

285. *The Viscosities of chemically related Liquids, and their Dependence on Molecular Weight and Molecular Volume. Part II.*

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It is suggested that any equation representing the variation of viscosity of liquids must contain fundamental terms representing temperature, molecular weight, and molecular volume. An equation is derived for chemically related series incorporating these essential terms, and the generality of its application is ascribed to similarity of cohesive pressures in such series. Fluorobenzene is shown to be a normal member of the halogenobenzenes when all factors operative are taken into account. Fused salts give some indication of obeying a similar relation, but lack of reliable parachor data prevents definite conclusions being drawn as to the influence of the molecular volume.

THE most satisfactory relation expressing the connexion between temperature and viscosity for normal liquids is that due to Andrade (*Nature*, 1930, **125**, 309, 582), *i.e.*,

$$\log \eta = \beta/T - \alpha \dots \dots \dots (1)$$

which was later extended (*Phil. Mag.*, 1934, **17**, 497, 698). Iyer (*Indian J. Physics*, 1930,

5, 371) has shown the applicability of this relation to 87 liquids of diverse chemical constitution, and Prasad (*Phil. Mag.*, 1933, **16**, 263) has also found good agreement in the case of a few fused salts.

Lewis (J., 1938, 1063), from a consideration of Chapman's equation for gaseous viscosity, derived the above equation in the form

$$\log \eta = (A \log M - B)/T - \frac{2}{3} \log CP \dots \dots \dots (2)$$

where  $A$ ,  $B$ , and  $C$  are constants and  $P$  is the parachor and  $M$  the molecular weight of the substance, and showed it to be generally applicable to all members of an homologous series. Equation (2) suggests that even in the liquid state the molecular weight and molecular volume exercise a profound influence on the viscosity and should be introduced into any equation intended to represent the variation of viscosity with other physicochemical constants. Hitherto, attempts to determine relations involving molar volume have been impeded by lack of precise dimensional data, but the parachors, being valuable indications of the relative magnitudes of molecules, may be utilised in attacking these complex problems.

Silverman and Roseveare (*J. Amer. Chem. Soc.*, 1932, **54**, 4460) combined Macleod's equation with that of Batschinski (*Z. physikal. Chem.*, 1913, **84**, 643) and derived the relation  $\gamma^{-\frac{1}{2}} = A/\eta + B$ , which is readily convertible into a parachor equation. A somewhat similar expression,  $\log(\log \eta) = 1.2\gamma^{\frac{1}{2}} - 2.9$  has been shown by Buehler (*J. Physical Chem.*, 1938, **42**, 1207) to be generally valid.

An attempt to derive an equation applicable to a series such as  $\text{CH}_3\text{F}$ ,  $\text{CH}_3\text{Cl}$ , etc., previously discussed (J., 1938, 262), led to an expression very similar to (2). For any one series, the plot of  $(\log M)/T$  against  $\log \eta$  gave a series of parallel lines of slope  $A$ , as shown in Table I, which was constructed from the data of Meyer and Mylius (*Z. physikal. Chem.*, 1920, **95**, 349) for the four halogenobenzenes; on the other hand,  $1/T$  plotted against  $\log \eta$  (equation 1) gives four lines of widely different slope. Table I shows the equations used, and the agreement between the experimental and the calculated values of  $\eta$  justifies the assumption of a constant slope,  $A = 231.7$ .

TABLE I.

