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

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There have been proposed many viscosity formulas for a physical mixture of two constituents:

I. $\log \eta = (1 - z_v) \log \eta_1 + z_v \log \eta_2$ (logarithmic formula),

II. $\eta = (1 - z_v) \eta_1 + z_v \eta_2$ (viscosity formula),

III. $\dfrac{1}{\eta} = (1 - z_v) \dfrac{1}{\eta_1} + z_v \dfrac{1}{\eta_2}$ (mobility or fluidity formula),

in which η_1, η_2 and η are viscosity coefficients of components 1, 2 and their mixture respectively; z_v a volume fraction of component 2.

Lees(1) deduced them theoretically, but discarded them because he found a more suitable expression :

$$\text{IV.} \qquad \eta^{\frac{1}{n}}=(1-z_v)\eta_1^{\frac{1}{n}}+z_v\eta_2^{\frac{1}{n}},$$

where n is an empirically determinate constant, varying for the most part between 2 and 5.

Kendall,(2) taking a molar fraction z_m in place of volume fraction z_v, gave a modified formula of I :

$$\text{V.} \qquad \log\eta=(1-z_m)\log\eta_1+z_m\log\eta_2 .$$

He abandoned it,(3) however, four years later and again proposed a well known formula :

$$\text{VI.} \qquad \eta^{\frac{1}{3}}=(1-z_m)\eta_1^{\frac{1}{3}}+z_m\eta_2^{\frac{1}{3}} .$$

Viscosity of a gas increases with rise of temperature, whilst that of a liquid decreases. This fact suggests that both depend alike on the molecular motion, but there must be some different points between them.

The kinetic theory of gases postulates that a molecular motion of gases is non-restrictive. Such consideration, however, may not be applicable to a molecule of liquids, whose molecular distance or a mean free path having been estimated by some investigators to be equivalent to or less than a diameter of a molecule. We consider, then, that a liquid molecule moves unfreely in an attraction field, i.e., its motion is restricted or bound by others.

Now we may allow the following two assumptions as to liquid molecules :

Assumption A. An associated molecule is a fast combined molecule, a single molecule in which is quite different in any property from a singly existing molecule and is regarded to be a constituent as if it were of a chemical compound molecule.

Assumption B. An associated molecule is a group of single molecules which have the self-same dimension with singly existing molecules and the difference between them is no other than the abrupt greatness of the cohesion force of the former in comparison with that of the latter.

Let us denote the association degrees and numbers of formal molecules of chemically indifferent two liquids by a_1, a_2, n_1 and n_2 respec-

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(1) Lees, *Phil. Mag.*, [VI] **1** (1901), 128.

(2) Kendall, *Meddelanden f. K. Velensk. Nobelinstitute*, **2** (1913), 23.

(3) Kendall, *J. Am. Chem. Soc.*, **39** (1917), 1790; ibid. **42** (1920), 1776.

tively. Then the numbers of molecules can be expressed by $\frac{n_1}{a_1}$ and $\frac{n_2}{a_2}$ according to assumption A; and n_1 and n_2 according to assumption B.

Since an associated molecule in the former case is counted only one just as a singly existing molecule, we are reduced to assume, in general, n kinds of molecular sizes in place of regarding no attraction field, in other words, for one component of a binary mixture we must consider a mixture of n kinds of ideal gases and the treatment becomes very complicate in consequence.

The suitability of assumption B has been justified in the writer's as yet unpublished paper "Refractivity of a binary mixture and its relations to the molecular size of components." In our present study we will also adopt it.

If we consider the viscosity of a binary liquid mixture to be composed of the constituent viscosities, the partition of each component may be assumed to be proportional to (i) the number of molecules and (ii) the mean intensity of attraction field, which, according to assumption B, is proportional to the association degree. In short, the viscosity shares of components are, respectively, expressed by $k_1\, a_1\, n_1$ and $k_2\, a_2\, n_2$, in which k_1 and k_2 are the characteristic "field-constants" of components 1 and 2—the constants which depend probably on the kind, form and size of constituent molecules.

Let us call such viscosity share "effective number of molecules" and denote by z'_m "effective molar fraction" of component 2, then we have

$$z'_m=\frac{k_2a_2n_2}{k_1a_1n_1+k_2a_2n_2}=\frac{k_2a_2z_m}{k_1a_1(1-z_m)+k_2a_2z_m}$$

where z_m is a formal molar fraction of component 2.

