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

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In the former paper,(1) the writer proposed a viscosity formula for physical binary mixtures of the form:

$$\eta=\eta_1+(\eta_2-\eta_1)\frac{k_2 a_2 z_m}{k_1 a_1(1-z_m)+k_2 a_2 z_m},$$

where η, a, k with suffixes 1 and 2 signify the viscosities, the association degrees and the field-constants of components 1 and 2 respectively; z_m a formal molar fraction of component 2. The present paper is a continuation of it.

The relation between k and molecular structure. The application of the formula to the hitherto published data in the literature having been

Table 1.

Substance	k	D ($\lambda=\infty$)	Observers	$\sigma\times10^8$	Observers
C_6H_6	1	2.25 (20°) 2.28 (25°)	Linebarger Krchma & Williams	4.10	Rappenecker
$C_6H_5CH_3$	1.23	2.36 (20°) 2.38 (25°)	Linebarger Krchma & Williams	——	
CH_3COOCH_3	1.67	6.68 (25°)	,, ,,	3.91	,,
$CH_3COOC_2H_5$	1.64	6.03 (25°)	,, ,,	4.27	,,
$CHCl_3$	1.50	5.13 (20°) 4.77 (25°)	Linebarger Krchma & Williams	——	
CCl_4	0.63	2.24 (20°) 2.23 (25°)	Linebarger Krchma & Williams	4.60	Ishikawa
CS_2	0.76	2.58 (20°) 2.63 (25°)	Linebarger Williams & Ogg	3.91	,,
CH_3OH	0.36	31.2 (20°)	Abegg & Seitz	3.04	,,
C_2H_5OH	0.34	25.8 (20°)	,, ,,	3.43	,,
n-C_3H_7OH	0.31	22.2 (20°)	,, ,,	3.72	,,
H_2O	0.21	81.1 (18°)	Turner	2.61	Rappenecker
$HCONH_2$	0.35			——	
CH_3COOH	0.57	9.7 (18°)	Francke	1.95	Ishikawa

Linebarger, *Z. physik. Chem.*, **20** (1896), 131.
Krchma & Williams, *J. Am. Chem. Soc.*, **49** (1927), 2408.
Williams & Ogg, *J. Am. Chem. Soc.*, **50** (1928), 94.
Rappenecker, "Landolt-Tabellen," recalculated by taking $N=2.705\times10^{19}$.
Ishikawa, As yet unpublished paper "Refractivity of binary mixture and its relation to molecular size of components."

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

made with satisfactory results, the field constant k proves to be, as is expected, a particular constant for a particular liquid.

Now, in order to find whether or no there exists any relation between k and molecular structure, we calculate the relative values of k by putting that of C_6H_6 as unity. The values thus obtained are collected in the following table. It also shows the molecular diameter σ and dielectric constant $D\,(\lambda=\infty)$. Comparing k with these two values we find an interesting relation: *k of homologous liquids is proportional to the product $D\cdot\sigma$* as recognized from Table 2.

Table 2.

Substance	k.	$D\cdot\sigma\cdot10^8$	$\frac{D\cdot\sigma}{k}\cdot10^8$	
CH_3OH	0.36	$31.2 \times 3.04 = 94.9$	264	263
C_2H_5OH	0.34	$25.8 \times 3.43 = 88.5$	260	
n-C_3H_7OH	0.31	$22.2 \times 3.72 = 82.6$	266	
CH_3COOCH_3	1.67	$6.68 \times 3.91 = 26.1$	15.6	15.6
$CH_3COOC_2H_5$	1.64	$6.03 \times 4.27 = 25.7$	15.7	

Extension to gaseous mixtures. The author's formula is transformed into

$$\eta=\frac{\eta_1}{1+\dfrac{k_2a_2}{k_1a_1}\dfrac{z_m}{1-z_m}}+\frac{\eta_2}{1+\dfrac{k_1a_1}{k_2a_2}\dfrac{1-z_m}{z_m}}.$$

