# 114. *The Dependence of the Viscosities of Liquids on Reduced Temperature, and a Relation between Viscosity, Density, and Chemical Constitution.*

By Leo H. Thomas.

An exponential equation is proposed representing the variation of the viscosities of liquids with reduced temperature in terms of two constants, one being characteristic of each liquid, and the other being approximately constant for all normal, non-associated liquids. The relation between the characteristic constant and molecular constitution is discussed.

In a review of the various formulæ connecting the viscosity of liquids with temperature, Srinivasan and Prasad (*Phil. Mag.*, 1942, **33**, 258) have shown that the most satisfactory are those derived by Andrade (*Nature*, 1930, **125**, 309, 582; *Phil. Mag.*, 1934, **17**, 497, 698), *viz.*,

$$\eta = Ae^{B/T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and its extension

$$v^{1/3}\eta = Ce^{D/vT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $v$ is the specific volume, and $A$, $B$, $C$, and $D$ are constants for each particular liquid. It was also shown that (1) and (2) reproduce the experimental viscosity results with equal accuracy.

Prasad (*J. Indian Chem. Soc.*, 1933, **10**, 143) indicated that the functions $B/T_b$ and $B/T_c$, where $T_b$ and $T_c$ are the absolute boiling points and critical temperatures respectively, are approximately constant for members of the paraffin and alkyl halide series, but that the constant $A$ decreases irregularly from member to member.

An equation incorporating reduced temperature is now proposed, *viz.*,

$$\log \eta\sqrt{v} = c + k(T_c/T - 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $k$ and $c$ are constants, and $T$ and $T_c$ the absolute temperatures. Rearrangement gives

$$\log \eta\sqrt{v} = (c - k) + kT_c/T = \alpha + \beta/T \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

which is a modification of (1). When $T = T_c$, $c = \log \eta_c\sqrt{v_c}$, so (3) becomes

$$\log \eta\sqrt{v}/\eta_c\sqrt{v_c} = k(T_c/T - 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

In testing the validity of (3), the critical temperatures were taken from the International Critical Tables, except those marked * which were calculated from the relationship $T_c/T_b = a - b \log [P]$ (Hertzog, *Ind. Eng. Chem.*, 1944, **36**, 997), where $a$ and $b$ are constants for a particular series or for a set of compounds closely related structurally, and $[P]$ is the parachor.

All specific volumes have been calculated from the reliable density–temperature equations of the International Critical Tables, or, when such equations were lacking, from the compilations of Thorpe and Rodger (*Phil. Trans.*, 1894, **185**, 397; 1897, **189**, 71) and Batschinski (*Z. physikal. Chem.*, 1913, **84**, 643) or from "Physicochemical Tables" (Castell-Evans; Griffin and Co. Ltd., 1902).

In Tables I and II, logarithms are to the base 10, and $\eta$ is in $10^3$ poise; $\alpha$ and $\beta$ are the constants in equation (4).

Table I shows the agreement between the experimental and calculated values of viscosity for a few typical cases, and Table II shows the characteristic constants for 123 substances together with the maximum positive and maximum negative percentage deviations between experimental and calculated values of viscosity. The

TABLE I.

| $T$. | $\eta$, calc. | $\eta$, found. | Error, %. | $T$. | $\eta$, calc. | $\eta$, found. | Error, %. |
|---|---|---|---|---|---|---|---|
| | *Hexane.* | | | | *Ethyl acetate.* | | |
| | $\alpha = -0{\cdot}6222$; $\beta = 356{\cdot}6$. | | | | $\alpha = -0{\cdot}7337$; $\beta = 412{\cdot}9$. | | |
| 273·8° | 3·940 | 3·931 | −0·2 | 273·2° | 5·757 | 5·763 | +0·1 |
| 282·1 | 3·585 | 3·581 | −0·1 | 281·9 | 5·144 | 5·144 | ±0·0 |
| 287·7 | 3·375 | 3·378 | +0·1 | 287·5 | 4·803 | 4·795 | −0·2 |
| 293·0 | 3·196 | 3·202 | +0·2 | 294·4 | 4·427 | 4·418 | −0·1 |
| 298·4 | 3·027 | 3·035 | +0·3 | 301·1 | 4·098 | 4·096 | −0·0 |
| 303·2 | 2·887 | 2·894 | +0·2 | 309·5 | 3·741 | 3·738 | −0·1 |
| 309·8 | 2·712 | 2·722 | +0·4 | 317·1 | 3·453 | 3·455 | +0·1 |
| 316·5 | 2·554 | 2·557 | +0·1 | 324·1 | 3·220 | 3·224 | +0·1 |
| 320·4 | 2·465 | 2·470 | +0·2 | 333·2 | 2·955 | 2·960 | +0·2 |
| 325·9 | 2·351 | 2·351 | ±0·0 | 341·4 | 2·741 | 2·741 | ±0·0 |
| 331·8 | 2·239 | 2·231 | −0·4 | 347·6 | 2·593 | 2·594 | +0·0 |
| 336·6 | 2·152 | 2·143 | −0·4 | | | | Mean error 0·1 |
| | | | Mean error 0·2 | | | | |
| | *Diethyl ketone.* | | | | n-*Undecane.* | | |
| | $\alpha = -0{\cdot}6403$; $\beta = 397{\cdot}0$. | | | | $\alpha = -0{\cdot}8549$; $\beta = 584{\cdot}3$. | | |
| 273·5° | 5·920 | 5·914 | −0·1 | 273·0° | 16·78 | 17·24 | +2·7 |
| 282·1 | 5·315 | 5·302 | −0·2 | 283·0 | 14·03 | 14·06 | +0·2 |
| 291·7 | 4·746 | 4·748 | +0·0 | 293·0 | 11·87 | 11·72 | −1·3 |
| 300·1 | 4·331 | 4·328 | −0·1 | 303·0 | 10·15 | 9·960 | −1·9 |
| 309·2 | 3·936 | 3·939 | +0·1 | 313·0 | 8·760 | 8·643 | −1·3 |
| 317·7 | 3·616 | 3·623 | +0·2 | 333·0 | 6·695 | 6·619 | −1·2 |
| 326·4 | 3·332 | 3·339 | +0·2 | 353·0 | 5·270 | 5·273 | +0·1 |
| 335·4 | 3·073 | 3·079 | +0·2 | 373·0 | 4·250 | 4·348 | +2·3 |
| 345·2 | 2·827 | 2·834 | +0·2 | | | | Mean error 1·4 |
| 354·5 | 2·619 | 2·623 | +0·2 | | | | |
| 364·0 | 2·432 | 2·426 | −0·2 | | | | |
| 371·8 | 2·294 | 2·279 | −0·7 | | | | |
| | | | Mean error 0·2 | | | | |

