539. *Interrelationship between Viscosity and Boiling Point of Homologous Liquids.*

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A number of empirical relations have been deduced between boiling point and viscosity for certain homologous series. Use has been made of a function ηM, where these symbols have their usual significance.

STARTING from Telang's absolute viscosity equation,[1] which is based on Eyring's rate theory and the " hole " structure of liquids,[2] Palit[3] deduced the following equation correlating the viscosity η, surface tension γ, density $\rho(= 1/v_{\text{sp.}})$, and molecular weight M, of a homologous series :

$$\log(\eta M) = k_1\gamma(Mv_{\text{sp.}})^{\frac{2}{3}} + k_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where k_1 and k_2 are constants whose values are given by the equations :

$$k_1 = 1{\cdot}091\boldsymbol{N}^{\frac{1}{3}}/2{\cdot}303\boldsymbol{R}T = 0{\cdot}165 \times 10^{-2} \text{ (at } 20°) \quad . \quad . \quad . \quad . \quad (2)$$

$$k_2 = (\log \boldsymbol{hN}b_{\text{sp.}})/v_{\text{sp.}}^{\frac{2}{3}}(v_{\text{sp.}} - b_{\text{sp.}})^{\frac{1}{3}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $\boldsymbol{N}$, $\boldsymbol{h}$, $\boldsymbol{R}$, and T have their usual significance and $b_{\text{sp.}}$ is the van der Waals constant per gram, *i.e.*, the actual volume of the molecule per gram. According to equation (1) log ηM should increase linearly with molar surface energy at a rate of about $\frac{1}{6}$% per unit change in molar surface energy. The available experimental data are found to be in very good agreement with the above equation.[3]

Viscosity and Boiling Point.—By combining with equation (1) the Eötvös equation, $\gamma(Mv_{\text{sp.}})^{\frac{2}{3}} = K_{\text{E}}(T_c - T)$, and the Guldberg equation, $T_c = \frac{3}{2}T_b$, where T_b is the boiling point (at 760 mm.) in °K, we obtain the following simple relation for a homologous series :

$$\log(\eta M) = m_1T_b + m_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

i.e.,

$$\eta M = \text{Const.} \times \exp.(m_1T_b) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4a)$$

where m_1 and m_2 are constants and m_1, if $K_{\text{E}} = 2{\cdot}1$, is given by

$$m_1 \simeq \tfrac{3}{2}k_1K_{\text{E}} = 5{\cdot}2 \times 10^{-3} \text{ per degree at } 20° \quad . \quad . \quad . \quad . \quad (5)$$

According to equation (4), log ηM should increase linearly with the b. p. at a rate of slightly more than 0·5% per degree, *i.e.*, about 3½-fold per 100° change in b. p. This equation assumes the validity of Eötvös and Guldberg's equations and that K_{E} is the same for all members of a homologous series : such conditions obtain approximately in non-associated liquids but not for associated liquids. Fig. 1 demonstrates the above linearity, and it is noteworthy that the slope of $6{\cdot}7 \times 10^{-3}$ at 20° is near the theoretically expected slope of $5{\cdot}2 \times 10^{-3}$. Unfortunately, we could not make a more extensive test of this very simple relation owing to lack of data for other non-polar homologous series.

This equation cannot be tested for higher hydrocarbons because the viscosity data are not available and the b. p.s under normal pressure are difficult to obtain. It has been shown[4] that ln η can be replaced by $100\rho_0[\eta]$ in the above equation, where ρ_0 is the density and $[\eta]$ is the intrinsic viscosity which is obtainable from viscosity measurements in solution; T_b can, of course, be determined at reduced pressures though the data available are not very accurate. It is noteworthy, however, that $100\rho_0[\eta] + \ln M$ is a linear function of T_b at 15 mm. for C_{17}—C_{35} straight-chain hydrocarbons. Data on $[\eta]$ are available from the work of Meyer and van der Wyk as recalculated by Mark and Tobolsky,[5]

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[1] Telang, *J. Chem. Phys.*, 1949, **17**, 556.

[2] Glasstone, Laidler, and Eyring, " Theory of Rate Processes," McGraw-Hill, New York, 1951, p. 488.

[3] Palit, *Indian J. Phys.*, 1952, **26**, 627.

[4] *Idem, ibid.*, 1955, **29**, 65.

