XVIII.—*Comparison of Some Physical Constants of Thiocyanate, Azide, and Nitrite Solutions.*

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CRANSTON and LIVINGSTONE recently published measurements of physical constants of azide and cyanate solutions which led them to infer that the two anions have the same spatial structure in solution (J., 1926, 501). About the same time, the $X$-ray investigations of Hendricks and Pauling (*J. Amer. Chem. Soc.*, 1925, **47**, 2904) definitely proved that in the crystalline state both these ions consist of atoms arranged in an open chain with very similar spacings, as theoretical considerations had first caused Langmuir (*ibid.*, 1919, **41**, 1543) to assume, discarding the old ring formula for the azides.

The correspondence of Cranston and Livingstone's conclusions with these results was probably fortuitous. The physical

characteristics of ionic solutions are in general greatly influenced by solvation of the ions, although this may in turn be dependent on the configuration of the atoms in the ion. It is nevertheless certain that considerable differences between ions can be concealed to a great extent by addition of water molecules. Yet if Cranston and Livingstone's conclusions were right in the case of the azide and cyanate ions, in that similarity in the configuration of the ions may be inferred from similarity in certain physical properties, we should be in possession of a very simple and convenient method for determining the structure of the thiocyanate ion also.

The following reasons may be given for doubting the validity of Cranston and Livingstone's deductions. In view of the fact that the cyanate is readily decomposed by water, a mixture of water and alcohol was employed as a solvent in determining the density and the refractive index. It would thus appear possible that the various ions would show preference in combining with one species of the molecules of the solvent. Moreover, the experiments only extended in the case of the potassium salts to $0.5N$-solutions, and in the case of the sodium salts to $1.0N$-solutions, whereas it is just the high concentrations that are of advantage in discovering the differences in the influence exerted by the solute on the character of the solutions.

In view of the possibility of determining the structure of the thiocyanate ion, we have tested the method employed by Cranston and Livingstone by comparing the physical properties of nitrite solutions with those of azide solutions. The nitrite ion differs little from the azide ion in weight, but in the configuration of its atoms it is certainly quite different, for its structure is very probably similar to that of the nitrate ion, which is known—at any rate in the crystalline state—not to have the nitrogen atom placed in a straight line between two oxygen atoms. We should thus expect nitrite solutions to have physical constants very different from those of azide solutions. With some degree of probability the following surmise can be made as to the difference between the structure of the thiocyanate and the cyanate ion, the latter of which is known to be the same as that of the azide ion, at least in the crystalline state. According to the measurements of Hendricks and Pauling, in the potassium cyanate crystal the centres of gravity of the atoms at the two ends of the cyanate chain are 2·32 Å.U. apart, whereas in the potassium azide crystal the corresponding distance between the two extreme nitrogen atoms is 2·34 Å.U. If we calculate the lengths of the cyanate and azide chains from the radii of the nitrogen, oxygen, and carbon atoms, as determined by Goldschmidt from other crystalline compounds of these elements

(" Geochemische Verteilungssätze der Elemente," VII, Die Gesetze der Krystallochemie, Oslo, 1926, pp. 26 *et seq.*), we find the length corresponding to the azide chain to be 2·84 Å.U., and in the case of the cyanate chain 2·85 Å.U. The radii of the atoms in the configurations in question are therefore smaller than usual, but the contraction is practically the same in both cases. Computing the length of the thiocyanate chain in the same way, using Goldschmidt's atomic radius of sulphur (1·04 Å.U.), we find 3·2 Å.U., a value some 18% greater ·than for the cyanate chain. If, on account of the equal contractions in the case of the azide and cyanate ions, we assume the same contraction to take place in the thiocyanate ion, the ratio of the chain lengths above computed would be more or less preserved.

The molecular weights of sodium azide and sodium thiocyanate are 65·0 and 81·1 respectively. Their influence on the density differences of solutions can be calculated for all concentrations.

In our experiments with sodium azide, thiocyanate, and nitrite we were able to work with pure water as solvent and to attain much higher concentrations than the above-named authors. The experiments show that the correct results which Cranston and Livingstone's method gave are hardly more than accidental. No conclusions can be drawn as to the similarity or dissimilarity of the atomic structure of the ions we investigated. We did not compare the densities of the solids, since, according to the crystallographic determination of Hendricks and Pauling, it is hardly possible that sodium thiocyanate can have the same arrangement of ions in the crystal as potassium cyanate; so we left out this comparison, carried out by Cranston and Livingstone, but we introduced another series of experiments, comparing the viscosities of the solutions.