As we have $a_1=a_2=1$ for a gaseous mixture,

$$\eta=\frac{\eta_1}{1+\dfrac{k_2}{k_1}\dfrac{z_m}{1-z_m}}+\frac{\eta_2}{1+\dfrac{k_1}{k_2}\dfrac{1-z_m}{z_m}}$$

Putting $\dfrac{k_2}{k_1}=K$, it becomes,

$$\eta=\frac{\eta_1}{1+K\dfrac{z_m}{1-z_m}}+\frac{\eta_2}{1+\dfrac{1}{K}\dfrac{1-z_m}{z_m}}\quad\ldots\ldots\ldots\ldots\ldots\ldots\quad(\mathrm{I})$$

Thiesen⁽¹⁾ proposed the following viscosity formula for a gaseous mixture:

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(1) Thiesen, *Verh. d.D. phys. Ges.*, **4** (1902), 357.

$$\eta=\frac{\eta_1}{1+A\frac{z_v}{1-z_v}}+\frac{\eta_2}{1+B\frac{1-z_v}{z_v}}, \quad A=\frac{a_{12}}{a_{11}}, \quad B=\frac{a_{21}}{a_{22}}.$$

In which a_{11}, a_{12}, a_{22}, a_{21} are empirical constants as defined by him "Diffusions-konstante," and z_v a volume fraction of component 2.

Now that the equality of molecular volumes of all the gases is univesally acceptable, the above formula can be rewritten as follows:

$$\eta=\frac{\eta_1}{1+A\frac{z_m}{1-z_m}}+\frac{\eta_2}{1+B\frac{1-z_m}{z_m}} \quad \cdots\cdots\cdots\cdots\cdots\cdots \text{(II)}$$

Comparing (I) and (II) we see that if $B=\frac{1}{A}$ holds good in (II) they are quite equivalent.

That Thiesen's formula gives more concordant values with experiments than those of Puluj's and of Sutherland's has been verified successively by Kleint,⁽¹⁾ Tänzler⁽²⁾ and Gille,⁽³⁾ from whose results we can examine in what pairs the equality of A to $\frac{1}{B}$ holds.

Table 3.

Pairs	$t°c.$	A	B	$B:\frac{1}{A}$	Observers
O_2 —— H_2	15	0.373	1.362	0.508	Kleint
	100	0.353	1.662	0.587	
	183	0.388	1.331	0.516	
O_2 —— N_2	15	0.456	2.443	1.11	Kleint
	100	0.93	1.10	1.02	
	183	0.48	2.32	1.11	
N_2 —— H_2	15	0.23	3.57	0.82	Kleint
	100	0.20	4.988	1.00	
	183	0.215	4.297	0.924	
A —— He	15	0.343	2.032	0.697	Tänzler
	100	0.375	1.957	0.734	
	183	0.446	1.692	0.747	
He —— H_2	10	0.847	1.170	0.991	Gille
	15	0.875	1.167	1.021	
	100	0.9203	1.110	1.021	

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(1) Kleint, *Verh. d. D. phys. Ges.*, **7** (1905), 145.
(2) Tänzler, *Verh. d. D. phys. Ges.*, **8** (1906), 222.
(3) Gille, *Ann. Phys.*, **48** (1915), 836.

As seen from the above table, that equality $B=\frac{1}{A}$, i.e.,

$$a_{12}=a_{22}, \qquad a_{21}=a_{11}$$

is not satisfied except in the cases O_2——N_2 and He——H_2.
The value $B:\frac{1}{A}$ seems to be apparently independent of temperature; its deviation from unity is the more distinct, the more difference there is in the molecular velocities of the components.

From this and the foregoing results we conclude that the diffusion effect of molecules which makes a great rôle in a gaseous mixture can be left out of consideration in a liquid mixture.

