mass spectrometer used in this research were supplied by the Atomic Energy Commission under contract AT(11-1)-92.

CONTRIBUTION FROM THE
GEORGE HERBERT JONES LABORATORY
UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS

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The Use of Ion Exchangers for the Determination of Physical-chemical Properties of Substances, Particularly Radiotracers, in Solution. IV. Activity Coefficients of Barium Nitrate in Uranyl Nitrate[1]

BY JACK SCHUBERT[2]

About 1931 it occurred to Vanselow that cation exchange reactions could be utilized for investigation of activity coefficients in mixed electrolytes.[3] The method was applied experimentally to the barium–cadmium exchange reaction with bentonite. Fair agreement between experimental and calculated activity coefficients was found. In paper I of this series,[4] it was suggested that Vanselow's approach could be applied even more successfully in conjunction with the synthetic organic cation exchangers and carrier-free radiotracers. The potentialities of this technique for elucidating the role of trace metals in biological systems are of particular interest. This communication presents the results of measurements on the activity coefficients of carrier-free $^{140}Ba^{++}$ in uranyl nitrate solutions by the use of uranyl form of the cation exchange resin, Amberlite IR-1.

The equilibrium reaction between tracer Ba and the cation exchanger is

$$Ba^{++} + UO_2R_2 \rightleftarrows BaR_2 + UO_2^{++} \qquad (1)$$

in which R is the insoluble anionic part of the exchanger. The thermodynamic exchange constant, K_a, for the reaction is[4,5,6]

$$K_a = (N_{BaR_2})(a_{UO_2^{++}})/(N_{UO_2R_2})(a_{Ba^{++}}) \qquad (2)$$

where N_{BaR_2} and $N_{UO_2R_2}$ are the mole fractions of Ba^{++} and UO_2^{++}, respectively, in the resin phase, and $a_{UO_2^{++}}$ and $a_{Ba^{++}}$ are the respective activities in solution. Since $UO_2R_2 >> BaR_2$ it follows that the mole fraction $m_{BaR_2}/(m_{UO_2R_2} + m_{BaR_2}) = m_{BaR_2}/m_{UO_2R_2}$, where m represents the moles of each cation in the resin phase. The concentration exchange constant, $K_{ex.}$, is defined as

$$K_{ex.} = (m_{BaR_2})(m_{UO_2^{++}})/(m_{UO_2R_2}(m_{Ba^{++}}) \qquad (3)$$

whence

$$K_a = K_{ex.} (\gamma_{\pm UO_2(N_2O_3)_2}/\gamma_{\pm Ba(NO_3)_2}{}^3 \qquad (4)$$

where $\gamma_\pm$ represents the mean activity coefficients of the ions of the specified electrolytes. It follows from equation (4) that

$$\gamma_{\pm Ba(NO_3)_2} = (K_{ex.}/K_a)^{1/3} \times \gamma_{\pm UO_2(NO_3)_2} \qquad (5)$$

The thermodynamic constant, K_a, is obtained by a plot of the experimentally determined values of $K_{ex.}$ against some function of electrolyte concentration and extrapolating to infinite dilution. The activity coefficients of uranyl nitrate are exactly those of its aqueous solution. Therefore, the only unknown in equation (5) is the activity coefficient of the barium salt.

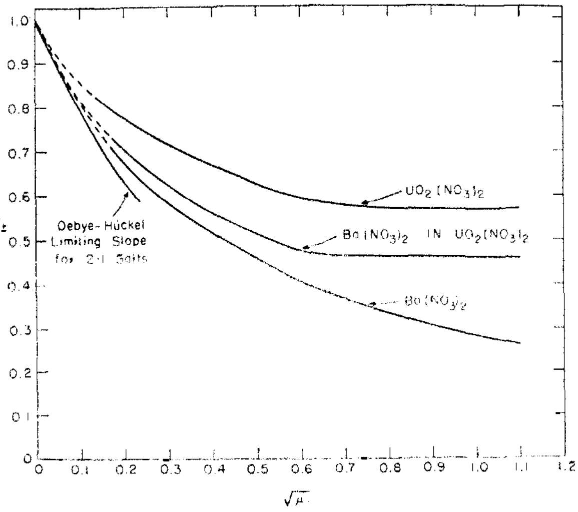

Fig. 1.

