

Solutions of Salts Fluid at the Temperature of Liquid Nitrogen Spectra of Solutions of Rare Earths

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The Scattering of Light by Sodium Silicate Solutions*

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May 12, 1949

USING a 90° turbidimeter built in this laboratory the scattering of light by sodium silicate solutions has been investigated. This method was applied in order to determine if and when structures—presumably combining Si, O, and H atoms—larger than ordinary ions are present in such solutions.

In the case of sodium metasilicate (Na_2SiO_3), prepared by fusion of a pure quartz with C.P. sodium hydroxide and crystallization of a hydrate from a solution of the melt, it is possible to obtain reproducible results from solutions filtered through a carefully cleaned sintered stainless steel filter. The solutions were prepared from freshly recrystallized undried $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ crystals by dissolving them in freshly redistilled water; they were stored under an atmosphere of nitrogen.

These filtered metasilicate solutions give results, some of which are shown in Fig. 1. Below a concentration of 0.10 g/cc these re-

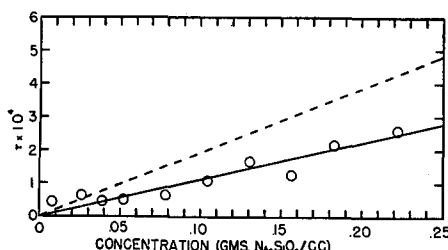


FIG. 1. Turbidity versus concentration for sodium metasilicate solutions. —Least squares line from all data. ---Calculated line for undissociated Na_2SiO_3 molecules.

sults have been reproduced using three other groups of solutions in the same concentration range; the data at concentrations greater than 0.10 g/cc are the result of only one series of measurements. It is observed that the solutions have very small turbidities even at very high concentrations. Representing the data by a straight line, we can relate the turbidity, τ , to a weight average molecular weight, M , by the equation¹

$$\tau = HM_c, \quad (1)$$

in which H is a refraction constant defined by the expression

$$H = \frac{32}{3} \pi^2 \frac{\mu_0^2}{N\lambda^4} \left(\frac{\mu - \mu_0}{c} \right)^2, \quad (2)$$

in which c is the concentration in g/cc, $\mu - \mu_0$ is the difference in index of refraction between the solution and the solvent, and λ is the wave-length in vacuum of the light used for the measurements. Using a τ/c value, namely 1.11×10^{-3} with a standard deviation in τ of $\pm 0.21 \times 10^{-4}$, obtained from a least squares straight line, shown in Fig. 1, through all the available data and using $H = 1.58 \times 10^{-5}$, calculated from $\mu - \mu_0$ measurements at a molecular weight of 70.5 is calculated. If undissociated Na_2SiO_3 molecules ($M = 122$) were present in the solutions, the $\tau - c$ relationship would be represented by the dotted line of Fig. 1 which corresponds to $\tau/c = 1.93 \times 10^{-3}$. It is indicated by the fact that the experimental points lie below the dotted line that there is not only no aggregation in these metasilicate solutions, but that there is dissociation.

However, the above calculation of the molecular weight 70.5 assumes one type of molecule with one H value considered to be sufficient for representing the scattering. In a solution of dissociated ions each ionic specie will have its own H value and corresponding contribution to τ . The data should therefore be treated differently. We will assume that the solutions contain Na^+ ions and negatively charged complexes of Si, O, and perhaps H atoms.

Measurements have been made of the refraction of silicate solutions with different $\text{SiO}_2/\text{Na}_2\text{O}$ ratios. In one type the ratio was 1:1, in another 3.3:1. Assuming that the difference in index of refraction between solution and solvent is a linear function of the composition, as indicated by the ratio, it follows from the $\mu - \mu_0$ measurements that the polarizability of the Na^+ ion, α_1 , is to the polarizability, α_2 , per Si atom of the silicon complex as 20.5×10^{-24} cc is to 8.1×10^{-24} cc. These values are obtained by solving the following equations simultaneously

$$(\text{for } \text{Na}_2\text{SiO}_3) \mu - \mu_0 = n_1 \alpha_1 + n_2 \alpha_2 = n \left(\frac{2}{3} \alpha_1 + \frac{1}{3} \alpha_2 \right)$$

$$(\text{for } \text{Na}_2\text{O } 3.3 \text{ SiO}_2) \mu - \mu_0 = n_1 \alpha_1 + n_2 \alpha_2 = n \left(\frac{2}{5.3} \alpha_1 + \frac{3.3}{5.3} \alpha_2 \right),$$

since $\mu - \mu_0 = n\alpha$. (n = number of molecules/cc.)