Application of the formula to any binary mixture accompanied with a chemical change. As stated before, the viscosity of a chemically indifferent (or physical) binary mixture can completely be expressible by

$$\eta=\eta_1+(\eta_2-\eta_1)\frac{\left(\frac{k_2a_2}{k_1a_1}\right)z_m}{(1-z_m)+\left(\frac{k_2a_2}{k\,a_1}\right)z_m}.$$

But when a chemical reaction takes place in admixture, the viscosity η is no more identical to that calculated by the above formula. The deviation $\delta=\eta-\eta_0$ which we call hereafter "solvation viscosity," here η_0 being the calculated value assuming there no chemical change on mixing, may depend entirely upon the mutual molecular reaction between the two constituents.

If a part of component 1 and a part of component 2, at z_m— concentration of component 2, enter into a reaction, which occurs among ν_1 molecules of the former and ν_2 molecules of the latter to form a molecular compound or aggregate, then the solvation viscosity may be assumed to be

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

in which C is a proportional constant.

For test of the postulation, three cases $CH_3COOH-H_2O$, CH_3OH-H_2O, and $C_2H_5OH-H_2O$ have been taken, the calculated results being recorded in the last column of each table of the following.

Table 4.

H_2O-CH_3COOH, 25°C (Noack).(1)

z-CH_3COOH	z_m-CH_3COOH	η	η_0	δ	$\frac{\delta}{z_m(1-z_m)}$
0.00	0.0000	0.00895	———		
0.10	0.0323	1076	0.00905	0.00171	0.055
0.20	0.0698	1282	917	365	0.057
0.25	0.0910	1359	923	436	0.053
0.30	0.1140	1497	930	567	0.056
0.40	0.1677	1701	946	755	0.054
0.50	0.2417	1905	967	938	0.051
0.60	0.3104	2092	986	1106	0.052
0.70	0.4120	2326	1013	1313	0.054
0.75	0.4737	2370	1028	1342	0.054
0.80	0.5455	2404	1046	1358	0.055
0.90	0.7300	2128	1088	1040	0.053
0.95	0.8510	1698	1113	585	(0.046)
1.00	1.0000	1143			0.054

$$\frac{k_2a_2}{k_1a_2}=\frac{0.57\times1.51}{0.21\times3.18}=1.29\,,\quad \eta_0=\eta_1+(\eta_2-\eta_1)\frac{1.29z_m}{(1-z_m)+1.29z_m}\,.$$

The constancy of $\frac{\delta}{z_m(1-z_m)}$ holds strictly at all concentrations, and hence a molecular compound or hydrate $CH_3COOH\cdot H_2O$ exists evidently in solution.

Table 5.

H_2O-CH_3OH, 25°C (Dunstan).(2)

z.CH_3OH	z_m-CH_3OH	η	η_0	δ	$\frac{\delta}{z_m(1-z_m)^2}$
0.0000	0.0000	0.00891	———		
0.0683	0.0396	0.01055	0.00878	0.00177	0.049
0.1007	0.0592	0.01157	872	285	0.054
0.1974	0.1216	0.01378	851	527	0.056
0.2147	0.1333	0.01403	847	556	0.055
0.3592	0.2398	0.01600	812	788	0.057
0.3782	0.2550	0.01567	807	760	0.054
0.3785	0.2553	0.01575	807	768	0.054
0.4071	0.2787	0.01570	799	771	0.053
0.4619	0.3257	0.01570	784	786	0.053

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(1) K. Noack, "Landolt-Tabellen."

