A VISCOSITY FORMULA FOR BINARY MIXTURES, THE ASSOCIATION DEGREES OF CONSTITUENTS BEING TAKEN INTO CONSIDERATION. XI.

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The nature of the solutional viscosity of solids in liquids. In the latest publication,(1) we have laid stress on the solutional viscosity in accordance with the Ishikawa's theory for elucidating the viscosity of aqueous solutions of electrolytes, and evaluated those values of a few strong electrolytes.

Table 1.

Substance	Solutional viscosity at t°C.	t°C.
Naphthalene	0.02653	25
Diphenyl	0.05413	25
KCl	0.01003	18
	0.00874	25
KI	0.00735	18
	0.00664	25
$RbNO_3$	0.00889	18
	0.00789	25
$CsNO_3$	0.00842	18
	0.00753	25

Since his formula for binary mixtures, the component viscosities of which being alike treated, has the validity for the solution of solids in liquids, one may arrive at the supposition that the solutional viscosity of a solid calculated by it touches a fundamental nature of the molecular constitution, and must have, in con-

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(1) T. Ishikawa and T. Baba, this Bulletin, **10** (1935), 153.

sequence, an intimate relationship with the viscosity of its molten state.

The equations expressing the viscosity variation of liquids with temperature have been proposed numerously. Among them the one proposed by Raman⁽²⁾ and developed by Andrade⁽³⁾ and his follower⁽⁴⁾ is simple but sufficient within the limit of experimental error:

$$\log \eta = \alpha + \frac{\beta}{T} \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (1)$$

in which η denotes the viscosity, T the absolute temperature, α and β constants. The equation also proved to be valid for molten salts such as $NaNO_3$, KNO_3, and $PbBr_2$, but failed for some salts such as $PbCl_2$, for which, however, a slightly modified formula which was also proposed by Andrade was shown to be applicable:

$$\log \eta = \alpha + \frac{\beta}{T-\theta} \quad \cdots\cdots\cdots\cdots\cdots \quad (2)$$

where θ is a constant.

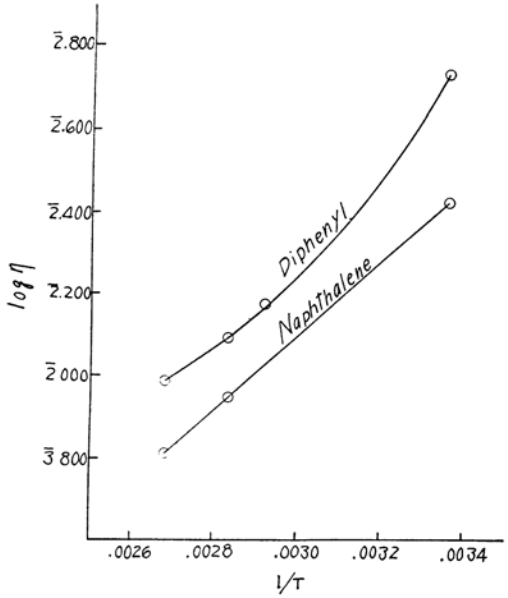

Table 2.

Naphthalene. Melting point: 80.1°C.

t°C.	$\eta_{obs.}$	$\log \eta$	$1/T$	$\eta_{calc.}$
25	0.02653	$\bar{2}.4237$	0.00336	0.02656
80	0.00886	$\bar{3}.9474$	0.00283	0.00886
100	0.00649	$\bar{3}.8125$	0.00268	0.00649

$$\log \eta_T = -4.5986 + 899.7\frac{1}{T}$$

Table 3.

Diphenyl. Melting point: 70.5°C.

t°C.	$\eta_{obs.}$	$\log \eta$	$1/T$	$\eta_{calc.}$
25	0.05413	$\bar{2}.7334$	0.00336	0.05413
70	0.01488	$\bar{2}.1727$	0.00292	0.01454
80	0.01243	$\bar{2}.0944$	0.00283	0.01243
100	0.00971	$\bar{3}.9872$	0.00268	0.00971

$$\log \eta_T = -2.6512 + \frac{88.85}{T-233.84}$$

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(2) C. V. Raman, *Nature*, **111** (1923), 532.

(3) E. N. Da C. Andrade, *Nature*, **125** (1930), 309.

(4) B. Prasad, *Phil. Mag.*, **16** (1933), 263.

Fortunately the viscosity measurements of molten naphthalene at different temperatures were done by Kurnakow(5) and by Scheuer,(6) from their data the values at regular intervals of temperature being recalculated by Bingham and Spooner,(7) and those of diphenyl by these authors.(7) Taking logarithms of the viscosities against $1/T$ of each substance, we find that in the former case the points with our value at 25°C. strictly lie on a straight line, and in the latter case on a curve on which our value at 25°C. also lies as seen from the figure. Tables 2 and 3 show how the calculated values by the formulae and the observed compare numerically.

As to the viscosity of molten inorganic salts, there have been known, except the salts above cited, the measurements by Lorenz(8) on KCl, KBr, NaCl, and NaBr. Among them KCl only is available for the present purpose. So that, in the following we will consider the solutional viscosity of KCl. For the viscosity of the molten KCl, formula (1) is valid:

$$\log \eta_T = -3.4530 + 1705\frac{1}{T},$$

and the calculated values are in good agreement with the observed as readily seen from Table 4.

