

above, it is essential to test for X-rays, and to shield against them if they present a hazard to personnel.

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¹ Dunsmuir, R., Milner, C. J., and Spayne, A. J., *Nature*, **161**, 244 (1948).

² Schneider, S., and Reich, B., *Proc. Inst. Rad. Eng.*, **43**, 711 (1955).

Existence of a Non-Electrostatic Stabilizing Factor in Hydrophobic Selenium Hydrosols

It is well known that the stability factor of hydrophobic sols decreases, at first, exponentially with the ionic strength of the solution, and reaches, rather suddenly, its limiting value for a certain concentration C_1 of the coagulating electrolyte¹. For concentrations lower than C_1 we have the so-called 'slow coagulation'; the interaction energy consists of long-range electrical repulsions, dependent on ionic strength, and of Van der Waals attractions. For concentrations higher than C_1 , the electrical repulsions have practically disappeared² and we have 'rapid coagulation'.

The kinetics of rapid coagulation have been studied theoretically. Each particle is assumed to be surrounded by a sphere of attraction having a radius r . If the centre of a second particle penetrates into this sphere of attraction, the two coalesce irreversibly. Treating the problem as one of simple diffusion, von Smoluchowski³ showed that the disappearance of primary particles must initially be a bimolecular process, characterized by a kinetic constant:

$$k_{1,1} = \frac{4kT}{3\eta} \cdot \frac{r}{a}$$

where k is Boltzmann constant, T is the absolute temperature, η is the viscosity of the medium and a is the radius of the particles.

The ratio r/a must obviously have a value of at least 2, and Hamaker⁴ has shown that it should be slightly larger. Experimental values between 2 and 3 have been found in a number of cases.

However, for selenium hydrosols, Krut and Van Arkel⁵ found very small values ranging from 0.55 to 1.3. With sols prepared in a similar manner, we have confirmed their results, obtaining values between 0.58 and 1.06, as shown in Table 1. It therefore appears that for selenium sols, some repulsive force unconnected with the charge of the double layer must be taken into account.

We have found that the abnormal stability is due to an impurity, probably hydrazine hydrate, which is used as a reducing agent for preparing the sols.

Table 1. EXPERIMENTAL VALUES FOR THE RATIO r/a , WITH NON-DIALYSED SELENIUM HYDROSOLS

Sol concentration (No. of particles/cm. ³)	Diameter of particles (m μ)	r/a
0.62×10^9	188	1.06
0.96	168	0.84
3.14	142	0.58
1.57	142	0.82
0.78	142	0.77

Table 2. VARIATION OF THE RATIO r/a DURING PURIFICATION OF A SELENIUM HYDROSOL

Time of electrodialysis (hr.)	Conductivity of the sol (ohm ⁻¹ cm. ⁻¹)	r/a
0	133.0×10^{-8}	1.5
22.5	118.0	1.8
29.75	95.5	2.1
46.0	57.0	2.3
71.0	8.8	2.2
78.5	8.0	(3.9)
118.5	6.5	2.1
167.0	4.2	2.2

The numerical data given in Table 2 show clearly that when the colloidal solutions are purified by prolonged electrodialysis, the ratio r/a increases regularly with the purity, as measured by specific conductivity.

In another series, r/a varied from 0.44 to 2.5 during purification.

It must be stressed that the purification has practically no influence on the stability factor in the region of slow coagulation, or on the limiting concentration C_1 . Therefore, it does not affect the Stern potential.

A tentative explanation of this behaviour is that each micelle is covered by an adsorbed layer of hydrazine, and this strongly polar substance modifies the local structure of water in the immediate neighbourhood of the colloidal particle. The 'hydration' shell may cause a repulsive action of entropic origin—a steric hindrance.

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¹ Reerink, H., and Overbeek, J. T. G., *Disc. Farad. Soc.*, **18**, 74 (1954).

² Verwey, E. J. W., and Overbeek, J. T. G., "Theory of the Stability of Lyophobic Colloids" (Elsevier, 1948).

³ Von Smoluchowski, M., *Phys. Z.*, **17**, 557, 585 (1916); *Z. phys. Chem.*, **92**, 129 (1918).

⁴ Hamaker, H. C., *Physica*, **4**, 1053 (1937).

⁵ Krut, H. R., and Van Arkel, A. E., *Rec. Trav. Chim.*, **39**, 656 (1920); **40**, 169 (1921).

Synthesis of 4-Methylumbelliferone β -D-Glucuronide, a Substrate for the Fluorimetric Assay of β -Glucuronidase

At the present time there is considerable demand for a suitable synthetic substrate for the routine assay of β -glucuronidase. The most common assay method employs phenolphthalein glucuronide isolated from rabbit urine¹. However, the preparation of 4-methylumbelliferone glucuronide from rabbit urine and its use in the fluorimetric assay of β -glucuronidase have been recently described². This substrate promises certain advantages over phenolphthalein glucuronide, and it is easy to synthesize by the method previously employed for (–)-menthol³ and phenol⁴ β -D-glucuronides.

