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

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The writer proposed[1] a viscosity formula for a chemically indifferent binary mixture of the form:

$$\eta=\eta_1+(\eta_2-\eta_1)\frac{k_2a_2z_m}{k_1a_1(1-z_m)+k_2a_2z},$$

where η, a and k with the suffixes 1 and 2 signify the viscosities, the association degrees and the field constants of components 1 and 2 respectively; z_m is the molar fraction of component 2.

The formula was confirmed with satisfactory results and also proved to be applicable for the mixture in which molecular compounds are formed.[2] Thus, the deviation δ of the measured viscosity (η) from that calculated from the formula (η_0) is expressible in the following form:

$$\delta=\eta-\eta_0=C\cdot(1-z_m)^{\nu_1}z_m^{\nu_2},$$

where ν_1 and ν_2 are the numbers of reactive molecules of each component to form a molecular compound and C is an empirical constant.

The field constant k which is a measure of molecular field of attraction was shown to be an important factor by which a liquid is particularized from other liquids.[3]

This paper is a further study on k for the mixture where one of its components suffers molecular dissociation.

If the associated molecules of one component, say, component 2 of a binary mixture dissociates in the solution, the values $\left(\frac{k_2a_2}{k_1a_1}\right)$ do not keep constant, since a_2 is a variable with concentration. Suppose the group of such points to lie on a straight line, the extrapolated values to $z_m=0$ and to $z_m=1$ are easily obtainable and are accurate at the same time.

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(1) This Bulletin, **4** (1929), 5.
(2) This Bulletin, **4** (1929), 25.
(3) This Bulletin, **4** (1929), 149.

Now consider three binary mixtures composed of three liquids A, B and C, among which only C dissociates in the admixtures of A and of B. Then we have

$$\left(\frac{k_c a_c}{k_A a_A}\right)_{z_m\text{-}C=1} \quad \text{and} \quad \left(\frac{k_c a_c}{k_B a_B}\right)_{z_m\text{-}C=1}.$$

Taking the ratio of these two, we get $\left(\frac{k_B a_B}{k_A a_A}\right)$.

The writer's theory demands that this value must coincide with that directly obtained from the viscosity of the mixture of A and B, provided that they are chemically non-reactive with each other.

It would be interesting to know whether the extrapolated values thus obtained obey the proposition, and the following six cases will be adopted from the literature.

Calculations of the degree of molecular dissociation.

Since the field constant k is invariable, it is easily understood that the degree of molecular dissociation of one component, say, component 2 in the admixture of infinite quantity of the other, component 1 which is non-dissociated, can be estimated by the following method: By extrapolation we get

$$\left(\frac{k_2 a_2}{k_1 a_1}\right)_{z_m=0} \text{and} \quad \left(\frac{k_2 a_2}{k_1 a_1}\right)_{z_m=1},$$

in which $(a_2)_{z_m=1}$ denotes the association degree of component 2 in singly existence,

and $(a_2)_{z_m=0}$, the decreased association degree of component 2 dissolved in infinite quantity of component 1.

If we denote the degree of molecular dissociation at infinite dilution by a_∞,

$$a_\infty = 1 - \frac{(a_2)_{z_m=0}}{(a_2)_{z_m=1}} = 1 - \left(\frac{k_2 a_2}{k_1 a_1}\right)_{z_m=0} \Big/ \left(\frac{k_2 a_2}{k_1 a_1}\right)_{z_m=1},$$

since $(a_1)_{z_m=0} = (a_1)_{z_m=1}$ by assumption.

Table 1.

