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Intermolecular Free Lengths in the Liquid State

III. Viscosity

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Many empirical and theoretical relations have been given for the viscosity of liquid systems (Partington,[1] Doolittle[2]). Much attention has thus been paid to the free volume, which is an essential feature in studying viscosity. However, we have found it better to relate viscosity to another similar property, namely the intermolecular free length. By employing this concept it is possible to formulate a simple equation that describes the viscosity of liquid systems as a function of this free length and of the molecular weight.

ABSOLUTE FREE LENGTHS AND FREE FLUIDITY LENGTHS

In studying compressibility[3] and surface tension[4] it was found suitable to use the concept of free length between the surfaces of the molecules $L = 2(V_T - V_0)/Y_0$. V_T and V_0 are the molar volumes at T°K and 0°K. Y_0 is the molar surface of one mole. L is called the absolute free length or often only the free length.

In studying physical properties that depend on molecular motions in a direction tangential to the surfaces of the molecules, *e.g.* viscosity and diffusion, the free length should be defined as

$$L_\Phi = 2(V_T - V_{\Phi_0})/Y \tag{1}$$

where L_Φ is called the free fluidity length as distinguished from the absolute free length. The molecular surface of one mole is $Y = (36\pi N V_{\Phi_0}^{\;2})^{\frac{1}{3}}$. V_{Φ_0} is the molar zero fluidity volume; it is a fundamental property which will therefore be discussed further.

The molar zero fluidity volume can be obtained from Friend's equation, which gives the change of fluidity Φ with density[5]

$$\Phi = \frac{1}{\eta} = k_1(V_T^{\frac{8}{3}} - V_{\Phi_0}^{\;\frac{8}{3}}) \tag{2}$$

where k_1 is a constant characteristic of each substance. In order to find the molar zero fluidity volume of a substance from this equation it is necessary to know the fluidities and densities at two different temperatures. Then the constant k_1 can be eliminated. To

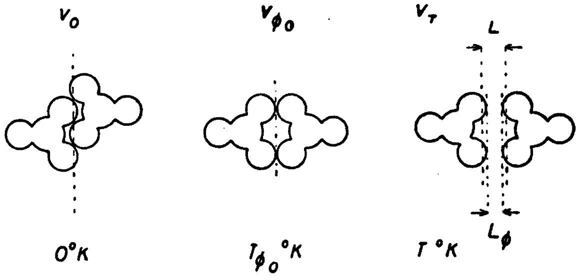

Fig. 1. The difference between the absolute free length L *and the free fluidity length* L_Φ *for polyatomic molecules. At 0°K the molecules have their closest packing possible and the molar volume is* V_0. V_{Φ_0} *is a theoretical molar volume at a temperature* T_{Φ_0} *when the molecules have just sufficient space to move tangentially against each others.* V_T *is the molar volume at* T°K.

obtain sufficient accuracy in V_{Φ_0} it is desirable to have fluidities and densities determined on the same sample and at exactly the same temperature.

The molar zero fluidity volume is a characteristic property of each substance. It is the molar volume of the supercooled liquid at the temperature of zero fluidity based on the assumption that the liquid does not solidify but continues to conform to equation (2). It should be observed that the zero fluidity volume is always smaller than the volume at the melting point, which is evident from the fact that it is possible to supercool a liquid.

The difference between the absolute free length and the free fluidity length is illustrated in Fig. 1. Some examples of values are given in Table 1. It should be observed that the definition of the free fluidity length involves an approximation in the same manner as the definition of the absolute free length. The free lengths will therefore be somewhat larger than the shortest possible perpendicular distance between the surfaces of the molecules. Both the absolute free length and the free fluidity length most closely resemble the free path in the liquid. Their error varies with the temperature and thus the definition according to (1) should be used only within limited temperature ranges. For a further discussion of the limitations see Jacobson [3].