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

Table 5. (*Continued.*)

z-CH_3OH	z_m-CH_3OH	η	η_0	δ	$\frac{\delta}{z_m(1-z_m)^2}$
0.4956	0.3560	0.01532	774	758	0.051
0.5131	0.3724	0.01540	768	772	0.053
0.5282	0.3865	0.01490	763	727	0.050
0.5535	0.4109	0.01475	755	720	0.051
0.5855	0.4430	0.01427	745	682	0.050
0.5861	0.4440	0.01399	744	655	0.048
0.6106	0.4686	0.01370	736	634	0.048
0.6653	0.5280	0.01282	716	566	0.049
0.7319	0.6056	0.01167	690	477	0.051
0.7741	0.6585	0.01105	671	434	0.057
0.7964	0.6876	0.01003	661	342	0.051
1.0000	1.0000	0.005525			0.052

$$\frac{k_2a_2}{k_1a_1}=\frac{0.36\times1.78}{0.21\times3.18}\doteqdot0.96\,,\quad \eta_0=\eta_1+(\eta_2-\eta_1)\frac{0.96z_m}{(1-z_m)+0.96z_m}\,.$$

For the range studied $\frac{\delta}{z_m(1-z_m)^2}$ keeps to be constant. The fact shows that a hydrate $CH_3OH\cdot2H_2O$ exists in solution.

Table 6.

$H_2O-C_2H_5OH$, 25°C (Dunstan).(1)

z-C_2H_5OH	z_m-C_2H_5OH	η	η_0	δ	$\frac{\delta}{z_m(1-z_m)^3}$	$\frac{\delta}{z_m(1-z_m)^2}$
0.0000	0.0000	0.00891	—			
0.2071	0.0986	1829	0.00907	0.00922	0.126	
0.2466	0.1159	1851	910	941	0.148	
0.2963	0.1415	2129	914	1215	0.136	
0.3240	0.1580	2162	917	1245	0.135	
0.3739	0.1893	2290	922	1368	0.136	
0.3826	0.1952	2301	923	1378	0.136	
0.3965	0.2044	2343	925	1418	0.138	
0.4121	0.2153	2327	927	1400	0.135	
0.4557	0.2468	2351	933	1418	0.134	
0.4617	0.2513	2368	934	1434	0.136	
0.4772	0.2631	2354	936	1418	0.135	
0.5020	0.2830	2337	939	1398	0.134	
0.5558	0.3284	2273	948	1325	0.133	
0.5583	0.3309	2273	948	1324	0.134	
0.5751	0.3462	2247	952	1295	0.134	
0.6015	0.3714	2243	956	1287	0.139	
0.6017	0.3714	2240	957	1287	0.139	
0.6049	0.3745	2226	957	1269	0.138	
0.6106	0.3802	2212	958	1254	0.138	(0.086)

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(1) A. E. Dunstan, & F.B. Thole, *J. Chem. Soc.*, **95** (1909), 1556.

Table 6. (*Continued.*)

z-C_2H_5OH	z_m-C_2H_5OH	η	η_0	δ	$\frac{\delta}{z_m(1-z_m)^3}$	$\frac{\delta}{z_m(1-z_m)^2}$
0.6185	0.3883	2173	960	1213	0.137	(0.084)
0.6536	0.4244	2104	967	1137	(0.140)	0.081
0.6585	0.4299	2112	968	1144	(0.140)	0.082
0.7054	0.4839	1995	979	1016	(0.153)	0.079
0.7390	0.5254	1957	988	969	(0.173)	0.082
0.7809	0.5825	1804	1002	802		0.079
0.8020	0.6132	1744	1010	734		0.081
1.0000	1.0000	1115			0.136	0.081

$$\frac{k_2a_2}{k_1a_1}=\frac{0.34\times 1.37}{0.21\times 3.18}=0.70\,, \quad \eta_0=\eta_1+(\eta_2-\eta_1)\frac{0.70z_m}{(1-z_m)+0.70z_m}.$$

The constancy of $\frac{\delta}{z_m(1-z_m)^3}$ holds for the range $z_m=0.1\sim 0.4$, and for higher concentrations $\frac{\delta}{z_m\,(1-z_m)^2}$ keeps to be constant.

This suggests that a hydrate $C_2H_5OH \cdot 3\,H_2O$ exists in solution up to 40 mol. % of C_2H_5OH, and a hydrate $C_2H_5OH \cdot 2\,H_2O$ exists at higher concentrations than 40 mol. % of C_2H_5OH.

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