4-Methylumbelliferone β -D-glucoside hemihydrate⁵ (1.5 gm.) in 60 ml. water was maintained at 90°C. and vigorously stirred. Oxygen was passed into the solution through a sintered glass disk, and freshly reduced platinum catalyst³ (0.4 gm.) was added. The pH was kept between 7 and 9 throughout the oxidation by the addition of 0.5 N sodium bicarb-

onate. After 1 hr., more catalyst (0.2 gm.) was added, and the reaction was complete 30 min. later, with an almost theoretical uptake of alkali. The filtered solution was reduced to half volume, treated with charcoal, and made acid to congo red with hydrochloric acid. The hydrated glucuronide was filtered off and recrystallized from 50 per cent (v/v) aqueous ethanol and then from water: yield 0.95 gm. (54 per cent). After drying at 105° over phosphorus pentoxide, the hemihydrate² had corrected and mixed melting points with a biosynthetic specimen of 139–140°, and $[\alpha]_D^{25} -119^\circ$ in water (c, 0.25): on acid hydrolysis 4-methylumbelliferone was obtained, melting point and mixed melting point 187–188°. Mead *et al.*² give a melting point of 139–140° (decomp.) for the hemihydrate of the biosynthetic glucuronide, and $[\alpha]_D^{25} -105^\circ$ for the completely hydrated compound.

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¹ di Somma, A. A., *J. Biol. Chem.*, **133**, 277 (1940).

² Mead, J. A. R., Smith, J. N., and Williams, R. T., *Biochem. J.*, **61**, 569 (1955).

³ Marsh, C. A., *J. Chem. Soc.*, 1578 (1952).

⁴ Tsou, K.-C., and Seligman, A. M., *J. Amer. Chem. Soc.*, **75**, 1042 (1953).

⁵ Robinson, D., and Williams, R. T., *Biochem. J.*, **61**, v (1955).

Phase-Change in 1,2,4,5-Tetrabromobenzene investigated by Pure Quadrupole Resonance

It is the purpose of this communication to mention a result of a type which we believe to be hitherto unreported, which we obtained when the temperature dependence of the bromine-81 pure quadrupole resonance at about 240 Mc./s. in 1,2,4,5-tetrabromobenzene was investigated. Here, on raising the temperature above 20° C., there is as usual a linear decrease of frequency. However, a very sudden discrete drop occurs at 46.5° C., after which there is again a linear decrease. On then reducing the temperature, the increase of frequency is linear as far as 33.5° C., where there is a sudden discrete rise, the frequency returning to the original line and completing a hysteresis loop.

The experimental results are shown in Fig. 1. The temperature coefficients of frequency are $-3.9 \times 10^{-5}/\text{deg. C.}$ and $-5.9 \times 10^{-5}/\text{deg. C.}$ for the upper and lower straight line portions respectively. The frequency jump is of the order of 1.5 parts in 10^5 . It is interesting to note that the temperature coefficient at temperatures above the discontinuity is of the order usually found in compounds where bromine is attached to the benzene ring, while that at temperatures immediately below is about 35 per cent lower.

The resonance was obtained by means of an externally quenched frequency-modulated super-regenerative oscillator using a cathode-ray oscillograph display. A push-pull arrangement was used employing type 955 'acorn' triodes, the sample being placed in a tuned

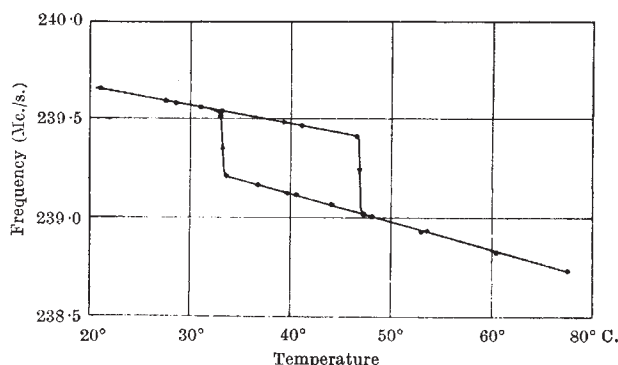


Fig. 1. Frequency of bromine-81 pure quadrupole resonance in 1,2,4,5-tetrabromobenzene as a function of temperature

coil at the far end of the anode lines. A simple oven surrounds the specimen. Comparison between frequency measurements made with slowly rising and slowly falling temperatures indicates that the error of temperature measurement is $\pm 0.2^\circ \text{C.}$

Frequency measurements were made by adjusting the amplitude and frequency of quench so that the resonance appeared as a single peak. This was then located at the centre of the cathode-ray oscillograph display. The sweep and quench were then switched off, and the frequency of the oscillator measured by obtaining zero beat with a harmonic of a calibrated wave-meter, type BC-221-C, detected by means of a G.E.C. very high frequency panoramic receiver, type BRT-652. The calibration of the wave-meter was set for each reading by means of the 2 Mc./s. crystal incorporated in the receiver. This was, in turn, checked against a B.B.C. transmission at 94.3 Mc./s., which afforded a sufficiently accurate standard at a convenient frequency. This system of measurement gives an error of about ± 5 parts in 10^5 , which includes that of setting the oscillator exactly upon the quadrupole frequency.

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Factors affecting the Permanency of Paper: Tests with Labelled Sulphur

PAPERS of good quality and high alpha-cellulose content can be kept under suitable storage conditions for several centuries. There are, however, differences of opinion on factors affecting storage, and a recent investigation by Langwell¹⁻⁵ claims that even good-quality papers can become brittle at the edges. He stated that this attacked portion of the paper in old documents and books has a scorched appearance resembling the product of the reaction between cellulose and strong acid. Analyses of these old papers reveals a high sulphate content indicative of attack by sulphuric acid from the atmosphere.

The concentration of sulphur dioxide in industrial atmospheres is of the order of 0.5 part per million⁶, and Langwell has suggested that catalysts in the paper accelerate the conversion of this sulphur