| $T^\circ, \text{K.}$  | $-\log \eta.$ | $10^3 \frac{(\log M)}{T}$ | $10^6 \eta.$ |        | $T^\circ, \text{K.}$   | $-\log \eta.$ | $10^3 \frac{(\log M)}{T}$ | $10^6 \eta.$ |        |
|---|---------------|---------------------------|--------------|--------|--|---------------|---------------------------|--------------|--------|
|   |               |                           | Found.       | Calc.  |  |               |                           | Found.       | Calc.  |
| <i>Fluorobenzene</i> : $\log \eta = (231.7 \log M)/T - 3.8110.$ |               |                           |              |        | <i>Bromobenzene</i> : $\log \eta = (231.7 \log M)/T - 3.6804.$ |               |                           |              |        |
| 282.3   | 2.1891        | 7.025                     | 6,470        | 6,561  | 273.1  | 1.8033        | 8.069                     | 15,730       | 15,440 |
| 288.9   | 2.2111        | 6.863                     | 6,150        | 6,012  | 278.9  | 1.8401        | 7.874                     | 14,450       | 13,920 |
| 292.9   | 2.2388        | 6.770                     | 5,770        | 5,728  | 283.1  | 1.8754        | 7.756                     | 13,320       | 13,080 |
| 302.1   | 2.2890        | 6.564                     | 5,140        | 5,129  | 291.2  | 1.9314        | 7.541                     | 11,710       | 11,700 |
| 306.2   | 2.3054        | 6.476                     | 4,950        | 4,900  | 301.3  | 1.9901        | 7.288                     | 10,230       | 10,200 |
| 311.1   | 2.3298        | 6.374                     | 4,680        | 4,634  | 316.6  | 2.0747        | 6.936                     | 8,420        | 8,445  |
| 317.0   | 2.3585        | 6.255                     | 4,380        | 4,355  | 334.4  | 2.1586        | 6.567                     | 6,940        | 6,944  |
| 323.2   | 2.3851        | 6.135                     | 4,120        | 4,083  | 344.2  | 2.2034        | 6.378                     | 6,260        | 6,275  |
| 333.5   | 2.4318        | 5.947                     | 3,700        | 3,690  | 353.7  | 2.2373        | 6.207                     | 5,790        | 5,728  |
| 344.9   | 2.4763        | 5.749                     | 3,340        | 3,320  | 415.3  | 2.4547        | 5.288                     | 3,510        | 3,513  |
| 353.9   | 2.5157        | 5.603                     | 3,050        | 3,076  |  |               |                           |              |        |
| <i>Chlorobenzene</i> : $\log \eta = (231.7 \log M)/T - 3.7185.$ |               |                           |              |        | <i>Iodobenzene</i> : $\log \eta = (231.7 \log M)/T - 3.6140.$  |               |                           |              |        |
| 273.0   | 1.9775        | 7.516                     | 10,530       | 10,530 | 277.6  | 1.6840        | 8.322                     | 20,700       | 20,620 |
| 277.7   | 2.0052        | 7.389                     | 9,880        | 9,851  | 300.5  | 1.8228        | 7.688                     | 15,040       | 14,690 |
| 282.7   | 2.0376        | 7.259                     | 9,170        | 9,194  | 309.8  | 1.8807        | 7.456                     | 13,160       | 13,000 |
| 289.3   | 2.0716        | 7.092                     | 8,480        | 8,405  | 321.1  | 1.9450        | 7.194                     | 11,350       | 11,270 |
| 290.6   | 2.0825        | 7.062                     | 8,270        | 8,270  | 331.1  | 1.9979        | 6.977                     | 10,050       | 10,050 |
| 293.1   | 2.0969        | 7.001                     | 8,000        | 8,007  | 341.2  | 2.0448        | 6.769                     | 9,020        | 8,995  |
| 298.1   | 2.1244        | 6.885                     | 7,510        | 7,525  | 353.6  | 2.1013        | 6.533                     | 7,920        | 7,943  |
| 303.1   | 2.1524        | 6.769                     | 7,040        | 7,071  | 371.0  | 2.1720        | 6.226                     | 6,730        | 6,730  |
| 313.2   | 2.2013        | 6.552                     | 6,290        | 6,311  |  |               |                           |              |        |

It is of fundamental importance to establish a connexion between the intercept  $\alpha$  and a physical property of the liquids under consideration. For homologous series, equation (2) suggests that this intercept should be a volume function raised to the  $\frac{2}{3}$  power, but this exponent does not give agreement with the chemically related series now being considered.

Nevertheless, the fact that this intercept may be a function of the molar volume is also implied by the equation derived theoretically by Eyring (*J. Chem. Physics*, 1936, **4**, 283; 1937, **5**, 726), viz.,  $\eta = (Nh/V)e^{E/kT}$ , where  $V$  is the molar volume and  $E$  an energy factor. Simha (*ibid.*, 1939, **7**, 202) proposed a similar equation,  $\eta = (6RT/nVv)e^{U/RT}$ , the volume function again appearing in the intercept.

These views are corroborated to some extent by the fact that the intercept is found to be a linear function of  $\log P$ , and the graphically determined intercepts for the halogenobenzenes have been used in Table II to calculate the parachors from the expression

TABLE II.

| Substance. | $\alpha$ . | $\log P$ . | $\log P$ (calc.). | Substance. | $\alpha$ . | $\log P$ . | $\log P$ (calc.). |
|------------|------------|------------|-------------------|------------|------------|------------|-------------------|
| $C_6H_5F$  | +3.8110    | 2.3338     | 2.334             | $C_6H_5Br$ | +3.6804    | 2.4116     | 2.411             |
| $C_6H_5Cl$ | +3.7185    | 2.3879     | 2.388             | $C_6H_5I$  | +3.6140    | 2.4487     | 2.449             |

