

[CONTRIBUTION FROM ARGONNE NATIONAL LABORATORY AND DUQUESNE UNIVERSITY]

Manganese-54, Uranium-233 and Cobalt-60 Complexes of Some Organic Acids¹

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By using Mn-54 with ion-exchange technique, we have determined the formation constants of manganous complexes of 20 organic acids at pH 7.2–7.3, $\mu = 0.16$. The effect of $-OH$, double bonds, configuration and chelate ring size on complex stability is brought out by comparison of the formation constants of the 20 acids. U-233 was used with ion-exchange and solvent-extraction methods for the study of uranyl complexes of bioxalate, glycolate and serine. Co-60 complexes of four organic acids were studied by ion-exchange and solvent-extraction techniques. Several of the complexes also have been studied by pH method. An important assumption in the use of ion-exchange method for complex study is that the complex itself is not taken up by the cation exchanger. This has been demonstrated experimentally for the first time for some metal complexes by means of acetate labeled with tritium and with C-14.

Introduction

By using Mn-54, U-233 and Co-60, in conjunction with the methods of ion-exchange² and solvent-extraction,³ we have determined the stability of manganous, uranyl and cobaltous complexes of some organic acids. Several of the complexes have also been studied by pH ⁴ methods.

The nature of the complexes which exist in the uranyl sulfate-oxalic acid solution recommended for actinometry has been the subject matter of several publications. Rollefson⁵ has referred to the work of McGinnis⁶ in which the conclusion was made that the photosensitive cluster is $UO_2 \cdot HC_2O_4^+$. Pitzer, Gordon and Wilson,⁷ from potential measurements, have shown that only divalent oxalate ions act as ligands in their experiments, while Heidt⁸ believed that the complexes present in solution are $UO_2H_2C_2O_4^{++}$, $UO_2C_2O_4$ and $UO_2(C_2O_4)_2^{--}$. Because of the disagreement among the various authors, we have re-investigated the uranyl complexes of the oxalic acid system by ion-exchange and solvent-extraction methods.

An important assumption in the use of the ion-exchange method is that the complex itself is not taken up by the cation exchanger. This has been demonstrated experimentally for the first time for some metal complexes by means of acetate labeled with tritium and with C-14.

Experimental

Materials.—High activity Co-60 and carrier-free Mn-54 were obtained from Oak Ridge National Laboratory in the form of cobaltous and manganous chloride, each in HCl solution. U-233 was obtained in the form of uranyl nitrate solution containing 4 M nitric acid. It was purified of pos-

sible α -emitting decay products by ether extraction just prior to use. Pulse analysis showed the purity of the U-233 isotope to be $99 \pm 1\%$. Potassium acetate labeled with tritium was prepared from malonic acid and tritiated water by a method similar to that employed by Halford and Anderson⁹ for the deuteration of acetate. Methyl C¹⁴-labeled sodium acetate was purchased from Tracerlab, Inc.

For the cation exchanger, Dowex-50, 8% cross-linked, 100–200 mesh, was used. The capacity of this type of resin has been found to be independent of pH over a wide pH range.¹⁰ The 2-thenoyltrifluoroacetone (TTA) was obtained from the Dow Chemical Co. It was very light yellow in color and homogenous in appearance, and was used without further purification. It was stored in the dark over phosphorus pentoxide. All other chemicals were of C.P. grade.

Procedure.—The Dowex-50 resin used for ion-exchange experiments was rendered iron-free by percolation with 6 N HCl at room temperature. The ion-exchange technique employed, except as otherwise noted, has been previously described.^{2b} It will be shown in a later section that the complexing action of the Veronal buffer,^{2b} where used, is negligible under the conditions employed. The flasks were agitated at $25 \pm 1^\circ$. After a three-hour shaking period a measured volume of supernate was removed from each flask for radiochemical analysis.

In solvent-extraction experiments for uranyl complexes, the aqueous phase was normally prepared to contain (a) U-233 in concentration of the order of $10^{-6} M$, (b) complexing agent in varying concentrations and (c) HClO₄ to maintain ionic strength and hydrogen ion concentration. The benzene phase, containing TTA, previously had been hydrated by shaking with dilute HClO₄ overnight. Equal volumes of aqueous and benzene phases were then placed in glass-stoppered erlenmeyer flasks and shaken at 25° for two hours, a period of time which had been found to be more than ample for equilibration. At the end of the shaking period, duplicate aliquots of the benzene phase were taken for counting. For complexing studies with Co-60, the above general procedure was followed, except that benzene with TTA was replaced by chloroform containing cupferron. In some experiments aliquots from the aqueous phase were counted and it was found that material balances were normally better than 95%. The precision attained in distribution coefficients was generally better than $\pm 5\%$.

Mn-54 or Co-60 were counted directly as liquid samples in a scintillation counter. For U-233, the liquid was deposited directly on steel planchets, dried by overhead heating with an infrared bulb, and assayed using a proportional α -counter. The samples were infinitely thin. Solutions containing C-14 were assayed by the thick sample technique.¹¹ Tritium in acetate was quantitatively converted to a mixture of methane and hydrogen by heating with zinc, nickel oxide and water in a sealed tube at 640° , according to the method of Wiltzsch, Kaplan and Brown,¹² and the mixture used for ion current measurements with a vibrating reed electrometer.

(1) (a) Work done in part at Argonne National Laboratory under the auspices of the U. S. Atomic Energy Commission. The work of N. C. Li and J. M. White was supported in part by the U. S. Atomic Energy Commission through Contract No. AT(30-1)-1922 with Duquesne University. (b) Presented at the XVth International Congress of Pure and Applied Chemistry at Paris, France, July 18–24, 1957.

