[CONTRIBUTION FROM THE RESEARCH LABORATORY AND THE KNOLLS ATOMIC POWER LABORATORY,[1a] GENERAL ELECTRIC COMPANY]

A Spectrophotometric Study of Three Zirconium Lakes

BY JOHN F. FLAGG, HERMAN A. LIEBHAFSKY AND EARL H. WINSLOW

Surprisingly enough, Beer's law holds over a considerable concentration range in the complex systems of alcohol–hydroxyanthraquinone–suspended zirconium (or hafnium) lake, and this fact forms the basis for a spectrophotometric determination of either metal in microgram amounts.[1] Furthermore, spectrophotometric evidence[2] has indicated that the hafnium–alizarin lake is a definite chemical compound, the combining ratio being unity. Similar evidence is given here for the lakes that zirconium forms with alizarin, with purpurin and with quinalizarin.

As for hafnium, lake formation was studied with zirconium in excess, and with zirconium and dye in stoichiometrically comparable amounts. In the former (limiting) case, all the dye is assumed to be combined so that the lake is the only colored substance present; in the latter (intermediate) case, there is free dye also. The experimental results are interpreted with the aid of data for the other limit, where dye is in excess and zirconium can be determined spectrophotometrically. The procedures for all cases have been fully described, and detailed references will consequently make repetition unnecessary.

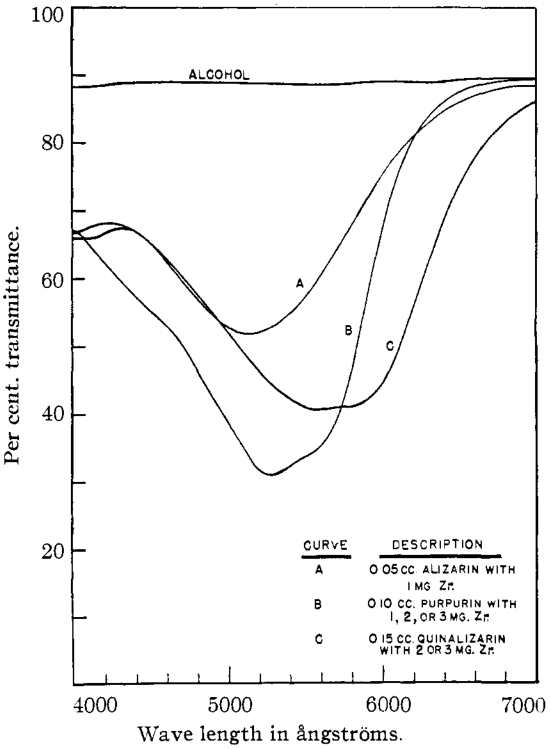

Fig. 1.—Transmittance curves for the three lakes, zirconium being in excess.

Experimental Results

Zirconium in Excess.—Transmittancies[3] were measured on a General Electric recording spectrophotometer for a series of suspensions prepared in the standard way by adding varying excess amounts of standard zirconium solution each to the same amount of dye. When increasing the excess of zirconium did not further increase the transmittance at the minimum in the curve for the dye (near 4360 Å. for alizarin; *cf.* ref. 2, Fig. 1), it was assumed that all the dye had combined to form a lake of formula $Zr_m(Dye)_n$. From the number of moles of dye added and the number of moles of zirconium combined (as obtained from Beer's law plots[1b]), values of the combining ratio n/m (Table I) were calculated (see ref. 2, Fig. 4, and the second paragraph beginning on p. 1131). Typical transmittance curves for the lakes are given in Fig. 1.