$1.714 \log P = 7.8125 - \alpha$ . The agreement leaves no doubt that the function  $\alpha$  of the Andrade equation is primarily determined by the molar volume. From a consideration of this group, Andrade (*Phil. Mag.*, 1934, **17**, 727) observes that "the fluoride shows an anomaly paralleled by other physicochemical properties, e.g., the boiling point." Lewis (J., 1938, 1061) has shown that the critical temperatures of this series are normal in obeying the equation  $T_c = kP - \lambda$ , and the following table shows that there is no anomaly when the boiling points ( $T_b$ ) are calculated from (i) the van der Waals volume function (b) and (ii) the parachor by means of the appended equations.

| Substance. | $b \times 10^6$ . | $P$ . | $T_b$ , calc.: |            | $T_b$ , exptl. |
|------------|-------------------|-------|----------------|------------|----------------|
|            |                   |       | from (i).      | from (ii). |                |
| $C_6H_5F$  | 5742              | 215.7 | 358.6°         | 359.7°     | 358.3°         |
| $C_6H_5Cl$ | 6485              | 244.3 | 405.0          | 404.9      | 405.1          |
| $C_6H_5Br$ | 6872              | 258.0 | 429.2          | 426.6      | 429.1          |
| $C_6H_5I$  | 7395              | 281.0 | 461.8          | 462.9      | 461.6          |

(i)  $T_b = 62,480 b - 0.2$ ; (ii)  $T_b = 1.58 P + 18.9$ .

Similarly, in the viscosity relation derived above, the fluoride is normal when compared with the other members of the series. This normality is undoubtedly brought about by the introduction of the essential terms,  $M$  and  $P$ , and it is suggested that uncertainty in the criteria of anomaly has led to the belief that fluorides are abnormal.

If we now define  $\alpha$  as a linear function of  $\log P$  given by

$$-\alpha = x \log P + y \log y \quad (3)$$

since  $x$  and  $y$  are constants for the series the general equation takes the form

$$\log \eta = A(\log M)/T + x \log P + \log y \quad (4)$$

To demonstrate the application of this equation, the values for a few of the viscosities of the propyl halide series (Thorpe and Rodger, *Phil. Trans.*, 1895, **185**, 397) have been calculated from

$$\log \eta = 187 (\log M)/T + 1.333 \log P - 6.6930 \quad (5)$$

and Table III represents the results over the entire temperature range, the values of the constants being obtained by the graphical methods previously described. The good agreement,

TABLE III.

| $10^6\eta$ .          |              | $10^6\eta$ .         |              | $10^6\eta$ .        |              | $10^6\eta$ .          |              |
|-----------------------|--------------|----------------------|--------------|---------------------|--------------|-----------------------|--------------|
| $T^\circ$ , K.        | Exptl. Calc. | $T^\circ$ , K.       | Exptl. Calc. | $T^\circ$ , K.      | Exptl. Calc. | $T^\circ$ , K.        | Exptl. Calc. |
| <i>Chloropropane.</i> |              | <i>Bromopropane.</i> |              | <i>Iodopropane.</i> |              | <i>Fluoropropane.</i> |              |
| 278.24                | 4104 4111    | 273.45               | 6414 6457    | 273.3               | 9340 9301    | 273                   | — 2972       |
| 287.65                | 3709 3733    | 298.44               | 4903 4900    | 283.98              | 8170 8166    | 293                   | — 2455       |
| 300.38                | 3344 3311    | 318.64               | 4032 4055    | 293.81              | 7300 7278    |                       |              |
| 308.38                | 3038 3083    | 334.98               | 3495 3524    | 328.59              | 5160 5152    |                       |              |
|                       |              |                      |              | 347.38              | 4390 4395    |                       |              |
|                       |              |                      |              | 356.88              | 4060 4093    |                       |              |

coupled with the conclusions of the previous paper (*loc. cit.*), establishes beyond doubt the physical constants upon which the  $\alpha$  and the  $\beta$  term of Andrade's equation depend, and the use of  $(\log M)/T$  as ordinate is to be preferred to that of  $1/T$  in graphical investigations of experimental data.

Few data are available to enable this equation to be tested for molten salts, but in Table IV the viscosities of the silver halides (Lorenz and Hoehberg, *Z. anorg. Chem.*, 1916, **94**, 317) have been calculated from the equations given, and the constancy of the slope  $A$  is again apparent. Though the values of the intercepts fall in the order to be expected from the parachor values, yet they do not show the expected linearity when plotted against  $\log P$ . On the other hand, there is some doubt about the parachor values of these fused salts, and erratic values have been reported; *e.g.*, Jaeger's data for silver nitrate lead to a parachor for silver of 64.7, whereas the value derived from the surface tensions of silver chloride is 46.1 (Sugden, "The Parachor and Valency," 1930, p. 186). The data therefore do not suffice for a crucial test, although the slope relation, which does not involve the parachor, again holds well.

