

ON THE RELATIONSHIP BETWEEN FLUIDITY OF LIQUIDS AND TEMPERATURE*

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Starting from Batschinski's equation, an equation relating fluidity (ϕ) with the coefficient of thermal expansion (α) of a liquid has been derived which gives a linear plot for ϕ against $e^{\alpha T}$. This relationship has been verified in the case of as many as 60 different liquids. From the intercept of the graph on the $e^{\alpha T}$ -axis, dimensions of molecules have been calculated and compared with the values obtained from other methods. Members of the same homologous series are found to yield the same intercept in each case as has been verified with five different homologous series.

Recently Eyring (*J. Chem. Phys.*, 1936, **4**, 283; Hirschfelder, Stevenson and Eyring, *ibid.*, 1937, **5**, 896) has proposed a picture of the liquid state in which he assumes liquids to be composed of molecules and some free space divided into smaller units of an enormous number of holes, mixed together and distributed at random. From this conception of holes in liquids he has been able to deduce an equation of state for liquids similar in form to Van der Waals' equation of state, the Hildebrand and Trouton rule for vapour pressure, the entropy change on melting, the temperature coefficient of viscosity, etc. The flow of a liquid has been regarded by him as due to jump of molecules from one hole into another by the action of some shearing stress and is thus dependent on the number of such holes in a given mass of liquid. This free volume in liquids has been related to the temperature and total volume of the liquid (Eyring and Hirschfelder, *J. Phys. Chem.*, 1937, **41**, 249; Hirschfelder, *J. Chem. Ed.*, 1939, **16**, 540) and a method for its experimental determination evolved based upon the velocity of sound in the liquid medium (Kincaid and Eyring, *J. Chem. Phys.*, 1938, **6**, 620).

The first empirical relationship between fluidity (ϕ) and free volume ($V - V_s$) as proposed by Batschinski (*Z. physikal. Chem.*, 1913, **84**, 643) in the equation

$$\phi = C. (V - V_s) \quad \dots (i)$$

assumes a linear relationship between the two, C being a constant and V and V_s , the molecular volumes of the liquid and solid states respectively, the latter being regarded as possessing little or no free volume.

In the present paper an attempt has been made to correlate fluidity (ϕ) with thermal expansion and free volume of the liquid. The relation thus obtained has been experimentally verified.

Let α be the coefficient of thermal expansion of a liquid. Then by definition of α we have,

$$\alpha = \frac{1}{V} \left(\frac{dV}{dt} \right)_P = \left(\frac{d \ln V}{dt} \right)_P \quad (ii)$$

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where V , P and T refer to the molecular volume, pressure and the temperature in the absolute scale respectively of the liquid

Assuming α to remain constant for small ranges of temperatures and assuming also that the volume of a liquid changes continuously with temperature in accordance with its own coefficient of expansion, we get by integration

$$V = A \cdot e^{\alpha T} \quad \dots (iii)$$

where A is the integration constant

Let us assume that there is a temperature T_s in the absolute scale, where the free space in the liquid vanishes altogether. By carrying out the integration between T_s and any higher temperature T for which the volumes of the liquid are V_s and V respectively, we get

$$V = V_s \cdot e^{\alpha(T - T_s)} \quad \dots (iv)$$

whence by equation (i)

$$\phi = C \cdot (V - V_s) = C V_s \{ e^{\alpha(T - T_s)} - 1 \} \quad \dots (v)$$

$$\text{or,} \quad e^{\alpha T_s} + \frac{e^{\alpha T_s}}{C \cdot V_s} \phi = e^{\alpha T}$$

$$\text{or,} \quad a + b \cdot \phi = e^{\alpha T} \quad \dots (vi)$$

$$\text{where} \quad a = e^{\alpha T_s} \quad \text{and} \quad b = \frac{e^{\alpha T_s}}{C \cdot V_s}$$

This gives a linear relationship between ϕ and $e^{\alpha T}$. It should be mentioned in this connection that in the above derivation the constancy of α implicitly assumes a constancy of the molecular species which does not change with change of temperature. As to the temperature T_s , the implication is that at this point the molecules are at their closest approach so that the free volume is the least at this point and the translatory energy is at its minimum.

