

less extension radially, and in fact may be complete disks, seen edgewise. In the latter case the rings mark, as it were, cellular partitions in the tube. The uppermost ring in one experiment (Fig. 3) shows such a partitioning film, which instead of remaining horizontal, had become conical after extending beyond the edge of the vial. The convection currents near the mouth of the vial were not horizontal. Within the vial each cell marks the boundaries of a system of vertical and horizontal convection currents, the necessary elements for the formation of which are a lateral temperature gradient and a vertical density gradient.

When these conditions are changed, even after a definite system of rings has formed, the rings will be readjusted, disappearing from the original location to reappear elsewhere; and, after several hours, a new system may have succeeded the old. It required from 6 to 8 hours for a complete system to form, but it is at times noticeable very much sooner than this.

The question may be asked: What part does the ammonia play in the stratification? It is very probable that it plays no part, if the explanation above given of the stratification is correct, *viz.*, that it is the resultant of two density gradients one due to gravity vertically, and one due to temperature laterally, together with the buoyant forces in the fluid. The stratification may then be already present in the vial containing the hydrochloric acid vapors and air. The diffusion of the ammonia into the vial is merely a means of making this stratification apparent.⁷

It would seem that, given the proper conditions, one may expect this same phenomenon of stratification to take place in pure gases that differ in density. Such cases may have meteorological significance. Finally, it may be of interest, too, to note that stratification in gas storage tanks is well known to gas engineers.

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NEGATIVE VISCOSITY

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Received August 25, 1921

The phenomenon which has received the wrong name of "negative viscosity" consists in the tendency of certain salts to lessen the viscosity of water, when dissolved in it. If we take the viscosity of water as unity, the viscosity of these solutions will be less than unity, in some cases by 24%, but of course not truly negative.

In non-aqueous solutions the phenomenon of negative viscosity oc-

⁷ (Note added March 1, 1922.) It appears that Dr. W. H. Chapin of Oberlin College, in using ammonium chloride and hydrochloric acid vapors to illustrate the laws of diffusion, had also observed and, I am told, exhibited this phenomenon in 1917.

curs very seldom. It has been observed so far only in glycerol for potassium iodide,¹ ammonium iodide, and rubidium chloride, bromide, nitrate and iodide,² and for naphthalene in alcohols.³

Many attempts at theoretical explanation have been made but none of them seems to be quite satisfactory. Lack of space prevents submitting them to critical examination, and therefore only the different factors acting upon the viscosity of solutions and especially those factors which are able to lower the internal friction of the solvent will be considered here.

1. One of the important factors which determine the viscosity of solutions is, obviously, the initial *viscosity of the solvent*. However, as this paper discusses only the relative viscosity of solutions (taking the internal friction of the solvent as unity), this factor will not be further considered.

2. The *viscosity of the solute* or the internal friction of the solution is not strictly an additive function of the coefficients of the components. All attempts to calculate accurately the viscosities of liquid mixtures on this basis have proved unsuccessful,⁴ but the certain influence of the viscosity of the solute on the internal friction of the solution is undeniable. In aqueous solutions of salts it manifests itself in the high internal friction of very concentrated solutions, even of those salts which, at smaller concentrations, lower the viscosity of water.

When the viscosities of very strong solutions of different salts are compared, the dependence of viscosity in solutions upon the viscosities of the respective salts in the fused state becomes clear.

TABLE I
VISCOSITIES OF CONCENTRATED SOLUTIONS AND FUSED SALTS

| Salt | η of fused salt at t | | η of 11.5 <i>N</i> sol. at 25° Cg. | η_a^5 at 25° |
|---------------------------------|-----------------------------|----------------|--|-------------------|
| | Cg. | ° C. | | |
| NH ₄ NO ₃ | 2.477 | 162 | 0.0452 | 2.5 |
| | 1.980 | 185 | | |
| | 0.9 | extrap. to 262 | | |
| ZnCl ₂ | 50.9 | 262 | 0.2769 | 153 |
| | 34.7 | 301 | | |
| | | | | |

The data for fused salts are taken from the work of Foussereau⁶ for solutions, but the calculations are mine. The figure for ammonium nitrate at 262 is extrapolated, using the known temperature coefficient of viscosity. The enormous difference in the internal friction of equiva-

¹ Getman, *THIS JOURNAL*, **30**, 1077 (1908).

