$$\mu = \frac{gr^2(1 + \beta)\gamma T}{8\left(L + z\,ln\dfrac{l_0 - z}{l_1 - z}\right)},$$

wherein

$$\beta = \left(\frac{r}{R}\right)^2 = \left(\frac{0.03475}{4.4}\right)^2 = 0.0000624.$$

The effect of β can obviously be neglected.   As γ and T will differ with different liquids, we will simply endeavor to express the coefficient of γT as a linear function of z. Δ are the differences in the coefficient per unit difference in z.

z.	$\dfrac{gr^2}{8\left[L + z\,ln\dfrac{l_0 - z}{l_1 - z}\right]}$	Δ.
0	0.002593	0.000060
1	0.002533	0.000059
2	0.002474	0.000060
3	0.002414	0.000061
4	0.002353	0.000061
5	0.002292	....

Then within reasonable limits:

$$\frac{gr^2}{8\left[L + ln\,z\dfrac{l_0 - z}{l_1 - z}\right]} = 0.002593 - 0.000060\,z = 0.002593(1 - 0.0231z).$$

Now,

$$z = h + c + \frac{8c\Theta l_a v_m}{gr^2} + \frac{v_m{}^2}{2g}\left[1 + \frac{0.005(l_1 + l_0)}{r}\right].$$

If the temperature is 20° C., $\Theta = 293.7$.   Also $g = 981$; then,

$$z = h + c + 0.062\,\frac{v_m}{r} + 0.008\,v^2.$$

When v_m is small, it can be neglected in commercial work, and if $h + c$ be made equal to 2.00 cm., then,

$$\mu = 0.00247\gamma T.$$

VISCOSITY OF SOLUTIONS OF THE METAL AMMONIA SALTS.

By ARTHUR A. BLANCHARD AND HAROLD B. PUSHEE.

In a previous article by one of the authors[1] it has been pointed out that in series of homologous liquid organic compounds, the viscosity is greater, the greater the molecular weight, and smaller, the greater the symmetry of the molecule.   From this it has been assumed to be a general principle that an increase in viscosity is due to an increase in the size

[1] THIS JOURNAL, 26, 1315 (1904).

of the molecules of a liquid, or to a decrease in their symmetry, and this principle has been applied in the study of solutions of inorganic compounds. It is generally believed to-day that in aqueous solutions a weak chemical union exists between solute and solvent, and that the molecules, and particularly the ions, of the solute are not as simple as would appear from the ordinary way in which their formulas are written. It should be possible by a careful interpretation of viscosity measurements to gain considerable insight into the complexity of the molecular or ionic aggregates existing in a solution.

The method employed by us in determining viscosity was the usual one of taking the time of flow through a capillary tube. The time for the flow of a definit volume of solution under its own head, divided by the time of flow for the same volume of pure water, multiplied by the specific gravity, gives the viscosity in terms of the viscosity of water. To this value a correction has been applied, with the end in view that the viscosity value shall always be based on the same amount of water rather than on the same volume of solution. A definit bulb full of solution contains less water than the same bulb when filled with pure water. The difference is readily calculated and in applying the correction, the time of flow of this amount of water through the capillary is added to the time of flow of the solution.[1]

The remarkable phenomenon of negative viscosity has been observed with a number of salts such as the nitrates, iodides, thiocyanates, etc., of potassium, ammonium, rubidium, caesium, and thallium, that is, solutions of these salts have a lower viscosity—in most cases even when the corrected viscosity is considered—than that of pure water. Addition of the salt thus decreases the internal friction of the water. According to the principle just stated, this must mean that aggregates of smaller size or greater symmetry are produced. The hydrated ions or molecules of the dissolved salt must be smaller or more symmetrical than the $(H_2O)_n$ molecules which are present in pure water.

A phenomenon similar to negative viscosity is observed when ammonia is added to solutions of copper, silver and zinc salts.[2] Initially a marked decrease in viscosity occurs, but after addition of two moles of ammonia for each mole of silver salt, and four moles of ammonia for each mole of copper or zinc salt, further addition of ammonia causes practically the same increase of viscosity as if it were added to pure water.

It is known that the ion complexes $[Ag.2NH_3]^+$, $[Cu.4NH_3]^{++}$, and $[Zn.4NH_3]^{++}$ exist in ammoniacal solutions. The viscosities of solutions of these ion complexes being less than of solutions of the supposedly simple metal ions Ag^+, Cu^{++}, and Zn^{++}, it is fair to assume that the

[1] Loc. cit., p. 1320.
[2] Blanchard, THIS JOURNAL, 26, 1315 (1904).

former must be smaller or more compact than the "simple" ions; and the most obvious explanation is, that the ordinary aqueous ion is a *complex* consisting of the metal ion plus bound water molecules, and that this complex is larger, or else more unsymmetrical, than the new complex formed by displacing the water molecules by ammonia molecules.

The new experimental work on this subject which has been carried out by Mr. Pushee at the Massachusetts Institute of Technology has consisted of the measurement of viscosities of solutions obtained by making successive additions of ammonia to solutions of salts of alkali and alkaline earth metals. The accompanying tables contain the experimental results.

The first column gives the concentration of ammonia in moles per liter.

The second column gives the specific gravity of the solution referred to that of water, both at the temperature of the experiment.

The third column gives the time of flow of the solution. The figure in parenthesis gives the time of flow of pure water in the same apparatus at the same temperature.

The fourth column gives the viscosity, η, as calculated in the more usual manner.

The fifth column gives the corrected viscosity, η', in which allowance is made for the water displaced by the solute.

AMMONIA IN WATER AT 25°.