FLUIDITIES OF LIQUID SYSTEMS

In a preliminary report [6] the following relation was given between the fluidity Φ and the free fluidity length L_Φ in a liquid

$$\Phi = KL_\Phi^p \tag{3}$$

At 20° C the values for the constants are $p = 1.27$ and $\log K = 13.104$ for cgs units. Equation (3) holds with rather good accuracy for most organic liquids. However, in some cases errors of 30 to 40 per cent for L_Φ are obtained, especially for certain halides. Systematic attempts have therefore been made to find a more universal relation.

Through empirical studies we have obtained the following equation

$$\Phi + c = kL_\Phi M^{-\frac{1}{2}} \tag{4}$$

Table 1. Examples of values for molar volumes at different states of some liquids and their free lengths.

Substance	Molar volume at absolut zero V_0	Molar zero fluidity volume V_{Φ_0}	Molar volume at melting point V_m	Molar volume at 20° C V_T	Fluidity Φ rhe	Absolute free length at 20° C L, 10^{-8}cm	Free fluidity length at 20°C, L_Φ 10^{-8} cm		Per cent deviation
							Calc. from definition Eq. (1)	Calc. from Φ Eq. (4)	
Pentane	86.7	92.1	96.6	115.2	417.5	0.713	0.555	0.537	− 3.3
Hexane	100.8	110.2	114.9	130.7	306.9	0.676	0.437	0.437	0
Cyclohexane	86.2	100.5	106.5	108.1	102.4	0.550	0.172	0.158	− 8.1
Benzene	71.3	79.6	87.5	88.9	153.0	0.501	0.246	0.218	−11.4
Aniline	77.4	89.0	89.4	91.1	21.8	0.370	0.052	0.053	+ 2.7
Pyridine	66.4	74.8	76.4	80.5	103.3	0.422	0.158	0.155	− 1.9
Iodobenzene	94.1	104.4	106.3	111.4	61.3	0.410	0.155	0.161	+ 3.9
Carbon tetrachloride	77.4	87.6	92.5	96.5	103.2	0.516	0.221	0.215	− 2.7
Ethyl acetate	76.4	85.0	87.4	97.8	220.0	0.583	0.325	0.323	− 0.6
Ethylether	77.2	82.9	87.0	103.9	408.5	0.722	0.541	0.533	− 1.5

where M is the molecular weight, $c = 15.8$ and $k = 6.85 \cdot 10^{-11}$ for cgs units. Equation (4) has been tested for 81 organic non-associated liquids of different types. In Fig. 2 the fluidities have been plotted as a function of the term $L_\Phi M^{-\frac{1}{2}}$. The necessary data have been taken from Timmermann[7] and Landolt Börnstein Tabellen. The equation holds with an average accuracy of about 5 per cent for L_Φ. For various reasons it is difficult to determine the degree of accuracy exactly. Thus, in several cases it has been impossible to obtain values for density and viscosity that have been measured on the same sample and at exactly the same temperature, as is desireable in calculating the zero fluidity volume. Furthermore we have abandoned the procedure of taking into account the form factors of the molecules. Since the molecules are not spherical the actual surface of the molecules is somewhat larger than that calculated and used in the definition (1). The actual free length is then smaller than that calculated from (1). This is apparent in the fact that the error is greater for compounds with asymmetric molecules *e.g.* benzene (see Table 1).

We have tried to use the factor $M^{-\frac{1}{3}}$ instead of $M^{-\frac{1}{2}}$ in equation (4). The results, however, are slightly in favour of the equation with $M^{-\frac{1}{2}}$.