EXPERIMENTAL

About sixty different liquids were examined for their viscosity and coefficient of expansion. More than a dozen (13) cases were locally examined, while the data for the rest were taken from Landolt-Bornstein Tabellen and from the data published under Project No. 44 of the American Petroleum Institute under the National Bureau of Standards, U.S.A

The liquids locally investigated were of B.D.H. Analytical quality, distilled twice or thrice till the constancy of the boiling point at their respective standard values was realised. Viscosity was measured relatively to water with the help of an Ostwald viscometer whose average time of flow for water at 30° was observed to be about 30 seconds. These relative values were then converted into centipoise from the absolute viscosity of water as given in the Landolt-Bornstein Tabellen. Reciprocals of these values yielded their fluidities.

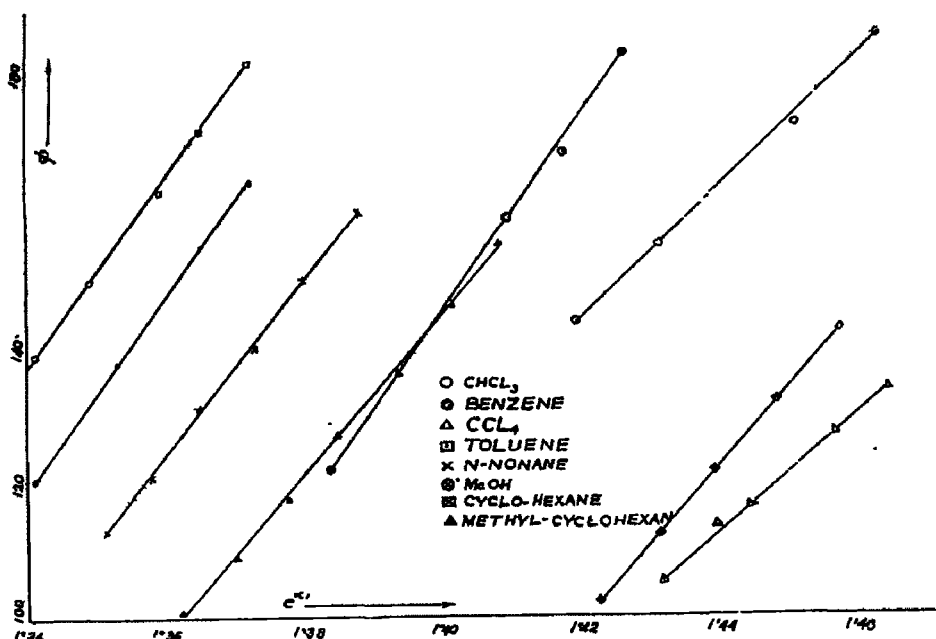
The coefficients of expansion were determined between 30° and 35° by determination of their densities at these temperatures. The coefficient of expansion for water was ascertained from its densities at 30° and 32°.

The equation (vi) has been verified within a temperature range of 0° to 40° with an average value of σ in the range assumed to be constant. For those liquids whose data were taken from the literature cited above, the temperature range has been extended or curtailed according to the availability of the relevant data

DISCUSSION

The Linear Relationship.—The plots of ϕ against a^{e^T} are straight lines as expected from equation (vi) with an intercept on the e^{e^T} -axis ($=a=e^{e^{T_0}}$). Some of the cases worked out here have been graphically presented in Fig. 1. From these graphs the values of T_0 were calculated and they were in all cases found to be lower than the