² Jones and Davis, *Carnegie Inst. Pub.*, **180**, 191 *et seq.* (1913).

³ W. Ostwald, "Grundriss der Kolloidchem." 2nd ed., p. 180.

⁴ For bibliography see the paper of Faust, *Z. physik. Chem.*, **79**, 97 (1912).

⁵ η_a is the relative viscosity of solution compared with the viscosity of water at the same temperature taken as unity.

⁶ Foussereau, *Ann. chim. phys.*, [6] **5**, 241 (1885).

lent solutions at 25° corresponds closely to the similar difference in fused salts, at 262°.

3. *Hydration* increases the viscosity of solutions. For most of them η_a (the relative viscosity) rises with rising temperature. Only those which contain highly hydrated salts (of lithium, calcium and magnesium) diminish their relative viscosities when heated, owing to the thermal decomposition of hydrates. Furthermore, when a comparison of salts with a common anion is made it is seen that the highly hydrated cations increase to a large degree the viscosity of water in a normal solution, while the least hydrated diminish it.

TABLE II
HYDRATION NUMBERS OF CATIONS

| Chlorides | η_a of <i>N</i> sol. | Hydration number ⁷ |
|-----------------|---------------------------|-------------------------------|
| Cs | 0.9775 | very small |
| Rb | 0.9846 | small |
| K | 0.9872 | 22 |
| NH ₄ | 0.9884 ⁸ | ... |
| Na | 1.0973 ⁹ | 70 |
| Li | 1.1423 | 158 |

Jones¹⁰ has interpreted this series in the directly opposite manner, taking into account only the atomic volumes of ions, without their hydrate envelopes. With regard to the mechanism of the increase in viscosity by hydration, it will be sufficient to call attention to the increase of the real concentration of the solution, *i. e.*, the diminution in the amount of free solvent, because a part is required for the formation of solvates (namely, hydrates) with the solute.

4. The *formation of complex ions and molecules* increases the viscosity when the volume of the complex ions is larger than the sum of the volumes of the simple ions composing it, and decreases the viscosity in the opposite case. Experimental evidence for these volume changes could be obtained from the change of relative viscosity with temperature, if the influence of temperature on the degree of complexity of some ions could be learned. Unfortunately, the only available data, those of Gordon¹¹ for cadmium salts, do not make it possible to solve this problem. In this connection, my own observation may present a certain interest, namely, that strong solutions of cadmium bromide show a decrease in relative viscosity, when the temperature is raised from 25° to 50°.

5. The *electric fields* of the ions may also affect the viscosity of solutions but cannot possibly diminish it, as Euler¹² supposed. The immedi-

⁷ According to Riesenfeld and Reinhold, *Z. physik. Chem.*, **66**, 672 (1909).

⁸ Kanitz, *ibid.*, **22**, 336 (1897).

⁹ Reyher, *ibid.*, **2**, 744 (1888).

¹⁰ Jones, *Carnegie Inst. Pub.*, **80**, p. 213; *Am. Chem. J.*, **37**, 405 (1907).

¹¹ Gordon, *Z. physik. Chem.*, **23**, 469 (1897).

¹² Euler, *ibid.*, **25**, 536 (1898).

ate influence of the ionic electric fields upon the internal friction of the liquid should result in an increase in viscosity owing to the attraction between the electric charges on ions and the induced charges of opposite sign on the neighboring particles of the liquid, as has been shown by Sutherland.¹³ Perhaps these attractions are manifested only in the formation, around the ions, of more or less stable envelopes of solvent particles, *i. e.*, in solvation or hydration.

