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

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Ideal Solutions of Solids in Liquids. Proposed formulas for the viscosities of ideal or chemically indifferent solutions of solids in liquids are numerous, among which, however, one attempt only at rational treatment has been made by Einstein.(1) According to him the viscosity η of a suspensoid increases linearly with the concentration expressed in a volume fraction z_v of the dispersion medium per unit volume of the solution.

$$\eta=\eta_0\,(1+2.5\,z_v),$$

where η_0 is the viscosity of the pure solvent. He deduced the formula from the hydrodynamical equation of motion by assuming (i) the particles are rigid spheres, (ii) the particles are few in number and (iii) the particles are great in comparison with the action spheres of molecules. Hatschek found the constant to be 4.5 instead of 2.5, but his procedure of calculation is false, so that his formula is considered to have no general meaning.(2)

A similar form of Einstein's formula is expressed by

$$\eta=\eta_0\,(1+c\,z_v),$$

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(1) A. Einstein, *Ann. d. Physik*, **19** (1906), 289; **34** (1911), 591; *Kolloid-Z.*, **27** (1920), 137.

(2) M. v. Smoluchowski, *Kolloid-Z.*, **18** (1916), 194.

where c is a constant which depends only upon the form of particles.

Though the above formula is theoretically interest, its validity is limited for very dilute solutions.

With the object of testing that Kendall's cube-root equation for a chemically indifferent binary mixture, $\eta^{\frac{1}{3}}=(1-z_m)\eta_1^{\frac{1}{3}}+z_m\eta_2^{\frac{1}{3}}$ (where η_1, η_2 and η are respectively the viscosities of components 1, 2 and the mixture, and z_m is a molar fraction of component 2) has applicability to ideal solutions of solids in liquids, Kendall and Monroe⁽¹⁾ carried out the viscosity measurements on solutions of naphthalene and of diphenyl in benzene and in toluene. The calculated values of η_2, by the formula, for either solute give good results for any system, those for benzene solutions are, however, different from the corresponding values for toluene solutions, namely, for naphthalene 2.25 in benzene and 1.825 in toluene, for diphenyl 3.44 in benzene and 2.82 in toluene. The authors pointed out that the ratio [η_2 on benzene basis]/[η_2 on toluene basis] is practically identical for the two solutes. While this agreement is of interest, it is difficult to accept the cube-root formula as anything but a further interpolation formula, considering that these solutions are undoubtedly ideal.

Application of the Writer's Formula to Ideal Solutions of Solids in Liquids. The writer has shown in the foregoing papers⁽²⁾ that his viscosity formula for a binary mixture where there form no new molecular compounds:

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

(where a and k with suffixes 1 and 2 denote the association degrees and the field-constants of components 1 and 2, and other symbols have the same meaning as above) affords the satisfactorily concordant results with the experimental data available in the literature. The next problem is whether or no the formula has validity for ideal or chemically indifferent solutions of solids in liquids.

For this purpose a transformation is made as in the following:

$$\frac{(1-z_m)(\eta-\eta_1)}{z_m(\eta_2-\eta)}=\frac{k_2a_2}{k_1a_1}\,.$$

For a chemically indifferent mixture $\frac{k_2a_2}{k_1a_1}$ is a constant independent of concentration, and we have, for two arbitrarily chosen concentrations z_m and z'_m and the respective viscosities η and η',

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(1) J. Kendall and K. P. Monroe, *J. Am. Chem., Soc.*, **39** (1917), 1802.

(2) This Bulletin, **4** (1929), 5; **4** (1929), 25; **4** (1929), 149; **4** (1929), 288.

$$\frac{(1-z_m)(\eta-\eta_1)}{z_m(\eta_2-\eta)}=\frac{(1-z'_m)(\eta'-\eta_1)}{z'_m(\eta_2-\eta')} .$$

Now, consider component 1 to be the pure solvent. Component 2 being a solid, η_2 is here of course the unknown. Yet an estimation of it can be made as follows:

Rewrite the above expression in the form,

$$\frac{(1-z_m)\,z'_m\,(\eta-\eta_1)}{z_m(1-z'_m)(\eta'-\eta_1)}=\frac{\eta_2-\eta}{\eta_2-\eta'} .$$

The left-hand side of the expression consists of the factors all experimentally measurable and let it be denoted by q, then we have

$$\frac{\eta_2-\eta}{\eta_2-\eta'}=q \qquad \text{or} \qquad \eta_2=\eta'+\frac{\eta'-\eta}{q-1} .$$

The above method of calculation can be also applied for any solution in which no abrupt change in molecular state occurs, by taking two concentrations close to each other. For the verification of the writer's formula, Kendall and Monroe's data will be adopted below.

Table 1.