(2) (a) J. Schubert, E. R. Russell and L. S. Myers, *J. Biol. Chem.*, **185**, 387 (1950); (b) J. Schubert, in "Methods of Biochemical Analysis," ed. by D. Glick, Vol. 111, Interscience Publishers, Inc., New York, N. Y., 1956, p. 247; (c) J. Schubert, *J. Phys. Chem.*, **56**, 113 (1952).

(3) R. A. Day, Jr., and R. M. Powers, *THIS JOURNAL*, **76**, 3895 (1954).

(4) (a) J. Bjerrum, "Metal Ammine Formation in Aqueous Solutions," P. Haase & Sons, Copenhagen, 1941; (b) N. C. Li, O. Gawron and G. Bascuas, *THIS JOURNAL*, **76**, 225 (1954).

(5) G. K. Rollefson, *Chem. Revs.*, **17**, 425 (1935).

(6) McGinnis, Thesis, University of California, 1935.

(7) F. C. Pitzer, N. E. Gordon and D. A. Wilson, *THIS JOURNAL*, **58**, 67 (1936).

(8) L. J. Heidt, *J. Phys. Chem.*, **46**, 624 (1942).

(9) J. O. Halford and L. C. Anderson, *THIS JOURNAL*, **58**, 736 (1936).

(10) W. C. Baumann and J. Eichhorn, *ibid.*, **69**, 2830 (1947).

(11) W. D. Armstrong and J. Schubert, *Anal. Chem.*, **20**, 270 (1948).

(12) K. E. Wiltzsch, L. Kaplan and W. G. Brown, *Science*, **118**, 522 (1953).

The pH method of Li, *et al.*,^{4b} was employed for the determination of the formation constants of several complexes. All titrations were performed in duplicate.

Results and Discussion

(A) **Mn(II) Complexes.**—Formation constants, k_f , were calculated from the equation

$$k_f = \frac{(K_d^0/K_d) - 1}{(A)^n} \quad (1)$$

where K_d^0 and K_d are the distribution coefficients of the divalent metal cation between resin and solution phases in the absence and presence of the ligand, A, respectively. The distribution coefficient is defined as

$$K_d = \frac{\% \text{ of tracer metal in resin phase } (M_r)}{\% \text{ of tracer metal in soln. phase } (M_s)} \\ \times \frac{\text{vol. of soln. phase}}{\text{mass of resin}} = \lambda \frac{v}{m}$$

where λ represents the ratio M_r/M_s . In the case of a reversible cation-exchange reaction involving a tracer amount of non-colloidal metal ion at constant ionic strength and pH, a variation in v/m is offset by a corresponding change in λ , so that the value of K_d^0 should remain unchanged. That this is so is brought out by the data of Table I, in which the value of K_d^0 remains practically constant despite a 5-fold variation in the v/m ratio.

TABLE I

EFFECT OF VARIATION IN THE v/m RATIO ON K_d^0 OF Mn-54 CATION, pH 7.2, $\mu = 0.16$, 25°

v , ml.	m , mg.	v/m	K_d^0
100	100	1.000	0.433
100	200	0.500	.445
100	300	.333	.445
100	400	.250	.419
75	400	.188	.433

Av. .435 ± 0.008

From plots of $1/K_d$ vs. (A) and from the constancy of k_f assuming various values of n in equation 1, it was found that in the concentration range listed in Table II, all of the manganous complexes were of the 1:1 type, *i.e.*, $n = 1$. In each case, the value of $1/K_d^0$ obtained by extrapolation of $1/K_d$ to zero concentration of the ligand was in agreement with the value measured directly. As a representative example, we give in Fig. 1 a plot of $1/K_d$ vs. (A) for manganous complex of tricarballylate. The results of manganous complexes studied in this investigation are summarized in Table II.

The value of $\log k_f$ for sodium diethyl barbiturate at pH 7.2–7.3 is only approximately 0.1, so that this buffer component exerts little, if any, complexing action. Any interaction of the Veronal buffer with Mn(II) cation then may be considered as due to the presence of the acetate in the buffer, and the formation constant of the Mn(II)-buffer complex, MnB^+ , may be assumed to be the same as for the Mn(II)-acetate complex. In the absence and presence of another ligand, A^b, respectively, we may define the distribution coefficients by the equations

$$K_d^0 = \frac{(MnR_2)}{(Mn^{++}) + (MnB^+)}; \\ K_d = \frac{(MnR_2)}{(Mn^{++}) + (MnB^+) + (MnA^{2-b})} \quad (2)$$

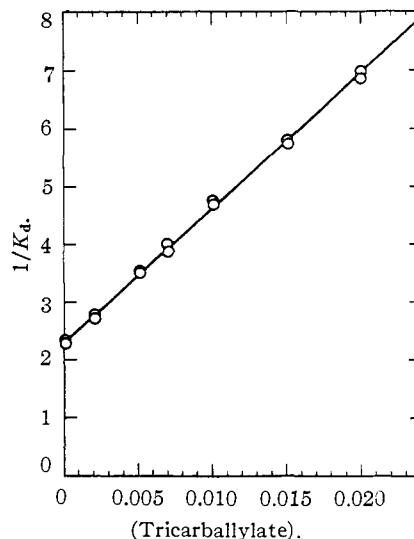


Fig. 1.— $1/K_d$ vs. (A) for Mn-54 complex of tricarballylate.