TABLE I

RATIO OF DYE TO ZIRCONIUM IN LAKES

Dye	Moles of dye taken × 10^7	Moles of Zr taken × 10^7	Moles of Zr combined × 10^7	n/m
Alizarin	2.88	37.2	2.58	1.1
Alizarin	4.03	37.2	3.77	1.1
Alizarin	5.75	74.4	5.06	1.1
Alizarin	5.32	74.4	5.14	1.0
Alizarin	7.83	330	5.72	1.4
Alizarin	7.87	55.8	8.10	1.0
Alizarin	8.62	37.2	7.73	1.1
Quinalizarin	1.81	330	1.26	1.4
Purpurin	2.94	330	2.68	1.1

Within the range of concentrations chosen, the combining ratio is essentially one for the alizarin lakes. As in the case of the hafnium lake, these ratios tend to exceed unity, perhaps owing to experimental error or to the incomplete realization of a fundamental assumption; *e. g.*, the absorption of dye by the lake may explain the value 1.4 found for the quinalizarin lake.

(1a) The Knolls Atomic Power Laboratory is operated by the General Electric Research Laboratory for the Atomic Energy Commission. Part of the work reported here was carried out under Contract No. W-31-109 Eng.-52.

(1b) Liebhafsky and Winslow, THIS JOURNAL, **60**, 1776 (1938); (c) see also Green, *Anal. Chem.*, **20**, 370 (1948).

(2) Liebhafsky and Winslow, THIS JOURNAL, **69**, 1130 (1947).

(3) National Bureau of Standards Letter Circular LC857 attempts to standardize the confused nomenclature in the field of absorptometry. The recommendations given there will be followed so far as is possible without complicating the references to previous work. Let I_1 and I_2 represent the radiant energy incident upon, and that leaving the filled cell. Then $T = I_2/I_1$ is the (over-all) *transmittance*. The transmittancy, T_S, is the ratio Tsoln./Tsolv., where "soln." in our case refers to a colored system and "solv." to alcohol. A_S = log $1/T_S$ is the *absorbancy*.

Zirconium and Dye in Comparable Amounts.—Lake and uncombined dye are both present, so that the absorbancy for a cell of unit length is given by

$$A_S = \epsilon_1(\Sigma[\text{Dye}] - n[\text{L}]) + \epsilon_2\,[\text{L}] \qquad (1)$$

in which ϵ_1 and ϵ_2 are, respectively, the molar absorbancy indexes of dye and lake, the brackets denote moles/l., Σ[Dye] represents dye added, and L the lake. Given a series of transmittance curves (*cf.* ref. 2, Fig. 2) for suspensions each prepared from a constant amount of dye and a different, comparable amount of zirconium, n/m at a suitable wave length can be obtained graphically from a plot of absorbancy against *combined* zirconium provided ϵ_2/m and ϵ_1 are known; see ref. 2, eq. 2 and 3, Fig. 5, and the neighboring text. The values of ϵ_2/m required for this evaluation were calculated from curves like those of Fig. 1 and are listed in Table II along with the molar absorbancy indexes (ϵ_1's) for the dyes.

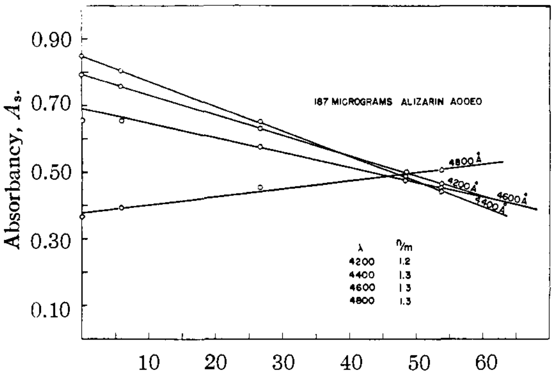

Fig. 2.—Determination of combining ratio, n/m, for the zirconium–alizarin lake at a higher amount of added alizarin.