If a mixture is chemically non-reactive, it readily follows:

$$\begin{aligned}\eta&=\eta_1(1-z'_m)+\eta_2 z'_m\\&=\eta_1\frac{k_1a_1(1-z_m)}{k_1a_1(1-z_m)+k_2a_2z_m}+\eta_2\frac{k_2a_2z_m}{k_1a_1(1-z_m)+k_2a_2z_m}\end{aligned}$$

or

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

Case I. $k_1 = k_2$

The assumption can only be allowed for homologous successive two liquids. In such cases,

$$\eta=\eta_1+(\eta_2-\eta_1)\frac{a_2z_m}{a_1(1-z_m)+a_2z_m}.$$

Special case: If $a_1=a_2$,

$$\eta=\eta_1+(\eta_2-\eta_1)\,z_m,$$

or the viscosity of such a mixture is additive with respect to formal molar fraction.

Case II. $k_1 \neq k_2$

This contains all the cases where two liquids are chemically indifferent. For the verification of the formula, I have consulted as much published data as seen in the literature.

The association degrees are all quoted from the writer's recent paper, "A theory of binary mixtures and its application to calculating the association degrees of liquids," *Sexagint, Y. Osaka, Chem. Inst. Dept. Science, Kyoto Imp. Univ.* (1927), 103-41.

The validity of the formula will readily be understood from the constancy of $\frac{k_2a_2}{k_1a_1}$ in each table, which also shows the values calculated from Kendall's formula:

$$\eta^{\frac{1}{3}}=\eta_1^{\frac{1}{3}}(1-z_m)+\eta_2^{\frac{1}{3}}z_m.$$

The sufficient condition that any one of $\frac{k_B}{k_A}$, $\frac{k_C}{k_B}$ and $\frac{k_A}{k_C}$, which are obtained separately from three pairs *A-B*, *B-C* and *C-A*, must be quite equivalent to that calculated from the other two is also realized as seen from the notes of tables 5 and 9.

Table 1.

$CH_3COOCH_3-CH_3COOC_2H_5$, 25°C. (Chadwell).⁽¹⁾

z_m-$CH_3COOC_2H_5$	$\eta_{obs.}$	$\frac{k_2a_2}{k_1a_1}$	$\eta_{calc.}$	η_k
0.0000	0.003594		—	—
0.0782	3638	(0.856)	0.003645	0.003645
0.1892	3713	0.960	3713	3709
0.3264	3801	0.965	3801	3804
0.4454	3876	0.954	3877	3877
0.5533	3943	0.936	3947	3944
0.7915	4098	0.909	4108	4104
0.8753	4158	0.935	4159	4158
1.0000	4244	0.943	—	—

$$\begin{cases} a_1=1.30 \\ a_2=1.25 \end{cases},\quad \frac{k_2}{k_1}=0.943\times\frac{1.30}{1.25}=0.98$$

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(1) H.M. Chadwell, *J. Am. Chem. Soc.*, **48** (1926), 1918.

Table 2.

$C_2H_5OH-CH_3OH$, 25°C. (Herz).⁽¹⁾

z-CH_3OH	z_m-CH_3OH	$\eta_{obs.}$	$\frac{k_2a_2}{k_1a_1}$	$\eta_{calc.}$	η_k
0.0000	0.0000	0.01092		—	—
0.0437	0.0617	0.01047	1.41	0.01050	0.01052
0.104	0.143	0.009845	1.52	998	1002
0.4102	0.5000	7885	1.34	792	797
0.8069	0.8572	6175	1.18	623	623
0.8477	0.8892	6050	1.41	608	610
0.9125	0.9376	5862	1.40	587	588
1.0000	1.0000	5621	1.38	562	—

$$\begin{cases} a_1=1.37 \\ a_2=1.78 \end{cases}, \quad \frac{k_2}{k_1}=1.38\times\frac{1.37}{1.78}=1.06$$

Table 3.

