number of coordinated nitrogen atoms, probably, does not increase and remains to be six, because, in the opposite case, the enthalpy of the reaction would be several times higher. Complexation can proceed *via* the following scheme:



(13)

Is chelate ring opening possible when the coordination sphere adds the ethylenediamine molecule as a monodentate ligand? According to the concepts on the chelate effect, an inverse process should occur: displacement of monodentate ligands and additional chelate ring closure usually increase the stability of a complex due to the entropic factor. Indeed, equilibrium (13) in aqueous solutions is shifted to the left. In a DMSO solution, it is shifted to the right due to the high positive entropic contribution $T\Delta_r S = 13.4—15.2$ kJ mol^{-1}.

The stability of the $[Cd(en)_4]^{2+}$ complex can be favored by the conformational mobility of two ethylenediamine fragments weakly solvated by dimethylsulfoxide. This mobility provides the existence of the complex as several conformers. The entropic stabilization of the complex due to conformational phenomena can be greater, most likely, than the stabilization accompanying additional chelate ring closure.

Coordinatively saturated complexes exhibit, as a rule, the highest increase in the stability on going from an aqueous medium to a DMSO solution, while monoligand complexes are characterized by the lowest stability increase. This regularity is observed for the complexes of Zn^{II} with ethylenediamine,[5] Ni^{II} with ethylenediamine or ammonia,[20] Ni^{II} with the acetate ion,[9] and Cu^{II} with ethylenediamine.[7] The stability of the nickel pyridine complexes in aqueous acetonitrile changes similarly.[21] The stepwise stability constants of these complexes are brought together with an increase in the concentration of an aprotic solvent.

The polythermal study of the $[Ni(en)_i]^{2+}$ complexes ($i = 1—3$) showed[22,23] that an increase in $\log K_i$ on going from water to DMF depends regularly on both the reaction step and temperature. The strongest dependence of $\log K_i$ on the composition of a mixed solvent is observed at low temperatures. The solvent effect on $\log K_3$ is stronger than that on $\log K_1$.

Probably, the stabilization of H bonding and strengthening of the structure of water at low temperatures reinforce the destructive effect of solvent on the complex. First of all, this concerns coordinatively saturated complexes. In the general case, aprotic solvents favor the alignment of $\log K_i$ values.

The stability of complexes in aqueous-alcohol solutions changes in different way as compared with water mixtures with an aprotic solvent. In aqueous ethanol, the stability constants of mono-, di-, and triethylenediaminecadmium change approximately by the same value.[6]

The stability of the coordinatively saturated copper(II) ammino and acetato complexes in water—isopropyl alcohol mixtures increases to a less extent than the stability of the monoligand complexes.[24,25] In this case, water rather than DMSO exerts a leveling effect on the stability of the complexes, whereas isopropyl alcohol has a differentiating effect.

An increase in the ethanol concentration in solution results in a faster increase in the $\log K_1$ constant than that in $\log K_3$ for the nickel ethylenediamine complexes.[26] In this case, differentiation of the complexes by stability in ethanol is stronger than in water.

Protic and aprotic solvents have basically different effects on the stability of metal halide complexes, which can be explained[27] by the ability of the ligand to form H bonds with a solvent. It was found[28] that the entropy-stabilized low-enthalpy halide complexes are predominantly formed in structurally disordered aprotic solvents.

An increase in the stepwise reaction constant depends on a change in the solvation of all reactants. The solvation in Eq. (2) and in

$$2.3RT(\log K_{\mathrm{solv}} - \log K_{\mathrm{H_2O}}) = -\Delta_{\mathrm{tr}}G^\circ{}_{\mathrm{r}} = \Delta_{\mathrm{tr}}G^\circ(\mathrm{L}) + [\Delta_{\mathrm{tr}}G^\circ(\mathrm{ML}_i) - \Delta_{\mathrm{tr}}G^\circ(\mathrm{ML}_{i+1})] \quad (14)$$

is characterized by $\Delta_{\mathrm{tr}}G^\circ(\mathrm{L})$, $\Delta_{\mathrm{tr}}G^\circ(\mathrm{ML}_i)$, and $\Delta_{\mathrm{tr}}G^\circ(\mathrm{ML}_{i+1})$.