TABLE II

1. MOLAR ABSORBANCY INDEXES OF THE DYES IN ETHYL ALCOHOL

Wave length, Å.	ϵ_1 of dye Alizarin	Quinalizarin	Purpurin
4060	4350	3595	2360
4200	5170	4610	3260
4400	5420	6240	5180
4600	4270	7720	7070
4800	2410	8880	8020
5000	960	8760	6070

2. ABSORBANCY INDEXES OF THE LAKES[a]

Wave length, Å.	ϵ_2/m of lake prepared from Alizarin[b]	Quinalizarin[c]	Purpurin[c]
4060	3280	4950	2350
4200	3260	4725	2890
4400	3190	5170	3630
4600	3580	6270	4300
4800	4310	7990	5460
5000	5030	9930	6910

[a] If m is (plausibly) taken as unity, then ϵ_2/m values are the molar absorbancy indexes. [b] Averaged values from seven curves. [c] Values from a single curve.

The results of the graphical evaluation of the combining ratios are given in Figs. 2–5. As in the case of the hafnium–alizarin lake, n/m tends to increase with wave length; possible reasons for this have been considered previously.[2] In general, these data support the conclusion drawn from the experiments with zirconium in excess—namely, that n/m = 1.

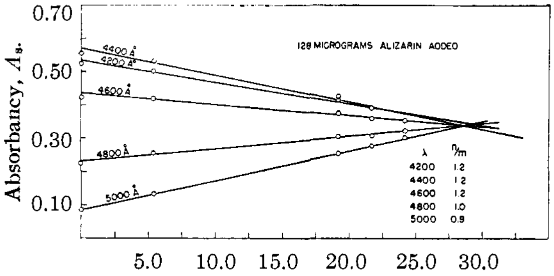

Fig. 3.—Determination of combining ratio, n/m, for the zirconium–alizarin lake at a lower amount of added alizarin.

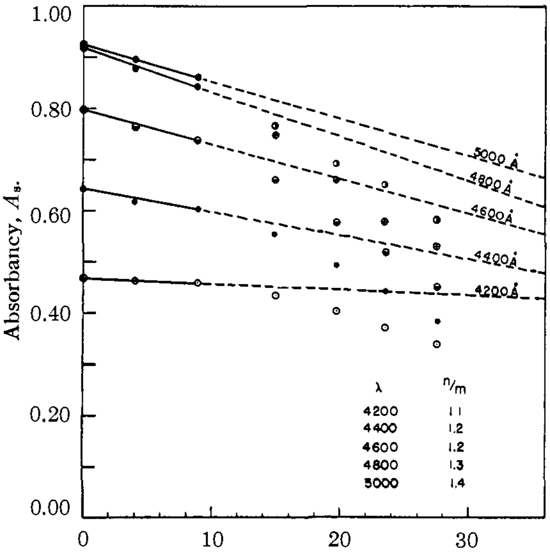

Fig. 4.—Determination of combining ratio, n/m, for the zirconium–quinalizarin lake.

Incomplete Lake Formation.—When a lake was formed from comparable amounts of zirconium and dye, the zirconium combined was less in each case than the zirconium added. Some of the complex situations that could lead to this result have been mentioned for the hafnium–alizarin case, where lake formation was incomplete also (see ref. 2, especially p. 1132). Of these situations, the following seems the most likely. When the lakes are formed in alkaline solution, equilibrium is reached (or at least approached) although the time allowed (two minutes) is short. Because acidification and dilution follow rapidly, these equilibria are "frozen" so that the concen-

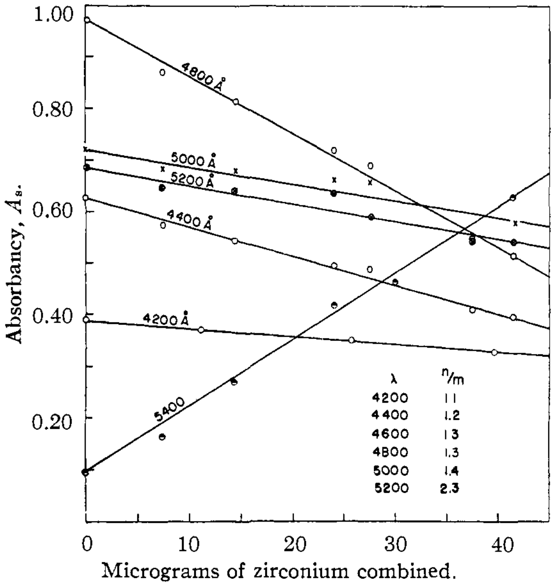

Fig. 5.—Determination of combining ratio, *n/m*, for the zirconium–purpurin lake.