$C_2H_5OH-n\text{-}C_3H_7OH$, 25°C. (Parks & Schwenck).⁽²⁾

z-C_3H_7OH	z_m-C_3H_7OH	$\eta_{obs.}$	$\frac{k_2a_2}{k_1a_1}$	$\eta_{calc.}$	η_k
0.0000	0.0000	0.01090		—	—
0.1250	0.0987	1169	(0.99)	0.01161	0.01157
0.2507	0.2041	1233	0.84	1238	1231
0.3760	0.3161	1319	0.86	1323	1314
0.4998	0.4337	1408	0.85	1414	1404
0.6251	0.5613	1522	0.90	1517	1506
0.7500	0.6971	1640	0.93	1630	1621
0.8746	0.8426	1759	0.90	1755	1750
1.0000	1.0000	1897	0.88	—	—

$$\begin{cases} a_1=1.37 \\ a_2=1.31 \end{cases}, \quad \frac{k_2}{k_1}=0.88\times\frac{1.37}{1.31}=0.92$$

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(1) W. Herz, *Z. anorg. allg. Chem.*, **104** (1918), 47.

(2) G.S. Parks & J.R. Schwenck, *J. Phys. Chem.*, **28** (1924), 720.

Table 4.

$CH_3OH-HCONH_2$, 25°C. (Merry & Turner).(1)

z_m-$HCONH_2$	$\eta_{obs.}$	$\frac{k_2a_2}{k_1a_1}$	$\eta_{calc.}$	η_k
0.0000	0.00557		—	—
0.1000	746	(0.65)	0.00705	0.00705
0.2000	861	0.49	868	879
0.3000	1055	0.50	1052	1076
0.3966	1247	0.50	1250	1260
0.4978	1484	0.50	1484	1556
0.6000	1749	0.49	1756	1348
0.7000	2067	0.50	2067	2168
0.7988	2431	0.51	2421	2520
0.9020	2874	0.52	2867	2929
1.0000	3359	0.50	—	—

$$\begin{cases} a_1=1.78 \\ a_2=0.93 \end{cases}, \quad \frac{k_2}{k_1}=0.50\times\frac{1.78}{0.93}=0.96$$

Table 5.

$C_2H_5OH-HCONH_2$, 25°C. (Merry & Turner).(2)

z_m-$HCONH_2$	$\eta_{obs.}$	$\frac{k_2a_2}{k_1a_1}$	$\eta_{calc.}$	η_k
0.0000	0.01086		—	—
0.1005	1229	(0.60)	0.01248	0.01243
0.1991	1376	(0.59)	1419	1409
0.3014	1563	0.62	1607	1597
0.4017	1816	0.71	1806	1798
0.4991	2010	0.69	2010	2010
0.6093	2259	0.68	2264	2269
0.7024	2515	0.72	2494	2498
0.8108	2782	0.67	2784	2789
0.9000	3054	0.72	3043	3049
1.0000	3359	0.69	—	—

$$\begin{cases} a_1=1.37 \\ a_2=0.93 \end{cases}, \quad \frac{k_2}{k_1}=0.69\times\frac{1.37}{0.93}=1.02$$

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(1) E.W. Merry & W.E.S. Turner, *J. Chem. Soc.*, **105** (1914), 748.

(2) Loc. cit.

From tables 4 and 5, we have

$$\frac{(k)_{CH_3OH}}{(k)_{C_2H_2OH}}=\frac{(k)_{HCONH_2}}{(k)_{C_2H_5OH}}\times\frac{(k)_{CH_3OH}}{(k)_{HCONH_2}}=1.02\times\frac{1}{0.96}=1.06,$$

which is exactly coincident with the corresponding value $\frac{k_2}{k_1}=1.06$ in table 2.

Table 6.

$H_2O-HCONH_2$, 25°C. (Merry & Turner).(1)

z_m-$HCONH_2$	$\eta_{obs.}$	$\frac{k_2a_2}{k_1a_1}$	$\eta_{calc.}$	η_k
0.0000	0.00891		—	—
0.1001	1044	(0.59)	1016	1048
0.1998	1161	0.49	1155	1222
0.3003	1315	0.48	1313	1416
0.3989	1463	0.46	1487	1623
0.4997	1698	0.49	1691	1855
0.5997	1927	0.48	1923	2111
0.6920	2142	0.46	2171	2363
0.8004	2508	0.47	2515	2686
0.9013	2906	0.49	2901	3012
1.0000	3359	0.48	—	—

$$\begin{cases} a_1=3.18 \\ a_2=0.93 \end{cases}, \quad \frac{k_2}{k_1}=0.48\times\frac{3.18}{0.93}=1.64$$

Table 7.

