curves as they stand, with few comments, pending further work on the preparation and study of the much needed nitroso derivatives of the methyl naphthyl ethers. It does seem in each case, however, that the curve of the tautomeric mixture resembles the curves of the quinonoid types more closely than those of the benzenoid types.

Experimental

No new or unpublished methods were used in the preparation of the compounds studied. Each was purified carefully. The solvents were also purified so that they were optically clear throughout the range of the spectrum for which they were used. The methods for obtaining the absorption spectra data have been described already from this Laboratory.[11] For the sake of simplicity not all the experimental points are shown in the curves. Table I summarizes the values of log ϵ at intervals of 100 Å. wave lengths, as well as the positions of the significant absorption maxima.

Summary

1. Absorption spectra curves are shown for the effect of solvent on nitrosobenzene, 1-nitrosonaphthalene, 1,2-naphthoquinone dioxime, and the three nitrosonaphthols.

2. From solvent effects, and from comparison of curves of compounds of fixed quinonoid and of fixed benzenoid structure, evidence is given for the state of the quinonoid–benzenoid equilibrium in the three nitrosonaphthols.

3. No very definite conclusions are possible without further work, but the quinonoid modification seems to predominate in the equilibria studied.

WELLESLEY, MASS. RECEIVED JANUARY 14, 1937

[11] Acly and French, THIS JOURNAL, **49**, 853 (1927).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY AND RADCLIFFE COLLEGE]

The Solubility of Barium Nitrate in Concentrated Nitric Acid

BY CHARLES H. GREENE

The determinations of the solubility of barium nitrate in nitric acid described in this paper were undertaken because of the value of this system for analytical purposes. The use of concentrated nitric acid to separate barium and strontium from calcium was first suggested by Rawson.[1] It is very convenient for the qualitative analysis of the alkaline earth group.[2] Willard and Goodspeed[3] have recently introduced a new technique for the precipitation of lead, barium, and strontium with 100% nitric acid and have shown that these metals may be separated quantitatively from calcium and most other metals by means of this reagent.

A number of investigators[4–8] have measured the solubility of barium nitrate in dilute nitric acid but no quantitative data appear to be available for concentrations of nitric acid above 50%, the range which is of interest for analytical purposes.

Experimental

Barium nitrate of reagent grade was purified by four recrystallizations with rinsing and centrifugal drainage. C. P. nitric acid, either fuming or concentrated as required, was purified by two or more distillations in an all glass still evacuated by a glass aspirator. Conductivity water, analytical reagent sodium carbonate and C. P. sulfuric acid were used.

Preliminary results upon the solubility of strontium nitrate in concentrated nitric acid indicated a slightly greater solubility in acid which had been exposed to full daylight for sixteen hours with consequent decomposition. For this reason, the acid for these experiments was distilled in a dark room and exposed only to red light. The solubility flasks were protected from white light at all times. All of the solutions containing more than 50% nitric acid were analyzed for nitrous acid by the following method.

Samples of 25.00 ml. taken from the flasks after the filtration of the saturated solution, were diluted with 100 ml. of water and oxidized for twenty minutes with 10.00 ml. of 0.1 *N* potassium permanganate. The excess permanganate was reduced with 10.00 ml. of 0.1 *N* oxalic acid and the oxalic acid back titrated with 0.1 *N* permanganate. The oxalic acid and permanganate solutions were compared each time by blank runs with 25 ml. of 18 *N* sulfuric acid in place of the nitric acid solution.

The largest amount of nitrous acid found in any sample was 0.003% while most of the samples contained less than 0.001%. It was thought that this small amount of decomposition would be without appreciable influence on the solubilities measured.

Sealed Pyrex Erlenmeyer flasks containing the acid with a liberal excess of solid barium nitrate were rotated about an inclined axis for twenty-four hours or more in a

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[1] Rawson, *J. Soc. Chem. Ind.*, **16**, 113 (1897).

[2] Greene, *Ind. Eng. Chem., Anal. Ed.*, **8**, 346 (1936).

[3] Willard and Goodspeed, *ibid.*, **8**, 414 (1936).

[4] Chlopin, *Z. anorg. allgem. Chem.*, **143**, 108 (1925).

[5] Fricke and Brummer, *ibid.*, **213**, 319 (1933).

[6] Friend and Wheat, *J. Chem. Soc.*, 501–2 (1933).

[7] Masson, *ibid.*, **99**, 1132 (1911).

[8] Tolmachev, *Compt. rend. acad. sci. U. R. S. S.*, 689 (1930A).

thermostat at 24.88 ± 0.02°. Preliminary experiments indicated that equilibrium was reached in four hours. The thermometer was compared with one calibrated by the Bureau of Standards. The flasks were then allowed to settle for at least twelve hours in the thermostat. In the experiments at 0° the flasks were shaken and allowed to settle with ice and water in large Dewar jars for the same lengths of time.

