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Stability Constants of Several Aliphatic Uranyl Carboxylates

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Synopsis. The stability constants of uranyl carboxylates were determined spectrophotometrically; for butyrate, they were $\log K_1=2.96$, $\log K_2=2.66$, $\log K_3=2.43$, and $\log K_4=2.23$; for isobutyrate, $\log K_1=2.74$, $\log K_2=2.20$, and $\log K_3=1.66$; for valerate, $\log K_1=2.91$ and $\log K_2=2.52$, and for isovalerate, $\log K_1=2.90$ and $\log K_2=1.91$.

The consecutive and gross stability constants of a number of mononuclear uranyl complexes with anions of common carboxylic acids, such as formic, acetic, propionic, lactic, oxalic, and succinic acids, were determined spectrophotometrically at an ionic strength of 1.0 in an aqueous solution.[1] As part of a series of studies we hereby report the stability constants of aliphatic uranyl carboxylates with the anions of butyric, isobutyric, valeric, and isovaleric acid obtained by the same method.

Experimental

Materials. All the chemicals were of an analytical grade, made by Nakarai Chemicals, Ltd., and were used without further purification. The solutions were prepared with double-distilled water. The uranyl perchlorate was recrystallized from water, and its constitution ($UO_2(ClO_4)_2$–$6H_2O$) was confirmed by the gravimetric determination of uranium as U_3O_8.

Measurements. Hitachi Perkin-Elmer 139 UV–VIS spectrometer was used to record the absorption spectra with cells 0.2, 0.5, and 1.0 cm thick, according to the respective concentration. The pH determinations were performed with a Hitachi pH meter, M-5. The temperature was controlled to $20+0.2$ °C for the spectrophotometric and pH measurements. The systems studied are listed in Table 1. The ionic strength was maintained at 1.0 by adding an appropriate amount of $NaClO_4$ solution to the buffer solution. The procedure of the measurement was as has been described in a previous publication.[1]

Results and Discussion

The data obtained spectrophotometrically and potentiometrically were analysed by Fronaeus' method.[2,3] The linear relationship obtained between the total effective ligand concentration and total uranyl ion concentration for various extinctions suggests the existence of only mononuclear complexes under these conditions. The consecutive stability constants thus obtained are given in Table 2. As is to be expected, the stability of the complexes decreases with an increase in the coordinated ligand number for a given anion. The maximum ligand number attained (Table 3) increases steadily with the length of the carbon chain, reaching 4 for propionate and butyrate, but the steric requirement may prevent the fatty acid with a carbon chain of a sufficient length to occupy more than four of the coordination sites.

Figure 1 shows the relationship between the stability constant, K_1, for the first uranyl complex (UO_2A^+) and the value of K_{1HA} for the corresponding carboxylic acid. As may be seen from the figure, the four carboxylate anions studied here may fall in the group that is classified as showing "normal" behavior, as defined by a previous paper.[1] It is interesting that water lies on this linear line extrapolated to $\log K_{1HA}$ of 16. According to Schwarzenbach's classification of cations into the A-character cations and B-character cations, on the basis of complex-formation behavior,[4] both the uranyl ion and the proton may be said to have the A-character, in which the formation reaction entropy term mainly contributes to the association with the ligand and in which the heat of reaction is positive or slightly negative. On the other hand, the B-character association is dominantly controlled by the negative heat of formation.

The relationship between the number of the carbon of monocarboxylic acid and the first stability constant, K_{1MA}, of the respective various metal complexes shown in Fig. 2. The iron(III) ion and the indium(III) ion

TABLE 2.

Complex	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$
UO_2-*n*-butyrate	2.96	2.66	2.43	2.23
	2.91[a]	1.62[a]		
UO_2-isobutyrate	2.74	2.20	1.66	
	3.40[a]	2.43[a]		
UO_2-*n*-valerate	2.91	2.52		
UO_2-isovelerate	2.90	1.91		

(at 20 ± 0.2 °C)

a) 31 ± 0.1 °C and $=0.1$ ($NaClO_4$); S. Ramamoorthy, A. Raghavan, and M. Santappa, *J. Inorg. Nucl. Chem.*, **31**, 1765 (1969).

TABLE 1.

System	Concentration of uranyl ion (mmol/l)	Concentration of organic Na salt (mmol/l)	Buffer solution (acid: salt)	pH range
UO_2-*n*-butyrate	0.2, 0.5, 1.5	1, 2, 4, 6, 8, 10, 12	2:1, 5:1, 20:1	2.7 to 4.2
UO_2-isobutyrate	0.2, 0.5, 1.5	0.5, 1, 2, 4, 6, 8, 10	2:1, 5:1, 20:1	2.9 to 4.2
UO_2-*n*-valerate	0.1, 0.3, 1.0	0.1, 0.2, 0.4, 0.8, 1.2, 1.4, 1.8	5:1, 10:1, 20:1	3.0 to 4.4
UO_2-isovalerate	0.1, 0.3, 1.0	0.1, 0.2, 0.4, 0.8, 1.2, 1.6, 2.0	2:1, 5:1, 20:1	3.0 to 4.4

Table 3.