6. A very important factor in the viscosity of solutions is *depolymerization*¹⁴ of the associated solvent, especially of water, by dissolved substances. The theory of depolymerization may be stated thus: some liquids, such as water, glycerol, the alcohols, the organic acids, etc., contain associated or polymerized molecules which may dissociate into simple ones under the influence of temperature or pressure increase or upon the introduction of dissolved substances. It is generally accepted that such association exists. We do not possess as yet an accurate method of determining the composition and the relative amounts of different polymers composing an associated liquid, but many formulas enable us to find approximately the mean factor of association.¹⁵ The same formulas which give inconsistent absolute values for this factor at a given temperature show concordant values for its decrease with rising temperature.

Change of pressure increases or decreases the factor of association of liquids in proportion to the relative size of the polymer and sum of the simple particles of a given liquid. In the case of water the relative sizes of particles of both kinds may be obtained by comparing the specific volume of liquid water with that of ice which is composed of more complex molecules. This has frequently been done.¹⁶ Ice has the smaller density and the larger molecular volume; *i. e.*, the polymerization of water is accompanied by dilatation. This is indicated by the increase of the coefficient of thermal dilatation of water with heating. At lower temperatures the normal thermal dilatation is counterbalanced by the volume contraction caused by depolymerization. The effect of contraction can even exceed that of dilatation. This is the case below 4°. At higher temperatures depolymerization decreases, owing to diminution in the number of associated particles, and the coefficient of dilatation approximates its normal value.

Thus, every polymerized molecule of water has a larger volume than the sum of the volumes of simple particles composing it. If we represent the process of depolymerization of water, $(\text{H}_2\text{O})_n \rightleftharpoons n(\text{H}_2\text{O})$, as an ordi-

¹³ Sutherland, *Phil. Mag.*, [6] **14**, 1 (1907).

¹⁴ The dissociation of molecular aggregates into simple particles.

¹⁵ See the paper by D. Tyrer, *Z. physik. Chem.*, **80**, 50 (1912), and later papers by the same author in different journals.

¹⁶ Witt, *Kg. Wetensk. Akad. Förh.*, 1900, 68. Sutherland, *Phil. Mag.*, [5] **50**, 460 (1900). Hudson, *Phys. Rev.*, **21**, 16 (1905). Duclaux, *J. chim. phys.*, **10**, 73 (1912).

nary process of dissociation (let us assume it to be isothermal), we can apply to it the well-known equation of Planck¹⁷

$$\frac{\partial(\ln K)}{\partial p} = - \frac{\Delta v}{RT}$$

from which it follows that if dissociation runs as it does here, under the volume contraction ($\Delta v < 0$), the constant K and the degree of dissociation increase with rising external pressure p .

The same conclusion can be reached by applying the principle of Le Chatelier-Braun in the improved form given to it by Ehrenfest.¹⁸

The depolymerization effect of dissolved substances can be deduced from the effect of temperature and pressure by means of a rule enunciated by Tammann:¹⁹ the introduction of soluble substances changes many properties of water such as its thermal dilatation, the temperature of maximum density, the compressibility, the specific heat, etc., in the same manner as does external pressure. Tammann explains this by the appearance of a real force, which he calls "internal pressure" (Binnendruck), and which is, in its action, analogous to external pressure.

The existence of such a force is quite probable, but Tammann overestimated its importance when he believed it to be the only one existing between the solvent and solute. This is shown by the discrepancy observed between the values of internal pressure when calculated by two different methods, amounting to 20-26% (in both directions) and even to 85% in one case. Moreover, solution of the alcohols in water lowers its internal pressure instead of increasing it, as would be expected if Tammann's effect were really the measure of attraction between the components of the solution.

The relations described by Tammann can be better explained by the theory of depolymerization, since the latter gives a simple and clear picture of the process, whereas Tammann's explanation is a purely formal description. Some facts (like the above-mentioned lowering of the internal pressure of water by alcohols), which are in contradiction to Tammann's view, can be readily accounted for on the basis of the theory of depolymerization. Thus, this theory is in perfect accord with the fact that a given solute has greater effect in raising the internal pressure the greater the association of the solvent (water > alcohol > ether > carbon disulfide).

