4. **Determination of Acid–Base Strengths.**—Potentiometric titrations were followed with a Leeds and Northrup N. 7662 *p*H indicator with calomel half-cell and glass electrode. The materials examined (I, II and IV) were taken as 25-ml. aliquots of 0.001 *M* solutions in water (0.0408 g. of I or II, or 0.0296 g. of IV, in 250 ml.), and were titrated with 0.001 *N* hydrochloric acid, made by dilution of standard 0.02 *N* acid or with sodium hydroxide solution standardized against the acid by potentiometric titration and found to be 0.0008 *N*. The averaged results of several titrations of each kind are plotted (*p*H *vs.* ml. of reagent) in Figs. 2 and 3.

5. **Ultraviolet Absorption Spectra.**—Absorptions were determined using a Beckmann quartz ultraviolet spectrophotometer with matched quartz cells. Results for the two nitrobenzimidazoles in ethanol under "neutral," acid (0.01 hydrochloric acid) and alkaline (0.10 *N* sodium ethoxide) conditions are shown in Figs. 4, 5 and 6.

6. **Association Factors from Molecular Weight Determinations.**—The Beckman apparatus[38] was somewhat modified to permit operation near 100°. Equipment included a cooling-bath and a heating-bath containing glycerol; the former was kept 1–1.5° below the crystallization temperature and the latter at 100°, *i.e.*, respectively, slightly below and slightly above the melting point of the phenanthrene (Eastman Kodak Co. No. 599, m.p. 98.5°) used as solvent. Samples of the nitrobenzimidazoles were compressed into tablets weighing 30 to 100 mg.; each tablet was brushed free of powder and was stored in a small stoppered vial. The rotary magnetic stirrer used was of new design.[39] To dissolve the pellet of sample the freezing-point tube containing the phenanthrene was withdrawn from the bath and was heated with a very small flame. During this operation it was necessary to raise the Beckman thermometer so that the bulb was about 7 cm. above the surface of the heated liquid. It was supported in this position by affixing one above the other three large-bore rubber stoppers slit through to the bore, with the lowermost resting on the rim of the tube. When the sample was in solution the liquid was allowed to cool to about 100°, the thermometer was lowered into the normal position and the freezing-point tube was introduced into the 100° bath. When equilibrium was attained, the tube was transferred to the cooling-bath, and two readings of the freezing point were taken. An additional pellet of sample was introduced and dissolved as described, and the process was repeated as many times as the solubilities of the nitrobenzimidazoles permitted. For 5(6)-nitrobenzimidazole the limit was 0.06 *M*, at which concentration mixed crystal formation occurred; for 4(7)-nitrobenzimidazole the limit was 0.08 *M*, at which concentration an appreciable color change made addition of further increments seem inadvisable. The freezing-point constant of the phenanthrene was determined empirically by use of triphenylmethane. Six trials, each in duplicate, yielded the averaged value 11.8; the reported value[40] is 12.0. Curves for the association factors plotted against concentration are shown in Fig. 7.

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[38] K. v. Auwers, *Z. physik. Chem.*, **18**, 595 (1895).

[39] A description for publication is in preparation.

[40] F. Garelli and A. Ferrantini, *Gazz. chim. ital.*, **23**, 442 (1893).

PHILADELPHIA, PENNA. RECEIVED NOVEMBER 2, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, BAYLOR UNIVERSITY COLLEGE OF MEDICINE]

A Study of the Solubility of Triethylenediaminenickel Thiosulfate[1,2]

BY JOSEPH H. GAST AND FRANK L. ALDRICH

Solubility studies on triethylenediaminenickel thiosulfate ($\mathrm{Ni\ en_3S_2O_3}$) have been carried out over a range from 15 to 50° and at 100° in water and at 20° in ethanol–water mixtures. The concentration of the complex was determined by iodometric titration and spectrophotometric measurements in the ultraviolet. Spectral absorption data are presented for both the thiosulfate and nitrate salts. The thiosulfate is soluble to the extent of 1.5 mg. per ml. at room temperature and shows an appreciable temperature coefficient of solubility. When equilibrium is approached from a higher temperature there is a definite tendency to supersaturation. The data on solubility in ethanol–water mixtures show that addition of an equal volume of redistilled ethanol to a water solution of the salt reduces its solubility to approximately one-tenth that of a water solution. Further depression of the solubility in water and ethanol–water mixtures can be obtained by the presence of excess triethylenediaminenickel ions.