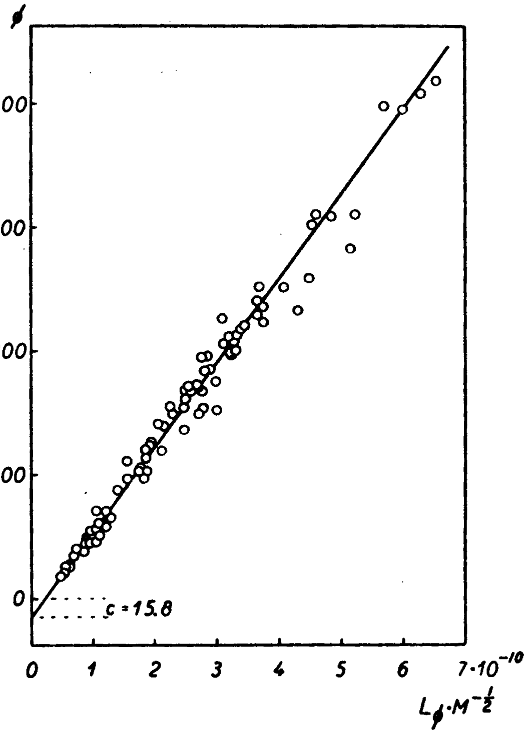

Fig. 2. Fluidities (Φ) *for 81 organic compounds plotted as a function of the factor* $L_\phi M^{-\frac{1}{2}}$ *at 20° C.*

The fluidity of associated liquids has also been investigated. However, equation (4) is not suitable for calculating association factors. This depends on the fact that with increasing association both the free length and the molecular weight increase and therefore the fluidity changes only slightly despite variation in the association factor. Also, Friend's equation (2) is not always valid for associated compounds and, it is difficult, therefore, to obtain accurate values for zero fluidity volumes.

We have also tested the given relation (4) on 20 liquid mixtures of the type benzene — chlorobenzene, benzene — cyclohexane, heptane — bromobenzene, heptane — α-bromonaphthalene and 2,2,4-trimethylpentane — ethyl acetate. The viscosities were determined with an Ostwald viscosimeter giving an accuracy of better than 1 per cent. The free lengths for the mixtures are obtained from a definition I(6)^3 corresponding to (1). In this it is assumed that the zero fluidity volumes are additive which, however, should not always be exactly the case. The molecular weight for a mixture is $M_{12} = m_1M_1 + m_2M_2$ where m_1 and m_2 are the molar fractions of the two liquids with the molecular weights M_1 and M_2 respectively.

For all series of liquid mixtures the fluidities have been a linear function of $L_\phi M^{-\frac{1}{2}}$. The average error in L_ϕ has been 2.4 per cent for the 20 mixtures. In Fig. 3 the results are given for mixtures of heptane-α-bromonaphthalene. Good results are also obtained in

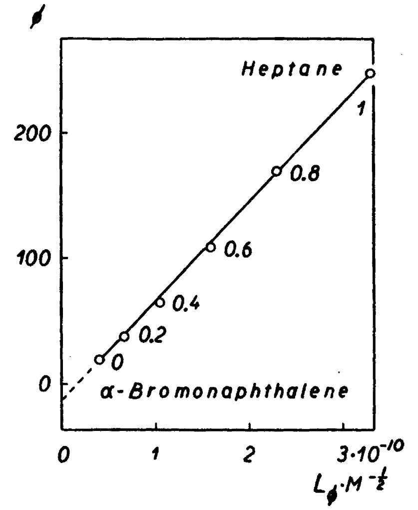

Fig. 3. Fluidities (Φ) at 20° C as a function of the factor $L_\Phi M^{-\frac{1}{2}}$ *for mixtures of heptane and α-bromonaphthalene at various volume fractions of heptane.*

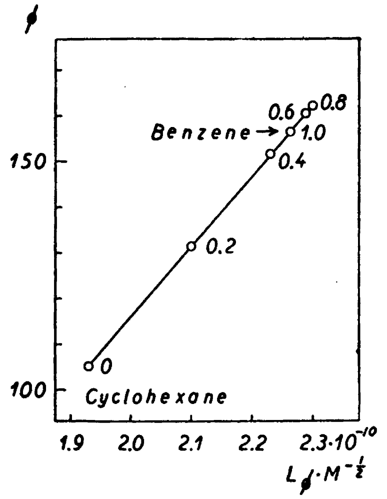

Fig. 4. Fluidities (Φ) at 20° C as a function of the factor $L_\Phi M^{-\frac{1}{2}}$ *for mixtures of benzene and cyclohexane at various volume fractions of benzene.*

cases in which the fluidities for some concentrations of the mixture are higher than the fluidities for the two pure liquids. Such systems are for instance 2,2,4-trimethylpentane-ethyl acetate and benzene-cyclohexane. For the latter system the results are given in Fig. 4.