TABLE IV.

| $T^\circ, K.$   | $-\log \eta.$ | $10^3 \frac{(\log M)}{T}.$ | $10^4 \eta.$ |       | $T^\circ, K.$ | $-\log \eta.$ | $10^3 \frac{(\log M)}{T}.$ | $10^4 \eta.$ |       |
|---|---------------|----------------------------|--------------|-------|---------------|---------------|----------------------------|--------------|-------|
|   |               |                            | Exptl.       | Calc. |               |               |                            | Exptl.       | Calc. |
| <i>Silver chloride</i> : $\log \eta = 415.3 (\log M)/T - 2.8179.$ |               |                            |              |       |               |               |                            |              |       |
| 876   | 1.7959        | 2.461                      | 160          | 160   | 942           | 1.8633        | 2.288                      | 137          | 136   |
| 905   | 1.8356        | 2.382                      | 146          | 148   | 1007          | 1.9281        | 2.141                      | 118          | 118   |
| <i>Silver bromide</i> : $\log \eta = 415.3 (\log M)/T - 2.8040.$  |               |                            |              |       |               |               |                            |              |       |
| 882   | 1.7305        | 2.578                      | 186          | 195   | 961           | 1.8268        | 2.367                      | 149          | 151   |
| 922   | 1.7799        | 2.467                      | 166          | 166   | 1076          | 1.9245        | 2.113                      | 119          | 119   |
| <i>Silver iodide</i> : $\log \eta = 415.3 (\log M)/T - 2.646.$    |               |                            |              |       |               |               |                            |              |       |
| 878   | 1.5200        | 2.674                      | 302          | 292   | 971           | 1.6253        | 2.418                      | 237          | 228   |
| 884   | 1.5452        | 2.656                      | 285          | 286   | 1003          | 1.6737        | 2.341                      | 212          | 212   |
| 903   | 1.5607        | 2.600                      | 275          | 272   | 1065          | 1.7328        | 2.205                      | 185          | 186   |

*Theoretical Discussion.*—The problem of the factors influencing viscosity may be approached from dimensional considerations. Let us assume that the viscosity  $\eta$  is a function of the mass  $m$ , the volume  $V$ , and the average velocity  $\omega$  of the molecules, so that  $\eta = km^p V^q \omega^r$ , where  $k$  is a constant. Dimensionally, this becomes  $ML^{-1}T^{-1} = kM^p L^{3q} L^r T^{-r}$  whence  $p = 1$ ,  $r = 1$ , and  $q = -\frac{2}{3}$ . Therefore

$$\eta = km\omega V^{-2/3} \quad \dots \quad (6)$$

For gases,  $\omega = \text{constant} \times \sqrt{\pi/\sigma}$ , where  $\sigma$  is the density of the gas and  $\pi$  is the pressure in dynes/sq. cm. If the diameter of the molecule is  $D$ , then  $D^2 = \text{const.} \times V^{2/3}$ . Substitution in equation (6) gives  $\eta D^2 = \text{const.} \times m\sqrt{\pi/\sigma}$ . If we now consider 1 c.c. of gas containing  $n$  molecules of mass  $m$ , then  $\sigma = nm$ , whence we have

$$\eta D^2 = \text{const.} \times (\sigma/n)\sqrt{\pi/\sigma} = \text{Const.} \times \sqrt{\pi\sigma/n}$$

which reduces to  $\eta = K\sigma\omega L$ , since the mean free path  $L = 1.319/\sqrt{2\pi} D^2 n$ . This is identical with the equation derived by Chapman (*Proc. Roy. Soc.*, 1916, *A*, **93**, 1) from kinetic considerations.

For liquids, although the dimensional equation (6) is very probably similarly applicable, the factors governing the magnitude of  $\omega$  and  $L$  are uncertain and probably very complex. At constant temperature, equation (6) in its logarithmic form  $\log \eta = \log m + \log k\omega V^{-2/3}$  is very similar in type to equation (4). If  $L$  is a more complex function of  $V$  than that given by this simple equation, then a more probable extension would be  $\log \eta = \log m + \log CV^z$ , where the exponent  $-\frac{2}{3}$  becomes modified for liquid media, and  $C$  is dependent on other factors, *e.g.*, the internal cohesive pressure existing between the various liquid molecules. Mortimer (*J. Amer. Chem. Soc.*, 1923, **45**, 633) has shown that for related compounds the internal cohesive forces are sensibly constant, and for chemically similar series a constant effect due to these forces would be produced.

It is suggested that the similarity of equation type for liquids and gases is not accidental and that it is due to a continuity existing between the gaseous and the liquid state, for although the molecules of a liquid are subject to pressure-volume laws which differ markedly from the simple gas laws, yet in the arrangement and order of the factors concerned, any equation which purports to represent the variation of viscosity in the liquid state must possess basic dimensional resemblances with the analogous gas function.

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