## TABLE II.

| Substance. | $T_c$. | *k*. | Anti-log *c*. | Max. error. | | (Andrade.) | | Mean error, % | Approx. temp. range (° C.). | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | + | − | + | − | | | |
| Propane | 369° | 0·6189 | 1·158 | 1·3 | 1·6 | — | — | 0·8 | −73—+16° | 1 |
| Butane | 426 | 0·6124 | 1·214 | 1·1 | 1·9 | — | — | 0·9 | −73—+48 | ,, |
| *iso*Butane | 407 | 0·7164 | 1·258 | 0·8 | 0·9 | — | — | 0·4 | −73—+ 4 | ,, |
| Pentane | 470 | 0·6787 | 1·141 | 0·2 | 0·2 | 0·4 | 0·2 | 0·1 | 1— 33 | 2 |
| *iso*Pentane | 461 | 0·6878 | 1·156 | 0·1 | 0·1 | 0·1 | 0·1 | 0·1 | 1— 26 | ,, |
| Hexane | 508 | 0·7020 | 1·201 | 0·4 | 0·4 | 0·3 | 0·4 | 0·2 | 1— 64 | ,, |
| *iso*Hexane | 498* | 0·7119 | 1·172 | 0·3 | 0·4 | 0·3 | 0·2 | 0·2 | 1— 55 | ,, |
| Heptane | 540 | 0·7364 | 1·190 | 0·7 | 0·7 | 0·5 | 0·8 | 0·4 | 6— 92 | ,, |
| *iso*Heptane | 530* | 0·7298 | 1·180 | 0·4 | 1·0 | 0·5 | 0·9 | 0·4 | 0— 88 | ,, |
| Octane | 569 | 0·7776 | 1·195 | 0·5 | 1·1 | 0·5 | 0·8 | 0·3 | 0— 122 | ,, |
| Nonane | 600* | 0·8198 | 1·166 | 1·1 | 1·0 | — | — | 0·8 | 0— 100 | 3 |
| Decane | 625* | 0·8724 | 1·127 | 2·1 | 2·0 | — | — | 1·3 | 0— 100 | ,, |
| Undecane | 649* | 0·9003 | 1·100 | 2·7 | 1·9 | — | — | 1·4 | 0— 100 | ,, |
| Dodecane | 667* | 0·9506 | 1·077 | 3·5 | 2·2 | — | — | 1·3 | 0— 100 | ,, |
| Methyl formate | 487 | 0·6832 | 1·245 | 0·3 | 0·1 | 0·2 | 0·3 | 0·1 | 0— 29 | 2 |
| Ethyl formate | 508 | 0·7288 | 1·221 | 0·3 | 0·3 | 0·3 | 0·2 | 0·1 | 0— 52 | ,, |
| Methyl acetate | 507 | 0·7438 | 1·135 | 0·2 | 0·3 | 0·1 | 0·1 | 0·2 | 0— 54 | ,, |
| Propyl formate | 538 | 0·7960 | 1·172 | 0·3 | 0·4 | 0·2 | 0·2 | 0·1 | 0— 77 | ,, |
| Ethyl acetate | 523 | 0·7895 | 1·137 | 0·2 | 0·2 | 0·4 | 0·3 | 0·1 | 0— 75 | ,, |
| Methyl propionate | 530 | 0·7553 | 1·166 | 0·5 | 0·3 | 0·5 | 0·6 | 0·1 | 0— 68 | ,, |
| Ethyl propionate | 546 | 0·7968 | 1·157 | 0·2 | 0·2 | 0·1 | 0·2 | 0·1 | 0— 90 | ,, |
| Methyl butyrate | 554 | 0·8268 | 1·114 | 0·2 | 0·7 | 0·6 | 0·4 | 0·2 | 0— 98 | ,, |
| Methyl *iso*butyrate | 540 | 0·7939 | 1·178 | 0·6 | 0·2 | 0·2 | 0·2 | 0·1 | 0— 89 | ,, |
| Propyl acetate | 549 | 0·8362 | 1·148 | 0·4 | 0·2 | 0·6 | 0·3 | 0·1 | 0— 97 | ,, |
| Butyl formate | 562* | 0·8776 | 1·149 | 0·9 | 0·7 | — | — | 0·5 | 0— 100 | 4 |
| Butyl acetate | 579 | 0·8592 | 1·137 | 1·3 | 0·9 | — | — | 0·6 | 0— 100 | ,, |
| *iso*Butyl acetate | 561 | 0·8997 | 1·158 | 0·6 | 0·7 | — | — | 0·3 | 20— 100 | 5 |
| Ethyl valerate | 602* | 0·8364 | 1·174 | 1·4 | 1·0 | — | — | 0·7 | 0— 100 | 4 |
| Butyl propionate | 599* | 0·8453 | 1·179 | 1·5 | 0·9 | — | — | 0·6 | 0— 100 | ,, |
| Butyl butyrate | 619* | 0·8794 | 1·153 | 1·8 | 1·3 | — | — | 0·9 | 0— 100 | ,, |
| Butyl valerate | 636* | 0·9099 | 1·147 | 2·2 | 1·5 | — | — | 1·1 | 0— 100 | ,, |
| Ethyl heptoate | 641* | 0·9122 | 1·120 | 2·3 | 1·6 | — | — | 1·2 | 20— 100 | ,, |
| Heptyl acetate | 645* | 0·9685 | 1·137 | 3·7 | 2·9 | — | — | 2·0 | 0— 100 | ,, |
| Amyl butyrate | 637* | 0·9175 | 1·105 | 2·3 | 1·4 | — | — | 1·1 | 0— 100 | ,, |
| Ethyl bromide | 504 | 0·6337 | 1·144 | 0·3 | 0·1 | 0·1 | 0·1 | 0·1 | 0— 36 | ,, |
| Propyl bromide | 542* | 0·6790 | 1·177 | 0·4 | 0·3 | 0·3 | 0·2 | 0·2 | 0— 68 | ,, |
| *iso*Propyl bromide | 525* | 0·7155 | 1·142 | 0·1 | 0·2 | 0·2 | 0·1 | 0·1 | 0— 57 | ,, |
