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On the Viscosity of Water

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SEZIONE II

(Fisica, chimica, geologia, paleontologia e mineralogia)

Fisica degli stati condensati. — *On the Viscosity of Water.* Nota (*) del Corrisp. MARIO AGENO.

RIASSUNTO. — La viscosità dell'acqua può rappresentarsi con grande precisione mediante una formula notoriamente valida nel caso di liquidi costituiti da polimeri lineari. Questo fatto è in accordo col modello collettivo del legame a idrogeno, secondo cui gli aggregati molecolari nell'acqua sono per lo più catene lineari.

In the present paper I propose to draw attention to an empirical formula which applies very well to the values of the viscosity of water expressed as a function of temperature. The formula is of the type which is known to hold for solutions of linear polymers as Dunstan has shown since 1906 [1–2]. First of all, I shall explain why such a formula was tested. In some previous papers [3–7] I developed a new model of hydrogen bond, which I called the collective model. Such a model was also tried on water, in order to see if its structure could be explained by it. Previously some remarkable results were obtained and satisfactory connections were found among very different quantities, such as the heats of vaporization of water, the viscosities of water-alcohol mixtures and their NMR spectra, the binding energy of two water molecules in the liquid and the temperature dependence of the chemical shifts of water protons in NMR. Furthermore, the main consequence of the collective model as far as the structure of water is concerned was somewhat supported by these results. This consequence is that in the liquid there are almost exclusively linear chains of molecules. As a matter of fact, according to the collective model other types of molecular aggregates (rings) are also possible in water, but one must think they become important only in the neighbourhood of the freezing point. It would be important if the main assumption of the theory, namely the linear structure of the molecular aggregates in water, could be tested as directly as possible. That is the point in which the present theory of the structure of water [7] differs from all other theories which have been proposed till now. Viscosity is a physical quantity which depends critically on the shape of molecules and molecular aggregates in a liquid. For this reason the viscosity of water at different temperatures was considered and the formulas which hold in the case of linear polymers were tested.

Experimental investigations on the viscosity η of long-chain polymers have been made by several Authors. Dunstan [1] was able to demonstrate

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(*) Presentata nella seduta del 10 gennaio 1970.

that in many cases η can be expressed quite well by the formula:

$$\eta = \eta_0 \, e^{\alpha L} \, e^{W/kT} \tag{1}$$

where L is the number of monomers in the chain and the activation energy W is independent of L [8].

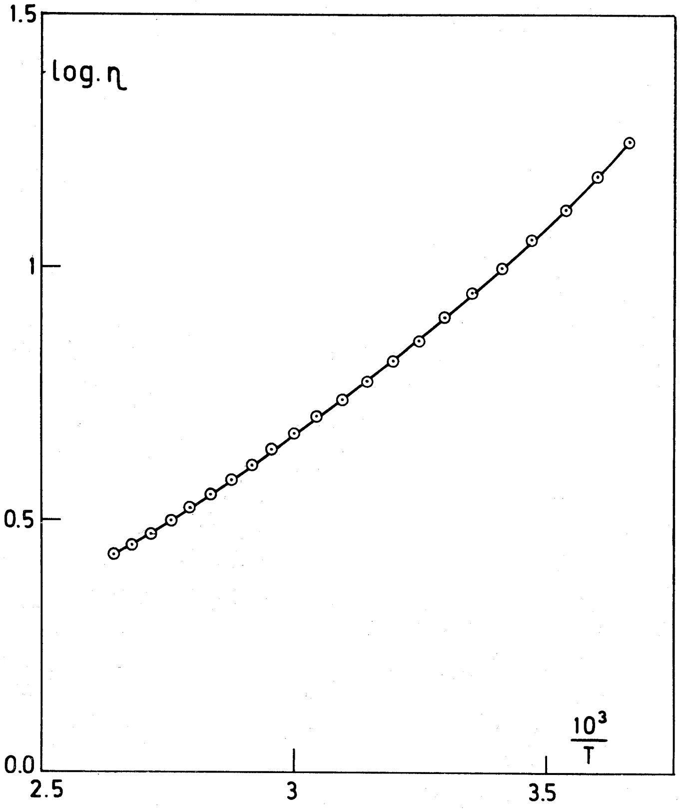

Fig. 1.

On the other hand, a theoretical treatment of the problem can be based on a formula derived for the first time by Einstein in 1905 for spherical particles. In the case of high concentrated solutions of linear polymers one obtains from it [9] at constant temperature:

$$\eta = \eta_0 \, e^{\gamma} \tag{2}$$

where γ is a convenient function of L. If the particles are rod-like in shape and contain more than a hundred monomers, it can be shown that

$$\gamma = \frac{L}{2 \log L} \tag{3}$$

while Flory's experimental results in the case of linear polyesters [2] are represented by the empirical formula:

$$\gamma = \frac{1}{4} \sqrt{L} \, . \tag{4}$$

The discrepancy between the experimental results represented by (1) and (4) and the theoretical formula (3) is generally interpreted as due to a partial curling of the molecular chains [9].

In the case of water, according to our theory, the mean number of molecules per polymer varies from five to eight depending on temperature. For such values of L, we must take into account formula (1) which was experimentally tested by Flory [9] using long-chain paraffins with relatively low values of L.

Very accurate values of the viscosity of water were available long since and a critical evaluation of all data between 0° C and 109° C is reported in the International Critical Tables [10]. The estimated accuracy is of the order of 0.1 % between 0° C and 40° C and of 0.5 to 1 % at higher temperatures. As is shown in fig. 1, a Vant'Hoff plot of such data is not a straight line.