Similar equations can be written for the first—fourth steps of complexation, and each expression contains $\Delta_{\mathrm{tr}}G^\circ(\mathrm{L})$. As shown for water—dimethylsulfoxide solvents, the difference $\log K_{\mathrm{solv}} - \log K_{\mathrm{H_2O}}$ is minimum in the first complexation step and maximum in the last step. Since the contribution of solvation of the ligand $\Delta_{\mathrm{tr}}G^\circ(\mathrm{L})$ is independent of the coordination step, the different increase in the stepwise constants is related to the values in Eq. (14), which characterize the solvation of complex ions. Therefore, $[\mathrm{Cd(en)_4}]^{2+}$ is unstable in an aqueous solution due to the specific interaction of the complex with an aqueous solvent.

The destabilizing effect of a protic solvent on the complexes decreases in the series $[\mathrm{Cd(en)_4}]^{2+} > [\mathrm{Cd(en)_3}]^{2+} > [\mathrm{Cd(en)_2}]^{2+} > [\mathrm{Cd(en)}]^{2+}$. The more H bonds are formed between the solvent and coordination sphere, the stronger destabilization of the complex on going from aprotic to protic solvent. Hydrogen bonding of the solvent is an important factor affecting the stability of the complex. However, in the general case, stability is determined by H bonding and also by the whole body of solvent properties.

The influence of a water—dimethylsulfoxide solvent on the stability of the $[\mathrm{Cd(en)_4}]^{2+}$ complex obeys the regularities of the series of above examples. A probable reason preventing the formation of this unusual compound in water is an H bond characteristic of protolytic solvents. It can be expected that similar complexes are stable in DMSO and other aprotic solvents as well.

The stability of a complex can change significantly, depending on the fact whether the complex and ligand are involved in the system of H bonds or not. The influence of H bonding of the free ligand is equally manifested in each step of complexation, whereas the participation of the coordination sphere of the complex in the network of H bonds provides an effect proportional to the number of donor atoms involved in H bonding.

The transfer of a complex from one solvent to another can destabilize the coordination sphere due to its involvement in the network of H bonds. This fact explains why the $[\mathrm{Cd(en)_4}]^{2+}$ complex, which is rather stable in DMSO, is not found in an aqueous solution.

References

1. T. R. Usacheva, S. F. Ledenkov, V. A. Sharnin, and A. Gzejdziak, *Koord. Khim.*, 2001, **27**, 222 [*Russ. J. Coord. Chem.*, 2001, **27** (Engl. Transl.)].
2. Yu. N. Kukushkin, *Khimiya koordinatsionnykh soedinenii* [*Chemistry of Coordination Compounds*], Vysshaya shkola, Moscow, 1985, 378 pp. (in Russian).
3. V. A. Sharnin, V. A. Shormanov, and G. A. Krestov, *Izv. Vuzov. Khim. Khim. Tekhnol.* [*Higher Education Bulletin. Chemistry and Chemical Technology*], 1978, **21**, 831 (in Russian).
4. G. A. Krestov, *Termodinamika ionnykh protsessov v rastvorakh* [*Thermodynamics of Ion Processes in Solutions*], Khimiya, Leningrad, 1984, 272 pp. (in Russian).
5. S. F. Ledenkov, V. A. Sharnin, V. A. Shormanov, and V. A. Isaeva, *Koord. Khim.*, 1993, **19**, 691 [*Russ. J. Coord. Chem.*, 1993, **19** (Engl. Transl.)].
6. S. F. Ledenkov, V. A. Sharnin, and V. A. Shormanov, *Zh. Neorg. Khim.*, 1994, **39**, 2028 [*Russ. J. Inorg. Chem.*, 1994, **39** (Engl. Transl.)].
7. S. V. Mikheev, S. F. Ledenkov, V. A. Sharnin, and V. A. Shormanov, *Koord. Khim.*, 1993, **19**, 800 [*Russ. J. Coord. Chem.*, 1993, **19** (Engl. Transl.)].
8. V. A. Isaeva, S. F. Ledenkov, V. A. Sharnin, and V. A. Shormanov, *Koord. Khim.*, 1995, **21**, 396 [*Russ. J. Coord. Chem.*, 1995, **21** (Engl. Transl.)].
9. V. A. Isaeva, V. A. Sharnin, V. A. Shormanov, and S. F. Ledenkov, *Zh. Fiz. Khim.*, 1996, **70**, 1320 [*Russ. J. Phys. Chem.*, 1996, **70** (Engl. Transl.)].
10. A. V. Nishchenkov, V. A. Sharnin, V. A. Shormanov, and G. A. Krestov, *Izv. Vuzov. Khim. Khim. Tekhnol.* [*Higher Education Bulletin. Chemistry and Chemical Technology*], 1985, **28**, 102 (in Russian).
11. M. V. Kilday, *J. Res. Nat. Bur. Stand.*, 1980, **85**, 467.
12. V. A. Borodin, E. V. Kozlovskii, and V. P. Vasil´ev, *Zh. Neorg. Khim.*, 1986, **31**, 10 [*J. Inorg. Chem. USSR*, 1986, **31** (Engl. Transl.)].
13. G. Ferroni and J. Galea, *Ann. Chimie (Paris)*, 1975, **10**, 41.
14. L. D. Petit and H. K. I. Powell, *SCQUERY, IUPAC Stability Constants Database*, IUPAC and Academic Software (UK), 1993.