| Butyl bromide | 576* | 0·6900 | 1·246 | 0·7 | 0·9 | — | — | 0·4 | 0— 100 | 6 |
| *iso*Butyl bromide | 560* | 0·7578 | 1·179 | 0·5 | 1·2 | 0·4 | 1·0 | 0·4 | 0— 88 | 2 |
| Amyl bromide | 609* | 0·7174 | 1·236 | 0·5 | 0·3 | — | — | 0·2 | 0— 100 | 6 |
| Hexyl bromide | 632* | 0·7619 | 1·227 | 1·0 | 0·8 | — | — | 0·5 | 0— 100 | ,, |
| Heptyl bromide | 662* | 0·8054 | 1·180 | 2·2 | 1·3 | — | — | 0·8 | 0— 100 | ,, |
| Octyl bromide | 683* | 0·8565 | 1·135 | 3·5 | 2·2 | — | — | 1·2 | 0— 100 | ,, |
| Propanethiol | 537* | 0·6673 | 1·227 | 0·1 | 0·0 | — | — | 0·0 | 0— 30 | 3 |
| Butane-1-thiol | 571* | 0·7028 | 1·185 | 0·7 | 1·0 | — | — | 0·5 | 0— 80 | ,, |
| Pentane-1-thiol | 605* | 0·6633 | 1·069 | 0·6 | 0·3 | — | — | 0·2 | 0— 100 | ,, |
| Pentane-2-thiol | 585* | 0·7034 | 1·192 | 0·7 | 0·7 | — | — | 0·3 | 0— 100 | ,, |
| Hexane-1-thiol | 631* | 0·7563 | 1·210 | 1·4 | 0·9 | — | — | 0·6 | 0— 100 | ,, |
| Hexane-2-thiol | 613* | 0·7471 | 1·175 | 1·4 | 0·7 | — | — | 0·5 | 0— 100 | ,, |
| Heptane-1-thiol | 659* | 0·7988 | 1·162 | 1·7 | 1·1 | — | — | 1·0 | 0— 100 | ,, |
| Heptane-2-thiol | 640* | 0·7848 | 1·162 | 1·7 | 1·2 | — | — | 0·9 | 0— 100 | ,, |
| Octane-1-thiol | 683* | 0·8494 | 1·104 | 2·2 | 1·7 | — | — | 1·2 | 0— 100 | ,, |
| Octane-2-thiol | 664* | 0·8399 | 1·100 | 2·3 | 1·6 | — | — | 1·2 | 0— 100 | ,, |
| Methyl iodide | 519* | 0·6247 | 1·068 | 0·1 | 0·0 | 0·1 | 0·0 | 0·0 | 0— 40 | 2 |
| Ethyl iodide | 550* | 0·6351 | 1·160 | 0·2 | 0·2 | 0·2 | 0·3 | 0·2 | 0— 69 | ,, |
| Propyl iodide | 584* | 0·6803 | 1·177 | 0·4 | 0·7 | 0·4 | 0·3 | 0·2 | 0— 99 | ,, |
| *iso*Propyl iodide | 564* | 0·7099 | 1·163 | 0·2 | 0·6 | 0·7 | 0·3 | 0·1 | 0— 89 | ,, |
| *iso*Butyl iodide | 599* | 0·7415 | 1·162 | 1·8 | 0·9 | 1·9 | 0·9 | 0·4 | 0— 116 | ,, |
| Ethyl ether | 467 | 0·6740 | 1·105 | 0·2 | 0·4 | 0·5 | 0·0 | 0·1 | 7— 32 | ,, |
| Methyl propyl ether | 473* | 0·6885 | 1·117 | 0·2 | 0·2 | 0·2 | 0·1 | 0·1 | 0— 35 | 2 |
| Ethyl propyl ether | 500 | 0·7354 | 1·118 | 0·2 | 0·5 | 0·2 | 0·3 | 0·1 | 0— 60 | ,, |
| Methyl *iso*butyl ether | 488* | 0·7375 | 1·157 | 0·3 | 0·4 | 0·3 | 0·3 | 0·1 | 0— 55 | ,, |
| Propyl ether | 529* | 0·7843 | 1·137 | 0·4 | 0·7 | 0·5 | 0·9 | 0·2 | 1— 88 | ,, |
| Ethyl *iso*butyl ether | 513* | 0·7857 | 1·133 | 0·3 | 0·4 | 0·2 | 0·1 | 0·1 | 0— 77 | ,, |
| Butyl ether | 592* | 0·8247 | 1·144 | 1·1 | 0·6 | — | — | 0·4 | 0— 100 | 5 |
| Acetaldehyde | 461 | 0·6323 | 1·095 | 0·1 | 0·1 | 0·1 | 0·1 | 0·1 | 0— 19 | 7 |
| Propaldehyde | 489* | 0·8106 | 1·087 | 0·5 | 0·4 | — | — | 0·2 | 15— 44 | ,, |
| Butaldehyde | 517* | 0·7705 | 1·289 | 0·1 | 0·0 | — | — | 0·0 | 18— 72 | ,, |
| *iso*Valeraldehyde | 532* | 0·8486 | 1·259 | 0·6 | 0·1 | — | — | 0·2 | 21— 85 | ,, |
| Methyl cyanide | 548 | 0·6676 | 1·131 | 0·2 | 0·3 | — | — | 0·2 | 16— 77 | ,, |
| Ethyl cyanide | 564 | 0·6770 | 1·148 | 0·2 | 0·2 | — | — | 0·1 | 20— 93 | ,, |
| Propyl cyanide | 582 | 0·7582 | 1·190 | 0·5 | 0·7 | — | — | 0·2 | 18— 113 | ,, |
| Butyl cyanide | 602* | 0·7814 | 1·264 | 1·0 | 0·2 | — | — | 0·2 | 19— 134 | ,, |
| Amyl cyanide | 622 | 0·8050 | 1·291 | 1·5 | 0·1 | — | — | 0·3 | 58— 157 | ,, |
| Phenyl cyanide | 699 | 0·7196 | 1·332 | 0·9 | 0·6 | — | — | 0·5 | 75— 181 | ,, |