where R is the immobile anionic part of the cation exchanger. If in addition we define the formation constants by the equations

$$k_f = \frac{(MnA^{2-b})}{(Mn^{++})(A^{b-})}; \quad k_{MnB} = \frac{(MnB^+)}{(Mn^{++})(B^-)} \quad (3)$$

equation (4) is derived readily

$$k_f = \frac{(K_d^0/K_d) - 1}{(A^{b-})} (1 + k_{MnB}(B^-)) \quad (4)$$

On comparison with eq. 1 it is seen that the correction term necessary for the Mn(II)-buffer interaction is

$$1 + k_{MnB}(B^-) \quad (5)$$

Since $k_{MnB} = k_{f,MnAc} = 10^{0.61}$, and since the concentration of acetate in the buffer used in a majority of the complexes listed in Table II is $9.52 \times 10^{-3} M$, the correction term is 1.04, a value which is certainly equal to unity within experimental error. This calculation of the magnitude of correction is verified by the values of $\log k_f$ determined under various conditions for the acetate and glycolate complexes, as listed in Table II.

If one considers that the dicarboxylic acids form chelates with Mn-54 cation through the two carboxylate groups, it is of interest to note that the order of chelate stability decreases with increase in chelate ring size, as one goes from oxalate to azelate. Figure 2 is a plot of $\log k_f$ vs. chelate ring size for a series of dicarboxylic acids, which differ from one another only by the number of intervening $-CH_2-$ groups. The greater stability of the 5- and 6-membered chelate rings probably is due to an entropy effect and frequently has been observed.¹³ The relative order of stability of oxalate and malonate chelates is in accord with the results of Li and Doody¹⁴ who found that α -amino acids (5-membered chelate ring) form more stable chelates than β -amino acids (6-membered ring). It is also interesting to note that as the distance between the two carboxylate groups in a dicarboxylic acid becomes "infinite," the value of $\log k_f$ be-

(13) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952.

(14) N. C. Li and E. Doody, *THIS JOURNAL*, **76**, 221 (1954).

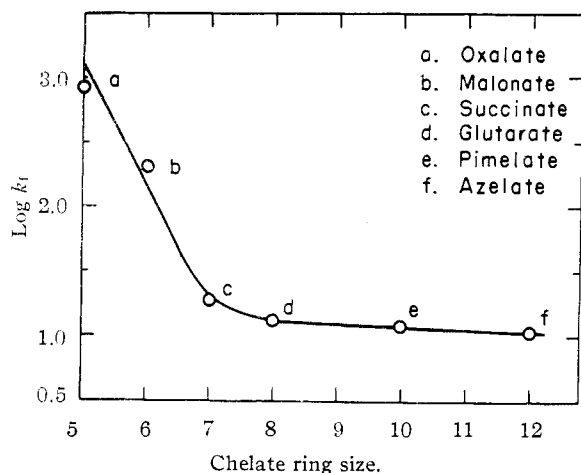
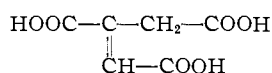


Fig. 2.— $\log k_f$ vs. chelate ring size for Mn(II) chelates.

comes almost twice the $\log k_f$ of a monocarboxylic acid. This is as expected.

The difference in formation constants between *cis* and *trans* aconitic acid is somewhat smaller than the difference between maleic and fumaric acid. Since aconitic acid (*trans*) is



it is apparent that two of the three carboxylate groups are always *cis* to each other whether the compound is *cis* or *trans*. In the *trans* compound, however, the chelate ring between the carboxylate groups in *cis* position would be 8-membered, whereas in the *cis* compound the corresponding ring is 7-membered. This might account for the slightly lower stability of the *trans*-aconitic acid compared to the *cis*-acid.

Complex formation between most of the other organic acid anions listed in Table II with Ca^{++} and with Sr^{++} have been studied by Schubert and Lindenbaum.¹⁵ In general the order of stability of the Mn-54 complexes of organic acids is about the same as that reported for the Ca^{++} and Sr^{++} complexes. The effect of $-\text{OH}$, double bonds and configuration on complex stability has been commented upon by earlier investigators.¹⁵⁻¹⁷

(B) **Uranyl Complexes of Oxalic Acid System.**—Numerous ion-exchange experiments were conducted in HClO_4 solutions of varying concentrations, in order to determine the formation constants of uranyl complexes of oxalic acid systems. In these experiments the cation exchanger was always washed and equilibrated with the HClO_4 solutions to be used as media. Some representative results are given in Table III.

In 0.16 M HClO_4 , $p\text{H}$ 0.90, if we assume that the possible complexes are $\text{UO}_2\text{HC}_2\text{O}_4^+$ and $\text{UO}_2(\text{HC}_2\text{O}_4)_2$, equation (6) is derived

$$\begin{aligned} \frac{K_{d1}^0}{K_d} &= \frac{(\text{UO}_2^{++}) + (\text{UO}_2\text{HC}_2\text{O}_4^+) + (\text{UO}_2(\text{HC}_2\text{O}_4)_2)}{(\text{UO}_2^{++})} \\ &= 1 + k_1'(\text{HC}_2\text{O}_4^-) + k_1'k_2'(\text{HC}_2\text{O}_4^-)^2 \end{aligned} \quad (6)$$

(15) J. Schubert and A. Lindenbaum, *THIS JOURNAL*, **74**, 3529 (1952).

(16) R. K. Cannan and A. Kibrick, *ibid.*, **60**, 2314 (1938).

