A VISCOSITY FORMULA FOR BINARY MIXTURES, THE ASSOCIATION DEGREES OF CONSTITUENTS BEING TAKEN INTO CONSIDERATION. VI.

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In an earlier paper,⁽¹⁾ the writer reduced Dunstan and Wilson's equation connecting logarithms of the absolute viscosity and the molecular weight into a form:

$$\log\eta = -3.22 + bM$$

(where η and M are the viscosity coefficient and the molecular weight of a liquid, and b is a particular constant for the particular liquid, depending upon the temperature) and showed that the values of b and the field-constant k are practically the same when both are compared with those for benzene.

Other formulas showing the relation between the viscosity coefficient and the molecular weight have been proposed by Gartenmeister⁽¹⁾ and Macleod.⁽³⁾

Gartenmeister deduced the following relation from his careful determinations of the absolute viscosity of various liquids:

$$\eta = k_G \ M, \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1)$$

where k_G is a particular constant within the observed temperature range for chlorine, bromine and iodine substitution compounds.

For those which do not obey the rule such as homologous series in which successive members differ by CH_2, he took M^2 in place of M, but the constancy of their proportional constants are not satisfactory.

Macleod, having drawn attention to the fact that the relation between the viscosity of liquids and their coefficients of expansions and densities can be explained on the assumption that the viscosity is a simple function of the free space within the liquid, proposed the expression:

$$\eta_t x_t^A = C,$$

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(1) This Bulletin, **4** (1929), 149.

(2) R. Gartenmeister, *Z. physik. Chem.*, **6** (1890), 524.

(3) D. B. Macleod, *Trans. Faraday Soc.*, **19** (1923), 6; **21** (1925), 145 and 151.

where η_t is the viscosity at a temperature t, x_t the free space at that temperature, C is a constant for the particular liquid, and A is approximately unity for unassociated substances. In this calculation he assumed that the expansion is wholly confined to the free space and the volume of the molecules remains constant, and put

$$x_t = x_0 + \frac{v_t}{v_0} - 1,$$

in which x_0 is the free space at 0°; v_t and v_0 are the specific volumes at $t°$ and 0° respectively.

Macleod further observed that by putting A as unity (which causes no serious error in finding x_0 for normal liquids) C is proportional to the molecular weight. He applied this method of calculation to any liquid, in this case, however, the discrepancy of the proportional constant from the value obtained for such a normal liquid as octane he attributed to the molecular complexity of the liquid and put forward the expression :

$$\eta = \frac{k_M a_M}{x}, \quad \dots\dots\dots\dots\dots\dots\dots\dots \quad (2)$$

where a is the degree of association and k_M is a constant for all liquids.

Comparing the equal terms in expressions (1) and (2), we get

$$k_G x = k_M a$$

With the object of testing which of the values k_G or $k_G\,x$ gives more constancy, the present writer will make use of the values at 0°C. tabulated by Macleod in his paper.⁽¹⁾

Table 1.

Substance	η_0	M	x_0	$10^5 \cdot k_G$	$10^6 \cdot k_G \cdot x_0$
C_2H_5Br	0·00478	109·0	0·1080	4·39	4·74
C_3H_7Br	0·00645	123·0	0·0908	5·24	4·76
i–C_3H_7Br	0·006045	123·0	0·0923	4·92	4·54
i–C_4H_9Br	0·008235	137·0	0·0829	6·01	4·98
CH_3I	0·005945	142·0	0·0967	4·19	4·05
C_2H_5I	0·00719	156·0	0·0907	4·61	4·18
C_3H_7I	0·00938	170·0	0·0782	5·52	4·31
i–C_3H_7I	0·008785	170·0	0·0836	5·17	4·32

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(1) D. B. Macleod, *Trans. Faraday Soc.*, **21** (1925), 154–155.

Table 1.—(*Continued*)

Substance	η_0	M	x_0	$10^5 \cdot k_G$	$10^6 \cdot x_0$
C_5H_{12}	0·00283	72·1	0·1207	3·93	4·74
i–C_5H_{12}	0·00273	72·1	0·1202	3·79	4·55
C_6H_{14}	0·003965	86·1	0·0979	4·60	4·51
i–C_6H_{14}	0·00371	86·1	0·1054	4·31	4·54
C_7H_{16}	0·00519	100·1	0·0863	5·19	4·48
i–C_7H_{16}	0·00477	100·1	0·0883	4·77	4·21
C_8H_{18}	0·00703	114.1	0·0744	6·16	4·58
CH_3OH	0·00813	32·0	0·0580	25·4	14·7
C_2H_5OH	0·01770	46·0	0·0450	38·5	17·3
C_3H_7OH	0·03882	60·0	0·0233	64·7	15·1
i–C_3H_7OH	0·04564	60·0	0·0252	76·0	19·1
C_4H_9OH	0·05185	74·0	0·0248	70·0	17·4
i–C_4H_9OH	0·08038	74·0	0·0243	108·6	26·4
$HCOO \cdot CH_3$	0·00429	60·0	0·0994	7·15	7·11
$HCOO \cdot C_2H_5$	0·00505	74·0	0·0936	6·83	6·39
$HCOO \cdot C_3H_7$	0·00668	88·0	0·0768	7·59	5·83
$CH_3CO_2 \cdot CH_3$	0·00478	74·0	0·0974	6·46	6·29
$CH_3CO_2 \cdot C_2H_5$	0·00578	88·0	0·0820	6·57	5·39
$CH_3CO_2 \cdot C_3H_7$	0·00770	102·0	0·0700	7.55	5·28
$H \cdot COOH$	0·02245	46·0	0·0356	48·8	17·4
$CH_3 \cdot COOH$	0·01219	60·0	0·0564	20·3	11·5
$CH_3 \cdot CH_2 \cdot COOH$	0·01519	74·0	0·0563	20·5	11·5
$CH_3(CH_2)_2 \cdot COOH$	0·02284	88·0	0·0417	26·0	10·8
$(CH_3)CH \cdot COOH$	0·01885	88·0	0·0463	21·4	9·92
$CH_3 \cdot CO \cdot CH_3$	0·00394	58·0	0·1134	6·79	7·70
$C_2H_5 \cdot CO \cdot CH_3$	0·005385	72·0	0·0827	7·48	6·19
$C_2H_5 \cdot CO \cdot C_2H_5$	0·00595	86·1	0·0800	6·91	5·53
$C_3H_7 \cdot CO \cdot CH_3$	0.00644	86·1	0·0754	7·48	5·64
C_6H_6	0·009025	78·0	0·0585	11·6	6·77
$C_6H_5CH_3$	0·007685	92·0	0·0642	8·35	5·36
$C_6H_5C_2H_5$	0·00874	106·0	0·0545	8·24	4·49
o-$C_6H_4(CH_3)_2$	0·011025	106·0	0·0486	10·4	5·06
m–$C_6H_4(CH_3)_2$	0·00802	106·0	0·0597	7·57	4·52