[References at foot of p. 577.

| Substance. | $T_c$. | *k*. | Anti-log *c*. | Max. error. | | (Andrade.) | | Mean error, % | Approx. temp. range (° C.). | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | + | − | + | − | | | |
| Acetone | 508 | 0·6718 | 1·164 | 0·2 | 0·3 | 0·5 | 0·2 | 0·1 | 8— 54 | 2 |
| Methyl ethyl ketone | 522* | 0·7554 | 1·205 | 0·2 | 0·2 | 0·1 | 0·1 | 0·1 | 0— 76 | ,, |
| Methyl propyl ketone | 547* | 0·7474 | 1·256 | 0·3 | 0·5 | 0·3 | 0·5 | 0·2 | 0— 99 | ,, |
| Ethyl ketone | 545* | 0·7286 | 1·226 | 0·3 | 0·7 | 0·8 | 0·7 | 0·2 | 0— 99 | ,, |
| Benzene | 561 | 0·9086 | 1·020 | 1·4 | 0·6 | 0·8 | 0·7 | 0·4 | 8— 75 | ,, |
| Toluene | 594 | 0·7333 | 1·114 | 0·7 | 0·5 | 0·7 | 0·3 | 0·2 | 0— 107 | ,, |
| Ethylbenzene | 614* | 0·7157 | 1·179 | 0·6 | 0·4 | 0·8 | 0·3 | 0·2 | 0— 131 | ,, |
| *o*-Xylene | 625* | 0·7678 | 1·164 | 2·4 | 0·9 | 1·7 | 1·1 | 0·6 | 0— 141 | ,, |
| *m*-Xylene | 620* | 0·6839 | 1·145 | 0·8 | 0·4 | 0·8 | 0·5 | 0·2 | 0— 135 | ,, |
| *p*-Xylene | 617* | 0·7186 | 1·111 | 0·5 | 0·4 | 0·5 | 0·4 | 0·1 | 8— 135 | ,, |
| Propyl chloride | 503 | 0·6808 | 1·213 | 0·6 | 0·6 | 0·7 | 0·4 | 0·3 | 0— 45 | ,, |
| *iso*Propyl chloride | 492* | 0·7286 | 1·112 | 0·0 | 0·0 | 0·1 | 0·1 | 0·0 | 0— 33 | ,, |
| *iso*Butyl chloride | 529* | 0·7734 | 1·162 | 0·1 | 0·2 | 0·3 | 0·3 | 0·1 | 0— 65 | ,, |
| Ethylene bromide | 628* | 0·8487 | 1·235 | 2·4 | 0·9 | 2·3 | 1·4 | 0·8 | 9— 127 | ,, |
| Propylene bromide | 636* | 0·8337 | 1·234 | 3·2 | 1·2 | 2·8 | 1·5 | 0·9 | 0— 137 | ,, |
| *iso*Butylene bromide | 635* | 0·9661 | 1·218 | 2·4 | 3·2 | 4·6 | 2·3 | 1·4 | 0— 142 | ,, |
| Allyl chloride | 511* | 0·6679 | 1·086 | 0·1 | 0·2 | 0·2 | 0·2 | 0·1 | 1— 42 | ,, |
| Allyl bromide | 544* | 0·6671 | 1·115 | 0·2 | 0·3 | 0·3 | 0·2 | 0·1 | 0— 69 | ,, |
| Allyl iodide | 585* | 0·6821 | 1·125 | 0·4 | 0·3 | 0·4 | 0·3 | 0·2 | 0— 98 | ,, |
| Diallyl | 498* | 0·6984 | 1·070 | 0·3 | 0·3 | 0·2 | 0·4 | 0·1 | 0— 56 | ,, |
| Isoprene | 475* | 0·6507 | 1·169 | 0·3 | 0·1 | 0·1 | 0·1 | 0·1 | 0— 32 | ,, |
| β-*iso*Amylene | 473* | 0·6152 | 1·085 | 0·1 | 0·1 | 0·1 | 0·1 | 0·1 | 0— 33 | ,, |
| Methylene chloride | 518* | 0·6401 | 1·212 | 0·3 | 0·1 | 0·2 | 0·1 | 0·1 | 0— 38 | ,, |
| Chloroform | 536 | 0·6659 | 1·294 | 0·1 | 0·2 | 0·2 | 0·2 | 0·1 | 0— 57 | ,, |
| Carbon tetrachloride | 556 | 0·9155 | 1·155 | 1·0 | 0·7 | 1·1 | 0·6 | 0·3 | 7— 74 | ,, |
| Ethylene chloride | 565* | 0·8494 | 1·215 | 1·0 | 0·5 | 1·0 | 0·6 | 0·4 | 0— 81 | ,, |
| Ethylidene chloride | 529* | 0·7286 | 1·170 | 0·1 | 0·1 | 0·1 | 0·2 | 0·1 | 7— 55 | ,, |
| 1 : 1 : 2 : 2-Tetrachloroethane | 626 | 0·9942 | 1·069 | 2·1 | 1·2 | — | — | 0·8 | 0— 80 | 5 |
| Chlorobenzene | 632 | 0·7191 | 1·125 | 0·9 | 2·0 | — | — | 0·5 | 0— 120 | 8 |
| *o*-Chlorotoluene | 650* | 0·7544 | 1·195 | 1·6 | 1·3 | — | — | 0·9 | 0— 100 | 5 |
| *m*-Chlorotoluene | 654* | 0·7127 | 1·120 | 1·6 | 1·5 | — | — | 1·0 | 0— 100 | ,, |
| Bromobenzene | 670 | 0·7230 | 1·104 | 2·5 | 1·7 | — | — | 1·4 | 0— 142 | 8 |
| *m*-Bromotoluene | 682* | 0·7319 | 1·129 | 2·3 | 1·5 | — | — | 1·2 | 0— 100 | 5 |
| *p*-Bromotoluene | 683* | 0·7122 | 1·180 | 0·8 | 0·3 | — | — | 0·4 | 30— 100 | ,, |
| Fluorobenzene | 559 | 0·7814 | 1·109 | 1·8 | 1·7 | — | — | 0·6 | 9— 81 | 8 |
| Iodobenzene | 721 | 0·7409 | 1·032 | 3·2 | 3·3 | — | — | 1·4 | 5— 149 | ,, |