While many of the coördination complexes of nickel have been studied by various investigators since Werner's original work[3] and the ethylenediamine complex has been recommended in the qualitative analysis and separation of thiosulfate from some inorganic sulfur compounds,[4,5] solubility measurements have not been reported.

In order to determine the conditions for more precise analytical use of triethylenediaminenickel(II) thiosulfate, $\mathrm{Ni\ en_3S_2O_3}$, further information concerning its solubility was essential.

In pure solutions, accurate measurements of the thiosulfate salt can be obtained readily by iodometric titrations, nickel analyses[6] and by optical density measurements (discussed below). Solubility determinations in water solutions were carried out using all three analytical procedures. However, in ethanol–water mixtures, iodometric titrations in dilute solutions can only be used after the removal of alcohol by evaporation.

None of these analytical procedures are satisfactory in the presence of an excess of the triethylenediaminenickel(II) ion, which must be used to obtain maximum precipitation of the thiosulfate.[7]

Experimental

The thiosulfate salt was formed by the addition of an excess of four times recrystallized triethylenediaminenickel(II) nitrate to a solution of sodium thiosulfate (Baker C.P). The $\mathrm{Ni\ en_3S_2O_3}$ thus precipitated was purified by fourfold recrystallization from water and its purity ascertained by solubility measurements in the presence of an excess of variable amounts of the solid salt, and by thiosulfate, nickel[6] and nitrogen analyses.[8]

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[1] This paper was presented at the 117th Meeting of the American Chemical Society, Houston, Texas, March, 1950.

[2] This work was supported in part by the grant from the Atomic Energy Commission administered by the Office of Naval Research as Research Project NR-122824. The authors are also indebted to the M. D. Anderson Foundation for financial support in this work.

[3] A. Z. Werner, *Anorg. allgem. Chem.*, **21**, 201 (1899).

[4] E. M. Chamot and C. W. Mason, "Handbook of Chemical Microscopy," 2nd Ed., Vol. II, John Wiley and Sons, New York, N. Y., 1940, p. 354.

[5] G. Spacu and P. Spacu, *Z. anal. Chem.*, **89**, 192 (1932).

[6] Determination of nickel colorimetrically with dimethylglyoxime (A. M. Mitchell and M. G. Mellon, *Ind. Eng. Chem.*, *Anal. Ed.*, **17**, 380 (1945)) on solutions of triethylenediamine salts requires destruction of ethylenediamine with nitrous acid for quantitative conversion of nickel to the dimethylglyoxime complex.

[7] J. H. Gast, "University Microfilms," Publication 214, 114 pages (1940).

[8] We are indebted to Miss Kazko Arai for the micro-Dumas and micro-Kjeldahl analyses and to Mr. C. E. Williams of the University of Houston for making the facilities available to us.

Anal. Calcd. for $C_6H_{24}N_6O_3S_2Ni$: $S_2O_3^=$, 31.89; Ni, 16.72; N, 23.95. Found: $S_2O_3^=$, 31.89; Ni, 16.74; N, 23.42.

The absorption spectra of the nitrate and thiosulfate were measured on a Beckman spectrophotometer with an ultraviolet attachment. The pertinent sections of the spectra are shown in Fig. 1, from which it can be seen that a wave length of 246 mμ (with 0.5 mm. slit width) is satisfactory for determination of the thiosulfate in pure solutions.