[5] Mark and Tobolsky, " High Polymers," Vol. II, Interscience Publ., New York, 1950, p. 289.

and T_b at 15 mm. is taken from Egloff's work.[6] This linear relation is shown as curve *B* in Fig. 1. Since T_b at 15 mm. is about $\frac{3}{4}T_b$ at 760 mm., we should expect the slope to be nearly thrice the theoretical slope, *i.e.*, $\frac{4}{3} \times 2{\cdot}303 \times 5{\cdot}2 \times 10^{-3} = 15{\cdot}9 \times 10^{-3}$. This compares well with the observed slope of $14{\cdot}7 \times 10^{-3}$.

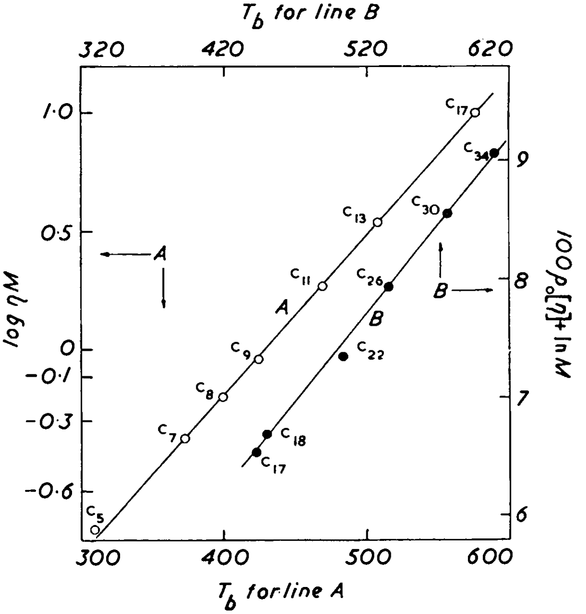

FIG. 1. *Relation between viscosity and boiling point of* n-*paraffins.*

Curve *A* : log (ηM) *versus* T_b for C_5—C_{17} hydrocarbons. (Data for η at 20° from Doolittle, *J. Appl. Phys.*, 1951, **22**, 1032; data T_b from Egloff.[6])

Curve *B* : $100\rho[\eta] + \ln M$ *versus* T_b at 15 mm. for C_{17}—C_{35} hydrocarbons. (Data for $[\eta]$ from Mark and Tobolsky;[5] data for T_b from Egloff.[6])

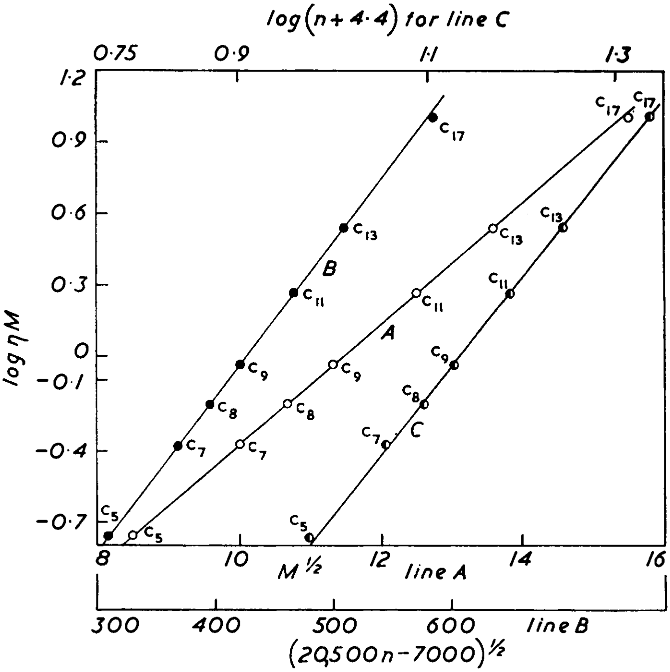

FIG. 2. *Relation between viscosity and molecular weight of* n-*paraffins.*

Curve *A* : log (ηM) *versus* $M^{\frac{1}{2}}$ for C_5—C_{17} hydrocarbons.

Curve *B* : log (ηM) *versus* $(20{,}500n—7000)^{\frac{1}{2}}$ for C_5—C_{17} hydrocarbons (*n* = no. of carbon atoms).

Curve *C* : log (ηM) *versus* [ln (*n* + 4·4)]. [Data for η at 20° from Doolittle *et al.* (see Fig. 1).]

