On the Viscosity of Solutions of Non-electrolytes⁽¹⁾

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1. Introduction

The viscosity of solutions composed of liquids (solvent) and solids (solute) can be treated from different standpoints: the first,⁽²⁾ in which the solvents are regarded as the continuous medium and, then, the equations of Einstein's type based on the hydrodynamics are used; and the second, in which the solutions are regarded as the special case of the liquid mixture. Since the molecular sizes of solvent and of solute are comparable, inasmuch as the ordinary solutions, except polymer solutions, are concerned, it is obvious that the second viewpoint is more excellent than the first. The theory of Kendall and Monroe proposed in 1917 is probably the only treatment based on the second standpoint.⁽³⁾ They extended their equation,

$$\eta^{1/3}=x_A\eta_A{}^{1/3}+x_B\eta_B{}^{1/3}, \tag{1}$$

(which had been proposed for the viscosity η of the binary liquid mixture) to solutions of non-electrolytes such as benzene solution of naphthalene and calculated the "viscosity coefficient of solute" η_B as a parameter. According to them, η_B is a constant, independent of the concentration. But η_B of the same solute given by them shows different values from solvent to solvent as will be shown in Table 1. This is nothing but the illustration of the defect of Eq. (1), for η_B must be characteristic of the solute and independent of the nature of the solvents according to its definition.

Two of the present authors⁽⁴⁾ proposed the following equation to represent the viscosity coefficient of a mixture of two liquids and showed that the equation agrees with the experimental data satisfactorily:

$$\eta=x_Aw_A\frac{d}{d_A}\eta_A+x_Bw_B\frac{d}{d_B}\eta_B+2\left(x_Ax_Bw_Aw_B\frac{d^2}{d_Ad_B}\right)^{1/2}\eta_{AB}, \tag{2}$$

where x's denote the molar fractions, w's denote the weight fractions, d, d_A and d_B are the densities of the solution, the solvent and the solute respectively. η_{AB} is a parameter called "mutual viscosity coefficient", which has its origin in the mutual interaction between solvent and solute molecules, and is independent of the composition of the solution. In this paper, we applied the equation (2) to the benzene or toluene solutions of naphthalene or diphenyl and obtained reasonable results.

2. Independency of η_B in relation to the Nature of Solvent

We applied at first the equation (2) to the experimental data obtained by Kendall and Monroe.⁽³⁾ In the case of a mixture of liquids, η_{AB} is the only unknown quantity that must be evaluated. In the present case, not only η_{AB} but also η_B is unknown. and we have two unknown parameters. To evaluate these, we rewrite Eq. (2) as follows:

$$\frac{\eta-(x_Aw_Ad/d_A)\eta_A}{x_Bw_Bd/d_B}=\eta_B+2\left(\frac{x_Aw_Ad/d_A}{x_Bw_Bd/d_B}\right)^{1/2}\eta_{AB}. \tag{3}$$

If there occurs neither contraction nor expansion on mixing, then w_Ad/d_A etc. can be replaced by the volume fractions, φ_A etc., and we get

$$\frac{\eta-x_A\varphi_A\eta_A}{x_B\varphi_B}=\eta_B+2\left(\frac{x_A\varphi_A}{x_B\varphi_B}\right)^{1/2}\eta_{AB}. \tag{4}$$

If we plot the value on the left hand side of the equation (4) against $(x_A\varphi_A/x_B\varphi_B)^{1/2}$, a straight line will be obtained so far as our equation is applicable. The results of our calculation give, indeed, straight lines as shown in Fig. 1; thus we can evaluate easily the values of η_B and η_{AB} in the usual way. As shown in Fig. 1, η_B, which is given by the ordinate of the point of intersection of the straight line and the ordinate, is constant, and is independent in relation to the nature of the

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(1) Read at the 3rd annul meeting of the Society in April, 1950.

(2) For example, H. L. Bredeé and J. de Booys. *Kolloid Z.*, **91**, 39 (1940).

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

(4) M. Tamura and M. Kurata, This Bulletin, **25**, 32 (1952).

solvent at a constant temperature. η_B is a kind of viscosity coefficient characteristic of the solute and should be independent of the solvent, as it is in our case, while η_B given by Kendall and Monroe depends upon the nature of the solvent, which is obviously inconsistent with the definition of η_B. The values of η_B and η_{AB} are given in Table 1.