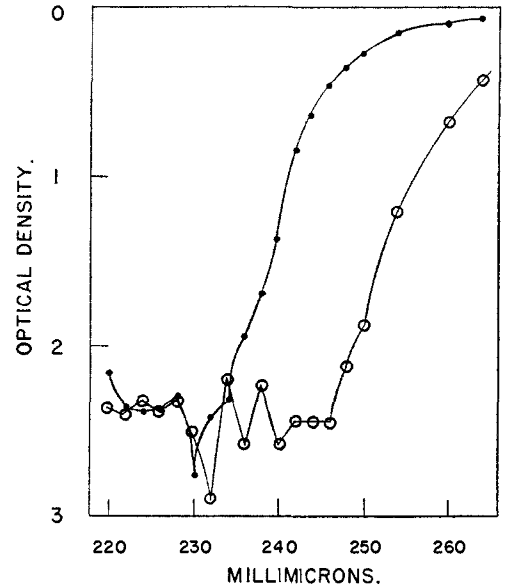

Fig. 1.—Ultraviolet absorption curve of ⊙ Ni $en_3S_2O_3$ (1.50 mg./ml.) and ● Ni $en_3(NO_3)_2$ (1.50 mg./ml.), cell thickness 1 cm.

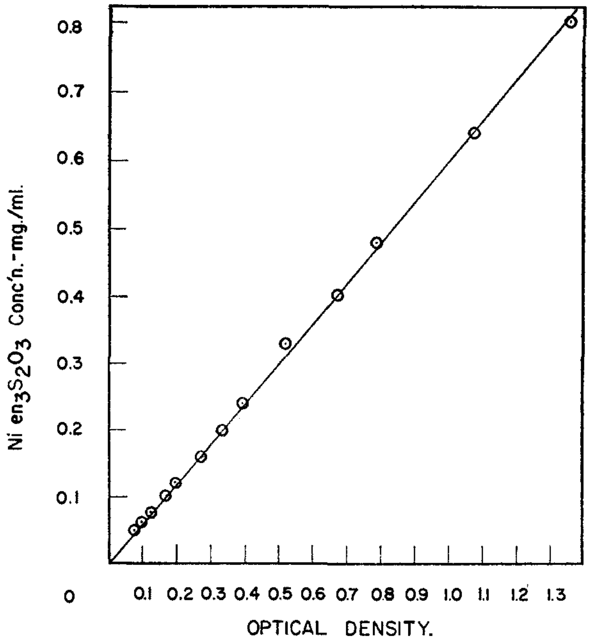

Fig. 2.—Cell thickness 1 cm., 246 mμ.

It was found experimentally (see Fig. 2) that concentration, in the range from 0.05 mg./ml. to 0.80 mg./ml. is strictly proportional to the optical density, $c = 0.595$ O.D. These results were reproducible, except when the salt remained in the light path for periods up to half an hour or longer, when an increase in the optical density was observed. It was suspected that the change was produced by the ultraviolet light. This was confirmed by irradiation of a sample with ultraviolet light from a carbon arc with a Cenco ultraviolet filter attachment for a few seconds. The O.D. reading changed from 0.323 to 0.337. The nature of the change taking place has not been investigated.

Equilibrium between solid Ni $en_3S_2O_3$ and its saturated solution was attained by continuous shaking in a water-bath maintained within ±0.1°. Aliquots of the supernatant were removed at varying intervals from two to 18 hours by suction filtration and analyzed spectrophotometrically and by iodometric titrations. Within the limits of experimental error, the same result was obtained by the two methods. An attempt to reach equilibrium by the crystallization of Ni $en_3S_2O_3$ from a saturated solution prepared at a higher temperature was not successful, since reproducible results were not obtained even after shaking for 18 to 24 hours. This seems to indicate a tendency toward supersaturation. All measurements reported were therefore obtained by equilibrating the solid phase with solvent at the given temperature. Figure 3 shows the data obtained for water solubility over a temperature range from 15 to 50° and at 100°. A similar study was carried out at 20° with varying concentrations of ethanol in water, and the data are plotted in Fig. 4.

