The effect of ligand solvation on the complexation of Dy^{3+} with benzoic, *p*-, *o*-, and *m*-aminobenzoic, and pyridine-4-carboxylic acids, and pyridine and 4-aminopyridine in aqueous and aqueous-organic media

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The effect of a substituent in *m*-, *o*-, and *p*-aminobenzoic and isonicotinic acids and 4-aminopyridine on the stability of their complexes with Dy^{3+} in H_2O and H_2O—DMSO(DMF) has been studied by pH-metric and magnetooptical titration. An increase in the efficiency of the solvation of a ligand decreases the effect of a substituent on the stability of the complex.

Key words: stability, structural thermodynamic parameters, solvation, ligand, aqueous-organic media.

It is known that structural dynamic parameters of complexes in solutions are determined by the nature of the central ion and the ligand and also by the nature of the solvent. The thermodynamics of complexation on going from aqueous to aqueous-organic solutions depends on the energy of solvation of the particles involved in the equilibrium. It is shown using Ni^{2+} [1] and Dy^{3+} [2,3] ions as examples that the change in the stability of complexes that occurs when the composition of the aqueous-organic solvent is varied is mainly associated with the solvation state of the ligand.

The purpose of this work is the qualitative and quantitative estimation of the effect of the electron-donating ability of the ligand and its solvation state on the stability of Dy(III) complexes with several derivatives of aromatic carboxylic acids and pyridine: benzoic, *p*-, *o*-, and *m*-aminobenzoic, and 4-pyridinecarboxylic acids, pyridine, and 4-aminopyridine.

The complexation was studied in water and in DMSO—H_2O and DMF—H_2O mixtures with up to 80 vol. % of the organic component. The main reasons for using these solvents were the following: the high solubility of the initial complexing reagents in these solvents; due to the dipolar aprotic character of DMSO and DMF their participation in the competition with water during the hydration of anions can be not taken into account,[4] and experiments on paramagnetic birefringence (PBR) and pH-metry in H_2O and H_2O—DMSO(DMF) media can be carried out.

Experimental

All compounds used (benzoic, *m*-, *o*-, and *p*-aminobenzoic, and pyridine-4-carboxylic acids, pyridine, and 4-aminopyridine) were industrial samples. Benzoic acid was recrystallized from water; *p*-, *o*-, and *m*-aminobenzoic acids were purified by double recrystallization from 20 % and 10 % ethanol solutions their melting points coincided with the published data. Pyridine was dried over KOH and distilled over BaO. Solvents were purified by the standard procedures.[5] Dysprosium nitrate (reagent grade) was used as a dysprosium salt. The concentration of dysprosium(III) was determined by trilonometry.[6] The pH of aqueous-organic solutions was measured on an I-130 ionometer by the described procedure.[7] The effect of paramagnetic birefringence relative to 1 mole was estimated by the formula

$$mP = \frac{6\lambda a M \Delta\varphi n_\lambda}{(n+2)^2 w d}, \qquad (1)$$

where a is a constant determined by calibration under standard conditions, λ is the wavelength of the testing radiation, n_λ is the refractive index, d is density, M and w are the molecular weight and the mass fraction of the studied compound, respectively, and $\Delta\varphi$ is the monitored angle of rotation of the polarization plane. The "CPESSP" program was used for computation of the experimental dependences.

Results and Discussion

Ligands in which the carboxyl group is the donor center in complexation with Dy(III), except for pyridine and 4-aminopyridine, were chosen as objects of the studies. Despite the fact that in the two latter cases both the n-donor center of the ligand and the medium were changed, the complexation of the Dy(III) ion with ligands of different electron-donating abilities was studied in the same media. Since the different stabilities of the complexes in the same medium can be caused by both the electron-donating ability of the ligand and its solva-

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tion state, the stabilities of the Dy(III) complexes with ligands of different electron-donating abilities were studied in aqueous and aqueous-organic media and compared, which made it possible to monitor the effect of the solvation state of the ligand. This also made it possible to use such ligands as pyridine and 4-aminopyridine.

