A VISCOSITY FORMULA FOR BINARY MIXTURES, THE ASSOCIATION DEGREES OF CONSTITUENTS BEING TAKEN INTO CONSIDERATION. III.[1]

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Viscosity and molecular structure. It was discovered by Dunstan and Wilson[2] that the viscosity coefficient and molecular weight of a liquid are related by the simple law :

$$M = A + B \log \eta ,$$

where M is the molecular weight, A and B are constants depending on the

(1) The former papers of this series have been published in this Bulletin, **4** (1929), 5 and 25.
(2) A. E. Dunstan & R. W. Wilson, *J. Chem. Soc.*, **91** (1907), 90.

particular series to which the liquid belongs, and η is the viscosity coefficient. They further noticed that B is almost the same in the various series, and has therefore a general nature, A being the specific constant for each family.

A mere transformation of the expression into

$$\log \eta = a + b\,M \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

brings us the following another noticeable result. The experimental data applied in the present calculation are quoted from the values obtained by Thorpe and Rodger.[1]

Paraffins.

t°C.	C_5H_{12}	a	b	C_6H_{14}	a	b	C_7H_{16}	a	b	C_8H_{18}
0	0.00283	−3.30	0.01044	0.003965	−3.12	0.00835	0.00519	−3.23	0.00940	0.00703
20	0.00232	−3.35	0.00996	0.00320	−3.16	0.00772	0.004105	−3.23	0.00838	0.00538
30	0.00212	−3.37	0.00971	0.00290	−3.18	0.00746	0.00369	−3.24	0.00805	0.004785

t°C.	i−C_5H_{12}	a	b	i−C_6H_{14}	a	b	i−C_7H_{16}
0	0.00273	−3.25	0.00950	0.00371	−3.10	0.00778	0.00477
20	0.00223	−3.31	0.00919	0.00300	−3.15	0.00724	0.00379
30	0.00204	−3.34	0.00897	0.002725	−3.17	0.00699	0.003415

Iodides.

t°C.	CH_3I	a	b	C_2H_5I	a	b	C_3H_7I
0	0.005945	−3.06	0.00589	0.00719	−3.43	0.00824	0.00938
20	0.00487	−3.10	0.00558	0.00583	−3.37	0.00726	0.00737
40	0.00409	−3.13	0.00521	0.00484	−3.34	0.00659	0.005985

t°C.	i−C_3H_7I	a	b	i−C_4H_9I
0	0.008785	−3.53	0.00870	0.011625
20	0.00690	−3.38	0.00718	0.00870
40	0.00559	−3.36	0.00654	0.006905

Monobromides.

t°C.	C_2H_5Br	a	b	C_3H_7Br
0	0.00478	−3.33	0.00929	0.00645
20	0.00392	−3.34	0.00857	0.00517
30	0.00357	−3.35	0.00832	0.00467

(1) T. E. Thorpe & J. W. Rodger, *Phil. Trans.*, **185** II (1894), 397.

t°C.	i−C_3H_7Br	a	b	i−C_4H_9Br
0	0.006045	−3.40	0.00958	0.008235
20	0.00482	−3.39	0.00869	0.00638
30	0.00435	−3.38	0.00832	0.00569

Sulphides.

t°C.	$(CH_3)_2S$	a	b	$(C_2H_5)_2S$
0	0.00354	−3.33	0.01416	0.00559
20	0.00293	−3.34	0.01291	0.004445
30	0.002685	−3.34	0.01243	0.00401

Fatty alcohols.

t°C.	CH_3OH	a	b	C_2H_5OH	a	b	n-C_3H_7OH
0	0.00813	−2.86	0.02411	0.01770	−2.87	0.02433	0.03882
20	0.00591	−2.92	0.02173	0.01192	−2.83	0.01976	0.02255
40	0.004505	−2.95	0.01884	0.008275	−2.84	0.01635	0.01403

a is regarded to be a universal constant, almost independent of temperature, while b which varies with temperature seems to be a particular constant for each homologous series.

Taking the mean value of a at 20°C. from the above figures, we obtain a reduced formula:

$$\log \eta = -3.22 + b\,M \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Relationship between b and the field-constant k. So far as a can be put to be a universal constant for all liquids, the factors which particularize a liquid are b and the molecular weight, and therefore b may well be said to play a great rôle in the molecular constitution of the liquid.

The writer, in his earlier papers,[1] defined the field-constant k of a liquid which presumably depends on the molecular structure, and evaluated those values of more than ten liquids by putting that of C_6H_6 as unity.

It is the purpose in this paper to find the relationship between k and b thus calculated. Two examples are taken below.

For benzene as we have η at 25°C=0.00599,

$$\log 0.00599 = -3.22 + b \times 78.05$$
$$b \text{ of } C_6H_6 = 0.0128.$$

And for water at the same temperature

(1) This Bulletin, **4** (1929), 5; **4** (1929), 25.

$$\log 0.00891 = -3.22 + b \times 18.02$$
$$b \text{ of } H_2O = 0.0649.$$

In the writer's opinion it is not likely to include water into a member of alcohol series and benzene into a member of substitutions of CH_3- or other groups.

b of other liquids can be estimated by the same method, the results of calculation from the viscosity data at 25°C. being recorded in the following table.

Substance	$\eta_{25°}$	b	$\frac{b_{C_6H_6}}{b}$	k
C_6H_6	0.00599	0.0128	1	1
$C_6H_5CH_3$	0.00541	0.01035	1.23	1.23
CH_3COOCH_3	0.003594	0.0105	1.22	1.67
$CHCl_3$	0.00540	0.00798	1.60	1.50
CCl_4	0.00883	0.00758	$1.69 = \frac{1}{0.59}$	0.63
CS_2	0.003656	0.0103	$1.24 = \frac{1}{0.80}$	0.76
CH_3OH	0.00557	0.0302	0.42	0.36
H_2O	0.00891	0.0649	0.20	0.21
$HCONH_2$	0.03359	0.0388	0.33	0.35
CH_3COOH	0.01121	0.0212	0.60	0.57

A simple test of comparison between k and b relative to that of C_6H_6 results in the fact that they are fairly concordant with each other as shown in this table.

As already observed, k or b being an important factor which characterizes a liquid, there may be introduced a "hypothetical or ideal liquid" which displays no particular nature as any real liquid does. For such liquid we may put $b=0$ in formula (2), so obtain

$$\log \eta = -3.22 = \bar{4}.78$$

or

$$\eta = 0.00060.$$

This values is far less than the viscosity coefficients of all liquids.

It will also be noticed that the degree of association has no important meaning in treating the viscosity of a single liquid.

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