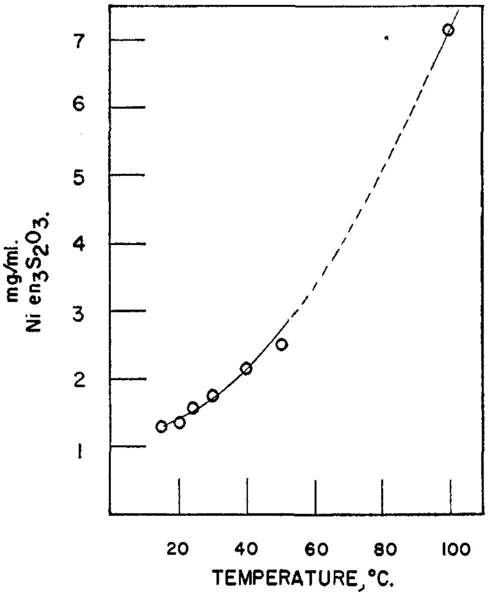

Fig. 3.—Water solubility of Ni $en_3S_2O_3$.

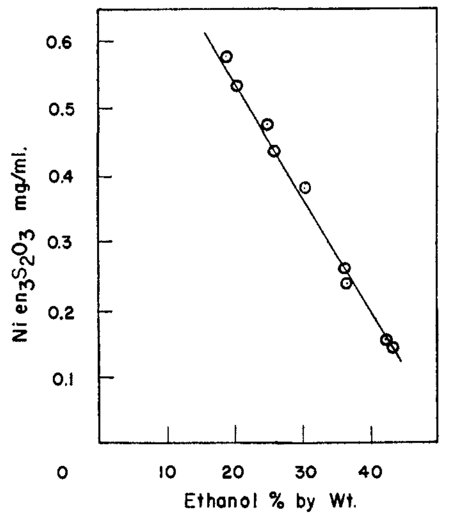

Fig. 4.—Ni $en_3S_2O_3$ solubility in ethanol–water 20 ± 0.10°.

Discussion

The data on water solubility of Ni $en_3S_2O_3$ indicated a temperature coefficient of approximately

0.034 mg./ml. per degree over the range from 15 to 50°, and a solubility of 1.35 mg./ml. at 20°. A tenfold reduction in the solubility can be obtained by the addition of an equal volume of ethanol to the water solution. Moreover the concentration of the thiosulfate in the supernatant can be decreased further by the presence of excess $(\text{Nien}_3)^{++}$. The fact that less than 0.1 mg./ml. of the thiosulfate ion remains in solution makes $\text{Ni en}_3(\text{NO}_3)_2$ a very suitable reagent for quantitative precipitation of thiosulfate.[7] However, in the presence of sulfate, some $\text{Ni en}_3\text{SO}_4$ is coprecipitated by alcohol from water solution, even though it is considerably more soluble than the thiosulfate. This precludes determination of the $\text{Ni en}_3\text{S}_2\text{O}_3$ spectrophotometrically because of the absorption of the sulfate salt in ultraviolet,[9] but it does not interfere with the determination of the thiosulfate iodometrically.[10]

No attempt has been made in this study to ascertain the solubility of thiosulfate salts containing less than three molecules of ethylenediamine. The presence of additional ethylenediamine in small amounts was found to have no effect on the solubility in water at 20°. This seems to indicate that lower complexes were not being formed to influence the solubility data. Alcohol precipitation did not affect the composition of the triethylenediaminenickel thiosulfate, since no change in the O.D. or iodine equivalent was observed.

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(9) J. H. Gast and F. L. Aldrich, unpublished data.

(10) K. Arai, F. L. Aldrich and J. H. Gast, *Federation Proc.*, **9**, 146 (1950).