Considering now the case of the metasilicate alone, it follows that instead of our old value of H a new value should be used; this value is obtained from the old H by multiplying it by the correction factor

$$\frac{2\alpha_1^2 + \alpha_2^2}{(2\alpha_1 + \alpha_2)^2}$$

provided that total dissociation is assumed and that each silicon complex contains only one Si atom. The correction factor is 0.376, so in this case we would expect $\tau/c = 0.73 \times 10^{-3}$ instead of the observed value $\tau/c = 1.11 \times 10^{-3}$. At this point it seems futile to speculate about the reality of differences between the observed value and that calculated on the assumption of complete dissociation.

The metasilicate solutions had been standing a week or more before turbidity measurements were made. Some of the measurements were repeated several days to a week after the first measurement with little change in results. We therefore as yet have no evidence that complexes develop in these solutions in the course of time.

The importance of proper preparation and cleaning must be stressed. Unreproducible molecular weights of 800 to 1800 are found in metasilicate solutions prepared from dried crystals or commercial samples.

Preliminary investigations indicate that the solutions of the 3.3/1 $\text{SiO}_2/\text{Na}_2\text{O}$ ratio sodium silicate have aggregates of a molecular weight $M = 1500$ containing about twenty silicon atoms.

McCartney's¹ and Halwer's² work on sucrose solutions show that it is feasible to determine low molecular weights by light scattering. Our experiments seem to indicate that the method also can be used in order to obtain information about ionic dissociation.

* This work was supported by the Sodium Silicate Manufacturers Institute.

¹ P. Debye, J. Phys. and Coll. Chem. **51**, 18 (1947).

² Murray Halwer, J. Am. Chem. Soc. **70**, 3985 (1948).

Solutions of Salts Fluid at the Temperature of Liquid Nitrogen Spectra of Solutions of Rare Earths

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May 2, 1949

THE solutions were prepared in two steps. First, the salt was dissolved under more or less normal conditions rather than at low temperatures so that the rate of solution of the solid would not be excessively slow. The second step was one of dilution, a more rapid process, achieved by lowering the temperature of the original solution and then bubbling and condensing in from the gaseous state, solvent substances having low melting points.

In our experiments thus far, either *n*-propyl alcohol, *n*-butyl alcohol or *n*-propyl ether served as solvent for the first step and for the second, pairs of the following hydrocarbons in various proportions—methane, propane, propene, butene-1, and isopentane. A number of combinations proved to be homogeneous and fluid at the temperature of liquid nitrogen.

One of the above combined solvents was tested and found to remain fluid at about five degrees below the freezing point of nitrogen. Its composition was 1 part by volume of *n*-propyl alcohol, 4.5-parts liquid propane, and 4.5-parts liquid propene.

A number of hexahydrated rare earth bromides and nitrates were dissolved in such solvents, and absorption spectra were taken at the temperatures of liquid nitrogen. Solubilities of some of the rare earths were sufficient at 77°K for obtaining spectra in a path length of 25 cm. At a given concentration of a rare earth, (neodymium nitrate hexahydrate) the solution kept at 77°K for nine days remained clear and continued to give the same spectrum. When somewhat more was dissolved at about 175°K, a reduction in temperature to 77°K brought a quick appearance of turbidity, indicating that transformations were occurring at the low temperatures. The spectra of some of the dissolved salts became comparable in sharpness with those from their crystals at the low temperature. Bands arising at higher temperatures became resolved into lines at 77°K.

The line widths in the spectra of neodymium and samarium salts ranged from about one to five angstroms. The dissolved praseodymium and thulium salts gave more diffuse lines. The bromide and nitrate of neodymium showed strikingly different structures within corresponding groups, both in the spacings and numbers of component lines, indicating different symmetries of the fields about the positive ions. There were marked changes in the spectra on reducing the temperature from that of dry ice to that of liquid nitrogen. The refinement in the spectrum of samarium bromide hexahydrate was especially great on lowering the temperature.