$C_6H_5CH_3-C_6H_6$, 25°C. (Linebarger).(2)

z_m-C_6H_6	$\eta_{obs.}$	$\frac{k_2a_2}{k_1a_1}$	$\eta_{calc.}$	η_k
0.00000	0.00541		—	—
0.12719	555	(1.7)	0.00547	0.00549
0.34229	558	0.80	558	560
0.70240	579	0.81	579	581
0.92750	594	0.83	594	595
1.00000	599	0.81	—	—

$$\begin{cases} a_1=1.00 \\ a_2=1.00 \end{cases}, \quad \frac{k_2}{k_1}=0.81\times\frac{1.00}{1.00}=0.81$$

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(1) Loc. cit.

(2) C.E. Linebarger, *Am. J. Sci.*, **4** (1896), 331.

Table 8.

$C_6H_5Br-C_6H_5CH_3$, 20°C. (Yajnik & coworkers).⁽¹⁾

z_v-$C_6H_5CH_3$	$\eta_{obs.}$	$\frac{(1-z_v)(\eta-\eta_1)}{z_v(\eta_2-\eta)}$
0.00	0.00880	
0.10	831	1.15
0.20	776	1.26
0.30	734	1.19
0.40	698	1.09
0.50	652	1.11
0.60	609	1.12
0.70	561	1.20
0.80	528	1.09
0.90	487	1.09
1.00	447	1.14

$$\begin{cases} a_1=\text{unknown} \\ a_2=1.00 \end{cases}, \quad \frac{k_2a_2}{k_1a_1}=1.14\times\frac{1.495\times92.06}{0.867\times157.0}=1.15,$$

taking the densities of C_6H_5Br and $C_6H_5CH_3$ to be 1.495 and 0.867 respectively (from Landolt, "Tabellen").

Table 9.

$C_6H_5Br-C_6H_6$, 18.2°C. (Yajnik & coworkers).⁽²⁾

z_v-C_6H_6	$\eta_{obs.}$	$\frac{(1-z_v)(\eta-\eta_1)}{z_v(\eta_2-\eta)}$
0.00	0.01129	
0.10	1086	0.90
0.20	1056	0.73
0.30	942	1.46
0.40	923	1.15
0.50	876	1.14
0.60	833	1.10
0.70	786	1.11
0.80	736	1.11
0.90	699	1.06
1.00	654	1.08

$$\begin{cases} a_1=\text{unknown} \\ a_2=1.00 \end{cases}, \quad \frac{k_2a_2}{k_1a_1}=1.08\times\frac{1.495\times78.05}{0.879\times157.0}=0.92.$$

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(1) N.A. Yajnik, M.D. Bhalla, R.C. Talwar, & M.A. Soofi, *Z. physik. Chem.*, **118** (1925), 305.

(2) Loc. cit.

The densities of C_6H_5Br and C_6H_6 are quoted from Landolt, "Tabellen." From tables 8 and 9, we get:

$$\frac{(k)_{C_6H_6}}{(k)_{C_6H_5CH_3}}=\frac{(k)_{C_6H_6}}{(ka)_{C_6H_5Br}}\times\frac{(ka)_{C_6H_5Br}}{(k)_{C_6H_5CH_3}}=0.92\times\frac{1}{1.15}=0.80.$$

This is concordant with the corresponding value $\frac{k_2}{k_1}=0.81$ in table 7.

Table 10.

$C_6H_6-CH_3COOC_2H_5$, 25°C. (Dunstan).(1)

z-$CH_3COOC_2H_5$	z_m-$CH_3COOC_2H_5$	$\eta_{obs.}$	$\frac{k_2a_2}{k_1a_1}$	$\eta_{calc.}$	η_k
0.0000	0.0000	0.005822		—	—
0.2704	0.2473	5181	1.94	0.005166	0.005388
0.3310	0.3049	4990	(2.38)	5022	5284
0.3584	0.3313	4990	2.11	5001	5241
0.4393	0.4099	4830	2.24	4865	5116
0.4830	0.4531	4803	2.01	4797	5046
0.4910	0.4610	4782	2.06	4785	5028
0.7595	0.7370	4446	1.94	4435	4590
1.0000	1.0000	4193	2.05	—	—

$$\begin{cases} a_1=1.00 \\ a_2=1.25 \end{cases},\quad \frac{k_2}{k_1}=2.05\times\frac{1.00}{1.25}=1.64$$

Table 11.