Table 1.—(*Continued*)

Substance	η_0	M	x_0	$10^5 \cdot k_G$	$10^6 \cdot k_G \cdot x_0$
CS_2	0·004295	76·0	0·1206	5·65	6·81
$(CH_3)_2S$	0·00354	62·0	0·1150	5·71	6·57
$(C_2H_5)_2S$	0·00559	90·0	0·0863	6·21	5·36
$C_2H_5{\cdot}O{\cdot}C_2H_5$	0·00286	74·1	0·1234	3·86	4·76
$C_3H_7{\cdot}O{\cdot}CH_3$	0·00307	74·1	0·1272	4·14	4·86
$C_3H_7{\cdot}O{\cdot}C_2H_5$	0·003965	88·0	0·0994	4·50	4·48
$C_3H_7{\cdot}O{\cdot}C_3H_7$	0·00540	102·0	0·0816	5·29	4·32
$i\text{-}C_4H_9{\cdot}O{\cdot}CH_3$	0·00381	88·0	0·1018	4·33	4·41
$i\text{-}C_4H_9{\cdot}O{\cdot}C_2H_5$	0·00482	102·0	0·0887	4·73	4·19

It is easily understood from the above table that Gartenmeister's exceptional cases, to which homologous series such as alcohols and acids belong, are sufficiently expressed by the formula $\eta = KM$, K being corrected for Macleod's free space and that for some substitution compounds such as formates and ketones more constancy of the values of the proportional constants is obtained by Gartenmeister's formula than by Macleod's. In short, it being difficult to justify which is the superior of the two so far as the present data are concerned, it seems highly probable, in accordance with the physical meaning that the viscosity is due to a transport of momentum, (i) that the viscosity η is proportional to the molecular weight M and (ii) that the proportional constant K in the expression $\eta = KM$ is a particular constant which plays a very important part.

Brillouin,(1) who made a success to interpret the negative temperature coefficient of viscosity of liquids from a theoretical standpoint of view, assumed that in liquids where the molecules are continually in collision and where the transfer of matter (diffusion) is ordinarily insignificant, when a molecule strikes all of the molecules in the vicinity are shaken and an elastic wave is found which is propagated through the medium, or, in other words, the molecules of liquids are never free and always under strong forces.

This intensity of attraction field must of course be taken into consideration in studying the viscosity of liquids. If the viscosity of a liquid is stoichiometrically related with the molecular weight as in the expression :

$$\eta = KM$$

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(1) L. Brillouin, *J. phys. radium* [6] **3** (1922), 326 and 362.

the factor depending on the intensity of attraction field may be included in no other than the constant K.

According to Macleod's idea the constant K depends on the free space and the relative value K of a liquid to K of octane is simply equal to the degree of association of the liquid, for which, however as stated above, his deduction formula $\eta\, x=\text{const.}$ (x being the free space) does not hold true.

For a further test the comparison among the particular constants at 0°C. (relative to those for benzene) calculated from the three formulas of Dunstan and Wilson, of Gartenmeister and of Macleod will be made in the following.

Table 2.

Substance	$\frac{(b)C_6H_6}{b}$	$\frac{(k_G)C_6H_6}{k_G}$	$\frac{(k_G\cdot x)C_6H_6}{k_G\cdot x}$
C_6H_6	1	1	1
$C_6H_5CH_3$	1·25	1·39	1·26
$CH_3GO_2C_2H_5$	1·35	1·76	1·26
$CHCl_3$	1·69	1·98	1·22
CCl_4	1·72	1·32	1·29
CS_2	1·34	2·05	0·99
CH_3OH	0·43	0·46	0·46
C_2H_5OH	0·47	0·30	0·39
H_2O	0·18	0·12	0·33
CH_3COOH	0·69	0·57	0·59

Though a quite satisfactory coincidence among the constants may not be hoped for, yet it is probable that they are the equivalent quantities with one another and are consequently the corresponding factors with the writer's field-constant k.(1) Similar consideration as above shown, if it extends to binary mixtures, accords with the writer's theory.(2)

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(1) This Bulletin, **4** (1929), 149.
(2) This Rulletin, **4** (1929), 5.