**Note on the Standard of Relative Viscosity, and on
"Negative Viscosity."** By W. W. Taylor, M.A., D.Sc.
Communicated by Professor CRUM BROWN.

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THE UNIT OF RELATIVE VISCOSITY.

The absolute viscosity calculated from the formula

$$\rho = \frac{\pi p r^4 t}{8 v l}$$

(where p = the pressure, t the time, r the radius, l the length of capillary, and v the volume of liquid), which connects the viscosity of a liquid with the rate of flow through a long capillary tube, is not often made use of, mainly on account of the difficulty of accurately determining some of the constants (r in particular). Further, a correction has to be made if the velocity of outflow is not sufficiently slow.* For most purposes the viscosity is referred to that of a given liquid as standard, and is calculated from the formula

$$\eta = \eta_0 \frac{st}{s_0 t_0}$$

where η_0 , s_0 , t_0 , are the viscosity, density, and time of flow through a tube of a given volume of the standard liquid, and η , s , t are the corresponding data for the other liquid. Of η_0 , Ostwald-Luther (*Phys. Chem. Messungen*, p. 260) say, "the viscosity of water at 0° C. (or at the temperature of experiment) is put = 1."

It is the general practice to take the viscosity of the solvent (whether water or other liquid) at the temperature of experiment as $\eta_0 = 1$. In place of this, it would be an advantage if the viscosity of water at 0° C. were taken as standard, and the relative viscosity of liquids and solutions referred to this alone.

For certain purposes, *e.g.* demonstration of the additive character of the viscosity of salt solutions, the relation between viscosity and atomic weight, or between viscosity and concentra-

* Cf. Ostwald-Luther, *Phys. Chem. Messungen*, p. 359.

tion, where all the experiments are made at one temperature, the general practice is not inconvenient, but it has several disadvantages:—

1. It is possible, and may be desirable, to determine the viscosity of a solution at temperatures below the freezing-point or above the boiling-point of the solvent; in this case s_0 , t_0 cannot be determined.

2. It affords no good way of graphically representing the relation between viscosity and temperature.

3. It may lead to misunderstanding. Most of the experiments on solutions have been made at 17° or 25° C., and a comparison of the relative viscosity of, *e.g.*, 1 n KCl is as follows:—

	Temp. 15°	Temp. 25°	
Water	1	1	
1 n KCl	0.972	1.001	
Water	0.640	0.501	} (water at 0° = 1);
1 n KCl	0.622	0.502	

from which it appears that the relative viscosity of the solution increases with increase of temperature. In this connection it may be remarked that Euler,* referring to the influence of temperature, says,—“whilst the specific viscosity of all solutions of non-electrolytes decreases with rise of temperature, the solutions of strongly-dissociated electrolytes are affected in the opposite direction.” Without a definition of “specific” viscosity this statement might be misunderstood.

If the viscosities are referred to water at 0° as unit, it is seen that they do not increase with rise of temperature, but that they do not diminish so rapidly as the solvent; in other words, the temperature coefficient of the solution is smaller than that of the solvent, but is of the same sign. Of course, there may still be a fundamental difference between the two classes of solutions.

As to the unit, no maximum of viscosity for water is known (as there is of density at +4° C.), and there is not much to choose between water at 0° and +4°; in either case, S_0 can be put = 1 without appreciable error in η , which is ordinarily not more accurate than one in 500 or 600.

* *Zeit. f. Phys. Chem.*, 25, p. 536 (1898).

There is no need to determine t_0 directly; the simplest way is to determine t for the solvent at the temperature of experiment, and to calculate t_0 from it by means of the table of viscosity of water at various temperatures.

“NEGATIVE VISCOSITY.”

The bearing of this on “negative viscosity” (a term frequently used to denote that the viscosity of the solution is less than that of the solvent at the same temperature) is indicated below.

In general, the temperature coefficient of the solution will be (a) less or (b) greater than that of the solvent.

(a) If at a given temperature the viscosity of the solution is greater than that of the solvent, and its temperature coefficient is smaller than that of the solvent, at higher temperatures the viscosity-temperature curves will diverge, but at lower temperatures they will approach, and finally intersect at some temperature, below which “transition temperature” the solution will exhibit “negative viscosity.”

(b) If, on the other hand, the temperature coefficient of the solution be greater than that of the solvent, the curves will diverge on lowering the temperature, whilst they will approach and intersect on raising the temperature. In this case the solution will exhibit “negative viscosity” at higher temperatures.

The particular case where the solution and solvent have the same temperature coefficient needs no discussion.

Aqueous solutions of electrolytes appear to belong to group (a), and in some cases, at any rate, a solution has “positive viscosity” at one temperature and “negative viscosity” at lower temperatures, e.g. KCl, KNO₃,* etc.

Until quite recently no solutions other than aqueous solutions of electrolytes were known to exhibit “negative viscosity,” and on this Euler† based his explanation,—“the electric charge of the ion causes a compression (electro-striction) of the water, on account of which the viscosity is diminished.” But Mühlenbein,‡

* Sprung, *Pogg. Ann.*, 159, p. 20 (1876).

† *Loc. cit.*, p. 541.

‡ Dissertation, Leipzig, 1901. Also Wagner, *Zeit. f. Phys. Chem.*, 46, p. 872 (1903).

a pupil of Wagner, has found that some organic substances in organic solvents do also exhibit it, *e.g.* cyanobenzol in ethyl alcohol.

In the known cases of group (a), increase of concentration raises the transition temperature: there is very little to show in what way concentration affects the transition temperature of solutions in class (b), whether decrease of concentration will lower it or not, but measurements by Rudolf* on aqueous solutions of carbamide indicate that at 25° C. the relative viscosity decreases with dilution, and even becomes "negative," *e.g.*—

Concentration.	η (Water at 25°=1).
0·937 <i>n</i>	1·010
·469	1·002
·234	0·996
·117	·993
·058	·995

—but the viscosity is so nearly the same as that of water that it is not safe to base any conclusions on these data.

Increase of molecular weight, in the known cases of class (a), raises the transition temperature, and this affords another means of bringing it within the range of experiment.

The general case, where the viscosity curves of solution and solvent intersect twice, is of some interest. According as the one curve or the other represents the solution, there will be a transition from "positive" to "negative" viscosity, or *vice versa*, at both high and at low temperatures. It may not be possible to realise this case, except perhaps with a very soluble substance, and a solvent which permits of a wide range of temperature, but there should not be much difficulty in realising the particular case of it where at one extreme of temperature and concentration the one part of the curve is obtained, and the other part at the other extreme.

I hope to commence experiments, in the near future, with a view to verifying these conclusions.

* *Zeit. f. Phys. Chem.*, 43, p. 257 (1903).

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