Table 1

η_B and η_{AB} at 25°C. (Comparison of Eq. (2) with the Kendall and Monroe equation)

Solute		Naphthalene		Diphenyl	
Solvent		Benzene	Toluene	Benzene	Toluene
K.-M. Eq.	η_B	2.25	1.825	3.44	2.82
Eq. (2)	η_B	1.98	1.92	2.87	2.85
	η_{AB}	1.030	0.912	1.197	1.004

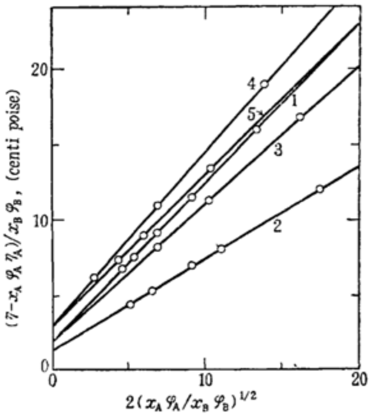

Fig. 1.—Comparison of Eq. (4) with experiments: lines 1, 2, benzene+naphthalene (25° and 60°C.); line 3, toluene+naphthalene (25°C.); line 4, benzene+Diphenyl (25°C.); line 5, toluene+diphenyl (25°C.).

3. Experimental

There are few data concerning the viscosity coefficient of such solutions as are under discussion, especially of solutions of high concentrations and those at various temperatures. So we conducted experiments on the viscosity of benzene solution of naphthalene. Benzene was purified in accordance with the instruction given by Richards and Schipley ("Organic Solvent" (1935)), and had melting point of 5.7°. Naphthalene was purified by sublimating twice in a vacuum and had a melting point of 80.0°.

In order to avoid the change in concentration due to the evaporation of benzene, we used the Ostwald type viscometer modified by Ostwald and Luther.(5) The temperature of the thermostat was regulated to ±0.005°. The measurements of the density and the viscosity were carried out at 25°, 30°, 40°, 50° and 60°. The results are shown in Table 2.

4. Temperature Dependency of η_B

In our calculation we used the equation (3). As for d_B at $t°$, the values calculated by the following equation were used,(6)

Table 2

Experimental Data of d, η and Calculated Values of η

A = Benzene and B = Naphthalene

100 x_B, %		0	2.82	6.90	8.98	13.41	15.87	20.89	25.33
100 w_B, %		0	4.55	10.85	13.93	20.27	23.63	30.23	35.76
25°C.	d	0.8733	0.8787	0.8883	0.8922	0.9009	0.9058	0.9169	0.9239
	η_{obs}	0.6020	0.6309	0.6732	0.6932	0.7423	0.7733	0.8330	0.8891
	η_{calc}		0.6298	0.6734	0.6957	0.7445	0.7730	0.8330	0.8871
	Δ		−0.2	0	+0.4	+0.3	0	0	−0.2
30°C.	d	0.8680	0.8736	0.8827	0.8872	0.8959	0.9007	0.9127	0.9170
	η_{obs}	0.5632	0.5882	0.6269	0.6448	0.6897	0.7181	0.7723	0.8222
	η_{calc}		0.5879	0.6268	0.6470	0.6912	0.7164	0.7723	0.8185
	Δ		−0.1	0	+0.3	+0.2	−0.2	0	−0.5
40°C.	d	0.8563	0.8634	0.8725	0.8771	0.8862	0.8908	0.9017	0.9097
	η_{obs}	0.4932	0.5160	0.5478	0.5665	0.6017	0.6263	0.6698	0.7200
	η_{calc}		0.5155	0.5487	0.5660	0.6041	0.6259	0.6749	0.7154
	Δ		−0.1	+0.2	−0.1	+0.4	−0.1	+0.7	−0.6
50°C.	d	0.8415	0.8529	0.8624	0.8666	0.8755	0.8807	0.8915	0.8992
	η_{obs}	0.4344	0.4564	0.4838	0.4993	0.5290	0.5509	0.5871	0.6319
	η_{calc}		0.4544	0.4824	0.4967	0.5296	0.5489	0.5909	0.6294
	Δ		−0.4	−0.3	−0.5	+0.1	−0.4	+0.6	−0.4
60°C.	d	0.8226	0.8425	0.8516	0.8551	0.8631	0.8705	0.8817	0.8894
	η_{obs}	0.3852	0.4059	0.4294	0.4418	0.4695	0.4925	0.5209	0.5572
	η_{calc}		0.4070	0.4308	0.4425	0.4695	0.4869	0.5211	0.5523
	Δ		+0.2	+0.3	+0.2	0	−1.2	0	−0.9

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(5) See, for example, E. Hatschek, "The Viscosity of Liquids (London, 1928)," p. 47.