| Methyl sulphide | 503 | 0·6038 | 1·174 | 0·2 | 0·3 | 0·1 | 0·1 | 0·1 | 0— 36 | 2 |
| Ethyl sulphide | 557 | 0·6881 | 1·165 | 0·2 | 0·3 | 0·3 | 0·6 | 0·1 | 0— 88 | ,, |
| Acetic anhydride | 569 | 0·8613 | 1·348 | 2·4 | 0·9 | 2·1 | 1·0 | 0·6 | 0— 133 | ,, |
| Propionic anhydride | 615* | 0·8728 | 1·220 | 4·4 | 1·5 | 3·1 | 1·7 | 1·0 | 0— 165 | ,, |
| Ethylene oxide | 465 | 0·6287 | 1·212 | 1·2 | 0·9 | — | — | 0·5 | −50—+ 9 | 9 |
| Carbon disulphide | 546 | 0·4671 | 1·291 | 0·8 | 0·3 | 0·5 | 0·2 | 0·2 | 0— 46 | 2 |
| Bromine | 575 | 0·6489 | 1·339 | 0·3 | 0·2 | 0·4 | 0·3 | 0·1 | 1— 56 | ,, |
| Thiophen | 590 | 0·7521 | 1·104 | 1·3 | 0·3 | 0·9 | 0·5 | 0·4 | 0— 80 | ,, |
| *cyclo*Hexanone | 654* | 1·0359 | 1·245 | 2·0 | 3·1 | — | — | 1·2 | 14— 90 | 10 |
| *cyclo*Hexane | 554 | 1·1270 | 1·127 | 0·9 | 1·3 | — | — | 0·6 | 11— 76 | 11 |
| *cyclo*Hexyl chloride | 626* | 0·9445 | 1·297 | 0·9 | 0·2 | — | — | 0·3 | 48— 133 | ,, |
| Anisole | 642 | 0·8668 | 1·058 | 0·2 | 0·2 | — | — | 0·1 | 56— 142 | ,, |
| Average values (Thorpe and Rodger's results only) | — | — | — | 0·6 | 0·5 | 0·6 | 0·4 | 0·2 | — | — |
| | | β. | − *a*. | | | | | | | |
| Nitromethane | — | 417·3 | 0·6334 | 0·2 | 0·6 | — | — | 0·2 | 0— 80 | 12 |
| Nitroethane | — | 448·6 | 0·6634 | 0·3 | 0·3 | — | — | 0·2 | 19— 109 | ,, |
| Nitropropane | — | 480·9 | 0·7049 | 0·4 | 0·3 | — | — | 0·2 | 15— 122 | ,, |
| Nitrobutane | — | 501·0 | 0·7120 | 0·7 | 0·6 | — | — | 0·4 | 15— 143 | ,, |
| Nitropentane | — | 535·0 | 0·7591 | 1·6 | 0·9 | — | — | 0·6 | 21— 161 | ,, |
| 3-Methylnitrobutane | — Calculated $T_c$ probably unreliable | 568·3 | 0·8002 | 0·7 | 0·4 | — | — | 0·2 | 40— 155 | ,, |
| Nitrobenzene | — | 533·9 | 0·6029 | 0·8 | 0·5 | — | — | 0·4 | 96— 208 | 13 |
| Propyl nitrite | — | 344·1 | 0·6534 | 0·0 | 0·1 | — | — | 0·0 | 16— 46 | 12 |
| Butyl nitrite | — | 384·9 | 0·6928 | 0·3 | 0·6 | — | — | 0·2 | 16— 71 | ,, |
| Amyl nitrite | — | 414·2 | 0·6689 | 0·5 | 0·4 | — | — | 0·3 | 19— 99 | ,, |
| *iso*Amyl nitrite | — | 389·5 | 0·6319 | 0·1 | 0·0 | — | — | 0·0 | 13— 79 | ,, |
| Nitric acid | — | 518·1 | 0·8863 | 0·6 | 0·4 | — | — | 0·3 | 18— 69 | ,, |
| Benzyl cyanide | — | 571·6 | 0·6585 | 0·6 | 0·5 | — | — | 0·2 | 90— 200 | 7 |
| Ethyl cyanoacetate | — | 645·7 | 0·8515 | 0·2 | 0·3 | — | — | 0·2 | 111— 201 | ,, |
| Diphenyl | — | 684·8 | 0·8555 | 0·2 | 0·2 | — | — | 0·1 | 139— 210 | 13 |
| *cyclo*Hexyl bromide | — | 598·0 | 0·7816 | 0·4 | 0·2 | — | — | 0·2 | 89— 155 | 11 |
| Phenyl ethyl ether | — | 556·8 | 0·8081 | 0·2 | 0·5 | — | — | 0·2 | 78— 165 | 13 |
| Acetophenone | — | 543·8 | 0·6507 | 0·2 | 0·2 | — | — | 0·1 | 99— 188 | ,, |
| *cyclo*Hexane | — | 475·7 | 0·7464 | 0·3 | 0·1 | — | — | 0·1 | 19— 80 | ,, |
| *p*-Methyl*cyclo*hexanone | — | 592·8 | 0·7778 | 2·1 | 1·5 | — | — | 1·6 | 20— 80 | 5 |
| Methylene bromide | — | 383·5 | 0·4907 | 0·1 | 0·2 | — | — | 0·1 | 19— 91 | 14 |
| Trichloroethylene | — | 324·1 | 0·4274 | 0·1 | 0·0 | — | — | 0·0 | 30— 80 | 5 |
| Pentachloroethane | — | 670·1 | 1·0260 | 1·4 | 1·6 | — | — | 1·0 | 0— 80 | ,, |
| Chloral | — | 525·4 | 0·8385 | 1·0 | 0·6 | — | — | 0·3 | 22— 95 | 7 |
| Furfural | — | 614·2 | 0·9137 | 3·1 | 2·8 | — | — | 1·7 | 0— 100 | 15 |
| Propane-2-thiol | — | 384·0 | 0·6892 | 0·1 | 0·2 | — | — | 0·1 | 0— 40 | 3 |