Naphthalene in Benzene, 25°C.

z_m-Solute	$\eta_{obs.}$	q	$\frac{k_2 a_2}{k_1 a_1}$
0.0000	0.006048	1.002	
0.0510	0.006565	1.052	0.482
0.1121	0.007261	1.017	0.498
0.1538	0.007707	1.043	0.485
0.1979	0.008263	1.014	0.491
0.2398	0.008764		0.484
0.2693	0.009178	1.026	0.489
			0.488

Table 2.

Naphthalene in Toluene, 25°C.

z_m-Solute	$\eta_{obs.}$	q	$\frac{k_2 a_2}{k_1 a_1}$
0.0000	0.005526	1.033	
0.0419	0.005848	1.026	(0.356)
0.1026	0.006394	1.029	0.377
0.1533	0.006866		0.377
0.2127	0.007470	1.029	0.378
			0.377

Since the values of q in each system and also in both the systems happen to be a constant within the limits of experimental error, I have taken $q=1.027$ as the mean value, with which calculated η_2 for successive two concentrations and obtained the mean value of them to be 0.02653. From the η_2 thus found $\left(\frac{k_2a_2}{k_1a_1}\right)$ can be calculated for each concentration, the values being recorded in the fourth column in each table. The constancy of $\left(\frac{k_2a_2}{k_1a_1}\right)$ is quite satisfactory.

Next consider $\frac{(k)C_6H_5CH_3}{(k)C_6H_6}$ from the two systems.

$$\frac{(ka)C_6H_5CH_3}{(ka)C_6H_6}=\frac{(k)C_6H_5CH_3}{(k)C_6H_6}$$

$$=\frac{(ka)\mathrm{solute}}{(ka)C_6H_6}\times\frac{(ka)C_6H_5CH_3}{(ka)\mathrm{solute}}=\frac{0.488}{0.377}=1.29.$$

This value is in good agreement with the already obtained value 1.23.

Table 3.

Diphenyl in Benzene, 25°C.

z_m-Solute	$\eta_{obs.}$	q	$\frac{k_2a_2}{k_1a_1}$
0.0000	0.006051		
0.1006	0.007585		0.295
0.1824	0.009014	1.033	0.294
0.3638	0.01298	1.096	0.295
			0.295

Table 4.

Diphenyl in Toluene, 25°C.

z_m-Solute	$\eta_{obs.}$	q	$\frac{k_2a_2}{k_1a_1}$
0.0000	0.005520		
0.1398	0.007335		0.244
0.2197	0.008587	1.025	0.239
0.2761	0.009627	1.012	0.242
			0.242

In these cases the concentrations measured are not so regularly chosen as those in the preceding solutions and the following calculations have been taken.

For diphenyl in benzene

$$\eta_2 = 0.009014 + \frac{0.009014 - 0.007585}{1.033 - 1} = 0.05231$$

$$\text{or} \quad = 0.01298 + \frac{0.01298 - 0.009014}{1.096 - 1} = 0.05433\ ,$$

and for diphenyl in toluene

$$\eta_2 = 0.008587 + \frac{0.008587 - 0.007335}{1.025 - 1} = 0.05867$$

$$\text{or} \quad = 0.009627 + \frac{0.009627 - 0.008587}{1.025 - 1} = 0.05123\ .$$

$\left(\frac{k_2 a_2}{k_1 a_1}\right)$ calculated from the mean value of the four, 0.05413, are shown in the fourth column in each table, the constancy of which is also satisfactory.

From these systems we get as above

$$\frac{(ka)_{C_6H_5CH_3}}{(ka)_{C_6H_6}} = \frac{(k)_{C_6H_5CH_3}}{(k)_{C_6H_6}} = \frac{0.295}{0.242} = 1.22\ ,$$

which is very satisfactory result.

Quite recently, Herz and Scheliga⁽¹⁾ made the viscosity determinations of the solutions of solids such as iodine, naphthalene and phenanthrene in benzene, toluene, carbon tetrachloride, carbon bisulphide and aceton, but attempted no stoichiometrical discussion, probably because of no suitable formula to represent their results.

It is interesting to see whether the calculated viscosity of the solutions of naphthalene in benzene and in toluene by the formula, whose empirical constants η_2 and $\left(\frac{k_2 a_2}{k_1 a_1}\right)$ are the same values obtained above, are concordant or not with the experimental data given by these authors.