Equation (4) is also approximately valid for the dependence of fluidity on temperature within moderate limits *e.g.* 0 to 60° C. Errors amounting to 3 per cent arise from the fact that L_Φ has such a large systematic error within the limits mentioned. This can be surmounted by selecting new values for the constants k and c for each compound. In this manner errors that depend on inaccurate values for the zero fluidity volumes are also eliminated.

DISCUSSION

The general applicability of the given relation as demonstrated here, has been achieved through the introduction of the concept of free fluidity length. This concept should also be of value in studying various other physical properties of liquids. Thus, for instance, preliminary investigations have shown that the diffusion constant of an organic compound is a linear function of the free fluidity lengths in the different diffusion media.

One disadvantage of equation (4) is the necessity of the constant c, due to inaccuracies in Friend's equation (2). To overcome this disadvantage a new method must be sought for obtaining the correct zero fluidity point

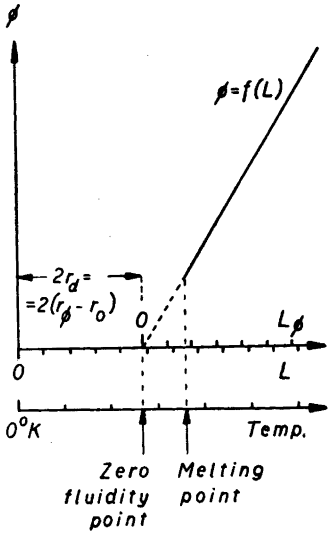

Fig. 5. The the difference between the apparent molecular radius at zero fluidity (r_Φ) *and the radius at absolute zero* (r_0) *can be obtained by extrapolating the absolute free length* (L) *to zero fluidity*

values. We are of the opinion that these could most conveniently be attained by extrapolating the absolute free length L to zero fluidity as indicated in Fig. 5. The intersection of the curve with the absolute free length axis gives the difference r_d between the molecular radius at absolute zero r_0 and the apparent molecular radius at zero fluidity r_Φ. Thus

$$2r_d = 2(r_\Phi - r_0) = L - L_\Phi \tag{5}$$

The apparent molecular radius at zero fluidity r_Φ should be a characteristic property of each compound, and is always larger than the molecular radius at absolute zero for polyatomic molecules. The difference r_d depends on the "roughness" of the molecular surface. The advantage in this procedure of using r_Φ instead of V_{Φ_0} lies in the fact that fluidity is an intermolecular phenomenon and should be related in a simpler way to the free lengths than to any function of the molar volumes. However, before this suggested method could be used to treat the fluidity problem the exact dependence of the free length on temperature must be known; this problem is not as yet satisfactorily solved.

SUMMARY

An empirical relation, $\Phi + c = kL_\Phi M^{-\frac{1}{2}}$ has been shown between the fluidity Φ, the intermolecular free fluidity lenght L_Φ and the molecular weight M of liquids. The relation has been tested on 81 non-associated organic liquids and it holds with an average accuracy of about 5 per cent for L_Φ, using the values

for the constants $c = 15.8$ and $k = 6.85 \cdot 10^{-11}$. The corresponding accuracy for 20 mixtures of organic liquids is 2.4 per cent. The relation is also approximately valid for the dependence of fluidity upon temperature. The concept of free fluidity length should also be of value in studying other physical properties of liquids.

REFERENCES

1. Partington, J. R. *An Advanced Treatise on Physical Chemistry* **2**, Longmans, Green and Co. London 1951.
2. Doolittle, A. K. in Alexander: *Colloid Chemistry*, Reinhold Publ. Corp. New York. **7** (1950) 149.
3. Jacobson, B. *Acta Chem. Scand.* **6** (1952) 1485.
4. Jacobson, N., and Heedman, P. A. *Acta Chem. Scand.* **7** (1953) 51.
5. Friend, J. N. *Trans. Faraday Soc.* **3** (1938) 813.
6. Jacobson, B. *Acta Chem. Scand.* **5** (1951) 1214.
7. Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds*, Elsevier Publ. Co. Inc. Amsterdam 1950.

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