(17) N. E. Topp and C. W. Davies, *J. Chem. Soc.*, 87 (1940).

TABLE II

FORMATION CONSTANTS BETWEEN Mn-54 CATION AND ORGANIC ANIONS AT $p\text{H}$ 7.2-7.3, $\mu = 0.16$, 25°

Unless otherwise stated, each solution contained a Veronal buffer (sodium diethyl barbiturate and sodium acetate, each 0.00952 M).

Parent acid	Concn. range of parent acid (moles/l.)	$\log k_f$
Monocarboxylic		
Acetic	0.010 - 0.060	0.61
	.032 - .112	.66 ^a .60 ^b
Glycolic	.012 - .060	1.06
		.99 ^c
Diethylbarbituric	.003 - .031	(0.1) ^d
Lactic	.025 - .060	1.19
Di-carboxylic		
Oxalic	.0015- .0055	2.93 ^e
Malonic	.005 - .050	2.30
Succinic	.002 - .020	1.26
Glutaric	.010 - .049	1.13
Pimelic	.012 - .040	1.08
Azelaic	.016 - .053	1.03
Citraconic	.002 - .020	1.77
Maleic	.005 - .050	1.68
Fumaric	.010 - .050	0.99
Malic	.005 - .040	2.24
Tri-carboxylic		
Aconitic (<i>cis</i>)	.0003- .009	2.47
Aconitic (<i>trans</i>)	.0015- .015	2.27
Citric	.0007- .003	3.54
Isocitric	.0016- .008	2.55
Tricarballic	.005 - .020	1.99
γ -Carboxypimelic	.003 - .015	1.91

^a Sodium acetate was omitted from the Veronal buffer. ^b This value was obtained for a 0.112 M NaAc over a 3-fold variation in the mass of resin and with NaAc omitted from the Veronal buffer. ^c This value was obtained for a 0.02990 M glycolate solution at $p\text{H}$ values varying from 6.33-7.76 using Veronal buffer, and at $p\text{H}$ 7.37 with no buffer present. ^d Number in parentheses is approximate because of large experimental errors. ^e The buffer contained 0.0016 M sodium diethylbarbiturate only.

where

$$\begin{aligned} k_1' &= (\text{UO}_2\text{HC}_2\text{O}_4^+)/(\text{UO}_2^{++})(\text{HC}_2\text{O}_4^-) \\ k_2' &= (\text{UO}_2(\text{HC}_2\text{O}_4)_2)/(\text{UO}_2\text{HC}_2\text{O}_4^+)(\text{HC}_2\text{O}_4^-) \end{aligned}$$

From a separate experiment at an ionic strength of 0.16, using the method of Li, *et al.*,^{4b} we have determined the pK_1 and pK_2 of oxalic acid to be 1.28 and 3.75, respectively. Therefore, at $p\text{H}$ 0.90, $(\text{HC}_2\text{O}_4^-) = 0.294T$; $(\text{H}_2\text{C}_2\text{O}_4) = 0.706T$. Equation 6 then becomes

$$\frac{(K_d^0/K_d) - 1}{T} = 0.294k_1' + 0.294^2k_1'k_2'T \quad (7)$$

A plot of $[(K_d^0/K_d) - 1]/T$ vs. T at $p\text{H}$ 0.90 ($\mu = 0.16$) should yield a straight line, from the intercept and slope of which the values of k_1' and k_2' can be calculated. The intercept and slope of such a plot are 740 and 7.9×10^4 , respectively, so that the following results are obtained: $k_1' = 2510$, $k_2' = 360$.

In 1 and 2 M HClO_4 , if we take pK_1 (oxalic acid) = 1.28, the concentrations of the bioxalate ion are calculated to be 0.05 T and 0.025 T , respectively.

TABLE III
 ION-EXCHANGE EXPERIMENTS WITH URANYL COMPLEXES

T (total concn. oxalic acid) $\times 10^2$	$1/K_d^a$	$(K_d^0/K_d)^{-1}/T$
(a) 1 M HClO ₄		
0	13.37 ^b	
1.25	19.05	34.0
2.50	29.03	46.8
5.00	37.03	35.4
6.25	41.89	34.1
7.50	46.30	32.8
	Av.	34.0
(b) 2 M HClO ₄		
0	42.22	
2.50	62.53	19.2
3.75	72.77	19.3
5.00	84.78	20.2
	Av.	19.6
(c) 0.16 M HClO ₄ , pH 0.90		
0	0.88	
0.20	2.45	894
.40	4.52	1038
.60	7.24	1208
.80	10.50	1370
1.00	14.66	1570

^a $\frac{1}{K_d} = \frac{\% \text{ U-233 in aqueous phase}}{\% \text{ U-233 in resin phase}} \times \frac{\text{mg. resin.}}{\text{ml. soln.}}$ This is $1/K_d^0$, and is identical with the value given in ref. 18, after converting to the same unit.

Equation 7 then becomes

$$\text{In } 1 \text{ M HClO}_4 \quad \frac{(K_d^0/K_d) - 1}{T} = 0.05k_1' + 0.05^2k_1'k_2'T \quad (8a)$$

$$\text{In } 2 \text{ M HClO}_4 \quad \frac{(K_d^0/K_d) - 1}{T} = 0.025k_1' + 0.025^2k_1'k_2'T \quad (8b)$$

Since the values of $[(K_d^0/K_d) - 1]/T$ listed in Table IIIa and IIIb are independent of T in the range of T investigated, the values of k_1' in 1 and 2 M HClO₄ are calculated to be 680 and 780, respectively. From the usual numerical relationship between the values of the first and second successive formation constants, $\log k_2 \sim \log k_1 - 1$, we may estimate the value of k_2' in 1 and 2 M HClO₄ to be about 70. When these values of k_1' and k_2' are substituted into eq. 8a and 8b, it is obvious that the values of $[(K_d^0/K_d) - 1]/T$ would be constant in the range of T investigated. The difference between the formation constants in 1 and 2 M HClO₄ and the values found in 0.16 M HClO₄ is probably due to the difference in ionic strengths.