## EXPERIMENTAL.

*Materials.*—Sodium azide was recrystallised from water by precipitation with alcohol and sodium thiocyanate was recrystallised from alcohol. The sodium nitrite was Kahlbaum–Schering's " purissimum." The purity of the azide was determined by precipitation as silver azide, which was converted into chloride and weighed as such, the analysis being checked by decomposing the azide with titrated sulphuric acid : the percentage varied between 97·0 and 98·2%. The sodium nitrite contained 97·8% of pure salt, and the thiocyanate 98%, as determined by titration with silver nitrate. Impurities certainly had no influence on the validity of the conclusions drawn from the experiments. 3$N$-Solutions of these salts were prepared, and diluted with distilled water as required.

*Densities.*—The following densities were determined with Mohr's specific gravity scales and, in part, checked with a pyknometer.

*Densities of aqueous solutions at* 20·1°.

| $M =$ | 3·0. | 2·0. | 1·0. | 0·5. | 0·25 (at 16·7°). |
|---|---|---|---|---|---|
| NaN$_3$ | 1·1137 | 1·0764 | 1·0380 | 1·0184 | 1·0099 |
| NaCNS | 1·1162 | 1·0786 | 1·0395 | 1·0198 | 1·0101 |
| NaNO$_2$ | 1·1273 | 1·0857 | 1·0427 | 1·0210 | — |

The densities of the azide and thiocyanate solutions differ very slightly—by less than 0·3% in the highest concentrations. The influence of the greater molecular weight of the thiocyanate is almost completely compensated for by the marked contraction taking place on dissolution, which amounts to as much as 3·85%. In comparing the azide with the nitrite solutions a discrepancy is observable, which can, however, be ascribed chiefly to the greater molecular weight of the latter substance; it is therefore impossible to draw any conclusions from these observations as to the configuration of the ions.

*Viscosity.*—The viscosities were determined with an Ostwald viscometer :

*Coefficients of viscosity at* 20·1° (*water* = 1).

| $M =$ | 3·0. | 2·0. | 1·0. | 0·5. |
|---|---|---|---|---|
| NaN$_3$ | 1·344 | 1·179 | 1·050 | 1·006 |
| NaCNS | 1·254 | 1·105 | 1·043 | 1·005 |
| NaNO$_2$ | 1·281 | 1·126 | 1·046 | 1·006 |

Corresponding to differences in the contraction occurring in solution, the azide ion has the greatest influence on the viscosity coefficient and the thiocyanate ion the smallest.

*Refractive Indices.*—The refractive indices were obtained with a Pulfrich refractometer. On account of the differences in density of the solutions, however, it was necessary to compare the values of the specific refractivity, $R$, and for this purpose the densities were redetermined at 25°.

$n_{\mathrm{D}}^{25°}$.

| $M =$ | 3. | 2. | 1. | 0·5. |
|---|---|---|---|---|
| NaCNS | 1·3831$_9$ | 1·3669$_9$ | 1·3500$_2$ | 1·3413$_1$ |
| NaN$_3$ | 1·3669$_0$ | 1·3560$_7$ | 1·3442$_8$ | 1·3385$_5$ |
| NaNO$_2$ | 1·3542$_4$ | 1·3475$_6$ | 1·3404$_9$ | 1·3365$_5$ |

$$R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}.$$

| $M =$ | 3. | 2. | 1. | 0·5. |
|---|---|---|---|---|
| NaCNS | 0·2096 | 0·2087 | 0·2074 | 0·2067 |
| NaN$_3$ | 0·2026 | 0·2036 | 0·2049 | 0·2056 |
| NaNO$_2$ | 0·1930 | 0·1970 | 0·2013 | 0·2036 |

The thiocyanate has the greatest and the nitrite ion the smallest influence on the refraction of light.

*Electrical Conductivity.*—The conductivities, which Cranston and Livingstone determined in methyl-alcoholic solution, were measured in a solution of conductivity water. The electrodes consisted of platinised platinum sheet, and in agreement with the results of Briner and Winkler (*J. Chim. physique*, 1923, **20**, 201), as against those of Cranston and Livingstone, the platinum coating was found not to decompose the azide solution. The conductivities were unchanged after $\frac{1}{2}$ hour, 1 hour, and 2 hours, and at the end of a series of experiments no ammonia could be determined in the solution even with the help of Nessler's reagent.

### Molecular conductivities.

| $M =$ | 0·5. | 0·25. | 0·125. | 0·063. |
|---|---|---|---|---|
| NaCNS .................. | 65·80 | 75·04 | 81·92 | 90·40 |
| NaN₃ ..................... | 65·54 | 74·84 | 81·52 | 90·40 |
| NaNO₂ .................. | 62·60 | 72·36 | 82·88 | 93·97 |

The conductivities of thiocyanate and azide agree up to $0·5M$, even better than those up to $0·1M$ in Cranston and Livingstone's experiments. The conductivity of the nitrite solution differs in magnitude as well as in its dependence on the concentration.

A survey of all the experimental results here given shows that experiments of this kind do not enable us to draw conclusions as to the configuration of atoms in the ion, as Cranston and Livingstone have done.

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