Conc. NH$_3$.	Sp. gr. 25°/25°.	Time (147.8).	η.	η'.	D'.
0	1.000	147.8	1.000	1.000	...
2	0.986	155.8	1.040	1.088	0.044
4	0.973	164.2	1.081	1.175	0.044
6	0.961	172.6	1.121	1.262	0.043
8	0.946	182.8	1.169	1.316	0.050

Average, 0.044

AMMONIA IN 1.048 MOLAL NH$_4$Cl AT 25°.

(147.4)

0	1.017	144.6	0.997	1.137	...
1.00	1.010	148.8	1.020	1.084	0.047
2.96	0.995	157.9	1.068	1.178	0.048
4.75	0.982	169.3	1.127	1.280	0.057

Average, 0.051

AMMONIA IN 0.548 MOLAL CaCl$_2$ AT 25°.

(147.8)

0	1.047	164.8	1.168	1.180	...
1	1.040	168.9	1.190	1.225	0.045
2	1.033	173.9	1.214	1.286	0.061
6	1.008	193.5	1.325	1.478	0.048

Average, 0.050

AMMONIA IN 1.097 MOLAL Li$_2$SO$_4$ AT 25°.

Conc. NH$_3$.	Sp. gr. 25°/25°.	Time (147.6).	η.	η'.	D'.
0.00	1.048	185.5	1.318	1.331	...
1.10	1.042	192.3	1.359	1.399	0.062
2.21	1.034	200.7	1.406	1.473	0.067
4.41	1.019	216.6	1.496	1.615	0.065
6.52	1.007	231.9	1.581	1.748	0.063

Average, 0.064

AMMONIA IN 0.5 MOLAL LiCl AT 1°.
(285.2)

0.00	1.014	302.0	1.073	1.081	...
1.00	1.006	314.3	1.110	1.143	0.062
1.97	1.001	325.4	1.142	1.197	0.056
2.50	0.998	331.6	1.161	1.229	0.060
2.96	0.995	335.7	1.172	1.250	0.046
4.06	0.989	349.7	1.215	1.318	0.062

Average, 0.058

AMMONIA IN 1.504 MOLAL LiCl AT 1°.
(285.2)

0.00	1.037	382.4	1.207	1.234	...
1.97	1.024	363.5	1.306	1.379	0.074
3.92	1.010	398.5	1.409	1.531	0.078
5.15	1.003	419.7	1.477	1.626	0.077
7.65	0.998	470.9	1.663	1.839	0.085

Average, 0.076

The sixth column gives the rate of increase, D', of the corrected viscosity. This is obtained by dividing the increase of viscosity over that of the previous measurement by the increase in the molal concentration of ammonia. The average value of D' is the rate of increase over the whole interval between zero concentration of NH$_3$ and the concentration of NH$_3$ which is nearest to 5-molal.

It is known from the lowering of the partial pressure of ammonia over such solutions as the above,[1] that the ammonia is to some extent bound by the metal salts, but the viscosity curves obtained by us show a not very great deviation from the curve of the viscosity when ammonia is added to pure water. Of course the complexes formed by these metals and ammonia are far less stable and not so well defined as the complexes with copper, silver, and zinc; still the interesting fact is that instead of getting a negative viscosity effect here, there is a slight *increase* in the viscosity.

This is the important evidence of the new work, that such unstable complexes as are formed between ammonia and lithium, potassium,

[1] Gans, *Z. anorg. Chem.*, **25**, 236 (1900). Abegg and Riesenfeld, *Z. physik. Chem.*, **40**, 84 (1902). Riesenfeld, *Ibid.*, **45**, 461 (1903).

ammonium and calcium salts are somewhat more viscous and must therefore be larger, or less symmetrical, than the ordinary complexes of the same salts with water in simple aqueous solutions.

It is not easy to assign a reason why salts of silver, copper and zinc, on the one hand, should show a preference to form compact complexes with ammonia, and, on the other hand, lithium, potassium, ammonium and calcium salts should show a preference to form compact complexes with water. Various analogies suggest themselves, for example, the difference between the sulfo- and the oxy-salts. Thus, tin, arsenic, and antimony show a marked tendency to form well defined sulfo-salts but very poorly defined oxy-salts; on the other hand, chromium and manganese show no tendency to form sulfo-salts, but they do form well defined oxy-salts, as in the chromates and permanganates.

To compare with the viscosity values for ammoniacal aqueous solutions, it seems of great importance to obtain the values for solutions in anhydrous ammonia, both with and without small additions of water. Work in this direction has already been begun in this laboratory.

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TWO NEW AND VERY DELICATE TESTS BY USE OF THE REAGENT, "TETRAMETHYL BASE."

BY ROBERT J. CARNEY.

An acetic acid solution of the organic base, tetramethyldiaminodiphenylmethane, $(CH_3)_4N_2(C_6H_4)_2CH_2$, was used by Trillat[1] in 1903 for the detection of traces of lead and manganese. His method is to convert the metals into the form of dry sulfates, then warm and treat with a few drops of a solution of sodium hypochlorite, remove the chlorine by washing and add the reagent and warm. A beautiful blue color develops, which disappears on cooling and reappears on warming. With manganese it is not necessary to add the hypochlorite, but merely to add sodium hydroxide and ignite before adding the reagent. Trillat found that this gave a very delicate test for both lead and manganese.

This base has also been used as a reagent for the detection of ozone in mixtures containing hydrogen peroxide and the oxides of nitrogen. For this purpose the base is dissolved in alcohol, and strips of paper are moistened with the alcoholic solution and held in the gas. Ozone gives a violet color, nitrogen dioxide a straw-yellow and hydrogen peroxide no color whatever. Arnold and Mentzel[2] were the first to use the reagent for this purpose. They named the reagent "tetra base," but

[1] Compt. rend., 136, 1205–1207; also J. Chem. Soc. Abstr., 1903, 512.

[2] Ber., 35, 1324.