The stoichiometry and complexation constants in the Dy^{3+}—HL system (HL are benzoic, *p*-, *o*-, and *m*-aminobenzoic, and pyridine-4-carboxylic acids) in the solutions in H_2O and H_2O—DMF(DMSO) mixtures were determined by the data of pH-metric titration. It has been established that the following equilibria occur for all acids studied at the metal ion—ligand concentration ratios = 1 : 1 and 1 : 2 (Table 1):

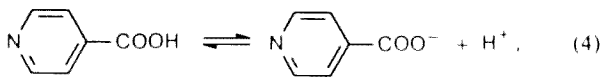
$$Dy^{3+} + L^- = [DyL]^{2+}, \quad (2)$$

$$[DyL]^{2+} + L^- = [DyL_2]^+. \quad (3)$$

The complexation of Dy(III) with nitrate ions was not taken into account, because, according to the published data,[10] it becomes noticeable at concentrations higher than 3 mol L^{-1}.

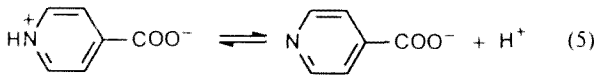
As can be seen from Fig. 1, the stabilities of benzoate and *m*-aminobenzoate complexes in aqueous solutions almost coincide, while the stabilities of *o*- and *p*-aminobenzoate complexes increase somewhat. The change observed is a result of the opposite action of two factors. An increase in the negative charge on the carboxyl group of *ortho*- and *para*-aminobenzoates due to the conjugation effect of amino groups favors the growth in the stabilities of the corresponding complexes. At the same time, an increase in the negative change on the carboxyl group results in the more efficient hydration of the anion, which decreases the stabilities of the corresponding complexes in aqueous solutions.[11]

Due to the noticeable contribution of the zwitterionic form, the acidity of pyridine-4-carboxylic acid, unlike aminobenzoic acids, is determined not only by the equilibrium



(4)

but also by the equilibrium



(5)

Correspondingly, the complexation of pyridine-4-carboxylic acid can be accompanied by the elimination of a proton from both the nitrogen atom and the carboxyl group due to the ionic character of the coordination bond in REE complexes.[12,13] The anion of pyridine-4-carboxylic acid is coordinated by the Dy^{3+} ion through oxygen atoms of the carboxylic group. It is known that the nitrogen atom exerts an "−I-effect," which decreases the negative charge on the X^- anion (see Ref. 14). In this case, it is reasonable to expect that the pK_a of HX would be lower than the corresponding value for benzoic acid. The experimentally observed pK_a value is much greater than the pK_a value of benzoic acid, which is probably caused by the contribution of equilibrium (5). If the value of the basicity of the nitrogen atom is taken into account, the increase in pK_a of HX becomes understandable. Therefore, the value of the stability constant of the complex with HX, which is lower than that with benzoic acid, and its drop out the correlation $\log\beta_{st}$—pK_a (Fig. 1) are caused both by the inductive effect of the nitrogen atom and by the contribution of the zwitterionic form in HX.

Since the substituent affects both the electron-donating ability of donor atoms and the solvation energy, it is reasonable to expect that the regularities of the complexation would noticeably change on going from derivatives of benzoic acid to neutral nitrogen-containing bases.

The computation of the dependences of the magnetooptical data on the concentrations of pyridine (Py) and 4-aminopyridine (Apy) at a dysprosium(III) con-

Table 1. Values of pK_a and stability constants of Dy^{3+} complexes with benzoic, *p*-, *o*-, and *m*-aminobenzoic, and pyridine-4-carboxylic acids in water (I) and water—80 vol. % DMF (II) and water—80 vol. % DMSO (III) mixtures

$pK_a \pm 0.05$			Stoichiometry*	$\log\beta_{st} \pm 0.1$		
I	II	III		I	II	III
Benzoic acid						
4.30	6.91	7.27				
			a	2.0	3.7	4.4
			b	3.9	7.0	8.6
p-Aminobenzoic acid						
4.95	8.15	8.49				
			a	2.2	5.0	5.5
			b	4.6	9.1	9.4
o-Aminobenzoic acid						
5.01	7.12	7.85				
			a	2.2	4.2	5.2
			b	4.5	7.8	9.9
m-Aminobenzoic acid						
4.84	6.84	7.77				
			a	2.1	3.8	4.6
			b	4.4	6.9	8.6
Pyridine-4-carboxylic acid						
4.94	5.79	5.93				
			a	1.5	2.0	3.1
			b	3.0	3.5	4.9

* Corresponds to the reactions

a: $Dy^{3+} + HL = [DyL]^{2+} + H^+$,

b: $Dy^{3+} + 2\,HL = [DyL_2]^+ + 2\,H^+$.