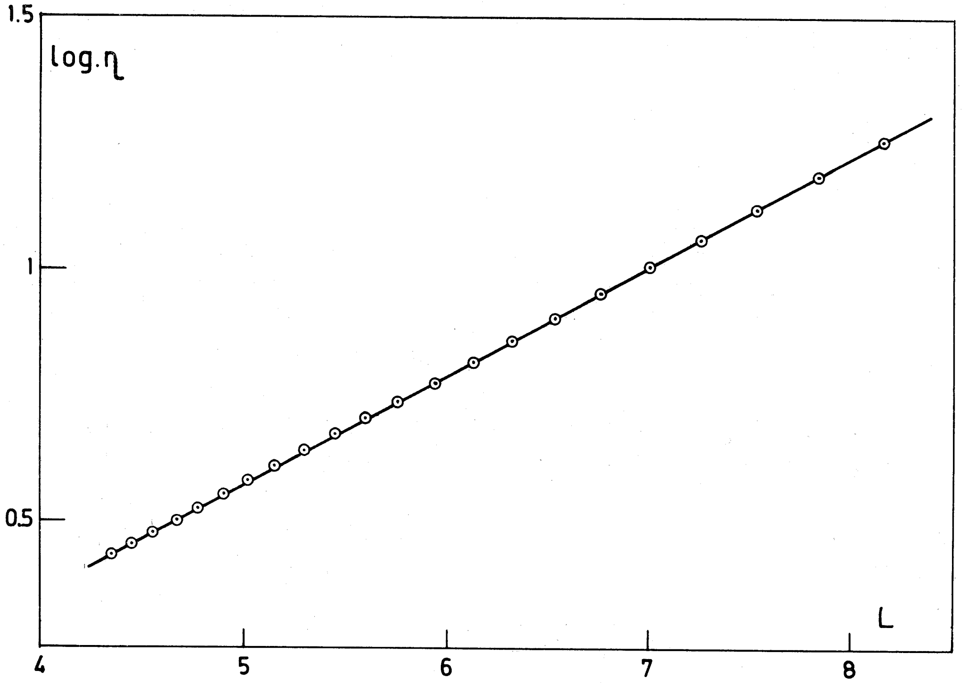

Fig. 2.

Viscosity increases more than usual as the temperature is decreased and this may be due to the fact that the mean polymer length increases correspondingly. It is remarkable, though not too easy to explain, that plotting log η against the mean number of molecules per polymer L, the resulting plot is linear with good accuracy (fig. 2).

According to our theory [7], L is given as a function of temperature by:

$$L = \frac{1}{2}\left[1 + \sqrt{1 + 2h}\right] \quad , \quad h = \frac{10^3 d}{18} K = 0.4703\, d\, e^{1318/T} \tag{5}$$

where d is the density and K the equilibrium constant of water at the absolute temperature T. A best fit shows that the viscosity of water between 0° C and 109° C can be suitably expressed by the empirical formula:

$$\eta = \eta_0 \, e^{\alpha \mathrm{L}} = (0.3167 \pm 0.001) \, e^{(0.4942 \pm 0.0005)\mathrm{L}} . \tag{6}$$

The root mean square deviation for the 110 points used in the fit is:

$$\sigma = 0.035$$

with a maximum deviation of 1.6%.

However the fit is not perfect although very good. Plotting the relative deviation $(\eta_{\mathrm{cal}} - \eta_{\mathrm{obs}})/\eta_{\mathrm{obs}}$ as a function of T, a regular trend is evident and the maximum deviation is more than three times greater than the accuracy of the experimental data.

This fact suggests that we should test Dunstan's empirical formula [1], which is known to hold for linear polymers with relatively low values of L. A best fit of the same points as before gives in this case:

$$\eta = (0.238 \pm 0.005) \, e^{(0.4425 \pm 0.0038)\mathrm{L}} \; e^{(189.6 \pm 13.8)/\mathrm{T}} \tag{7}$$

with:

$$\sigma = 0.034$$

and a maximum deviation of 1.2%. The improvement is poor. It must be observed however that systematic deviations occur now mainly near 0° C; where the hypothesis of the occurrence of exclusively linear polymers in the liquid is less realistic, owing to the presence of a substantial fraction of hexagonal rings, deriving from the demolition of the lattice of ice. A new fit was then made using only a hundred experimental points, between 10° C and 109° C, at which the contribution of hexagonal rings to the viscosity can be neglected. The result was:

$$\eta = (0.2138 \pm 0.0045) \, e^{(0.4192 \pm 0.0042)\mathrm{L}} \; e^{(269 \pm 15)/\mathrm{T}} \tag{8}$$

and

$$\sigma = 0.018$$

with a maximum deviation of 0.51%, which is the same order of magnitude as the accuracy of the measurements. Thus, the fit is as good as one can hope, and the residual trend in the distribution of the deviations of the single points may also be due in part to the use of a not very accurate value of the equilibrium constant K of water.

We are thus led to the conclusion that the viscosity of water is expressed with a very high degree of accuracy by a formula which holds in the case of linear polymers. Obviously, this fact does not prove that molecular aggregates in water are linear. However if the aggregates of water molecules are linear, it is to be expected that Dunstans' formula would hold. No difficulties then from this side to the collective model of the hydrogen bond.

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