In the above calculations the complex UO₂-(H₂C₂O₄)⁺⁺ is assumed not to exist. Such a complex would carry a net charge of +2, and would have been expected to be taken up in part by the cation exchanger (see the ion-exchange behavior of a +2 complex, Co(imidazole)⁺⁺, described at the end of section (D)). In 1 and 2 M HClO₄, no complex is taken up by the cation-exchanger, since a series of solvent-extraction experiments conducted with 1 M HClO₄ as the aqueous phase, gave 40 as the average values of $[(K_d^0/K_d) - 1]/T$.

(18) J. C. Sullivan, D. Cohen and J. C. Hindman, THIS JOURNAL, **77**, 6203 (1955).

Ahrland¹⁹ has shown that the uranyl ion UO₂⁺⁺ is the only existing complex of U(VI) in acid solutions, up to pH of about 2. Since the degree of hydrolysis is certainly greater for the uranyl ion itself than for the bioxalate complex, and since in each of the experiments of Table IIIa, b, c, a constant high acidity (pH << 2) is maintained, we believe that only mononuclear complexes of bioxalate exist under the conditions of the experiment.

Heidt⁸ states that HC₂O₄⁻ is not a ligand except perhaps in more acid solution. From our results it is seen that even in 1 and 2 M HClO₄, UO₂-(H₂C₂O₄)⁺⁺ does not exist, only HC₂O₄⁻ is the ligand. It seems that our results are more reasonable, inasmuch as the negatively charged HC₂O₄⁻ anion would be expected to exert a greater affinity for a divalent metal cation than the uncharged oxalic acid.

McGinnis,^{5,6} from photochemical studies on uranyl-oxalic acid system over a range of 0.01 to 2 *m* hydrogen ion concentration, concluded that the uranyl complex present is UO₂HC₂O₄⁺. This is in agreement with our results in HClO₄ media.

Additional ion-exchange experiments were carried out at pH 4.45. The resin had previously been washed with dilute NH₄OH, water and equilibrated with 0.16 M NH₄Cl. The results are given in Table IV.

 TABLE IV
 ION-EXCHANGE EXPERIMENTS WITH URANYL-OXALATE COMPLEXES

T (total concn. (NH ₄) ₂ C ₂ O ₄) $\times 10^3$	$1/K_d$	$\frac{(K_d^0/K_d) - 1}{T} \times 10^{-3}$
0	0.63	
0.68	1.58	2.26
1.35	2.72	2.47
2.70	5.28	2.74
4.05	11.1	4.13
5.40	20.9	5.98
8.10	40.8	7.90

At pH 4.45, if we assume that only the bioxalate and oxalate complexes are present, the equation is obtained

$$\frac{K_d^0}{K_d} = \frac{(\text{UO}_2^{++}) + (\text{UO}_2\text{HC}_2\text{O}_4^+) + (\text{UO}_2(\text{HC}_2\text{O}_4)_2 + \text{UO}_2(\text{C}_2\text{O}_4)_n^{(2n-2)-}}{(\text{UO}_2^{++})}$$

A plot of $[(K_d^0/K_d) - 1]/T$ vs. T will give an S-shaped curve, if $n > 2$, and this is obtained for the data of Table IV. While it is mathematically possible to derive the formation constants of the oxalate complexes from the curve, the accuracy of the experimental data does not justify such a treatment. Furthermore, at this high pH, some polymerization of the complexes may occur.

(C) **Uranyl Complexes of Glycolate and Serine.**—Table V lists the results of the distribution of uranyl ion between the resin (200 mg.) and the aqueous phase (25 ml.) containing various concentrations of glycolate ion. The glycolate stock solution was 1.222 M glycolic acid and 0.2387 M sodium hydroxide. The pH of the stock solution and of all the solutions listed in Table V was 2.97.

If we consider that 1:1 and 1:2 uranyl complexes of glycolate exist with successive formation con-

(19) S. Ahrland, *Acta Chem. Scand.*, **3**, 374 (1949).

TABLE V
ION-EXCHANGE EXPERIMENTS WITH URANYL COMPLEXES OF
GLYCOLATE, NaCl ADDED TO MAINTAIN $u = 0.16$, 25°

(Glycolate) = (A ⁻) × 10 ²	1/K _d	(K _d ⁰ /K _d) - 1 (A ⁻)
0	0.80	
0.955	6.23	710
1.432	9.40	750
2.387	17.6	880
2.864	22.3	940

stants k_1 and k_2 , we may derive the equation²⁰

$$\frac{(K_d^0/K_d) - 1}{(A^-)} = k_1 + k_1 k_2 (A^-) \quad (9)$$

Under these conditions then we would predict a linear plot of $[(K_d^0/K_d) - 1]/(A^-)$ vs. (A^-) , from the intercept and slope of which the values of k_1 and k_2 can be calculated. The intercept and slope of such a plot are 600 and 12,000, respectively, so that the following results are obtained: $k_1 = 600$, $k_2 = 20$.