Certain experimental data also strongly support this theory, such as cryoscopic determinations made on highly concentrated solutions, where water can be considered as the solute. Thus it has been shown by Jones

¹⁷ M. Planck, "Thermodynamik," 4th ed., 1913, p. 235.

¹⁸ Ehrenfest, *Z. physik. Chem.*, **77**, 227 (1911).

¹⁹ Tammann, "Ueber die Beziehungen zwischen den inneren Kräften und Eigenschaften der Lösungen," 1907.

and Murrey²⁰ that when the molar concentration of water in acetic acid changes from 12.65 to 0.64, its molecular weight falls from 38.8 to 21.7. In formic acid water has the molecular weight 21.9 in a 6.18 *N* solution, and 19.7 in a 0.93 *N* solution.

Rozsa²¹ has shown that the degree of association of water falls in acetic acid from 1.80 to 1.03 when the concentration changes from 15.13 to 0.213%, while in phenol it changes from 1.80 to 1.02 when the concentration diminishes from 16.10 to 0.406%.

It should be possible to make indirect cryoscopic determinations with inorganic salts as a solvent and small amounts of water as solute, thus measuring the solubility of salts at high temperatures. The depression of the melting point would correspond then to the freezing-point depression. For most salts these determinations would have to be made under pressure to prevent the evaporation of water at the high temperatures approximating the melting point of the salt. Such is the curve for silver nitrate drawn by Etard²² for temperatures of 198°.

Unfortunately, these and similar measurements cannot be used to prove the depolymerizing influence of the change of concentration, as a quite analogous action is produced by pressure increase.

Far better results could be obtained with the double salt silver thallium nitrate, which is miscible with water in all proportions and melts at 82.5°. The quantity of this salt at my disposal was not great enough to allow cryoscopic determinations to be made.

Duclaux²³ indicated the depolymerization of water by dissolved substances, using a colorimetric method. He showed that the change of color of water to greenish was the same whether he raised its temperature or dissolved in it various salts. As the first influence is known to cause depolymerization, the author concluded that this is also the case with the second.

Of the possible causes of depolymerization of water, the effect of the volume of the dissolved substance may be mentioned first, as it is always acting, independently of the kind of solute. The concentration of the solvent is always diminished by the presence of the solute. If we suppose the mass-action law to be at least qualitatively applicable to the equilibrium between simple and polymeric molecules, the decrease in concentration must favor the decomposition of aggregates, *i. e.*, depolymerization. If V_1 is the molecular volume of the solute, V_0 that of the solvent, V that of the solution, then $V_0 < V < V_0 + V_1$. The influence is evidently the greater, the larger V_1 and the smaller the contraction upon solution, that is $(V_0 + V_1) - V$. Such is the case with cane sugar,

²⁰ Jones and Murrey, *Am. Chem. J.*, **30**, 193 (1903).

²¹ Rozsa, *Z. Elektrochem.*, **17**, 934 (1911).

²² Etard, *Compt. rend.*, **108**, 176 (1889).

²³ Duclaux and Wollman, *J. Physik*, [5] **2**, 263 (1912).

which causes strong depolymerization of water, as far as we can judge of it by the lowering of the temperature of maximum density.

The second possible cause of depolymerization is the effect of the hydration of the solute in taking away a part of the solvent which is connected to the solute particles and lessening, therefore, the solvent concentration. Its necessary consequence, according to the mass-action law, is the displacement of equilibrium towards simple molecules. This factor has been considered by Traube,²⁴ Blanchard²⁵ and Bousfield.²⁶

Third, a series of investigations has indicated that the degree of association of highly associated substances is lowered materially when they are dissolved in solvents possessing high dielectric constants. On the other hand, a solute of high dielectric constant must cause the depolymerization of the solvent, especially in concentrated solutions. Among soluble substances, inorganic salts are remarkable for their high dielectric constants. Thus,²⁷ the dielectric constant of potassium nitrate is 2.56; potassium chloride, 4.94; sodium nitrate, 5.18; sodium chloride, 6.12-6.29; and lead chloride, 4.20. At the first glance, it would seem that these dielectric constants are very small in comparison with that of water which is about 80. However, these values are for the solid state and, in the case of water, solidification causes the dielectric constant to decrease from 80 to 3.2.²⁸ It is apparent that all the above-named salts (except perhaps potassium nitrate) possess *higher* dielectric constants than does water, when considered in comparable states.