Without removing the flasks from the thermostat they were opened by applying a hot glass rod to a scratch on the neck. Samples were withdrawn through sintered Pyrex filters directly into calibrated 250-ml. volumetric flasks.

Small samples withdrawn in adjusting the solutions to the mark in the 250-ml. flasks served for the determination of nitric acid. After weighing, these were diluted with great care to avoid loss by evaporation. They were titrated with 0.5 *N* carbonate free sodium hydroxide measured in weight burets. The sodium hydroxide was stored in a paraffin lined bottle and standardized frequently against constant boiling hydrochloric acid. The average difference between duplicate analyses for nitric acid was 0.03%.

Densities were determined by weighing the 250-ml. flasks filled with the solutions. Unfortunately the temperatures of the filtrates changed somewhat during the slow filtrations so that the densities are less accurate than would otherwise have been the case. The room temperature, however, was close to 25° during the filtrations so that the errors in the densities reported are in the last decimal place. The solutions saturated at 0° were brought to 24.88° before adjusting the volume to 250 ml.

The weighed samples of the concentrated nitric acid solutions were transferred quantitatively from the volumetric flasks to one liter distilling flasks with long necks constricted to fit directly to Pyrex condenser tubes. Ninety per cent. of the acid was removed and recovered by distillation. Experiments in which the first distillate was redistilled proved that there was no loss of barium nitrate when the solutions were distilled in this apparatus.

The remaining 10% of the acid solution was rinsed quantitatively into a small beaker and evaporated to dryness in a stream of filtered air. The residue of barium nitrate was dissolved in water with the addition of a drop of nitric acid. The solution was filtered through a tiny filter arranged so that the filtrate ran directly into hot dilute sulfuric acid in a small platinum crucible.

Any insoluble residue in the beaker was scrubbed out with bits of quantitative filter paper and ashed with the filter. Barium in this residue was converted to barium carbonate by fusion with a small amount of sodium carbonate. The melt was dissolved in water and any barium carbonate present filtered off on another tiny filter and washed a few times with small portions of water to remove most of the sodium carbonate solution. It was then dissolved with a few drops of dilute nitric acid and washed into the crucible in which the main part of the barium had already been precipitated as sulfate.

After the precipitate had been digested sufficiently the supernatant liquid was drawn off through a fine porcelain filter stick. The precipitate was washed with 0.06 *N* sulfuric acid and dried by heating the crucible in a quartz capsule. The crucible was weighed against a tare of similar material upon a micro balance reliable to a few thousandths of a milligram.

The precipitates were examined with a quartz spectrograph and found to be free from significant quantities of metals other than barium. Weights and volumetric apparatus were standardized. Weights have been reduced to vacuum.

Results

The results of these determinations are given in Table I and are plotted in Fig. 1 upon a logarithmic scale. The results of Tolmachev,[8] which have also been plotted in Fig. 1, are consistent with the results of the present investigation for the concentration range which they cover. The results at 0° indicate that the temperature coefficient of solubility is moderate in this system so that little is to be gained from an analytical point of view by cooling.

TABLE I

THE SOLUBILITY OF BARIUM NITRATE IN NITRIC ACID

Temperature, 24.88°

HNO_3, %	Density, g./ml.	$Ba(NO_3)_2$, mg./l.	$Ba(NO_3)_2$, %	6 + log (% $Ba(NO_3)_2$)	
				Exptl.	Calcd.
0.00	1.0769	99,400[b]	9.23	6.97[a]	..
20.65	1.1221	5,560[b]	0.495	5.69[a]	..
32.71	1.1966	2,380[b]	.199	5.30[a]	..
47.60	1.2907	624[b]	.0484	4.68[a]	..
56.60	1.343	197	.0147	4.17	4.18
56.98	1.346	187	.0139	4.14	4.15
59.06	1.355	136	.0100	4.00	3.99
61.67	1.372	87.3	.00636	3.80	3.79
62.77	1.373	72.8	.00532	3.73	3.70
64.36	1.385	51.5	.00372	3.57	3.57
66.05	1.394	33.5	.00241	3.38	3.43
67.12	1.394	31.7	.00228	3.36	3.34
67.30	1.395	31.0	.00223	3.35	3.33
71.15	1.413	14.1	.00100	3.00	2.99
71.45	1.415	12.2	.000865	2.94	2.96
75.14	1.430	5.78	.000404	2.61	2.61
78.29	1.445	2.87	.000199	2.30	2.30
78.51	1.442	2.85	.000197	2.29	2.28
85.37	1.463	0.376	.0000257	1.41[a]	1.56
91.69	1.485	.108	.0000072	0.86[a]	0.85
92.10	1.480	.283	.0000191	1.28[a]	.80
Temperature, 0.00°					
56.42	1.3416	132	0.00982	3.99	3.99
59.00	1.3558	86.1	.00635	3.80	3.80
63.21	1.3763	30.8	.00224	3.35[a]	3.47
67.88	1.3975	16.5	.00118	3.07	3.07
71.93	1.4143	7.15	.000506	2.70	2.70
72.82	1.4177	5.75	.000406	2.61	2.61

[a] These experiments were omitted in computing the coefficients for equations (1) and (2).