corresponding deviations when using equation (2), taken from Andrade's data, are given for purposes of comparison. Mean percentage deviations are listed in col. 9. The constants $c$ and $k$ were evaluated by application of Campbell's " zero sum " method (*Phil. Mag.*, 1920, **39**, 177; 1924, **47**, 816).

It appears that (3) fits the experimental results as accurately as do the Andrade equations, and it is clear that the introduction of the $v$ term into the variable, log $\eta$, has an effect well within the limits of experimental accuracy in the determination of viscosity. This might have been anticipated, for, within any temperature range, the variation in viscosity is many times greater than the corresponding change in density. However, (3) has the marked advantage that $c = \log \eta_c\sqrt{v_c}$ is approximately a constant for all the normal non-associated substances examined. Of the 123 liquids for which critical temperatures are known or can be calculated as above, 96 possess values of $\eta_c\sqrt{v_c}$ differing from the mean figure 1·167 by less than 6% and 112 by less than 9%. The remaining 11 liquids, which include benzene, carbon disulphide, chloroform, and bromine, differ from the mean by 9—16%.

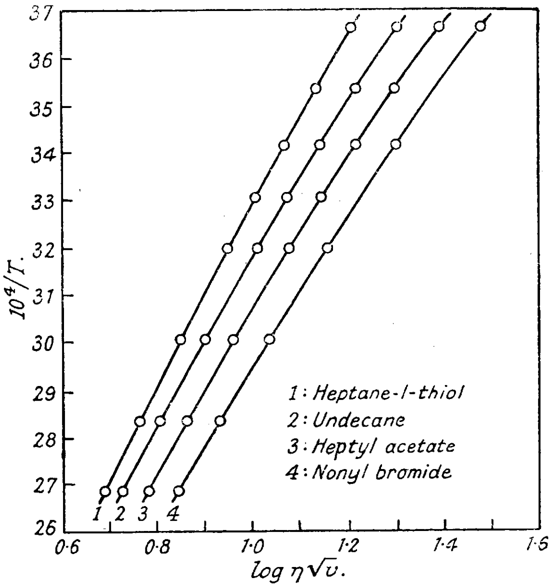
It therefore becomes possible, as a fair approximation, to express the viscosity of a liquid by an equation involving only one characteristic constant; *i.e.*,

$$\log \eta\sqrt{v} = 0{\cdot}0670 + k(T_c/T - 1) \quad \ldots \ldots \ldots \quad (6)$$

The calculated value of the intercept $c$ for a particular compound depends on the accuracy of measurement of $\eta$, $v$, and $T_c$, and considerable extrapolation is involved in its evaluation. Possibly then, for most of the substances, (6) is within the limits of experimental accuracy; but this not at all likely for, *e.g.*, benzene, chloroform, and bromine.

It is noteworthy that the mean value of $c$ for the 49 compounds whose critical temperatures are known is 1·168 as compared with 1·166 for the 74 compounds whose critical temperatures were calculated as above.

The agreement between the calculated values of viscosity and the experimental results of Thorpe and Rodger (*locc. cit.*) is highly satisfactory, the average mean error being 0·2%. These measurements were carried out at 0—100° on liquids of low molecular weight and therefore low boiling point. Similar measurements have since been made on liquids of higher boiling point, notably by Bingham and his co-workers. The agreement here is not so satisfactory, and the $\log \eta\sqrt{v}$–$1/T$ curves are decidedly convex to the $1/T$ axis, the curvature for the range 0—100° being the more pronounced as the temperature drops and as the boiling points of the liquids increase (see figure). Such a curvature is also exhibited by a small number of the higher-boiling liquids, *e.g.*, the alkylene bromides (Thorpe and Rodger). The typical case of *n*-undecane is shown in Table I.



Examination of the mean deviations between experimental and calculated viscosities shows that this departure from linearity occurs with all liquids having mean errors greater than 0·3—0·4%. In fact, the curvature is so regular that the mean error over a given range in temperature may be taken as a rough measure of its extent.

In certain cases, *e.g.*, hexane, the $\log \eta\sqrt{v}$–$1/T$ curves are concave to the $1/T$ axis, but the mean errors are only 0·1—0·3%, probably within the limits of experimental accuracy. It seems fairly certain then that the simple exponential expressions (1) and (5) are true only at temperatures approaching the boiling point.