Walden²⁹ arrived at the same conclusion from measurements of dielectric constants of concentrated solutions.

Some of the theories of negative viscosity ascribed this effect to *electrostriction* due to the electrical charges on the ions. However, many facts are known which are quite incompatible with the conclusion from Drude and Nernst's³⁰ theory of electrostriction, that the total dissociation of one gram mol of every salt must cause the same contraction. Some salts give values very different from the mean, and many salts of ammonium, lithium, cesium, etc., even produce dilatation instead of contraction. This suggests the idea that changes in volume upon solution of other salts are also caused by other factors than electrostriction. The theory of electrostriction is based upon the assumption that every dielectric contracts under the influence of electrical polarization, if its dielectric constant increases under compression. All attempts, however, to observe

²⁴ Traube, *Phil. Mag.*, [6] **8**, 158 (1904).

²⁵ Blanchard, *THIS JOURNAL*, **26**, 1315 (1904).

²⁶ Bousfield, *Trans. Roy. Soc. (London)*, **206A**, 101 (1906).

²⁷ Landolt-Börnstein, "Tabellen," 3rd ed., p. 766.

²⁸ Abegg, *Wied. Ann.*, **65**, 229 (1898).

²⁹ Walden, *Bull. Acad. Sci. Petrograd*, **64**, 305, 1055 (1912).

³⁰ Drude and Nernst, *Z. physik. Chem.*, **15**, 79 (1894).

directly the compression of water under the influence of electrical charges, made by Quincke,³¹ Roentgen³² and Drude and Nernst,³⁰ proved unsuccessful. Therefore we cannot regard as established the existence of electrostriction and its depolymerizing action upon water. Depolymerization is rather the result of volume changes upon solution (decrease of water-concentration), of hydration and, especially in the case of dissolved salts, of the high dielectric constant of the solute.

It will now be shown that depolymerization is really able to lessen the internal friction of water, *i. e.*, to be the cause of "negative viscosity."

Applebey³³ stated that viscosity is increased by the presence of polymer molecules and, generally, of particles of large size, because (1) high values of viscosity are characteristic of associated liquids; (2) the viscosity of water falls more rapidly in the interval 0–50° with temperature increase than at higher temperatures, as heating produces here two effects which are additive, namely, the ordinary decrease of viscosity, and depolymerization which also tends to diminish viscosity; (3) pressure lowers the viscosity of water, as has been proved by Roentgen,³⁴ Warburg and Sachs,³⁵ Cohen³⁶ and others; (4) different ions change the viscosity of water in the reverse order of their mobilities.

The dependence of viscosity upon the size of particles can also be treated in a purely theoretical way. Einstein³⁷ has deduced from the fundamental equations of hydrodynamics a relation determining the viscosity η of a system composed of a liquid of the internal friction η_0 and a great number of suspended solid spheres of a size very large in comparison with the particles of the liquid, the total volume φ of these particles being, however, but a small part of the volume of the liquid taken as unity.

$$\eta = \eta_0(1 + 2.5\varphi)$$

This equation has been tested on systems which best satisfy the named conditions, *i. e.*, on suspensions, and was brilliantly confirmed in some cases. Bancelin³⁸ in the laboratory of Perrin applied it with success to suspensions of various sized granules of gamboge in water. Experiments of Mifka³⁹ on weak colloidal solutions of noble metals also gave results which do not contradict this formula. In other cases such as the deter-

³¹ Quincke, *Wied. Ann.*, **10**, 521 *et seq.* (1880).

³² Roentgen, *ibid.*, **11**, 771 *et seq.* (1880).

³³ Applebey, *J. Chem. Soc.*, **97**, 2020 *et seq.* (1910).

³⁴ Roentgen, *Wied. Ann.*, **22**, 510 (1884).