FIG. 1

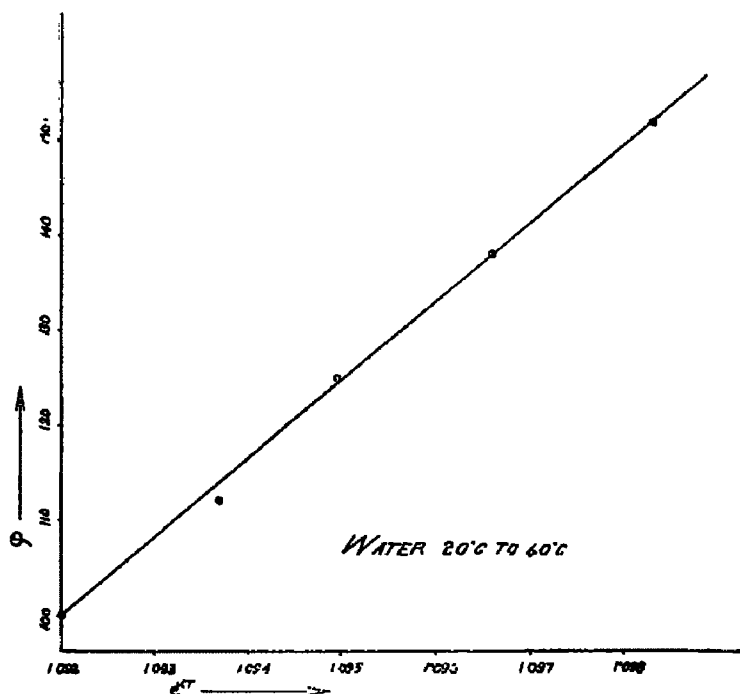


corresponding melting points under atmospheric pressure, excepting in the case of water and acetone, where they were found to be much above their melting temperatures. This fact is significant because the volume V_0 of the liquid at temperature T_0 has been assumed to contain no holes and hence the densities at this temperature ought to be maximum. In the case of water, it is well known that the maximum density is reached at 4° under atmospheric pressure, while extrapolation from the present curve for water gives a value of T_0 equal to 14°. This discrepancy might be attributed to the fact that the extrapolation has in this case been actually performed on the data for coefficient of viscosity observed between 20° and 40°. This temperature of maximum density should be best compared with that obtained by extrapolation of the density-temperature curve

for water, specially of the region between 20° and 40° . Such an extrapolation has been actually carried out on the density-temperature curve given in the Landolt-Bornstein Tabellen (Eg. IIIa, 53) which yielded a value of 13° as the temperature of maximum density. The agreement is therefore satisfactory.

Another important feature to be noticed in the case of water is that although water is known to be a highly associated liquid, still it gives a linear relationship (vide Fig. 2) according to equation (vi). This evidently suggests that within a range of 20° to 40° its molecular species does not alter appreciably. Methyl and ethyl alcohols have also been

FIG. 2



found to give straight lines according to this equation within a range of -30° to 25° and 0° to 30° respectively; they are also known to be highly associated liquids. The case of mercury is interesting from this point of view because liquid mercury is known to be composed of monatomic particles and as such they are much simpler than those of most of the liquids known. It is interesting to notice that mercury maintains a strictly linear relationship throughout the major temperature range over which it remains in the liquid state under atmospheric pressure. The T_0 calculated for mercury comes out to be 18°K ($= -255^{\circ}\text{C}$) which is much below its melting point (-39°).

Significance of V_0 .—As already referred to, V_0 is the volume which the liquid will occupy at the hypothetical temperature T_0 , where its fluidity totally disappears. On the assumption of a proportionality between ϕ and the free volume in a liquid, according to Batschinski's equation, the volume V_0 at T_0 should not have any free volume and the molecules will be packed together in the closest possible orientation. Even at this volume the

free space will not entirely disappear because at the closest packing of spherical molecules there will be gaps in between, though such space may be very small.

It will not be irrelevant to refer here to the superior advantages for using this V_s for calculation of molecular dimensions over the method based upon the law of rectilinear diameter of Callitot and Mathius (cf. Moelwyn Hughes, *loc. cit.*, p. 30) which rests upon an assumed validity of extrapolation of the mean density over as large a temperature range as from 0°K to the critical temperature of the liquid. The values of molecular radii calculated from V_s have been given in Table I and compared with those obtained from viscosity of gases and also from Van der Waals' 'b'.

TABLE I

Liquid,	† r calculated from		
	Eqn. (v) ₁ ,	Viscosity.	'b'.
Mercury	1.778 \AA	1.80 \AA	1.79 \AA
Acetone	1.70	1.90	—
Benzene	3.098	2.95	1.07
CCl ₄	2.22	2.38*	1.096
n-Pentane	2.33	2.25	1.14
Ether	3.40	3.10	1.10
Chloroform	2.13	2.14	—

*The value of r for CCl₄ in this case has been taken from polarisation data (Moelwyn Hughes, "Introduction to Physical Chemistry", 1940, p. 105).