Ahrland²¹ has shown that for $\delta = 4$, ($\delta =$ ratio of the glycolic acid to glycolate concentrations), the pH does not permit any perceptible hydrolysis. He concludes that the complex formation curve with $\delta = 4$, obtained from e.m.f. measurements, is indubitably the curve of uranyl glycolate system, undisturbed by hydrolysis, and that its independence of uranyl ion concentration proves that all the uranyl complexes of glycolate are mononuclear. Since the data of Table V are for $\delta = 5.1$, the complexes are certainly mononuclear.

Ahrland²¹ has shown that 1:1, 1:2 and 1:3 uranyl complexes of glycolate exist, with the following values for the successive formation constants (at $u = 1$): $k_1 = 265$, $k_2 = 34$, $k_3 = 18$. If we include the presence of 1:3 complex, equation 9 becomes

$$\frac{(K_d^0/K_d) - 1}{(A^-)} = k_1 + k_1 k_2 (A^-) + k_1 k_2 k_3 (A^-)^2 \quad (9a)$$

By a least square treatment of a $[(K_d^0/K_d) - 1]/(A^-)$ vs. (A^-) plot, one could then evaluate k_1 , k_2 , k_3 . However, our experimental data do not warrant this treatment.

Figure 3 summarizes the solvent-extraction results with uranyl complex of serine at pH 2.05. The ionic strength was maintained at 0.45 by the addition of NaCl. The stock solution of serine was 0.950 *M*, containing 0.560 *M* HClO₄, pH 2.05. The value of pK_1 of serine, calculated from these data in the usual manner, was 2.21, in exact agreement with that listed by Cohn and Edsall.²²

Since the solvent-extraction method³ is analogous to the ion-exchange method, we have preferred to adapt the same terminology to both. In Fig. 3,²³

(20) The derivation of equation 9 is similar to that of equation 6, except that at pH 2.97, UO₂(glycolic acid)⁺⁺ complex is assumed not to exist.

(21) S. Ahrland, *Acta Chem. Scand.*, **7**, 485 (1953).

(22) E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides," Reinhold Publ. Corp., New York, N. Y., 1943.

(23) In the absence of serine, pH 2.00, $1/K_d^0 = 0.99$. From the discussion of solvent-extraction technique in ref. 3, it can be shown that, under the conditions of the experiment, $1/K_d^0 \propto (H^+)^2$. The value of $1/K_d^0$ at pH 2.00, when corrected to pH 2.05, becomes 0.79, and the corrected value is inserted in Fig. 3.

then K_d is the distribution coefficient of uranyl ion between the organic and aqueous phases, that is

$$\frac{1}{K_d} = \frac{\% \text{ U-233 in aqueous phase}}{\% \text{ U-233 in organic phase}} \times \frac{\text{ml. org. phase}}{\text{ml. aq. phase}}$$

If we assume that the cationic species of serine, CH₂OH-CH-(NH₃⁺)-COOH, does not interact with the divalent metal cation, then at pH 2.05 the only ligand would be the isoelectric serine. Since Fig. 3 shows that $1/K_d$ is a linear function (of serine), formation of only 1:1 complex is indicated. The value of k_f for the uranyl complex of serine is calculated by means of equation 1 to be 7.4 ± 0.2 .

Li and Doody²⁴ found that, while the serinate-Cu⁺⁺ complex is very stable, the serine-Cu⁺⁺ complex is not stable enough to be measured potentiometrically, due to the presence of -NH₃⁺ in serine. Presumably, then, the same generalization may be applied to the uranyl complexes. However, we have now advanced one step further in that, by the use of solvent-extraction method, we are able to assign a value to the formation constant of even a very weak complex.

(D) **Co(II) Complexes.**—Table VI lists the results of the distribution of cobaltous ion between the resin (150 mg.) and the aqueous phase (25 ml.) containing various concentrations of acetate ion. The acetate stock solution was 0.642 *M* acetic acid and 0.500 *M* sodium acetate. The pH of the stock solution and of all the solutions listed in Table VI was 4.52.

TABLE VI
ION-EXCHANGE EXPERIMENTS WITH COBALTOUS COMPLEXES
OF ACETATE, NaClO₄ ADDED TO MAINTAIN $u = 0.15$, 25°

(Acetate) = (A ⁻)	1/K _d	(K _d ⁰ /K _d) - 1 (A ⁻)
0	1.30	
0.04	1.73	8.25
.06	1.95	8.33
.08	2.14	8.08
.10	2.36	8.15
.11	2.43	7.91
.13	2.65	7.99
.15	2.90	8.20

Av. 8.13 ± 0.12

A plot of $1/K_d$ vs. (acetate) is linear and the value of K_d^0 obtained by extrapolation of $1/K_d$ to zero concentration of acetate is in agreement with the value measured directly. Table VII summarizes all of the cobaltous complexes studied in this investigation. In the concentration range listed in Table VII, all of the complexes were of the 1:1 type, and equation 1 was used to calculate the formation constant.

The decrease in $\log k_f$ with increase in ionic strength and the greater stability of glycolate complex over acetate complex are both as expected.

In the use of ion-exchange method for calculation of complex formation constants, it always has been tacitly assumed that the complex itself is not taken up by the resin to any appreciable extent. In order to test this assumption experimentally, we have carried out ion-exchange experiments in which resin is shaken with solutions of 0.02 *M*

(24) N. C. Li and E. Doody, *THIS JOURNAL*, **74**, 4184 (1952).