$C_2H_5OH-CS_2$, 25°C. (Dunstan).(2)

z-CS_2	z_m-CS_2	$\eta_{obs.}$	$\frac{k_2a_2}{k_1a_1}$	$\eta_{calc.}$	η_k
0.0000	0.0000	0.01113		0.01113	0.01113
0.1691	0.1096	0.009448	(2.30)	968	1003
0.1929	0.1263	9535	1.88	948	988
0.2564	0.1726	9065	1.83	896	945
0.3231	0.2241	8407	1.98	842	898
0.3950	0.2832	7621	2.24	787	845
0.5282	0.4040	6659	2.20	687	745
0.6995	0.5848	5669	1.93	564	611
0.7350	0.6266	5466	1.86	541	583
0.8193	0.7328	4926	1.78	483	514
1.0000	1.0000	3656	1.96	366	366

$$\begin{cases} a_1=1.37 \\ a_2=1.20 \end{cases},\quad \frac{k_2}{k_1}=1.96\times\frac{1.37}{1.20}=2.24$$

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(1) A.E. Dunstan, *J. Chem. Soc.*, **85** (1904), 817.

(2) Loc. cit.

Table 12.

$CS_2-C_6H_6$, 25°C. (Linebarger).⁽¹⁾

z-C_6H_6	$\eta_{obs.}$	$\frac{(1-z)(\eta-\eta_1)}{z(\eta_2-\eta)}$
0.000	0.00358	
0.089	376	(0.83)
0.349	446	1.07
0.759	544	1.07
1.000	599	1.07

$$\begin{cases} a_1=1.20 \\ a_2=1.00 \end{cases}, \quad \frac{k_2}{k_1}=1.07\times\frac{78.05\times1.20}{76.12\times1.00}=1.32.$$

Table 13.

$C_6H_6-CCl_4$. 60°C. (Thorpe & Rodger).⁽²⁾

z-CCl_4	z_m-CCl_4	$\eta_{obs.}$	$\frac{k_2a_2}{k_1a_1}$	$\eta_{calc.}$	η_k
0.0000	0.0000	0.00391		—	—
0.3229	0.1949	422	0.79	422	425
0.5621	0.3944	456	0.78	456	461
0.7763	0.6377	503	0.79	503	508
1.0000	1.0000	584	0.79	—	—

$$\begin{cases} a_1=1.00 \\ a_2=1.24 \end{cases}, \quad \frac{k_2}{k_1}=0.79\times\frac{1.00}{1.24}=0.64$$

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(1) C.E. Linebarger, *Am. J. Sci.*, **4** (1896), 331.

(2) T.E. Thorpe & J.W. Rodger, *J. Chem. Soc.*, **71** (1897), 360.

Table 14.

$CHCl_3-CCl_4$, 25°C. (Linebarger).⁽¹⁾

z_m-CCl_4	$\eta_{obs.}$	$\frac{k_2a_2}{k_1a_1}$	$\eta_{calc.}$	η_k
0.00000	0.00540		—	—
0.15663	569	0.50	570	586
0.50989	659	0.51	661	698
0.76985	761	0.54	758	794
1.00000	883	0.52	—	—

$$\begin{cases} a_1=1.00 \\ a_2=1.24 \end{cases}, \quad \frac{k_2}{k_1}=0.52\times\frac{1.00}{1.24}=0.42$$

Table 15.

$CH_3COOC_2H_5-CH_3COOH$, 25°C. (Kendall & Brakeley).⁽²⁾

z_m-CH_3COOH	$\eta_{obs.}$	$\frac{k_2a_2}{k_1a_1}$	$\eta_{calc.}$	η_k
0.0000	0.004236		0.004236	0.004236
0.1049	0.004590	(0.456)	0.004563	0.004769
0.2070	0.004949	(0.436)	0.004925	0.005323
0.3037	0.005331	0.427	0.005316	0.005888
0.3990	0.005762	0.422	0.005756	0.006486
0.4985	0.006289	0.420	0.006289	0.007154
0.5996	0.006890	0.411	0.006926	0.007880
0.6988	0.007668	0.418	0.007676	0.008627
0.8011	0.008590	0.413	0.008616	0.009460
0.8742	0.009430	0.420	0.009426	0.01008
1.0000	0.01121	0.42	0.01121	0.01121

$$\begin{cases} a_1=1.25 \\ a_2=1.51 \end{cases}, \quad \frac{k_2}{k_1}=0.42\times\frac{1.25}{1.51}=0.35$$

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(1) Loc. cit.

(2) J. Kendall & E. Brakeley, *J. Am. Chem. Soc.*, **43** (1921), 1826.