$C_6H_5CH_3-C_6H_5CH_2\cdot C_7H_5O_2$ (Benzyl benzoate), 25°C.
(Kendall & Monroe).[1]

z_m-Ester	η	$\left(\frac{k_2a_2}{k_1a_1}\right)_{obs.}$	$\left(\frac{k_2a_2}{k_1a_1}\right)_{calc.}$
0.0000	0.005520		
0.2367	0.01183	0.280	0.282
0.4261	2015	0.306	0.310
0.6502	3614	0.341	0.341
0.7890	5080	0.359	0.360
0.9002	6660	0.378	0.376
1.0000	8450		

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=0} = 0.250, \qquad \left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=1} = 0.390$$

and $$\left(\frac{k_2a_2}{k_1a_1}\right)_{calc.} = 0.250+(0.390-0.250)z_m .$$

Table 2.

$C_6H_6-C_6H_5CH_2\cdot C_7H_5O_2$ (Benzyl benzoate), 25°C.
(Kendall & Monroe)[2].

z_m-Ester	η	$\left(\frac{k_2a_2}{k_1a_1}\right)_{obs.}$	$\left(\frac{k_2a_2}{k_1a_1}\right)_{calc.}$
0.0000	0.006044		
0.1886	0.01196	0.343	0.345
0.4124	2301	0.392	0.386
0.5832	3584	0.437	0.418
0.7827	5478	0.455	0.455
0.8952	6883	0.468	0.476
1.0000	8454		

(1), (2) J. Kendall and K. P. Monroe, *J. Am. Chem. Soc.*, **39** (1917), 1787.

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=0} = 0.310\,, \qquad \left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=1} = 0.495$$

and $$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{calc.}} = 0.310+(0.495-0.310)z_m\,.$$

From the values

$$\left|\frac{(ka)\text{Ester}}{(ka)_{C_6H_5CH_3}}\right|_{z_m\text{-Ester}=1} = 0.390 \quad \text{and} \quad \left|\frac{(ka)\text{Ester}}{(ka)_{C_6H_6}}\right|_{z_m\text{-Ester}=1} = 0.495$$

we obtain, since $(a)_{C_6H_6}=(a)_{C_6H_5CH_3}=1$,

$$\frac{(ka)_{C_6H_5CH_3}}{(ka)_{C_6H_6}}=\frac{(k)_{C_6H_5CH_3}}{(k)_{C_6H_6}}=\frac{0.495}{0.390}=1.27\,.$$

Satisfactory coincidence is found between this value and $k=1.23$ obtained in the previous paper for the field-constant of $C_6H_5CH_3$. Also

$$\left|\frac{(ka)\text{Ester}}{(ka)_{C_6H_5CH_3}}\right|_{z_m\text{-Ester}=0} = \frac{(ka')\text{Ester}}{(ka)_{C_6H_5CH_3}}=0.250\,,$$

where (a') =the decreased association degree of the ester at zero concentration in $C_6H_5CH_3$.

$$\left|\frac{(ka)\text{Ester}}{(ka)_{C_6H_6}}\right|_{z_m\text{-Ester}=0} = \frac{(ka'')\text{Ester}}{(ka)_{C_6H_5CH_3}}=0.310\,,$$

where (a'') =the decreased association degree of the ester at zero concentration in C_6H_6.

From these two we get

$$\left(\frac{a''}{a'}\right)_{\text{Ester}}\cdot\frac{(k)_{C_6H_5CH_3}}{(k)_{C_6H_6}}=\frac{0.310}{0.250}=1.24\,.$$

This value is in good agreement with the above, so that $a'=a''$, i. e. benzyl benzoate dissociates in equal amount at zero concentration in $C_6H_5CH_3$ and in C_6H_6; the degree of the molecular dissociation,

$$a_\infty=1-\frac{0.250}{0.390} \quad \text{or} \quad 1-\frac{0.310}{0.495}=0.36 \quad \text{or} \quad 0.37\,.$$

Table 3.