A further verification can also be tried with their results of naphthalene in carbon tetrachloride and in carbon bisulphide, the association degrees and the field-constants of these solvents having been known, for whether the following conditions required by the theory are realized or not:

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(1) W. Herz and G. Scheliga, *Z. anorg. allg. Chem.*, **169** (1928), 161.

$$\frac{(ka)_{\text{naphthalene}}}{(ka)_{\text{CCl}_4}} = \frac{(ka)_{\text{naphthalene}}}{(ka)_{\text{C}_6\text{H}_6}} \times \frac{(ka)_{\text{C}_6\text{H}_6}}{(ka)_{\text{CCl}_4}} ,$$

and

$$\frac{(ka)_{\text{naphthalene}}}{(ka)_{\text{CS}_2}} = \frac{(ka)_{\text{naphthalene}}}{(ka)_{\text{C}_6\text{H}_6}} \times \frac{(ka)_{\text{C}_6\text{H}_6}}{(ka)_{\text{CS}_2}} .$$

In these calculations it must be remembered that between a weight fraction z and a molar fraction z_m there exists a relation:

$$\frac{1-z}{z} = \frac{1-z_m}{z_m} \frac{M_1}{M_2} ,$$

where M_1 and M_2 are the formal molecular weights of components 1 and 2 respectively. So that

$$\left(\frac{k_2a_2}{k_1a_1}\right) = \frac{(1-z_m)}{z_m} \frac{(\eta-\eta_1)}{(\eta_2-\eta)} = \left(\frac{k_2a_2}{k_1a_1}\right)_z \frac{M_2}{M_1}, \quad \left(\frac{k_2a_2}{k_1a_1}\right)_z = \frac{(1-z)(\eta-\eta_1)}{z(\eta_2-\eta)} .$$

Table 5.

Naphthalene in Benzene, 20°, 40° and 60°C.

z-Solute	η_{20}		η_{40}		η_{60}	
	obs.	calc.	obs.	calc.	obs.	calc.
0.0000	0.00645	—	0.00495	—	0.00395	—
0.0102	653	650	501	500	399	401
0.0198	660	655	505	506	401	406
0.0403	674	660	514	515	408	418

$$\left(\frac{k_2a_2}{k_1a_1}\right)_z = 0.488 \times \frac{78.08}{154.1} = 0.247 , \quad \text{and} \quad \eta_2 = 0.02653 .$$

Table 6.

Naphthalene in Toluene, 20°, 40° and 60°C.

z-Solute	η_{20}		η_{40}		η_{60}	
	obs.	calc.	obs.	calc.	obs.	calc.
0.0000	0.00584	—	0.00468	—	0.00386	—
0.0103	591	590	474	474	388	392
0.0200	596	595	478	480	392	398
0.0392	608	607	487	492	399	411

$$\left(\frac{k_2a_2}{k_1a_1}\right)_z = 0.377 \times \frac{92.10}{128.1} = 0.271 \,, \quad \text{and} \quad \eta_2 = 0.02653 \,.$$

Table 7.

Naphthalene in Carbon Tetrachloride, 20° and 40°C.

z-Solute	η_{20}		η_{40}	
	obs.	calc.	obs.	calc.
0.0000	0.00968	—	0.00745	—
0.0104	979	979	754	757
0.0209	991	990	768	770
0.0412	1011	1012	777	795

$$\left(\frac{k_2a_2}{k_1a_1}\right)_z = \left\{\frac{k_2a_2}{(ka)_{C_6H_6}}\right\}_z \times \left\{\frac{(ka)_{C_6H_6}}{(ka)_{CCl_4}}\right\}_z = 0.247 \times \frac{1}{0.63 \times 1.24} \times \frac{153.8}{78.08}$$
$$= 0.623 \,, \quad \text{and} \quad \eta_2 = 0.02653 \,.$$

Table 8.

Naphthalene in Carbon Bisulphide, 20° and 40°C.

z-Solute	η_{20}		η_{40}	
	obs.	calc.	obs.	calc.
0.0000	0.00389	—	0.00344	—
0.0102	392	395	345	350
0.0201	395	401	349	356
0.0391	404	413	355	359

$$\left(\frac{k_2a_2}{k_1a_1}\right)_z = \left\{\frac{k_2a_2}{(ka)_{C_6H_6}}\right\}_z \times \left\{\frac{(ka)_{C_6H_6}}{(ka)_{CS_2}}\right\} = 0.247 \times \frac{1}{0.76 \times 1.20} \times \frac{76.14}{78.08}$$
$$= 0.264 \,, \quad \text{and} \quad \eta_2 = 0.02653 \,.$$

As seen from each table, fair agreement between the observed and calculated values is interesting. The most discrepancy among them is observed in the case of carbon bisulphide solutions.

According to Thorpe and Rodger⁽¹⁾ the viscosities at 20° and 40°C. of benzene, toluene, carbon tetrachloride and carbon bisulphide are 0.00649,

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

0·00492; 0·00586, 0·00466; 0·00969, 0·00738; and 0·00367, 0·00319 respectively. Judging from these data in comparison with those obtained by Herz and Scheliga, the above discrepancy comes probably, in the writer's opinion, from the purity of carbon bisulphide used by these authors.

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