15. V. A. Borodin, V. P. Vasil´ev, and E. V. Kozlovskii, in *Matematicheskie zadachi khimicheskoi termodinamiki* [*Mathematical Problems of Chemical Thermodynamics*], Nauka, Novosibirsk, 1985, 219 (in Russian).
16. V. P. Vasil´ev, E. V. Kozlovskii, and V. A. Borodin, *Zh. Neorg. Khim.*, 1988, **33**, 1047 [*J. Inorg. Chem. USSR*, 1988, **33** (Engl. Transl.)].
17. A. K. Maheshwari, D. S. Jain, and J. N. Gaur, *Monatsh. Chem.*, 1977, **108**, 297.
18. V. Yu. Frolov, Author´s Abstract, Ph. D. (Chem.) Thesis, Ivanovo Chemical Technological Institute, Ivanovo, 1988, 14 pp. (in Russian).
19. A. E. Shvelashvili and M. A. Porai-Koshits, *Koord. Khim.*, 1975, **1**, 467 [*Sov. J. Coord Chem.*, 1975, **1** (Engl. Transl.)].
20. A. V. Nishchenkov, V. A. Sharnin, V. A. Shormanov, and G. A. Krestov, *Koord. Khim.*, 1990, **16**, 1264 [*Sov. J. Coord. Chem.*, 1990, **16** (Engl. Transl.)].
21. S. N. Pukhov, Author´s Abstract, Ph. D. (Chem.) Thesis, Ivanovo Chemical Technological Institute, Ivanovo, 1984, 27 pp. (in Russian).
22. T. S. Karabinova, Author´s Abstract, Ph. D. (Chem.) Thesis, Ivanovo Chemical Technological Institute, Ivanovo, 1977, 28 pp. (in Russian).
23. V. A. Shormanov, T. S. Karabinova, and G. A. Krestov, *Izv. Vuzov. Khim. Khim. Tekhnol.* [*Higher Education Bulletin. Chemistry and Chemical Technology*], 1977, **20**, 327 (in Russian).
24. A. Ya. Fridman, E. V. Kozlovskii, and T. V. Volkova, *Zh. Neorg. Khim.*, 1991, **36**, 1519 [*J. Inorg. Chem. USSR*, 1991, **36** (Engl. Transl.)].
25. A. Ya. Fridman, E. V. Kozlovskii, and T. V. Volkova, *Zh. Neorg. Khim.*, 1991, **36**, 1231 [*J. Inorg. Chem. USSR*, 1991, **36** (Engl. Transl.)].
26. A. V. Nevskii, V. A. Shormanov, and G. A. Krestov, *Koord. Khim.*, 1989, **15**, 1576 [*Sov. J. Coord. Chem.*, 1989, **15** (Engl. Transl.)].
27. S. Ahrland, *Pure Appl. Chem.*, 1990, **62**, 2077.
28. S. Ahrland, Sh. Ishiguro, and I. Persson, *Acta Chem. Scand.*, 1986, **A40**, 418.

Received November 24, 2002;
in revised form March 4, 2003