³⁵ Warburg and Sachs, *ibid.*, **22**, 518 (1884).

³⁶ Cohen, *ibid.*, **45**, 666 (1892).

³⁷ Einstein, *Drude's Ann.*, **19**, 289 (1906); **34**, 591 (1911).

³⁸ Bancelin, *Compt. rend.*, **152**, 1382 (1911); *Kolloid Z.*, **9**, 154 (1911).

³⁹ Mifka, *Sitzb. Akad. Wiss. Wien, Abt. IIa*, **120**, 1173.

minations of Wondstra,⁴⁰ Oden,⁴¹ Freundlich and Ishizaka,⁴² and Bingham and Durham⁴³ the observed values of η were higher than those calculated using the formula of Einstein, which is quite natural, as Einstein's formula was deduced under assumptions which are rarely satisfied, namely, the large relative size and the spherical form of the suspended particles, total absence of interaction between them and the medium, exceedingly small concentration, etc.

Einstein himself, however, made a successful attempt to apply his equation to a system of a notably different character, a solution of sugar in water. Combining this equation with his well-known formula of diffusion, he calculated the size of sugar particles and found the number of particles in a gram-molecule, N , to be 6.56×10^{23} , a figure which is in good accord with values obtained by the most reliable methods. It does not, therefore, seem too audacious to apply the equation of Einstein to solutions of salts in water and to water itself, as a system of large, associated molecules suspended in smaller simple water particles. It is clear that in such a case associated molecules, having larger values of φ , cause a higher viscosity of the system. Upon their dissociation (or depolymerization), φ falls, and with it η .

Jones⁴⁴ has put forward the opposite view, that the viscosity of water is increased by depolymerization owing to the increase of the "total frictional surface." This increase in frictional surface has been only assumed by Jones, but even if it should be proved, the conclusion of Jones could not be regarded as correct, as he connects the internal friction of a solution with the *surface* of particles which compose it, whereas the equation of Einstein, the only one having a serious theoretical basis,⁴⁵ shows that η of the solution is a linear function of the volume of the particles, not of their surface.

The same objection may be urged against Jones' theory of "negative viscosity" caused by salts, a property which he ascribes to the decrease of the "total frictional surface" owing to the introduction of large particles of salts into a solvent consisting of relatively small molecules.

7. The *depolymerization of the solute* by the solvent must be added to the factors influencing the viscosity of solutions. According to the above considerations, it can affect the viscosity in both directions, depending on the relative sizes of polymer and simple solute particles.

⁴⁰ Wondstra, *Z. physik. Chem.*, **63**, 619 (1908).

⁴¹ Oden, *Nova Acta R. Soc. Upsala*, [7] **3**, No. 4, 103 (1913).

⁴² Freundlich and Ishizaka, *Kolloid Z.*, **12**, 230 (1913).

⁴³ Bingham and Durham, *Am. Chem. J.*, **46**, 278 (1911).

⁴⁴ Jones and Veazey, **37**, *ibid.*, 405 (1907); Jones *et al.*, *Carnegie Inst. Pub.*, **80**, 207, 214, 225.

⁴⁵ Cf. a quite (formally) analogous equation of Hatschek, *Kolloid Z.*, **7**, 301 (1910), which is deduced by a different method.

The fact that water depolymerizes salts is beyond doubt. All osmotic methods show for salts dissolved in water molecular weights less than normal. This, indeed, is due to electrolytic dissociation, but if the salts in water should be highly associated, the sum of the molar weights should be greater than unity, as is the case for the same salts in non-aqueous solutions.

In the fused state, however, most salts are highly associated, as has been shown by Bottomley,⁴⁶ Walden⁴⁷ and others. Consequently, solution in water lowers their degrees of association, and depolymerization increases further with increasing dilution.