Table 4.

Potassium chloride. Melting point: 768°C.

t°C.	$\eta_{\text{obs.}}$	$\log \eta$	$1/T$	$\eta_{\text{calc.}}$
790	0.0142	$\bar{2}.1523$	0.000941	0.0142
835	0.0121	$\bar{2}.0828$	0.000907	0.0124
920	0.0099	$\bar{3}.9956$	0.000838	0.0095
1035	0.0071	$\bar{3}.8513$	0.000765	0.0071

By the use of the equation, the extrapolated values at 25° and 18°C. are estimated thus:

$$\eta_{25} = 1.89 \times 10^2 \qquad \text{and} \qquad \eta_{18} = 2.55 \times 10^2,$$

respectively. These show too much higher values than would be expected from the consideration just made on organic non-electrolytes. And if we take the ratios at respective temperatures, they are respectively

$$\text{ratio at } 25^\circ = 2.16 \times 10^4 \quad \text{and} \quad \text{ratio at } 18^\circ = 2.53 \times 10^4.$$

The recent conception on the physics of solids(9) shall be introduced here.

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(5) N. S. Kurnakow, *Z anorg. allg. Chem.*, **135** (1924), 84, 89.

(6) O. Scheuer, *Z. physik. Chem.*, **72** (1910), 553.

(7) E. C. Bingham and L. W. Spooner, *Physics*, **4** (1933), 393, 394.

(8) R. Lorenz, *Z. physik. Chem.*, **79** (1912), 65.

(9) "Handbuch der Physik", XXIV (Berlin, 1933), 803; F. Zwicky, *Rev. Mod. Physics*, **6** (1934), 193; A. Goetz, *Phys. Rev.*, **45** (1934), 138.

The existence of a crystalline state attributes mainly to the cooperative actions between many elementary particles such as atoms, ions, etc. These interactions extend over distances which are enormously greater than usual action radii of elementary particles, and the cooperative actions, in general, necessitate the introduction of a secondary structure of crystals, or without such conception real crystals which display structure sensitive properties such as the elastic limit, the breaking strength, the thermal and the electrical conductivity, etc. cannot satisfactorily be described by the theory of ideal lattices. By this theory the energetic aspects of the ideal states are already roughly realized in a statistical manner in the melt. It follows that the heat of fusion of the crystal is roughly the same as the gain in energy by a variation leading from the ideal state to the secondary structure, and that an aggregation of groups of approximately equal size which is essential for the formation of a solid crystal takes place during an interval of temperature of a few degrees above the melting point, and that if their formation is prevented, undercooling results down to a temperature at which the group formation is more probable. As regards the dimension of the secondary structure, the theory tells us that a secondary structure superposes on top of the ordinary primary structure, showing perfect regularity also, or in other words the surface density of the plane of it is the same as the planes of free ionic lattices, and its dimension is for most of the crystals found in the region between 100 and 10000 Å, e.g. the plane of a secondary structure of NaCl is divided into 35 primary lattice spacings of cubic block of equal size or in a block of a secondary structure there are 2×10^4 ionic pairs in round number.

Now, the extrapolation of the Raman-Andrade formula far below the melting point as above treated simply means a supposed continuation of the molten state as in like manner as above the melting point, indifferent to the actual phenomenon whether or not the formation of the secondary structure occurs. But, so far as the formula is valid at or about the melting point, its employment far below the melting point should be based on the assumption that although the secondary structure already forms yet the solidification does not appear even at that temperature. This assumption is allowable also from the viscosity theory of simple liquids recently developed by Andrade,(10) who assumes that when a solid is melted it still retains in the liquid form sufficient of its crystalline character for the atoms or the molecules to possess a frequency of atomic or molecular vibration which is practically the same as that of the solid

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(10) E. N. Da C. Andrade, *Nature*, **128** (1931), 835; *Phil. Mag.*, **17** (1934), 497.

form at the melting point, and derives a theoretical equation $\eta = \frac{4}{3}\frac{m\nu}{\sigma}$, m being the mass of an atom or a molecule, σ the average distance between the centers of atoms or molecules, and ν the frequency of vibration nearly concordant with the Lindemann formula.(11) Thus, for KCl $\nu(\text{obs.}) = 4.74 \times 10^{12}$, $m = \frac{74.56}{6.06 \times 10^{23}}$, $\sigma = \left(\frac{74.56}{1.97 \times 6.06 \times 10^{23}}\right)^{1/3}$ and, therefore, the calculated viscosity at the melting point $\eta = 0.0196$, which gives a fair agreement with the extrapolated value 0.0153 from the exponential formula now in question.

From the above considerations together with the fact that the crystal structure of KCl is quite similar to that of NaCl, the ratios above obtained 2.16×10^4 and 2.53×10^4 at 25° and 18°C. respectively may undoubtedly correspond to the number of ionic pairs in a block of the secondary structure, taking for granted that the solutional viscosity of this salt is the viscosity due to its ionic pair.

Hence the following conclusion may be drawn: The solutional viscosity derived from the Ishikawa formula is the viscosity due to the block of a secondary structure in accordance with the secondary structure theory on crystals when the substance is an organic non-electrolyte, or is the viscosity due to the ionic pair when the substance is an ionic salt.

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(11) F. A. Lindemann, *Physik. Z.*, **11** (1910), 609.