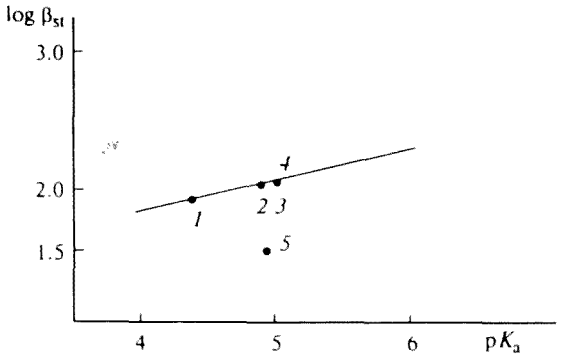


Fig. 1. Dependences of the stability constants of Dy(III) complexes on the deprotonation constants of the corresponding acids. Complexes in aqueous solutions with benzoate (*1*), *m*-aminobenzoate (*2*), *p*-aminobenzoate (*3*), *o*-aminobenzoate (*4*), and pyridine-4-carboxylate (*5*) anions.

centration of 0.026 mol L^{-1} showed that the complexation in the system occurs *via* the reactions

$$Dy^{3+} + B = [DyB]^{3+}, \quad (6)$$

$$[DyB]^{3+} + B = [DyB_2]^{3+}, \quad (7)$$

whose constants are presented in Table 2.

As should be expected, the low basicity and the nature of the donor atom of pyridine cause the stability of its complexes with the dysprosium(III) ion to be lower than that of carboxylate anions. The conjugation effect of the amino group in 4-aminopyridine (Apy) results in a considerable increase in its basicity (pK_a for pyridine and 4-aminopyridine are 5.20 and 9.26, respectively),[15] which can result in an increase in the stability of its complexes and also in the hydrolysis of the aqua ion of Dy^{3+} due to the equilibrium

$$B + H_2O = BH^+ + OH^- \quad (8)$$

which is observed at an excess of 4-aminopyridine. We varied the concentration of 4-aminopyridine and also the pH of the solution by acidification with nitric acid

$$Dy^{3+} + BH^+ = [DyB]^{3+} + H^+, \quad (9)$$

$$Dy^{3+} + 2BH^+ = [DyB_2]^{3+} + 2H^+. \quad (10)$$

to exclude the hydrolysis and to take into account the effect of the acidity of the medium on the concentration of 4-aminopyridine due to equilibrium (8).

The constants of equilibria (9) and (10) and the corresponding stability constants of the complexes formed are presented in Table 2. The increase in the stability of the complexes on going from Py to Apy is approximately 4.5 logarithm units, while it is 0.2 logarithm units on going from benzoic acid to *para*-aminobenzoic acid. It is reasonable to assume that, unlike the carboxylate anion, the "M-effect" of the amino group is not accompanied (or is accompanied to a considerably lesser extent) by a change in the hydration of 4-aminopyridine compared to that of pyridine.

Table 2. Values of pK_a, Py, and Apy, and stability of their complexes with Dy^{3+} in water (I) and water—80 vol. % DMF (II) and water—80 vol. % DMSO (III) mixtures

pK_a			L	Dy : L	$\log\beta_{st}\pm0.1$		
I	II	III			I	II	III
5.2	3.2	3.2	Py				
				1 : 1	0.2	0.2	0.2
				1 : 2	0.4	0.4	0.4
9.26	7.97	7.81	Apy				
				1 : 1	4.8	3.4	3.3
				1 : 2	10.2	7.2	7.1

An increase in the stability of complexes of substituted benzoic acids, which depends on the nature and position of the substituent in the aromatic ring, is observed on going from aqueous to aqueous-organic solutions. The maximum increase in the stability is established for *ortho*- and *para*-aminobenzoates, and the minimum increase is typical of pyridine-4-carboxylate (Fig. 2, Table 1). Now pyridine-4-carboxylic acid does not drop out of the correlation, because, unlike benzoic and aminobenzoic acids, the pK_a value of pyridine-4-carboxylic acid almost does not increase on going to an aqueous-organic solvent (Fig. 3). It is likely that this is caused by a decrease in the fraction of the bipolar form of HX on going from aqueous to aqueous-organic solutions. A decrease in the bipolar form of HX in these mixed solutions is explainable, if it is taken into account that in H_2O—DMSO(DMF) solutions both the basicity of the "pyridine" nitrogen (which will be discussed later) and the acidity of the carboxyl group decrease.