HOUSTON, TEXAS RECEIVED DECEMBER 20, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Wall Effects in Photochemically Induced Chain Reactions

BY RICHARD M. NOYES

A mathematical solution has been developed for the situation in which photochemically produced atoms or radicals may combine homogeneously at a rate which is second order in the reactants, and simultaneously may combine heterogeneously on the wall by a first order mechanism. The treatment suggests that the walls may serve to remove those atoms or radicals located in a shell of thickness $0.9(D^2/Qk)^{1/4}$ where D is the diffusion coefficient, Q is the rate of production of chains and k is the rate constant for homogeneous termination. If the volume of this shell is significant compared to the total volume of the system, the walls may be responsible for terminating an important fraction of the chains which are formed. It appears that even in vessels having diameters of several centimeters a very large fraction of photochemically produced chains may terminate on the wall unless the absorption of radiation is much greater than 10^{12} quanta/ml. sec. and/or the pressure is considerably in excess of atmospheric. The treatment also shows the applicability of kinetic data to determine the probability that an atom or radical striking the wall of the vessel will undergo recombination.

A great many gas-phase photochemical reactions involve chain mechanisms in which the active intermediates are atoms or radicals produced by the primary photochemical process. The chains may be terminated either homogeneously in the gas phase or heterogeneously on the walls of the vessel. The homogeneous termination reaction is usually second order in the active intermediate. The heterogeneous termination reaction is usually first order in the active intermediate except at elevated temperatures.[1] As a result of the heterogeneous termination a gradient will be established in the concentration of active intermediate.

The exact mathematical treatment of this situation is complex, and experimenters have frequently claimed that wall effects could be ignored but have failed to provide adequate justification. Rashevsky[2] has integrated the diffusion equation for a number of biological systems; however, he does not consider the combined generation and destruction of substances according to the kinetics discussed above. Hill[3] has made detailed calculations of a special case in the photochemical decomposition of acetone; but, because of mathematical difficulties, he only allowed first order kinetics for the homogeneous termination process in the region near the walls.

While we were considering the interpretation of data on some gas-phase chlorination reactions,[4] we developed some expressions which are of general applicability to photochemical reactions of this type. This treatment should directly apply to some systems, and at the very least it will provide criteria to determine whether more complicated calculations are necessary.

NOMENCLATURE

c = local concentration of atoms or radicals per ml.
k = rate constant for second-order homogeneous termination of chains in $(\text{atom/ml.})^{-1}$ sec.^{-1} (This is twice the customary rate constant based on number of collisions)
r = distance from center of reaction vessel in cm.
$t = cr$
$v = (8RT/\pi M)^{1/2}$ = average velocity of atom or radical in cm./sec.
D = diffusion coefficient of atom or radical in cm.^2/sec.
Q = rate of production of chains in atom/ml. sec. (This may be as great as twice the rate of absorption of radiation in quanta/ml. sec.)
α = recombination coefficient or probability that an atom or radical striking the wall will undergo recombination
β = fraction of chains terminating on the wall
$\gamma = \tau/\rho = (k/Q)^{1/2}c$ = ratio of local concentration to concentration which would prevail in absence of wall reaction
$\mu = v/4(D^2Qk)^{1/4}$
$\rho = (Qk/D^2)^{1/4}r$
$\sigma = \rho - \tau$
$\tau = (k^3/D^2Q)^{1/4}t$

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(1) K. E. Shuler and K. J. Laidler, *J. Chem. Phys.*, **17**, 1212 (1949).

(2) N. Rashevsky, "Mathematical Biophysics," Revised edition, University of Chicago Press, Chicago, Ill., 1948.

(3) T. L. Hill, *J. Chem. Phys.*, **17**, 1125 (1949).

(4) L. Fowler and J. J. Beaver, THIS JOURNAL, **73** in press; R. M. Noyes and L. Fowler, *ibid.*, **73**, 3043 (1951).