TABLE VII

FORMATION CONSTANTS BETWEEN Co-60 CATION AND ORGANIC ACID ANIONS AT 25°

Unless otherwise stated, $u = 0.16$, and the ion-exchange method was used.

Parent acid	Concn. range of parent acid (moles/l.)	log k_1
Acetic	0.04-0.15 ^a	0.91
	.10- .42 ($u = 0.50$) ^a	.55
Glycolic	.03 - .12	1.64
Malonic	.003- .006 ^b	2.85
Citric	.00024- .00003 ^b	4.61
		4.52 ^c

^a The stock solution was 0.642 *M* acetic acid, 0.500 *M* sodium acetate, *pH* 4.52. ^b Sodium diethyl barbiturate, 0.01 *M*, was used as buffer, *pH* 7.2. ^c Solvent extraction method was used; the organic phase was chloroform containing cupferron.

sodium acetate (labeled with tritium), both in the presence and absence of 0.02 *M* CoCl₂ (non-radioactive). After equilibration, the resin phase was filtered, washed quickly with water, and tested for tritium activity. It was invariably found that less than 1% activity was in the resin phase, and that the % activity was about the same, regardless of whether the metal ion was present or not. The same results were obtained when sodium acetate was labeled with C-14, and when MnCl₂ was used instead of CoCl₂. We must conclude therefore that at least for the acetate complex, the complex itself is not taken up by the cation exchanger.

It may be appropriate to mention here that in the ion-exchange experiments we have done with Co-60 complex of imidazole, the values of $1/K_d$, for imidazole concentrations varying from 0.01-0.80 *M*, were always smaller than the value of $1/K_d^0$. The explanation that can be given to account for this exceptional behavior is that the Co-imidazole complex itself must have been taken up by the cation-exchanger. This is reasonable in that, since imidazole molecule is uncharged, the cobalt-imidazole complex would retain the +2 charge.

(E) *pH* Titrations of Some Metal Complexes.—

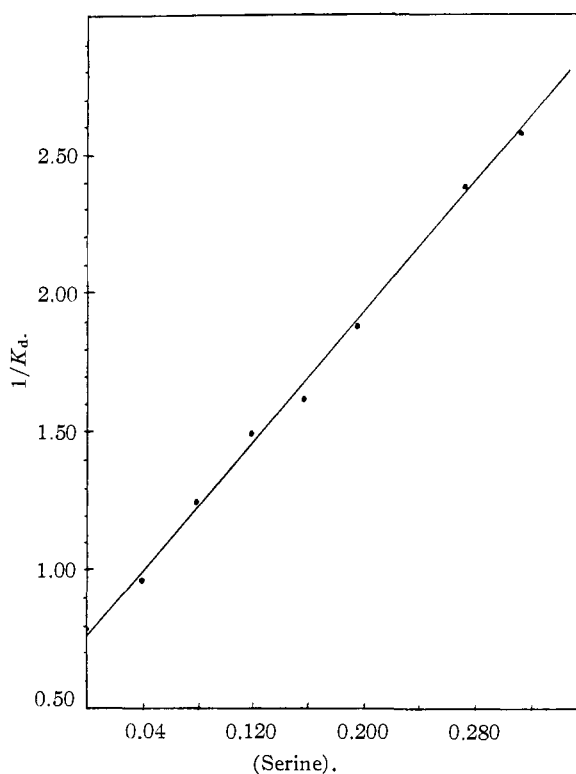
The formation constants of the complexes listed in Sections A to D have been determined with the use of radioactive elements. We have carried out *pH* titrations of some metal complexes, using non-radioactive metal cations. As an example, the *pH* titration data for the manganous complex of malonate at 25° are given in Table VIII. The symbols (A^{--}) and \bar{n} represent the total concentration of free malonate in solution and the average number of moles of malonate bound per mole of manganous ion, respectively. These are calculated by means of the equations

$$(A^{--}) = \frac{(2T - (NaOH) - (H^+))K_1K_2}{K_1(H^+) + 2(H^+)^2} \quad (10)$$

$$\bar{n} = \frac{T - A(K_1K_2 + K_1(H^+) + (H^+)^2)/K_1K_2}{T_m} \quad (11)$$

$$k_1 = \frac{\bar{n}}{(1 - \bar{n}) (A^{--})} \quad (12)$$

where T and T_m are the total concentration of malonic acid and Mn(II) in solution, respectively; K_1 and K_2 are the two ionization constants of malonic acid and were found from a separate experi-

Fig. 3.— $1/K_d$ vs. (serine), in solvent-extraction experiments for uranyl-serine complex, *pH* 2.05.

ment to be 2.04×10^{-3} and 5.75×10^{-6} , respectively. The derivations of equations 10, 11, 12 are similar to those of equations 22, 23, 24 in the paper of Li, Gawron and Bascuas.^{4b}

TABLE VIII

TITRATION OF MANGANOUS CHLORIDE-MALONIC ACID MIXTURES

50 ml. solution containing 0.0200 *M* MnCl₂; 0.0200 *M* malonic acid; 0.100 *M* NaCl; titrated with 0.9860 *M* NaOH under nitrogen, 25°

NaOH, ml.	<i>pH</i>	(A^{--}) $\times 10^3$	\bar{n}	k_1
0.00	2.24			
1.00	3.64	0.403	0.067	180
1.30	4.32	1.595	.218	175
1.50	4.70	2.838	.339	181
1.60	4.90	3.690	.390	174
1.70	5.12	4.71	.435	163
1.90	Precipitate			

Av. 175 ± 5

Table IX summarizes the *pH* results obtained in this investigation, together with those available in the literature and the ion-exchange results.

