potential in either HCl or $HClO_4$ were in error by 4.5 millivolts, the Pu(III)–Pu(VI) potential in both systems could be equal. This would correspond to an error in the ratio of concentration of Pu(III) to Pu(IV) in the e.m.f. determination of 20%, if the entire error were assumed to be in this ratio. An error of 4.5 millivolts seems too large, so this is probably the least likely explanation for the observed results.

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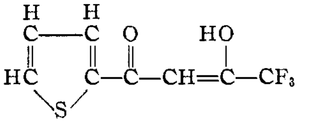
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA]

The Activity Coefficient of Thenoyltrifluoroacetone in Benzene Solution[1]

BY EDWARD L. KING[2] AND WILLIAM H. REAS[3]

The activity coefficient of thenoyltrifluoroacetone in benzene solution has been determined by a study of the distribution of thenoyltrifluoroacetone between benzene and aqueous solutions. This activity coefficient may be calculated by using the empirical equation, $y_B = 1 - 0.24(TTA)_B^{0.48}$, which represents the experimental data quite well. The activity coefficients are required data in the interpretation of metal ion extraction studies in which this substance is used as the chelating agent.

The distribution of metal ions between an aqueous solution and an organic solvent containing a derivative of acetylacetone is useful for the separation of metals from one another as in the work on zirconium and hafnium by Huffman and Beaufait[4] and Larsen and Schultz.[5] Fundamental data on complex ion and hydrolysis equilibria involving metal ions as in the work on zirconium by Connick and McVey[6] may also be obtained from distribution studies. If, in such studies, the concentration of the chelating agent is varied, its activity coefficient may vary in one or both phases. If this is the case, the variation in the activity coefficient must be known before the metal ion distribution coefficient data can be interpreted in anything more than qualitative terms. The derivative of acetylacetone which has been studied in the present work is thenoyltrifluoracetone; this was first prepared by Reid and Calvin.[7] This compound, hereafter referred to as TTA, is a weak acid having the following structure in the enol form



The purpose of the present work was to determine the activity coefficient of TTA in its benzene solutions.

The equilibrium which is established when TTA is distributed between an aqueous solution and a benzene solution may be represented by the equation

$$\text{TTA (in water)} = \text{TTA (in benzene)}$$

for which the equilibrium constant is

$$K = (TTA)_B y_B/(TTA)_W y_W$$

where $(TTA)_B$ and $(TTA)_w$ are the concentrations of TTA in moles per liter of solution in the benzene and water phases, respectively. The y_B and y_W are the activity coefficients of TTA in benzene and water. Defining the distribution coefficient, D, as $D = (TTA)_B/(TTA)_W$ it is seen that $K = Dy_B/y_W$. Since the distribution coefficient is approximately 40, it would be expected that variations in the activity coefficient of TTA in the benzene phase would become appreciable under concentration conditions for which the activity coefficient of the TTA in the aqueous phase in equilibrium is unity. This assumption that y_W is unity in the aqueous phase is supported on the findings of Saylor, Stuckey and Gross[8] who have measured the Henry's law constants for benzene, ethylene dichloride and diethyl ketone in aqueous solution by direct vapor pressure measurements. It was found that the first two substances obeyed Henry's law over the concentration ranges studied, that is, up to concentrations of 0.024 and 0.091 mole/1000 g. water, respectively. The Henry's law constant for diethyl ketone started to deviate at concentrations above 0.4 mole/1000 g. water. It seems reasonable, therefore, to assume that Henry's law is obeyed by TTA in water solution up to a concentration of 0.03 mole/liter, the highest concentration studied here. If the activity coefficient for the TTA in the benzene phase is chosen as unity in the infinitely dilute solution, the activity coefficient at a concentration c is given by the equation $(y_B)_c = D_0/D_c$ where D_0 and D_c are the distribution coefficients at infinite dilution and the concentration c in the benzene phase, respectively.

Experimental Work.—The distribution coefficient of TTA between benzene and a 0.115 M HCl solution has been determined at various concentrations of TTA. Experiments were carried out by shaking in sealed containers known volumes of a benzene solution of TTA and an aqueous solution in a thermostat at 25.0°. As is described elsewhere,[9] the behavior in short time distribution experiments is unusual. In the experiments described here aliquots were removed at various times until equilibrium was established. This generally requires less than 4 days.

The TTA used in this experimental work was prepared and purified (by vacuum distillation) by Dr. J. C. Reid. Reagent grade thiophene free benzene was used. The standard solutions of TTA were prepared by dissolving weighed quantities of dry TTA in benzene or dilute aqueous acid.

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[1] This research was carried out in the Radiation Laboratory and the Chemistry Department of the University of California under the auspices of the Manhattan District, Corps of Engineers during 1945 and 1946.

[2] Department of Chemistry, University of Wisconsin, Madison, Wisconsin.

[3] General Electric Company, Hanford Works, Richland, Washington.