Complex	Maximum ligand number attained $n_{\max}$
UO_2-formate	2
UO_2-acetate	3
UO-propionate	4
UO_2-*n*-butyrate	4
UO_2-isobutyrate	3
UO_2-*n*-valerate	2
UO-isovalerate	2

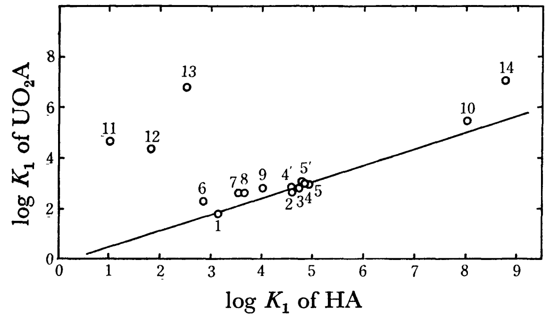

Fig. 1. Relationship between the stability constant K_1 of MA-type uranyl complexes and the first stability constant K_1 of the corresponding carboxylic acid, HA.

1: formate, 5′: isovalerate, 11: oxalate,
2: acetate, 6: salicylate, 12: maleate,
3: propionate, 7: glycollate, 13: citrate,
4: *n*-butyrate, 8: lactate, 14: acetylacetonate,
5: *n*-valerate, 9: succinate,
4′: isobutyrate, 10: glycineamide,

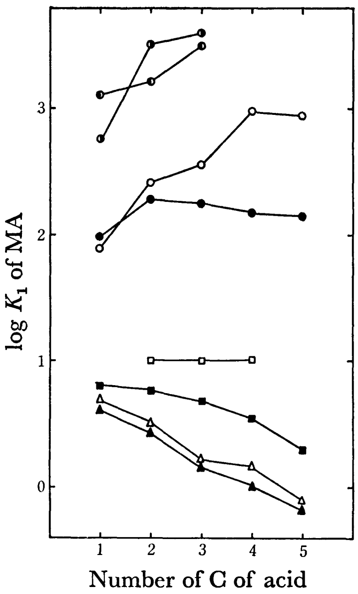

Fig. 2. Relationship between the number of carbon of monocarboxylic acid and the first stability constant of various metal complexes.

◑: In^{3+} at 20 °C and $\mu=2$. N. Sunden, *Svensk. Kem. Tidskr.*, **65**, 257 (1953).

◐: Fe^{3+} at 20 °C and $\mu=1$. D. D. Perrin, *J. Chem. Soc.*, **1959**, 1710.

●: Cu^{2+} at 25 °C and $\mu \rightarrow 0$. M. Llovd, V. Wycherley, and C. B. Monk, *J. Chem. Soc.*, **1951**, 1786.

□: Zn^{2+} at 25 °C and $\mu=0.2$. P. K. Cannon and A. Kibrick, *J. Amer. Chem. Soc.*, **60**, 2314 (1938).

■: Ca^{2+}, △: Sr^{2+} and ▲: Ba^{2+} at 25 °C and $\mu \rightarrow 0$. C. A. Coleman-Porter and C. B. Monk, *J. Chem. Soc.*, **1952**, 4363.

○: UO^{2+} at 20 °C and $\mu=1$.

behave much like the uranyl ion does, corresponding to the fact that these ions are classified as having the A-character. The copper(II) ion and the zinc(II) ion, belonging to the B-character group, remain nearly constant, independently on the temperature. Apart from Schwarzenbach's consideration, there is a possibility of interpreting these tendencies on the basis of the electronic energy level scheme of the metal ion. Alkali earth metal ions, Ca(II), Sr(II), and Ba(II), have stable configurations, with completely-filled $3s^2$-$3p^6$, $4s^24p^6$, and $5s^25p^6$ shells respectively. Since the levels of the 3d, 4d, and 5d orbitals, which accept the electrons of the approaching ligands, lie considerably higher than the filled 3p, 4p, and 5p levels respectively, the stability of the complex may not be affected by the dissociation behavior of carboxylic acid, log K_{1HA}, thus, they are decreased with the length of the carbon chain, which generally causes an increase in the stability of the acid. In the copper(II) ion, however, the unfilled 3d shell with 9 electrons has some capacity to accept electrons from ligands, so the tendency of the stability of the complex to decrease with the length of the carbon chain is compensated for by the increased donating properties of the corresponding acid. The zinc(II) ion seems also to fall in this category, because superposed 3d—4s levels may have the capacity to accept some electrons.

On the other hand, the iron(III) ion with a half-filled 3d shell can accept more electrons within the same 3d shell than can the copper(II) ion or the zinc(II) ion, even if some energy levels are more or less raised by the ligand-field effect. In the uranyl ion, 5f, 6d, and 7s orbitals are distributed in nearly equal energy levels, so there is much capacity to accept the electrons of ligands, though some of the orbitals are used to construct strong bonds of the uranyl ion by hybridization. In the indium(III) ion, which is completely filled up to the 4d shell, the 5s shell is more easily occupied by electrons from ligands than the 4s shell of the zinc(II) ion which is adopted by ligand electrons.

References

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2) S. Fronaeus, Dissertation, Univ. Lund (1944).
3) S. Ahrland, *Acta Chem. Scand.*, **7**, 485 (1953).
4) G. Schwarzenbach, Plenary Lecture at XII International Conference on Coordination Chemistry, Sydney, Australia (1969).