Experimental

Ten-ml. volumes of uranyl nitrate solutions (*p*H varied from 1.9–2.4 containing carrier-free ^{140}Ba were added to weighed samples (0.05–0.5 g.) of the uranyl saturated form of Amberlite IR-1 (Rohm and Haas Co., Philadelphia, Pa.). The mixtures were shaken until the absorption of ^{140}Ba reached a constant value. Assay for ^{140}Ba was made by precipitating the tracer with added barium chloride carrier and counting the radioactivity of the mounted precipitate with an end-mica window G. M. counter tube. All of the radioactive measurements were made on a strictly relative basis, thus minimizing errors due to decay, self-absorption, scattering, etc.

The UO_2R_2 contained 1.19 millimoles of UO_2^{++} per gram of oven-dried resin. The air-dried resin, 60–80 mesh, contained 15.5% moisture.

The concentrations of uranyl nitrate in solution at equilibrium were determined gravimetrically by ignition of measured aliquots to U_3O_8.

Results and Discussion

The experimental and derived data are summarized in Table I. The value of $K_a = 14$ was obtained from a plot of log $K_{ex.}$ *versus* $\sqrt{m}$ and an extrapolation to infinite dilution. We can arrive independently at an approximate value of K_a by inserting in equation (4) the known activity coefficient of barium nitrate in a dilute binary solution of the same ionic strength. This procedure for $\mu = 0.03$ gives $K_a = 15$.

The γ^+ of $Ba(NO_3)_2$ in the ternary solution is greater than its value in the binary solution. This effect is similar to that found by Harned[7] for strong acids.

The accuracy of the ion exchange method for measuring activity coefficients in mixed electrolytes can be improved by the use of monofunctional ex-

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(1) This investigation was performed under the auspices of the Manhattan District at the Clinton Laboratories during the period December, 1944, to January, 1945, Oak Ridge, Tenn., and reported in CN-1873 and CN-2563 in January, 1945, and February, 1945, respectively.

(2) Argonne National Laboratory, P. O. Box 5207, Chicago 80, Illinois.

(3) A. P. Vanselow, THIS JOURNAL, **54**, 1307 (1932).

(4) J. Schubert, *J. Phys. Colloid Chem.*, **52**, 340 (1948).

(5) A. P. Vanselow, *Soil Sci.*, **33**, 95 (1932).

(6) G. E. Boyd, J. Schubert and A. W. Adamson, THIS JOURNAL, **69**, 2818 (1947).

(7) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1943, p. 453.

TABLE I

DATA FOR THE CATION EXCHANGE REACTION, $Ba^{++} + UO_2R_2 \rightleftarrows BaR_2 + UO_2^{++}$ AT 25°

Molality, m	Exchange[a] constant $K_{ex.}$	Activity[b] coefficient of uranyl nitrate (binary solution) $\gamma_\pm$	Activity[c] coefficient of barium nitrate (binary solution) $\gamma_\pm$	Calcd. activity coefficient of barium nitrate (ternary solution) $\gamma_\pm$
0	(14)	1.0	1.0	1.00
0.01	10.8	0.80	0.71	0.73
.02	10.0	.75	.63	.67
.04	8.95	.69	.55	.59
.06	8.40	.66	.50	.56
.08	8.15	.64	.46	.53
.10	8.00	.60	.43	.50
.20	7.70	.57	.34	.47
.30	7.55	.57	.29	.46
.40	7.30	.57	.26	.46
.50	7.05	.55	(.24)	(.44)

[a] The exchange constant $K_{ex.}$ is for solutions containing $UO_2(NO_3)_2$ at the stated molalities and $Ba(NO_3)_2$ in tracer quantities (*ca.* 10^{-8} molal). Values for $K_{ex.}$ were read from a smooth curve drawn through the experimental data. The observed average deviation was ±5%. The value of $K_{ex.}$ for $m = 0$ was obtained by extrapolation. [b] Landolt-Börnstein, "Tabellen," Erg. II, Part 2, Fifth Ed., p. 1129 (1931); R. A. Robinson, THIS JOURNAL, 64, 1469 (1942). [c] Landolt-Börnstein, "Tabellen," Erg. III, Part 3, Fifth Ed., p. 2141 (1936); R. H. Stokes, *Trans. Faraday Soc.*, **54**, 295 (1948).

change resins (*e.g.*, Dowex 50 or Amberlite IR-120), so that the capacity of the ion exchange resin is independent of *p*H. Since both exchanging cations were of the same valence in the present study, it is reasonable to expect that changes in resin capacity because of varying *p*H are largely cancelled. The activity of the ions in the resin phase is a point of uncertainty. It appears safe to assume, however, that for the conditions employed in this investigation the activity of the cations in the resin phase is equal to their mole fractions.