[b] These values were obtained by evaporating 58-ml. samples to dryness and weighing the residue.

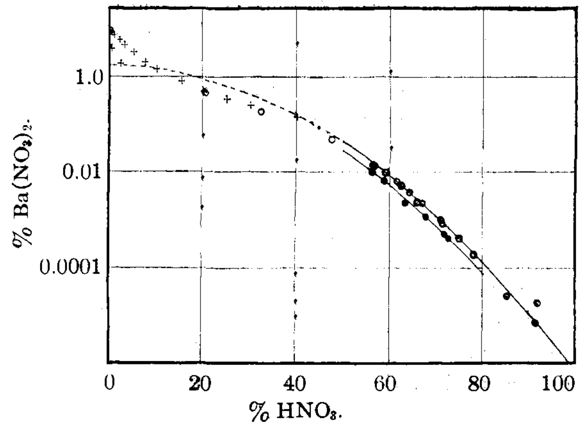

Fig. 1.—The solubility of barium nitrate in nitric acid: ○, experiments at 24.88°; ●, experiments at 0.00°; +, experiments of Tolmachev.[8]

From 55 to 80% of nitric acid the logarithms of the solubilities fall upon a smooth curve which may be expressed well by a quadratic function of the per cent. of nitric acid. Coefficients for this function were determined by the method of least squares omitting the points above 80% of acid because of the obvious experimental uncertainties in this range. The resulting equations have been used to compute the values in column 6 of Table I and the solubilities at round concentrations of nitric acid in Table II.

TABLE II

THE SOLUBILITY OF BARIUM NITRATE IN NITRIC ACID CALCULATED BY EQUATIONS (1) AND (2)

HNO_3, %	% $Ba(NO_3)_2$ 24.88°C.	% $Ba(NO_3)_2$ 0.00°C.
50	0.0423	0.0260
60	.00835	.00533
70	.00123	.000759
80	.000135	.0000747
90	.0000111	(.00000509)
100	(.00000068)	(.00000024)

At 24.88° the solubility is given by the equation

$$\log(\%\ Ba(NO_3)_2) = 0.24537 - 0.0006232\ (\%\ HNO_3) - 0.0006351\ (\%\ HNO_3)^2 \quad (1)$$

while at 0.00° the equation is

$$\log(\%\ Ba(NO_3)_2) = -0.53778 + 0.0189055\ (\%\ HNO_3) - 0.00079706\ (\%\ HNO_3)^2 \quad (2)$$

These equations represent well the results of the present experiments in the concentration range from 50 to 90% nitric acid. As is shown by the dashed curve in Fig. 1 they are entirely unreliable in dilute nitric acid. The extrapolation to 100% HNO_3 in Table II is interesting but uncertain.

Summary

The solubility of barium nitrate has been measured at 0.00 and 24.88° in concentrations of nitric acid ranging up to 92%. Equations have been derived which express the logarithm of the solubility as a quadratic function of the per cent. of acid.

CAMBRIDGE, MASS.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

The Normal Potential of the Mercury–Mercurous Iodide Electrode at 25°[1]

BY ROGER G. BATES AND WARREN C. VOSBURGH

For the normal potential of the mercury–mercurous iodide electrode, the value of 0.0416 v. at 25° is given by "International Critical Tables."[2] This value was calculated from the electromotive force of the lead–mercurous iodide cell measured by Vosburgh[3] and a value for the normal potential of the lead amalgam–lead iodide electrode. However, values for the latter electrode calculated from data for different cells[4] do not agree well. In view of the resulting uncertainty, it was decided to determine the normal potential of the mercurous iodide electrode directly, since its value was needed in another investigation.

Materials.—Mercury was purified by washing with an acidified mercurous nitrate solution and distilling twice at reduced pressure in a current of air. Mercurous iodide was prepared by precipitation and digestion as described by Vosburgh[3] for his Preparation 7. Potassium iodide was recrystallized twice from redistilled water and dried for about a week at 110–125°. Analysis by the Volhard method indicated a purity of at least 99.9%. Hydrogen was prepared by the electrolysis of 30% sodium hydroxide solution and was passed through a tube containing a hot platinum wire for removal of oxygen.

Preparation and Measurement of the Cells.—Two series of cells were made, one with electrolytes of potassium

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[1] Part of a thesis submitted by Roger G. Bates in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University.

[2] "International Critical Tables," Vol. VI, p. 332.

[3] Vosburgh, THIS JOURNAL, **50**, 2391 (1928).

[4] (a) Gerke, *ibid.*, **44**, 1701–1703 (1922); (b) Getman, *J. Phys. Chem.*, **32**, 944 (1928); (c) Jones and Kaplan, THIS JOURNAL, **50**, 2076 (1928); (d) Owen, *ibid.*, **57**, 1526 (1935).