It will be noticed from Table IX that our *pH* and ion-exchange results for log k_1 of Mn⁺⁺-malonate and Co⁺⁺-malonate are about 1 log unit smaller than those reported by Stock and Davies,²⁵ who used a colorimetric method. For log k_1 of Ca⁺⁺-malonate, Schubert and Lindenbaum¹⁵ report the value 1.36 ($u = 0.16$) obtained by the ion-exchange method, which is in agreement with the value 1.46 ($u = 0.2$), obtained by Cannan and Kibrick,¹⁶ using the *pH* method. These values how-

(25) D. I. Stock and C. W. Davies, *J. Chem. Soc.*, 1371 (1949).

TABLE IX
pH RESULTS OF SOME METAL COMPLEXES, 25°

Complex	$\log k_1$ $u = 0.16-0.19$	$\log k_1$, as reported in lit.	$\log k_1$ (ion- exchange results, this investi- gation) $u = 0.16$
Mn ⁺⁺ -malonate	2.24	3.29 ($u = 0.04$) ²⁵	2.30
UO ₂ ⁺⁺ -glycolate	2.75	2.42 ($u = 1,20^\circ$)	2.78
log k_2 :	1.52	1.53 ($u = 1,20^\circ$)	1.30
Co ⁺⁺ -acetate	1.10		0.91
glycolate	1.62		1.64
malonate	2.85	3.72 ($u = 0.04$) ²⁵	2.85

ever are again about 1 log unit smaller than that reported by Stark and Davies,²⁵ $\log k_1 = 2.49$ ($u = 0.04$). Part of the difference between the ion-exchange and pH values on the one hand, and the colorimetric value on the other hand, is probably due to the difference in ionic strength.

All the values of $\log k_1$, determined by the pH method in this investigation, are in good agreement with those determined by the ion-exchange method. For these complexes therefore, two conclusions may

be made: (1) the complex itself is not taken up by the resin to any noticeable extent, and (2) the nature and stability of complexes of radioactive metal cations are identical with complexes of non-radioactive metal cations.

Ahrland,²⁶ *et al.*, have shown that the complex formation curve is dependent on concentration of metal ion, if polynuclear complexes exist; while if the complex formation curve is independent of metal ion concentration, the complex is mononuclear. The difference in the metal ion concentration used in ion-exchange and pH methods is clearly very great, and the agreement in the formation constant values obtained by the two methods must mean therefore that the Mn(II), uranyl and Co(II) complexes listed in Table IX are mononuclear.

Acknowledgment.—The authors are indebted to Dr. K. E. Wilzbach of Argonne National Laboratory for the preparation and analysis of tritium-labeled acetate.

(25) S. Ahrland, R. Larsson and K. Rosengren, *Acta Chem. Scand.*, **10**, 705 (1956).

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, UNION OIL COMPANY OF CALIFORNIA]

Separation of Xylenes, Cymenes, Methyl-naphthalenes and Other Isomers by Clathration with Inorganic Complexes

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Xylenes, cymenes, methyl-naphthalenes and other isomers have been separated from mixtures by clathration with appropriate inorganic complex compounds. *p*-Xylene concentrates have been recovered from either C₈ aromatic hydrocarbons or from gasolines by single step operations. Each of the C₈ aromatic hydrocarbons has been preferentially clathrated by selection of the proper complex. High selectivity and recovery have been achieved by proper selection of complex and manipulative conditions for the separation at hand. Many new complexes of inorganic salts and basic nitrogen compounds have been prepared.

The use of urea, thiourea, 4,4'-dinitrodiphenyl, hydroquinone and various other materials for selective inclusion in a solid phase of various types of compounds is now widely recognized and documented.^{1,2} This phenomenon which has more recently been dubbed "clathration" by Powell³ has developed into a powerful tool for the separation and purification of organic compounds.

Prior to this report the only reported inorganic complex compound known⁴ to form clathrates with organic compounds was the mono-ammino complex of nickel cyanide, Ni(NH₃)(CN)₂. This compound forms crystals in the presence of certain organic molecules, which contain both the components of the complex and the organic molecule. Organic molecules clathrated by this inorganic compound include thiophene, benzene, phenol, aniline and

furan, all of which occupy about the same molecular volume. The molecular volume appears to be the basis for the selective clathration.^{3,4}

It has now been discovered⁵ that other inorganic complex compounds will form clathrate compounds with organic compounds. This new class of clathrate formers exhibits a sharp selectivity for forming crystals containing certain organic molecules, the selectivity being based, apparently, on the shape rather than on the molecular volume occupied by the organic moiety. By means of these complexes good separation of isomers such as the xylenes, cymenes, methyl-naphthalenes and others has been realized.⁵ The complexes employed here are also of the Werner type but differ from the Ni(NH₃)(CN)₂ complex in that a plurality of neutral molecules (usually four) plus anions, are coordinated with the metal ion.

The three constituents of these complexes (the metal atom, a basic nitrogen compound and the

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(4) K. A. Hofmann, *Z. anorg. Chem.*, **15**, 204 (1897).

(5) W. D. Schaeffer, Belgian patent 553,481, June 17, 1957, U. S. patent 2,798,891 (July 9, 1957); C. G. Christian, U. S. patent 2,774,802 (December 18, 1956); W. D. Schaeffer, *et al.*, U. S. patent 2,798,103 (July 2, 1957); U. S. patent 2,798,102 (July 2, 1957); and others pending.