$C_6H_4(OCH_3)OH$ (Guaiacol)$-C_6H_6$, 30°C. (Puschin & Pinter).[1]

z_m-C_6H_6	η	$\left(\frac{k_2a_2}{k_1a_1}\right)_{obs.}$	$\left(\frac{k_2a_2}{k_1a_1}\right)_{calc.}$
0.00	0.0445		
0.10	0.0340	3.34	3.64
0.20	0.0249	4.08	3.88
0.30	0.0197	4.13	4.12
0.40	0.0157	4.32	4.36
0.50	0.0129	4.38	4.60
0.60	0.0104	4.82	4.84
0.70	0.00873	5.04	5.08
0.80	742	5.36	5.32
0.90	641		
1.00	569		

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=0} = 3.40 \quad \text{and} \quad \left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=1} = 5.80$$

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{calc.} = 3.40 + (5.80-3.40)z_m .$$

Table 4.

$C_6H_4(OCH_3)OH$ (Guaiacol)$-C_6H_5CH_3$, 30°C. (Puschin & Pinter).[2]

z_m-$C_6H_5CH_3$	η	$\left(\frac{k_2a_2}{k_1a_1}\right)_{obs.}$	$\left(\frac{k_2a_2}{k_1a_1}\right)_{calc.}$
0.00	0.0445		
0.10	0.0317	4.36	4.35
0.20	0.0247	4.08	4.50
0.30	0.0183	4.69	4.65
0.40	0.0150	4.54	4.80
0.50	0.0120	4.82	4.95
0.60	0.00981	5.08	5.10
0 70	815	5.39	5.25
0.80	700	5.39	5.40
0.90	599		
1.00	526		

(1), (2) N. A. Puschin and T. Pinter, *Z. physik. Chem.*, Abt. A, **142** (1929), 211.

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=1} = 4.20 \text{ and } \left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=1} = 5.70 .$$

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{calc.}} = 4.20 + (5.70-4.20)z_m .$$

We obtain, from the values

$$\left|\frac{(ka)_{C_6H_6}}{(ka)_{\text{Guaiacol}}}\right|_{z_m\text{-}C_6H_6=0} = \left|\frac{(ka)_{C_6H_6}}{(ka)_{\text{Guaiacol}}}\right|_{z_m\text{-Guai.}=1} = 3.40$$

and

$$\left|\frac{(ka)_{C_6H_5CH_3}}{(ka)_{\text{Guaiacol}}}\right|_{z_m\text{-}C_6H_5CH_3=0} = \left|\frac{(ka)_{C_6H_5CH_3}}{(ka)_{\text{Guaiacol}}}\right|_{z_m\text{-Guai.}=1} = 4.20 ,$$

$$\frac{(ka)_{C_6H_5CH_3}}{(ka)_{C_6H_6}} = \frac{(k)_{C_6H_5CH_3}}{(k)_{C_6H_6}} = \frac{4.20}{3.40} = 1.24 .$$

This is strictly concordant with the known value of field constant of $C_6H_5CH_3$.

$$a_\infty \text{ in } C_6H_6 = 1-\frac{\frac{1}{5.80}}{\frac{1}{3.40}} = 1-0.586 = 0.41 ,$$

while $$a_\infty \text{ in } C_6H_5CH_3 = 1-\frac{\frac{1}{5.70}}{\frac{1}{4.20}} = 1-0.737 = 0.26 .$$

Table 5.

$C_2H_5OH-(C_2H_5)_2O$, 25°C. (Baker).[1]

z-$(C_2H_5)_2O$	z_m-$(C_2H_5)_2O$	η	$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{obs.}}$	$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{calc.}}$
0.0000	0.0000	0.01112		
0.2315	0.1577	0.007414	3.84	3.84
0.4743	0.3593	4782	4.48	4.48
0.5751	0.4569	4005	4.84	4.78
0.6448	0.5302	3590	5.02	5.02
0.7299	0.6269	3152	5.32	5.32
0.7837	0.6925	2897	5.73	5.53
0.8639	0.7978	2635	5.73	5.86
1.0000	1.0000	2260		

(1) F. Baker, *J. Chem. Soc.*, **60** (1912), 1409.