[4] E. H. Huffman and L. J. Beaufait, THIS JOURNAL, **71**, 3179 (1949).

[5] E. M. Larsen and B. Schultz, *ibid.*, **72**, 3610 (1950).

[6] R. E. Connick and W. H. McVey, *ibid.*, **71**, 3182 (1949).

[7] J. C. Reid and M. Calvin, *ibid.*, **72**, 2948 (1950).

[8] Saylor, Stuckey and Gross, *ibid.*, **60**, 373 (1938).

[9] E. L. King and W. H. Reas, *ibid.*, **73**, 1806 (1951).

The analyses for TTA were carried out by measuring the optical transmission of aqueous solutions with a Beckmann quartz spectrophotometer which was not equipped for maintaining the cells at constant temperature. The spectrum of TTA in aqueous solution exhibits maxima at 267 mμ and 292 mμ. The values of ϵ, the molar extinction coefficient ($\epsilon = (cl)^{-1} \times \log I_0/I$), of TTA in 0.133 M HCl have been determined and are presented in Table I. The absorption at 292 mμ was used in the analyses.

TABLE I

MOLAR EXTINCTION COEFFICIENTS OF SOLUTIONS OF TTA IN 0.13 M HCl

Concn. TTA, in moles/l. × 10⁶	Cell length in cm.	267 mμ	292 mμ
5.93	5.0	10260	8100
7.90	5.0	10000	7990
19.8	5.0	10080	8000
19.8	2.0	10300	8040
35.2[a]	2.0	10080	7940
49.4	2.0	10060	7940

[a] Values determined by E. Zebroski; solution is 10^{-3} M HClO$_4$.

TABLE II

DISTRIBUTION OF TTA BETWEEN BENZENE AND 0.115 M HCl.

Concn. of TTA in Moles/L.			
	At equilibrium		
Aq. phase initially × 10³	Aq. phase × 10³	Benzene phase	D
33.3	30.5	1.79	58.7
33.3[a]	30.0	1.75	58.3
0.00	29.8	1.75	58.7
0.00	30.0	1.73	57.8
33.3	17.9	0.910	50.9
0.00	16.6	.875	52.7
33.3[a]	8.11	.384	47.4
0.00	7.5	.347	46.3
33.3[a]	4.75	.216	45.5
0.00	3.92	.173	44.1
6.6[a]	2.30	.100	43.5
0.00	1.97	.0856	43.6
1.5[a]	0.92	.0372	40.5
0.00	0.83	.0341	41.1
8.3[a]	0.59	.0244	41.4
0.00	0.41	.0171	41.7
0.00	0.213	.00863	40.5
0.00	0.021	.00084	40

[a] In these experiments the benzene solution was pre-equilibrated with a different aqueous phase. See reference 9 for significance of this operation.

The distribution coefficients are presented in Table II and in Fig. 1. It is seen that D does not deviate widely from 40 at concentrations lower than 0.04 moles/l. At greater concentrations, the distribution coefficient becomes significantly larger. This trend is expected if association of TTA molecules were occurring in the more concentrated benzene solutions. In order to establish the nature of this association and the equilibrium constant for the association reaction(s), knowledge regarding the activity coefficients of the individual species is necessary. These activity coefficients of the individual species cannot be predicted with any certainty. It can be said, however, that association does occur in the more concentrated benzene solutions.

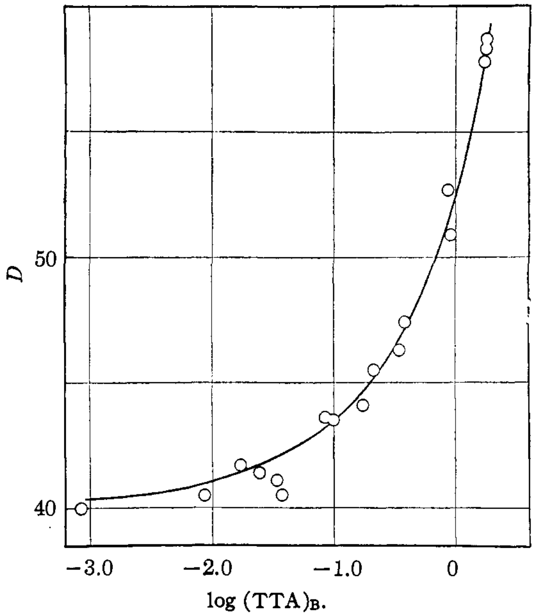

Fig. 1.—Distribution coefficient, D, $vs.$ (TTA)$_B$: solid curve calculated using equation; $40D^{-1} = 1 - 0.24 \cdot (\text{TTA})_B^{0.48}$.

For the purpose of calculating the activity coefficient, y_B, at any concentration, it is desirable to have an empirical equation which represents the experimental data. An equation which may be used for this purpose is: $y_B = 1 - 0.24(\text{TTA})_B^{0.48}$. The solid curve in Fig. 1 has been calculated using this equation.

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