

## Letters to the Editor.

## Negative Viscosity of Solutions.

JONES AND DOLE (*J. Amer. Chem. Soc.*, **51**, 2950, 1929) and Falkenhagen and Dole (*Phys. Z.*, **30**, 611, 1929; also see Falkenhagen, *Phys. Z.*, **32**, 745, 1931) have treated the problem of the variation with concentration of the relative viscosity of electrolytes from the standpoint of the ion-atmosphere theory of Debye and Hückel and shown that at high dilutions the electrolyte must always increase the viscosity of the solvent and that the relative viscosity of an electrolyte solution at high dilution must be represented by an equation of the form

$$\eta_c/\eta_0 = 1 + K\sqrt{C}$$

where  $\eta_c$  is the viscosity of the solution,  $\eta_0$  is the viscosity of the solvent,  $C$  is the equivalent concentration, and  $K$  is a constant which can be determined in terms of certain constants of the electrolyte and the solvent.

It is well known that certain salts of some of the alkali metals show "negative viscosity" within a certain range of concentration, *i.e.*, the solutions are less viscous than the pure solvent. According to the theory of Falkenhagen and Dole, in very dilute solutions the viscosity should increase with concentration upto a certain stage even in instances of negative viscosity. A tendency to this effect was noticed by Schneider ("Dissertation", Rostock, 1910) in the case of potassium chlorate and by Bousfield (*J. Chem. Soc.*, **107**, 1781, 1915) in the case of nitric acid.

Recently Joy and Wolfenden (*Nature*, **126**, 994, 1930; *Proc. Roy. Soc.*, **134**, 413, 1932) have shown by very accurate measurements that the viscosity of solutions of potassium chloride, potassium chlorate, rubidium nitrate and nitric acid at high dilutions is greater than that of pure water and that the limiting slopes of the  $\eta_c/\eta_0$ ,  $\sqrt{C}$  curves and their temperature coefficients agree, within the experimental error, with the values predicted by the Falkenhagen-Dole equation.

In our laboratory we have carried out recently measurements of viscosity at 30°C with an Ostwald viscometer of solutions of chlorides, iodides and nitrates of potassium and ammonium in water and methyl, ethyl and n-propyl alcohols and observed the following:—

(1) Chlorides, iodides and nitrates of potassium and ammonium in aqueous solu-

tions show negative viscosity within a certain range of concentration (*cf.* Getman, *J. de Chim. phys.*, **5**, 344, 1907; *J. Amer. Chem. Soc.*, **30**, 721, 1908; Herz and Martin, *Z. anorg. Chem.*, **132**, 31, 1924; Simon, *C. R.*, **176**, 437, 1923 and others).

(2) In methyl and ethyl alcohols potassium chloride and ammonium chloride alone show negative viscosity.

(3) In n-propyl alcohol only a tendency for negative viscosity is marked in the case of potassium chloride.

(4) In all the above cases of negative viscosity, the relative viscosity increases with concentration upto a certain stage in very dilute solutions.

The last observation is in agreement with the requirements of the Falkenhagen-Dole theory. The observations with the Ostwald viscometer in dilute solutions are however not so accurate as can be used to test the theory quantitatively. These cases of negative viscosity are being investigated by using a more appropriate type of viscometer with an automatic arrangement to record time of flow.

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#### A Formula for the Variation in the Scattering of Light in Colloids during Ageing and Slow Coagulation.

In a previous communication I have stated that the time-Tyndall intensity curves obtained with silicic acid sols during ageing are distinctly S-shaped, being curved convex to the time axis at the commencement and becoming concave towards the end. An explanation for this was offered, and an equation was then derived, which was found to represent the variation of the intensity of scattered light with time very well. The general equation is:—

$$I = c + \frac{k}{1 + b \cdot e^{at}}$$

where  $I$  is the intensity of scattered light,  $t$  is the time from the start, and  $a$ ,  $b$ ,  $c$  and  $k$  are constants, which could be found by

calculation for a particular sol. The following tables give the calculated and observed values of the Tyndall intensity, and it will be seen that the agreement is good.

*Sol. A.*—

$$I = 5.7 + \frac{24.28}{1 + 126.71 \cdot e^{-0.1146 \cdot t}}$$

Time	I (Cal.)	I (Obs.)
10 days	8.1	8.0
13 "	10.5	10.5
16 "	14.2	14.3
18 "	17.3	17.4
20 "	20.4	20.0
23 "	24.5	25.0
27 "	27.7	27.6
30 "	28.9	29.0

*Sol. B.*—

$$I = 7.4 + \frac{18.63}{1 + 146.82 \cdot e^{-0.1271 \cdot t}}$$

Time	I (Cal.)	I (Obs.)
8 days	8.6	8.7
9 "	9.0	9.0
10 "	9.5	9.5
11 "	10.1	10.0
13 "	11.7	11.6
14 "	12.8	12.8
15 "	14.0	14.0
18 "	18.0	19.0
20 "	20.5	20.5
22 "	22.5	22.0
29 "	25.5	24.6

Similar S-shaped curves have been obtained by me while examining the variation of the scattering of light and viscosity with time during the formation, ageing, and slow coagulation of colloidal solutions, and have also been observed by others in the case of the change of viscosity with time during coagulation. It has already been recognised that results such as those given above cannot be represented by von Smoluchowski's equation for coagulation. But the equation suggested above, fits in very well with the data on ageing and slow coagulation obtained by me and other workers, and can easily be derived from theoretical considerations, as will be shown in a paper to be published shortly.

I pointed out the usefulness of this equation in an address to the Nagpur Chemical Society about three years ago. Recent investigations have convinced me that it could be applied with advantage to the results giving the variation of light-scattering in sodium oleate solutions with time at 20°C, and in the formation and slow coagulation of sols.

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### Physics of the "Smell".

PROF. BOHR in his recent address<sup>1</sup> on 'Life and Light' has emphasised the peculiar organisation of living beings with a view to understanding their essential characteristics. This organisation exhibits typical atomistic and quantum traits combined with the ordinary mechanical characteristics, in a manner having no counterpart in inorganic matter.

As an illustration of the refinement to which this organisation is developed, Prof. Bohr has considered the case of the human eye. The eye is an ideal and perfect optical instrument inasmuch as its resolving power and its sensitiveness have reached the limit imposed by the wave and quantum nature of light. It has been found that the eye can be stimulated by a few light quanta (or possibly a single light quantum?). Further the optical resolving power  $[(5/d)^2]$  where  $d$  is the aperture of the eyelens in inches] and the physiological resolving power (angle subtended by the "cone" in the retina at the eyelens) of the eye are almost the same. This perfection of the eye naturally leads one to expect that the other organs also may reveal similar characteristics, the study of which will greatly help in establishing the relation between organic evolution and physics.

A consideration of the construction and function of the nose may also afford another interesting example. The human nose appears to be very sensitive to smell. However, physics corresponding to the sensation of smell does not exist at all, though physics of the eye and the ear (being simpler) has developed so much.

It is of interest to see whether the sensitiveness of the nose has also reached a

<sup>1</sup> *Nature*, March 25 and April 1, 1933.