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OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENN.
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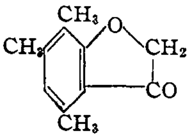
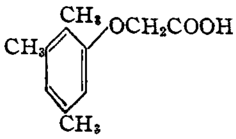
2,4,5-Trimethyl-6-hydroxybenzoic Acid

BY LEE IRVIN SMITH AND RICHARD REMSEN HOLMES

Some time ago there was described preparation of 4,6,7-trimethylcoumaran-3-one (I) by action of sulfuric acid upon 2,3,5-trimethylphenoxyacetic acid (II).[1] The structure of I was established beyond any doubt, but ozonolysis of III, the isopropylidene derivative of I, led to a trimethylsalicylic acid melting at 181–182°. In conformity with the structure assigned to I, this acid was regarded as 2,4,5-trimethyl-6-hydroxybenzoic acid (IV). But an acid, supposed to be IV, had been prepared by Jacobsen and Schnapauff[2] by fusion of durenol with alkali, and this acid was reported to melt at 148°. The isomeric acid, 2,3,5-trimethyl-6-hydroxybenzoic acid (V) had been prepared by Krohn *via* Kolbe synthesis from 2,4,5-trimethylphenol, and reported to melt at 181°.[3] Hence, it appeared that the salicylic acid obtained by ozonolysis of III was V and not IV, and the possibility of migration of a methyl group during cyclization of II to I had to be considered. Krohn's work was repeated and his acid melting at 181° was obtained. But a mixed melting point of Krohn's acid with the acid IV obtained from III showed that the two were not identical, and made it clear that IV was actually 2,4,5-trimethyl-6-hydroxybenzoic acid. It, therefore, became necessary to assume either that Jacobsen and Schnapauff had not actually prepared IV, or else this acid existed in polymorphic forms.


I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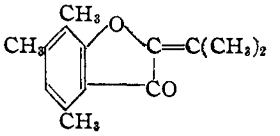
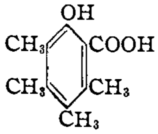
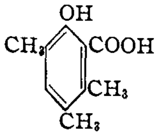
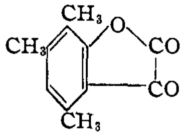

III


IV


V


VI

Since the earlier work[1] durenol has become available, and in order to clear up the uncertainty regarding the structure of IV, the work of Jacobsen and Schnapauff was repeated. Fusion of durenol with alkali, as described by these authors, led to a trimethylsalicylic acid melting at 184°, together with a small amount of a hydroxydibasic acid melting at 276–280° (dec.). It thus appears that there is a typographical error in the paper of Jacobsen and Schnappauf, and that the melting point given there for IV—and of course copied by Beilstein—as 148° should have read 184°. Additional evidence that the structure of I is correct has been provided[4] by conversion of I to the same coumarandione VI as that obtained by action of oxalyl chloride upon 2,3,5-trimethylphenol.

Experimental Part

A mixture of durenol (19 g., m.p. 117°) and potassium hydroxide (150 g.) was fused in a large nickel crucible. The melt was stirred and kept at 180–220° for two hours; evolution of gas (hydrogen) was steady, and at the end of the reaction the dark upper layer of potassium phenolate disappeared. The melt was dissolved in water (1.5 l.) and the solution was acidified. Separation of a very small amount of durenol (m.p. 117°) occurred; this was removed and the filtrate was extracted with three 100-cc. portions of benzene. The combined benzene solutions were extracted several times with aqueous sodium bicarbonate (5%). Acidification of the bicarbonate extracts produced a white solid which, after crystallization from aqueous ethanol, melted at 184°.

Anal. Calcd. for $C_{10}H_{12}O_3$: neut. equiv. (one), 180. Found: neut. equiv., 188.

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(1) L. I. Smith, J. A. King, C. O. Guss and J. Nichols, THIS JOURNAL, **65**, 1594 (1943).

(2) O. Jacobsen and E. Schnapauff, *Ber.*, **18**, 2841 (1885).

(3) C. Krohn, *ibid.*, **21**, 884 (1888).

(4) L. I. Smith and R. R. Holmes, THIS JOURNAL, **73**, 4294 (1951).