Arrhenius⁴⁸ states that depolymerization of solute always causes an increase of viscosity; the opposite phenomenon—coagulation (*i. e.*, aggregation of small particles into large ones) diminishes the viscosity of the solution, as has been shown for some suspensions by Wondstra⁴⁹ and Oden.⁴¹

This, however, is far from general. Freundlich and Ishizaka,⁴² working on colloidal aluminum hydroxide, and Bingham and Durham,⁴⁸ working with suspensions of infusorial earth and graphite, have found an enormous increase of viscosity to take place upon coagulation. Changes of viscosity in the same direction have been found by Biltz and Vegesack⁴⁹ for some aniline dyes and by Friedlaender⁵⁰ for emulsions of butyric acid in water. This shows that upon coagulation different substances undergo volume changes in opposite directions. Moreover, many conditions may act indirectly, such as the decrease of accuracy of determinations owing to the clinging of suspended particles to the walls of the capillary tube, electrical phenomena, form changes, etc.

If all such factors could be subjected to quantitative estimation, calculation of the viscosity of a solution might be attempted. The present state of our knowledge, however, does not allow this to be done, and all attempts to make such a calculation over a wide range of concentration, using one or two of the named factors only, have proved unsuccessful.⁵¹

It has been necessary, therefore, to limit this paper to qualitative considerations only, concerning the causes of the increase or decrease of the internal friction of solvents by solutes, and a determination of which of the enumerated factors of the viscosity of solutions are able to account for the phenomenon of "negative viscosity."

The viscosity of a solute, mentioned in the last paragraph, cannot be used for this purpose, as it can act in both directions and even for the less

⁴⁶ Bottomley, *J. Chem. Soc.*, **83**, 1421 (1903).

⁴⁷ Walden, *Z. Elektrochem.*, **14**, 715 (1908).

⁴⁸ Arrhenius, *Biochem. J.*, **11**, 112 (1912).

⁴⁹ Biltz and Vegesack, *Z. physik. Chem.*, **73**, 500 (1910).

⁵⁰ Friedlaender, *ibid.*, **38**, 430 (1901). Rothmund, *ibid.*, **63**, 54 (1908).

⁵¹ See the works of Applebey, Ref. 33; Einstein, Ref. 37; Grüneisen, *Wiss. Abhandl. Reichsanstalt*, **4**, 237 (1905); Bousfield, Ref. 26.

viscous salts exceeds by many hundred times the viscosity of water. Thus, ammonium nitrate has been shown to have the coefficient of internal friction $\eta = 2.477$ abs. units at 162° , while the viscosity of water from the data of DeHaas⁵² at 142° and 153° , is calculated by extrapolation to 162° to be 0.00172, *i. e.*, 1440 times lower.

The depolymerization of the salt by water can lower the viscosity of the solution, but only in comparison with the salt in the liquid state and not with the solvent. If we assume, indeed, in the case of ammonium nitrate dissolved in water, a very high degree of association of the salt, its total depolymerization by water, and the largest imaginable influence of depolymerization upon the viscosity of the solute, assuming total depolymerization to diminish the viscosity as much as 10 times, we shall find the theoretical liquid component of the solution to be still 140–150 times more viscous than water. This is true notwithstanding the fact that salts lower the viscosity of water in an indirect way when they are present in a sufficiently small amount. At higher concentrations their own high viscosity predominates, and "negative viscosity" is no longer observed.

Of the other factors, hydration and the electrical field of ions are able only to increase, not to diminish, the initial viscosity of water, as has been said above. The decomposition of complexes can diminish the internal friction in some cases, but only with regard to the solute, which at sufficiently great dilutions forms but a small part of the whole solution. Only the *depolymerization of the solvent, i. e.*, of the component quantitatively prevailing in the solution and therefore materially influencing its viscosity, is able to produce *by itself* negative viscosity.⁵³ Other factors can favor or hinder and, in many cases, overbalance it, giving rise even to a positive viscosity effect.

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⁵² De Haas, *Comm. Leyden*, No. 12 (Landolt-Börnstein "Tabellen," 3rd ed., p. 76).

⁵³ The important part played by depolymerization has been acknowledged by many authors and most clearly expressed by Kraus. Our views about negative viscosity are in full accord except for the causes of depolymerization, which Kraus ascribes principally to the action of Tammann's "Binnendruck."