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=0} = 3.34\,, \qquad \left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=1} = 6.50$$

and $$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{calc.}} = 3.34 + (6.50-3.34)z_m\,.$$

Table 6.

n-C_3H_7OH—$(C_2H_5)_2O$, 25°C. (Baker).[1]

z-$(C_2H_5)_2O$	z_m-$(C_2H_5)_2O$	η	$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{obs.}}$	$\left(\frac{k_1a_1}{k_2a_2}\right)_{\text{obs.}}$	$\left(\frac{k_1a_1}{k_2a_2}\right)_{\text{calc.}}$
0.0000	0.0000	0.01971			
0.1193	0.0991	0.01404	4.39	0.228	0.228
0.2299	0.1949	0.01024	4.90	0.204	0.204
0.3492	0.3032	0.007528	5.32	0.188	0.188
0.4716	0.4198	5619	5.78	0.173	0.173
0.5989	0.5475	4274	6.33	0.158	0.158
0.7297	0.6864	3356	6.80	0.147	0.147
0.8622	0.8354	2717	7.30	0.137	0.137
1.0000	1.0000	2260			

Since $\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{obs.}}$ are not strictly linear, their reciprocals are taken.

$$\left(\frac{k_1a_1}{k_2a_2}\right)_{z_m=1} = 0.258 \quad \text{and} \quad \left(\frac{k_1a_1}{k_2a_2}\right)_{z_m=0} = 0.129\,.$$

$$\left(\frac{k_1a_1}{k_2a_2}\right)_{\text{calc.}} = 0.258 - (0.258-0.129)z_m\,.$$

The four values above obtained are rewritten as follows:

(i) $\left|\frac{(ka')_{\text{Ether}}}{(ka)_{C_2H_5OH}}\right|_{z_m\text{-}C_2H_5OH=1} = 3.34$, where $(a')_{\text{Ether}}$ = the association degree of ether at zero concentration in ethyl alcohol.

(ii) $\left|\frac{(ka)_{\text{Ether}}}{(ka')_{C_2H_5OH}}\right|_{z_m\text{-Ether}=1} = 6.50$, where $(a')_{C_2H_5OH}$ = the association degree of C_2H_5OH at zero concentration in ether.

(1) Loc. cit.

(iii) $\left|\frac{(ka)_{C_3H_7OH}}{(ka'')_{Ether}}\right|_{z_m\text{-}C_3H_7OH=1} = 0.258$, where $(a'')_{Ether}$=the association degree of ether at zero concentration in *n*-propyl alcohol.

(iv) $\left|\frac{(ka'')_{C_3H_7OH}}{(ka)_{Ether}}\right|_{z_m\text{-}Ether=1} = 0.129$, where $(a'')_{C_3H_7OH}$=the association degree of *n*-C_3H_7OH at zero concentration in ether.

We have from the preceding papers

$$\frac{(ka)_{C_3H_7OH}}{(ka)_{C_2H_5OH}}=\frac{0.31\times 1.31}{0.34\times 1.37}=0.87$$

While from (ii) and (iv) we get

$$\frac{(ka'')_{C_3H_7OH}}{(ka)_{C_2H_5OH}}=6.50\times 0.129=0.84,$$

which is fairly concordant with the above. Hence we may say that the molecular dissociation of these alcohols does not take place in ether solution.

Again from (i) and (iii) we get

$$\left(\frac{a'}{a''}\right)_{Ether}\frac{(ka)_{C_3H_7OH}}{(ka)_{C_2H_5OH}}=3.34\times 0.258.$$

$$\left(\frac{a'}{a''}\right)_{Ether}=\frac{3.34\times 0.258}{0.87}=0.99.$$

This tells that the decreased association degrees of ether at zero concentration in C_2H_5OH and in *n*-C_3H_7OH are the same, a_∞ having the value 0.50.

The two more examples, C_6H_5Cl-C_6H_5OH and C_6H_6-C_6H_5OH will be quoted.