The basicities of both pyridine and 4-aminopyridine decrease on going to H_2O—DMSO(DMF) solutions (Table 2). The difference in pK_a of 4-aminopyridine

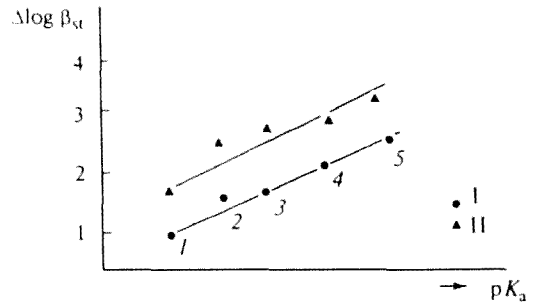


Fig. 2. Dependences of the changes in the stability constants of Dy(III) complexes on the deprotonation constants of the corresponding acids in going from water to aqueous-organic solutions: H_2O—80 vol. % DMF (I), H_2O—80 vol. % DMSO (II). Complexes with benzoate (*1*), *m*-aminobenzoate (*2*), *p*-aminobenzoate (*3*), *o*-aminobenzoate (*4*), and pyridine-4-carboxylate (*5*) anions.

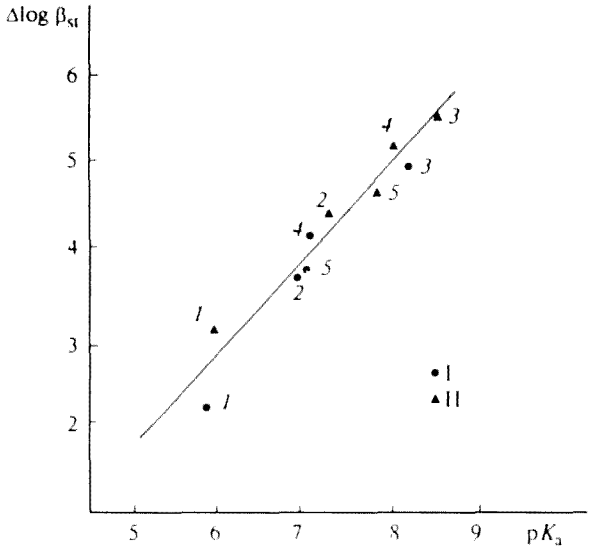


Fig. 3. Dependences of the stability constants of Dy(III) complexes on the deprotonation constants of the corresponding acids in water-dimethylformamide and water-dimethylsulfoxide solutions: I, 80 vol. % DMF; II, 80 vol. % DMSO. Complexes with benzoate (*1*), *m*-aminobenzoate (*2*), *p*-aminobenzoate (*3*), *o*-aminobenzoate (*4*), and pyridine-4-carboxylate (*5*) anions.

and pyridine on going from aqueous to the aqueous-organic solutions studied increases from 4 to 4.8 pK units in the H_2O—DMSO and H_2O—DMF solutions, respectively. The stability of the complexes with pyridine remains almost unchanged on going from aqueous to aqueous-organic solutions, while the stability of the aminopyridine complexes decreases. It can be assumed that the decrease in the pK_a values and in the stability of the complexes in aqueous-organic solvents is a consequence of the more efficient solvation of pyridine and 4-aminopyridine. However, it is of interest that the aqueous-organic solvent exerts a differentiating effect on the basicity of pyridine and 4-aminopyridine, but levels out the stabilities of their complexes with Dy^{3+} (Table 2). Thus, the mesomeric effect of the amino group of aminopyridine in the aqueous-organic solvent stabilizes the protonated form to a greater extent than the complex with Dy^{3+}.

It is evident that the observed dependence of the stability of the complex on the nature of the solvent is caused by the different solvation energies of the corresponding ligands. As has been mentioned above, the effect of the conjugation of the amino group in aminobenzoates on the stability of their complexes with Dy^{3+} is wiped out in aqueous solutions, but manifests itself in the H_2O—DMF(DMSO) media, while the similar effect in *para*-aminopyridine is manifested to a greater extent in aqueous solutions.

Thus, as follows from the pH-metric and magnetooptical data obtained, the more efficient the solvation of the ligand, the less the extent of the effect of the substituent on the stability of the complex.

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