Electrical conductances were measured over a range of temperatures and were found to drop rapidly at the lowest temperature, finally reaching in one solution 2×10^{-11} mhos for the specific conductance at 77°K.

Detailed descriptions of methods and results will be given in full detail in future papers.

We wish to express our indebtedness to Dr. Fred J. Leitz for his collaboration in the early stages of this work.

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milligram amounts, was evaporated onto a circular filter paper and placed in the center of the stack which had been previously moistened with a suitable electrolyte. A direct current of 0.04 ampere/cm² for a half hour was sufficient to move ions through about 15 layers of filter paper. By a proper choice of complexing ions and pH, the desired activity could be moved to either one of the electrodes or retained at the initial position in the center of the stack. In some mixtures, one activity migrated to one of the electrodes, milligram amounts of non-isotopic elements to the other, while impurity activities remained at the initial position. Recovery of the desired fraction consisted simply of removing filter papers from the appropriate region of the stack. The activity was usually concentrated in less than five adjacent papers.

In each of the separations described below, 0.20 ampere was passed for one half hour through a stack of 30 filter papers, 2.6 cm in diameter.

(1) Separation of carrier-free radio-columbium from manganese dioxide precipitate: A solution of the precipitate in 5 percent oxalic acid was evaporated onto a filter paper and placed in the middle of the stack which had been saturated with 1*M* ammonium oxalate solution. Under these conditions, columbium migrated to the anode region and manganous ions migrated to the cathode.

Another sample of precipitate was dissolved in concentrated hydrochloric acid and was placed in a stack saturated with 3*N* hydrochloric acid. The columbium activity remained on the original papers and the manganous ions migrated to the cathode.

(2) Separation of carrier-free radio-columbium and radio-zirconium from radio-yttrium and rare earth activities: A sample of solution was electrolyzed in a stack saturated with 1*M* ammonium oxalate. Columbium and zirconium were recovered in the anode papers. Yttrium and rare earth activities (Eu, Nd, and Pr) remained on the original paper.

(3) Separation of carrier-free radio-arsenic from milligram amounts of copper hydroxide carrier: The precipitate was dissolved and electrolyzed in 3*N* hydrochloric acid. The arsenic activity remained in original position. Cupric ions migrated to the cathode.

The technique has also been used as a rapid preliminary test in establishing the chemical identity of carrier-free radio-isotopes. For example, an activity which is found to migrate in dilute hydrochloric acid cannot be radio-arsenic.

Other applications of this type are obvious.

We are grateful to Dr. J. G. Hamilton for his interest in this problem.

* Lieutenant Colonel, U. S. Army.

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¹ Kendall and Crittenden, *Proc. Nat. Acad. Sci.* **9**, 75 (1923).

² Kendall and Clarke, *Proc. Nat. Acad. Sci.* **11**, 393 (1925).

³ Kendall and West, *J. Am. Chem. Soc.* **48**, 2619 (1926).

A Rapid Electrical Method of Separating Carrier-Free Radioactivities

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May 3, 1949

ELEMENTS with similar chemical properties may be separated by electrical transference methods as shown by the work of Kendall and co-workers.¹⁻³ We have found a modification of their technique to be of value for rapid separations of carrier-free radioisotopes from other activities and from milligram amounts of non-isotopic carriers.

Our apparatus consists of a stack of filter papers moistened with electrolyte and placed between two platinum electrodes. In a typical separation, a sample of solution containing one or more carrier-free radio-elements, and possibly other stable elements in

Selection Rules for Singlet-Triplet Perturbations in Polyatomic Molecules

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May 13, 1949

IN a recent paper¹ Shull has shown that the triplet-singlet emission band of benzene has the vibrational structure of a ¹B_{1u}—¹A_{1g} transition thus showing that the perturbing singlet state is a ¹B_{1u} state. The question of the symmetry of the triplet state required by this observation was not definitely decided, although by analogy with the rule for diatomic molecules that ³Σ⁺ states perturb ¹Σ⁻ states, Shull tentatively concluded that