trations of lake, dye and zirconium remain at the equilibrium values for the alkaline medium. To test this explanation, the "equilibrium quotients" (Q = moles of lake divided by the product of moles uncombined zirconium and moles free alizarin) in Table III were calculated, $n/m = 1$ being assumed. The constancy of the Q's, especially of those for the alizarin lake, makes the explanation seem reasonable.

In parallel experiments at different temperatures, lake formation from comparable amounts of zirconium and alizarin was found to be 67% complete at room temperature and 83% complete at 75°.

Summary

TABLE III

EQUILIBRIUM QUOTIENTS AT ROOM TEMPERATURE

Moles dye added × 10^7	Moles Zr added × 10^7	Moles lake × 10^7	Moles Zr un-combined × 10^7	Moles dye un-combined × 10^7	$Q \times 10^{-6}$
5.32	0.93	0.59	0.34	4.73	3.7
(Alizarin)	3.72	2.10	1.62	3.22	4.0
	4.65	2.37	2.28	2.95	3.5
	6.50	2.66	3.84	2.66	2.6
7.80	0.93	0.646	0.284	7.15	3.2
(Alizarin)	4.65	2.92	1.73	4.88	3.5
	9.30	5.32	3.98	2.48	5.4
	12.10	5.91	6.20	1.90	5.0
5.58	0.11	0.058	0.052	5.52	2.0
(Quin-	0.55	0.397	0.153	5.18	5.0
alizarin)	1.10	0.954	0.145	4.63	14.2
	2.20	1.65	0.055	3.93	7.6
	3.30	2.19	1.10	3.39	5.9
	4.40	2.61	1.79	2.97	4.9
	6.60	3.08	3.51	2.50	3.5
5.89	1.10	0.814	0.286	5.08	5.6
(Purpurin)	2.20	1.57	0.626	4.32	5.8
	4.40	2.65	1.75	3.24	4.7
	5.50	3.02	2.47	2.87	4.3
	7.70	4.13	3.57	1.76	6.6
	8.80	4.56	4.22	1.33	8.1

Spectrophotometric evidence indicates that the lakes formed by zirconium with each of the dyes, alizarin, purpurin and quinalizarin, are definite compounds, the two constituents being combined in equimolal amounts.

The spectrophotometric behavior, and the incomplete lake formation observed under some conditions, resemble closely experimental results obtained on the hafnium–alizarin lake. On this basis, it is logical to assign the three lakes studied here a chelate-ring formula analogous to that given the lake formed by hafnium and alizarin.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

The Partial Pressure of Hydrogen Chloride from Its Solutions in Aprotic Solvents: Comparison of Solubility and Infrared Absorption Studies[1]

BY S. JAMES O'BRIEN[2] AND CECIL V. KING

Data were presented in previous papers[3] which indicated that the entropy of solution of hydrogen chloride in aprotic solvents is related linearly to the shift produced by the various solvents in the position of the 3.46 μ absorption band as measured by Gordy and co-workers.[4] In further work along these lines, measurements have been made at two or more temperatures of the partial pressure of hydrogen chloride above its solutions in four more aprotic solvents for which infrared absorption values are available. These determinations provide additional facts pertinent to the relationships between the entropy of solution of hydrogen chloride and the shift of its 3.46 μ absorption band. It is the purpose of this paper to

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(1) Abstracted from a dissertation submitted by S. James O'Brien in December, 1946, to the Graduate School of New York University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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(3) S. J. O'Brien, THIS JOURNAL, **63**, 2709 (1941); **64**, 951 (1942).

(4) W. Gordy and P. C. Martin, *J. Chem. Phys.*, **7**, 99 (1939); W. Gordy, *ibid.*, **9**, 215 (1941).