† r 's denote the molecular radii calculated on the assumption of spherical molecules and r 's in column 3 signify the radii calculated from the viscosity of these substances in the gaseous state and taken from Landolt-Bornstein Tabellen (Eg III 5 Auf., p. 105)

Obviously the values of r calculated from V_s are in general larger than those obtained from Van der Waals' 'b', but show satisfactory agreement so far as the data from viscosity of gases are concerned.

Encouraged by these results the chain lengths of some normal paraffins were also calculated by first ascertaining their molecular volumes from V_s and dividing this by 21 sq. \AA ., the cross-section of these hydrocarbon chains, as determined by the surface film method (vide Glasstone, "Recent Advances in Physical Chemistry", 1933, 2nd Edition, p. 332). The area of cross-section as measured by the film method has been preferred in this case because in a surface film under limiting conditions the molecules are assumed to be in closest packing, as has been pictured in the conception of V_s . The values appear in Table II below and have been compared with those calculated with the help Mark's formula ("Physical Chemistry of High Polymeric Systems", Part III, 1940, p. 141): $l = 1.26n + 1.83$, where n denotes the number of carbon atoms in the chain and l , the chain length in \AA .

TABLE II

Hydrocarbon.	l calc. from Eqn (vi).	l calc. by Mark's Eqn.	Hydrocarbon	l calc. from Eqn. (vi).	l calc by Mark's Eqn.
<i>n</i> -Pentane	7.6 Å	8.13 Å	<i>n</i> -Undecane	15.51 Å	15.69 Å
<i>n</i> -Hexane	8.98	9.39	<i>n</i> -Dodecane	16.87	16.95
<i>n</i> -Heptane	10.25	10.65	<i>n</i> -Tridecane	18.00	18.63
<i>n</i> -Octane	11.7	11.9	<i>n</i> -Tetradecane	19.62	19.47
<i>n</i> -Nonane	12.8	13.17	<i>n</i> -Pentadecane	20.9	20.73
<i>n</i> -Decane	14.08	14.43			

The values of l are in excellent agreement. The equation (vi) can therefore be regarded as a suitable method for computing the dimensions of molecules. The only experimental data that we require for this purpose comprise viscosity and density at least at two different temperatures from which by linear extrapolation the value of V_0^* is obtained. The assumption of an approximate constancy of the values of α , on which the present calculations are all based, appears to be justified by the close agreement of the data presented in the above tables.

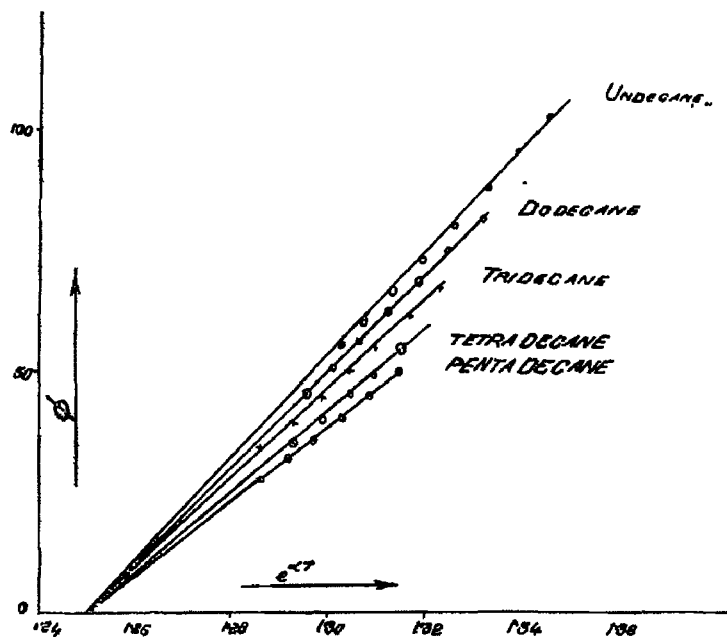
Significance of T_ .*—The concept of T_* , as already referred to, becomes also of an hypothetical nature where the liquid loses its free space as envisaged by the viscous properties of liquids. If V_* be regarded as the volume of the solid obtained from the liquid state in which the molecules are in the closest possible packing, T_* may be looked upon as analogous to the critical temperature between the solid and the liquid states, as their specific volumes at this temperature are equal. It is, however, highly improbable that there would be any relationship between T_* and T_c , the gas-liquid critical temperature, because the constancy of α is not maintained near the critical temperature beyond which the value of α is known to be as high as $1/273.16$ which is the accepted value of α for gases. Extrapolation of T_* from T_c does not therefore appear to be justified.