Equation (6) enables one to calculate $\eta\sqrt{v}$ for a given compound at any temperature (say, the b. p.) from one measured value at another temperature $T$, provided $T_c$ can be estimated as above. Let

$$[\log_{10} \eta_c v_c] - 0{\cdot}0670 = \Delta \log_{10} \eta_c\sqrt{v_c}$$

Then it may easily be shown that

$$\Delta \log \eta_B\sqrt{v_B} = \Delta \log \eta_c\sqrt{v_c}\left[1 - \frac{T_c/T_B - 1}{T_c/T - 1}\right]$$

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[1] Lipkin, Davison, and Kurtz, *Ind. Eng. Chem.*, 1942, **34**, 976. [2] Thorpe and Rodger, *locc. cit.* [3] Bingham and Fornwalt, *J. Rheol.*, 1930, **1**, 372. [4] Bingham and De Turck, *ibid.*, 1932, **3**, 479. [5] After the compilation of Bingham and Spooner (*Physics*, 1933, **4**, 387). [6] Bingham and Stookey, *J. Amer. Chem. Soc.*, 1939, **61**, 1625. [7] Friend and Hargreaves, *Phil. Mag.*, 1944, **35**, 619. [8] Meyer and Mylius, *Z. physikal. Chem.*, 1920, **95**, 349. [9] Maass and Boomer, *J. Amer. Chem. Soc.*, 1922, **44**, 1709. [10] Huckel and Wunsch, *J. pr. Chem.*, 1935, **142**, 225. [11] Friend and Hargreaves, *Phil. Mag.*, 1944, **35**, 57. [12] *Idem, ibid.*, 1944, **34**, 810. [13] *Idem, ibid.*, 1944, **35**, 136. [14] *Idem, ibid.*, 1943, **34**, 643. [15] Bingham and Rogers, *J. Rheol.*. 1932, **3**, 113.

Put $T_c/T = 2$, then, since $T_c/T_B \approx 1{\cdot}5$, $\Delta \log \eta_B\sqrt{v_B} = \frac{1}{2}\Delta \log \eta_c\sqrt{v_c}$, but as the average value of $\Delta \log \eta_c\sqrt{v_c}$ is 0·0158, we have $\Delta \log \eta_B\sqrt{v_B} = 0{\cdot}0079$, or $\Delta\eta_B v_B = 1{\cdot}8\%$.

Hence the viscosity of a given liquid at its b. p. may be calculated from a given value at the reduced temperature ½ with an average accuracy of approximately 1·8%. For toluene, for example, $\frac{1}{2}T_c = 24°$ C. and $T_B = 120°$ C., and as $\Delta \log \eta_c\sqrt{v_c} = 0{\cdot}0201$,

$$\Delta \log \eta_B\sqrt{v_B} = 0{\cdot}0201/2 = 0{\cdot}0100, \text{ or } \Delta\eta_B\sqrt{v_B} = 2{\cdot}3\%.$$

*The Dependence of* k *on Molecular Constitution.*—In equation (3), putting $T_c/T = 2$, we have

$$\log\,(\eta\sqrt{v})_{T=\frac{1}{2}T_c} = c + k \tag{8}$$

so $(c + k)$ is a measure of the function $\log \eta\sqrt{v}$ at the reduced temperature $T_r = \frac{1}{2}$.

Examination of the constants in Table II shows that $k$ increases fairly regularly with each increment of $CH_2$, and, as far as can be ascertained, is the same for all homologous series. The increment in $k$ for $CH_2$, *i.e.*, $k_{CH_2}$ was found for the paraffin series by applying Campbell's zero-sum method to the nine equations of the type $k_{\text{butane}} = k_{2H} + 4k_{CH_2}$ for the hydrocarbons from butane to dodecane. This procedure gives $k_{CH_2} = 0{\cdot}039$. By a similar method, the alkyl bromides give a value 0·031, thiols 0·037, esters 0·031, and cyanides 0·040. Other series were not taken into the calculation, for no data beyond those for the fourth members are available. The mean $k = 0{\cdot}036$ was adopted as the most probable value.

From equation (8), for two successive members of any homologous series, we may write

$$k_2 - k_1 = \log\,(\eta_2\sqrt{v_2})_{T=\frac{1}{2}T_c} - \log\,(\eta_1\sqrt{v_1})_{T=\frac{1}{2}T_c} - (c_2 - c_1) \approx 0{\cdot}036$$

But $c_2 - c_1 \approx 0$, therefore

$$10^{(k_2 - k_1)} = \left(\frac{\eta_2\sqrt{v_2}}{\eta_1\sqrt{v_1}}\right)_{T=\frac{1}{2}T_c} = 10^{0\cdot036} = 1{\cdot}086$$

Hence there is an approximately constant increase in $\eta\sqrt{v}$ at a reduced temperature of ½ from one member of any homologous series to the next of 8·6%.

TABLE III.