Since the slope is expected to be practically the same for all non-associated liquids, it can be shown that log ($\eta'M'/\eta M$) would be linear with ΔT_b, where ΔT_b is the difference in T_b values for the monohalogen derivative and the parent hydrocarbon, and η' and M' are

[6] Egloff, " Physical Constants of Hydrocarbons," Vol. I, Reinhold Publ. Corp., New York, 1939.

values for the monohalogen derivative corresponding to η and M. Varshni [7] has, however, shown empirically that on passing from a hydrocarbon to a monohalogen derivative, ΔT_b is inversely proportional to $T_b + T_b'$; we should therefore expect the above logarithmic quantity to increase linearly with $1/(T_b + T_b')$; *e.g.*, ηM(hexane)/ηM(chlorohexane) should be less than ηM(heptane)/ηM(chloroheptane) and so on, *i.e.*, the viscosity of the hydrocarbon should approach that of the monohalogen derivative the more closely as we ascend the series. Though the scanty data available tend to support this conclusion, no systematic data are available to test it adequately.

Viscosity and Molecular Weight.—Many empirical relations between T_b and M or n (the number of carbon atoms) have been proposed. If we eliminate T_b between any of these relations and our equation (4), we obtain an equation correlating η and M or n.

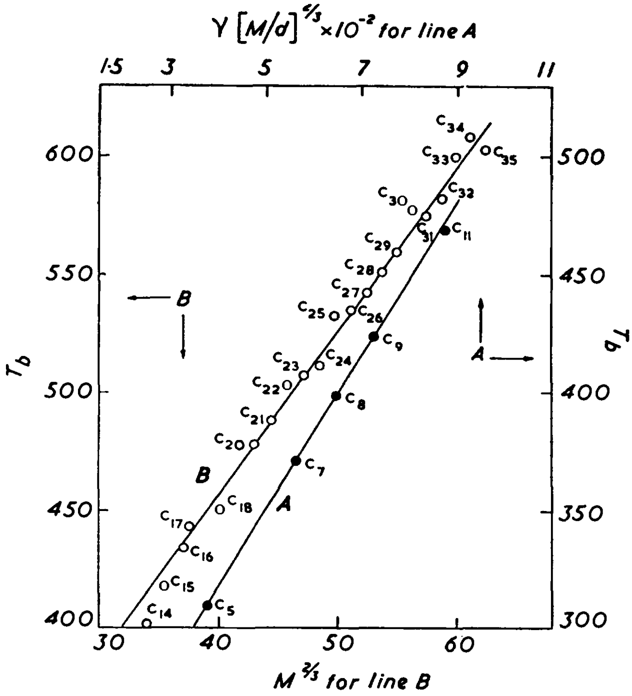

FIG. 3. *Relation between boiling point and* (*A*) *molar surface energy and* (*B*) *molecular weight.*

Curve A: T_b *versus* molar surface energy for C_5—C_{11} hydrocarbons. [Surface tension and density data from Quale, Day, and Brown (*J. Amer. Chem. Soc.*, 1944, **66**, 938), and for b. p. from Egloff.[6]]

Curve B: T_b at 15 mm. *versus* $M^{\frac{2}{3}}$ for C_{14}—C_{35} hydrocarbons. (Data for T_b from Egloff.[6])

However, such equations are quite different from ours, for we have introduced the function ηM, which has not been used before. For example, Walker's equation,[8] that of Aten [9] for paraffin mono-derivatives, and that of Egloff, Sherman, and Dull [10] for hydrocarbons give, respectively, equations (6), (7), and (8), which are illustrated in Fig. 2 and are seen to be fairly accurate.

$$\log \eta M = AM^{\frac{1}{2}} + C \qquad (6)$$

$$\log \eta M = A(20{,}500n)^{\frac{1}{2}} + C \qquad (7)$$

$$\log \eta M = A \log (n + 4{\cdot}4) + C \qquad (8)$$

One simple corollary of equations (1) and (4) may be pointed out. Since $\log \eta M$ is linear with molar surface energy and also with boiling point, it follows that T_b is linear with molar surface energy, as can be shown also by combination of Eötvös and Guldberg's equations. Although this relation is empirical, we may remark, first, that it is quite accurate at least for hydrocarbons as is shown in Fig. 3, Curve A, and secondly, that it

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[7] Varshni, *J. Indian Chem. Soc.*, 1953, **30**, 169.

[8] Walker, *J.*, 1894, **65**, 193, 795.

[9] Aten, *J. Chem. Phys.*, 1937, **5**, 260.

[10] Egloff, Sherman, and Dull, *J. Phys. Chem.*, 1940, **44**, 730.

indicates that b. p. should increase linearly with $M^{\frac{2}{3}}$ as we ascend a homologous series, *i.e.*, Lt $M \longrightarrow \infty$, $T_b \simeq aM^{\frac{2}{3}} + b$. This is shown for a few straight-chain hydrocarbons from C_{14} to C_{35} in Fig. 3, wherein we have plotted T_b at 15 mm. against M; it is seen that the curve tends to a constant slope with increasing M.

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