An interesting feature in the $\phi - e^{aT}$ plots is that the straight lines obtained for the members of the same homologous series have been found to intersect the e^{aT} -axis at approximately the same point. Five different homologous series have been studied in this connection, two of which have been shown in Figs. 3 and 4. The values of the intercepts are presented in Table III.

TABLE III

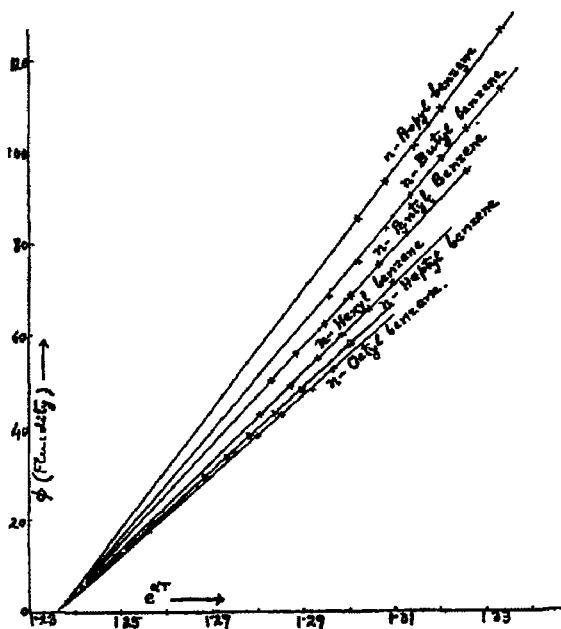
Homologous series.	e^{aT} .	No. of C atoms where T_* becomes const.
Normal paraffins	1.250	> 21
<i>cyclo</i> Pentanes	1.252	21
<i>cyclo</i> Hexanes	1.252	19
Benzene homologues	1.236	19
Normal mercaptans	1.262	—

FIG. 3.



The three aliphatic homologous series viz., *n*-paraffins, cyclopentanes and cyclohexane homologues have identical values for their intercepts, while that of benzene homologues have slightly lower and the normal alkyl mercaptans, a slightly higher value.

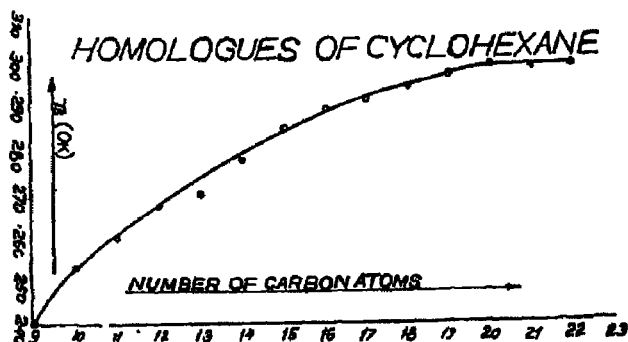
FIG. 4.



These observations are interesting in as much as they indicate constancy of $e^{\alpha T}$ for a homologous series which again indicates that αT , should be constant. The values of T_s

have been calculated for the different series and have been observed to change with the number of carbon atoms in the chain in the typical manner as shown for the different series studied herein (Fig. 5). The number of carbon atoms at which the curve shows a tendency to reach a constant value have been shown in column 3 of Table III. The constancy of the product αT_s and the manner of variation of T_s with the number of carbon atoms in the chain are suggestive that T_s might be a fundamental and charac-

FIG. 5



teristic quantity for a definite homologous series. Further work is necessary for elucidation of this aspect which is in progress and will be reported in a future communication.

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