| Substance. | $k$, calc. | $k$, found. | $(\eta\sqrt{v})_{300}$, calc. | $(\eta\sqrt{v})_{300}$, found. | Error, % (to nearest 1%). |
|---|---|---|---|---|---|
| Propane | 0·606 | 0·619 | 1·61 | 1·61 | ± 0 |
| Butane | 0·642 | 0·612 | 2·17 | 2·19 | + 1 |
| Pentane | 0·678 | 0·679 | 2·82 | 2·77 | − 2 |
| Hexane | 0·714 | 0·702 | 3·65 | 3·69 | + 1 |
| Heptane | 0·750 | 0·736 | 4·65 | 4·62 | − 1 |
| Octane | 0·786 | 0·778 | 5·92 | 5·96 | + 1 |
| Nonane | 0·822 | 0·820 | 7·74 | 7·71 | − 0 |
| Decane | 0·858 | 0·872 | 9·91 | 9·93 | + 0 |
| Undecane | 0·894 | 0·900 | 12·8 | 12·4 | − 3 |
| Dodecane | 0·930 | 0·951 | 16·0 | 15·7 | − 2 |
| Ethyl iodide | 0·656 | 0·635 | 4·10 | 3·93 | − 4 |
| *iso*Butyl iodide | 0·728 | 0·741 | 6·21 | 6·37 | + 3 |
| Ethyl bromide | 0·647 | 0·634 | 3·21 | 3·08 | − 4 |
| Amyl bromide | 0·755 | 0·717 | 7·00 | 6·78 | − 3 |
| Octyl bromide | 0·863 | 0·856 | 14·8 | 14·1 | − 5 |
| Propanethiol | 0·649 | 0·667 | 3·80 | 4·13 | + 9 |
| Hexane-1-thiol | 0·757 | 0·756 | 7·98 | 8·26 | + 3 |
| Octane-1-thiol | 0·829 | 0·849 | 13·3 | 13·5 | + 1 |
| Acetone | 0·675 | 0·672 | 3·43 | 3·40 | − 0 |
| Diethyl ketone | 0·783 | 0·729 | 5·09 | 5·18 | + 2 |
| Methyl formate | 0·693 | 0·683 | 3·16 | 3·32 | + 5 |
| Ethyl acetate | 0·765 | 0·790 | 4·32 | 4·39 | + 2 |
| Propyl acetate | 0·801 | 0·836 | 5·40 | 5·67 | + 5 |
| Ethyl valerate | 0·873 | 0·836 | 8·83 | 8·17 | − 8 |
| Heptyl acetate | 0·945 | 0·968 | 14·3 | 14·8 | + 4 |
| Amyl butyrate | 0·945 | 0·918 | 13·4 | 11·9 | −13 |
| Methyl propyl ether | 0·696 | 0·689 | 2·94 | 2·79 | − 5 |
| Butyl ether | 0·840 | 0·825 | 7·66 | 7·26 | − 5 |
| Methyl cyanide | 0·666 | 0·668 | 4·15 | 4·03 | − 3 |
| Amyl cyanide | 0·810 | 0·805 | 8·65 | 9·44 | + 9 |
| Isoprene | 0·638 | 0·651 | 2·45 | 2·50 | + 2 |
| Diallyl | 0·674 | 0·698 | 3·25 | 3·10 | − 5 |
| *iso*Butyl chloride | 0·733 | 0·773 | 4·23 | 4·53 | + 7 |
| Methylene chloride | 0·716 | 0·640 | 3·86 | 3·54 | − 9 |
| Carbon tetrachloride | 0·898 | 0·916 | 6·81 | 7·00 | + 3 |
| Chloroform | 0·807 | 0·666 | 5·03 | 4·33 | −16 |
| Ethyl benzene | 0·706 | 0·716 | 6·40 | 6·61 | + 3 |
| *m*-Xylene | 0·706 | 0·684 | 6·61 | 6·14 | − 8 |
| Chlorobenzene | 0·725 | 0·719 | 7·41 | 7·03 | − 5 |
| *m*-Bromotoluene | 0·747 | 0·732 | 10·4 | 9·66 | − 8 |

The above argument clearly applies equally well to any other reduced temperature, the value of log $\eta\sqrt{v}$ for $CH_2$ being less or greater than 0·036 according as $T_r$ is greater or less than ½. Thus at corresponding temperatures for any homologous series, there is a constant percentage increase in $\eta\sqrt{v}$ from one member to the next, this percentage being 8·6 at the reduced temperature ½.

In view of the constancy of $k_{CH_2}$, it seemed reasonable to assume that $k$ could be evaluated from a list of atomic and structural constants. By proceeding in the usual way, the following list has been drawn up :

$C = -0{\cdot}462$
$I = 0{\cdot}335$
$H = 0{\cdot}249$
$O = 0{\cdot}054$
$Cl = 0{\cdot}340$
$S = 0{\cdot}043$
$Br = 0{\cdot}326$
Double bond = 0·478
$C_6H_5 = 0{\cdot}385$
CO (ketones and esters) = 0·105
CN (cyanides) = 0·381

The measure of agreement between the calculated and observed values of $k$ is shown for a few typical cases in Table III. Clearly, by employing the above list of constants, $\eta\sqrt{v}$ for a substance at any temperature may be evaluated, provided $T_c$ can be estimated as above. Thus, *e.g.*, at 27° C., we can write $\log (\eta\sqrt{v})_{300} = 0{\cdot}067 + k(T_c/300 - 1)$.

Table III also shows the percentage deviations between the values of $\eta\sqrt{v}$ at 27° C. so calculated, and the actual values [as calculated from (3)] at that temperature. In ascertaining the mean percentage error thus involved, all the substances listed in Table II were included, with the exception of the following whose $k$ values could not be calculated : carbon disulphide, thiophen, *cyclo*hexane, *cyclo*hexanone, and *cyclo*hexyl chloride.

Large errors are exhibited by benzene (52%), ethylene chloride (27%), ethylene bromide (45%), propylene bromide (28%), *iso*butylene bromide (60%), *iso*valeraldehyde (29%), and anisole (32%).

The exceptional behaviour of benzene and the alkylene halides was also observed by Thorpe and Rodger (*locc. cit.*). The behaviour of the latter may be due to the accumulation of " negative " groups, and it may be significant that parachor and molecular refractivity anomalies are also associated with such molecules (Mumford and Phillips, *J.*, 1929, 2112).

The remaining 108 liquids, of which 72 show errors of less than 5%, 91 less than 9%, and 102 less than 14%, show a mean error of 5%. The agreement is perhaps better than could have been expected in view of the nature of the approximations made, and the uncertainty involved in the evaluation of $T_c$. At least, the method is not without practical value in viscometry, where choice of viscometer capillary dimensions for a given liquid would be facilitated. Further, the temperature–viscosity behaviour can be predicted from the relationship $\beta = kT_c$.

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