Table 7.

C_6H_5Cl–C_6H_5OH, 20°C. (Bramley).[1]

z-C_6H_5OH	z_m-C_6H_5OH	η	$\left(\frac{k_2a_2}{k_1a_1}\right)_{obs.}$	$\left(\frac{k_2a_2}{k_1a_1}\right)_{calc.}$
0.0000	0.0000	0.00768		
0.0493	0.0584	0.00825	0.090	0.088
0.0978	0.1148	0.00888	0.091	0.094
0.2173	0.2493	0.01122	0.107	0.107
0.3043	0.3435	0.01374	0.116	0.117
0.3890	0.4324	0.01673	0.127	0.126
0.4990	0.5437	0.02218	0.138	0.137
0.5815	0.6243	0.02748	0.144	0.146
0.7141	0.7493	0.04070	0.158	0.158
0.8145	0.8400	0.05555	0.166	0.168
1.0000	1.0000	0.1104		

(1) A. Bramley, *J. Chem. Soc.*, **109** (1916), 10.

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=0} = 0.082 \quad \text{and} \quad \left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=1} = 0.184 .$$

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{calc.}} = 0.082 + (0.184-0.082)z_m .$$

$$a_\infty \text{ of } C_6H_5OH = 1-\frac{0.082}{0.184} = 0.55 .$$

H. Hirobe[1] studied the partition of phenol between water and chlorobenzene and concluded that if phenol in chlorobenzene solution is assumed to consist of two kind of molecules of monomol and trimol which are in the equilibrium:

$$3\ C_6H_5OH \rightleftarrows (C_6H_5OH)_3 ,$$

$$\frac{C_1^3}{C_3} = K ,$$

where C_1 and C_3 are the numbers of mols of monomol and of trimol, the equilibrium is sufficiently explained, giving $\log K = \bar{1}.44$ at 30°C.

Now, put $C_1+C_3=1$ in order to find the fraction of respective molecules, then we get

$$C_1 + \frac{C_1^3}{0.276} = 1 .$$

The solution of the equation is $C_1=0.51$. The coincidence of this and the above obtained value is satisfactory.

Table 8.

$C_6H_6-C_6H_5OH$, 20°C. (Bramley).[2]

z-C_6H_5OH	z_m-C_6H_5OH	η	$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{obs.}}$	$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{calc.}}$
0.0000	0.0000	0.00629		
0.0604	0.0506	0.00683	0.098	0.094
0.0984	0.08305	0.00724	0.102	0.099
0.2001	0.1723	0.00865	0.111	0.111
0.3240	0.2877	0.01126	0.124	0.127
0.4209	0.3762	0.01401	0.133	0.139
0.5302	0.4836	0.01911	0.150	0.154
0.6365	0.5775	0.02642	0.175	0.168
0.7411	0.7037	0.03811	0.185	0.185
0.8320	0.8043	0.0535	0.202	0.200
1.0000	1.0000	0.1104		

(1) H. Hirobe. *J. Coll. Sci., Imp. Univ. Tokyo,* **25** (1908), Art. 12, p. 35.
(2) A. Bramley, *J. Chem. Soc.* **109** (1916), 10.

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=0} = 0.087 \quad \text{and} \quad \left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=1} = 0.227 .$$

$$a_\infty \text{ of } C_6H_5OH = 1 - \frac{0.087}{0.227} = 0.62 .$$

K. Endo,[1] in his study on the partition of phenol between water and benzene, assumed that phenol in benzene takes similar molecular state as that in chlorobenzene as was discussed by Hirobe, and observed

$$\frac{C_3}{C_1^3} = K = 1.072 \ (25°\text{C.}) .$$

From this and $C_1+C_3=1$,

we get $1.072\,C_1^3+C_1=1$

Whence $C_1=0.67$,

which is in fair agreement with the value above obtained.

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(1) K. Endo, this Bulletin, **1** (1926), 25.