(6) International Critical Tables, Vol. III, (1928).

Table 3

Values of d_B, η_B and η_{AB} at Various Temperatures

Temp.	d_B	η_B	η_{AB}
25°C.	1.018	1.975	1.026
30	1.014	1.830	0.941
40	1.007	1.587	0.819
50	1.000	1.384	0.715
60	0.993	1.215	0.619

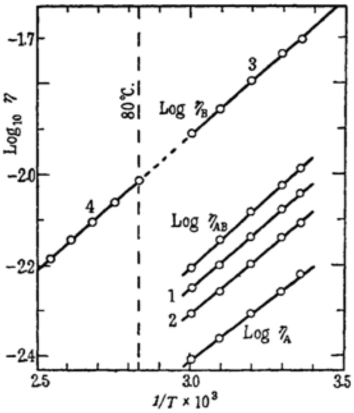

Fig. 2.—Temperature dependence of η of the system, benzene+naphthalene: line 1, $\log\eta$ ($x_B=0.2533$); line 2, $\log\eta$ ($x_B=0.1587$); line 3, $\log\eta_B$ (obtained by Eq. (3)); line 4, $\log\eta_B$ (liquid naphthalene)

$$\mathrm{d}_B=0.9779+0.7670\times10^{-3}\times(80-t)-0.755\times10^{-6}\times(80-t)^2. \quad (5)$$

This equation holds for temperature higher than 80° (melting pt.). We extrapolated to lower temperatures to get d_B, for we thought it might be reasonable to use the densities of supercooled liquid naphthalene in our case. The values of d_B are shown in Table 3, with the values of η_B and η_{AB} at various temperatures which are obtained by the method mentioned in **2**. Using these values, we calculated the viscosity coefficient of the solutions. The results are given in Table 2 compared with the observed values. Δ in the table represents $100\times(\eta_{calc}-\eta_{obs})/\eta_{obs}$. The coincidence between the calculated and the observed values is very satisfactory.

Now let us investigate into the relation between η_B and the absolute temperature T. If η_B represents the "viscosity coefficient of naphthalene", it may satisfy the following equation, as is often the case with the viscosity coefficient of pure liquid in general.

$$\log\eta_B=a+(b/T), \quad (6)$$

where a and b are constants. In fact, the equation (6) is satisfied as shown in Fig. 2. (See the straight line No. 3 which lies to the right hand side of the dotted line indicating the melting point of naphthalene.) The straight line No. 4 in Fig. 2 is the plot of $\log\eta_B$ of the liquid naphthalene at temperatures higher than the melting point against $1/T$. Two plots, No 3 and No. 4, lie on a straight line, and this fact suggests an interesting conclusion that η_B, which we evaluated in **2** and in this section, may be none other than the viscosity coefficient of supercooled liquid naphthalene. And this shows that the coincidence between the observed values of η and the calculated values by eq. (2) is not a fictitious result coming from the regulation of the values of two parameters, η_B and η_{AB}.

In the lower part of the right hand side of Fig. 2, we plotted $\log\eta$ at various concentrations, $\log\eta_A$ and $\log\eta_{AB}$ against $1/T$, respectively. These give straight lines, whose slopes give the following activation energies of flow:

$$\varepsilon_A=2.50,\quad \varepsilon_B=2.74 \text{ and } \varepsilon_{AB}=2.75\,\text{kcal./mole}.$$

Even in such a case as under discussion, where two components are rather similar to each other in construction, ε_{AB} is not always equal to $(\varepsilon_A+\varepsilon_B)/2$, and this fact indicates that the introduction of the term containing η_{AB} is necessary even in the case of apparently ideal solutions.

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(7) The experimental values of η_B of liquid naphthalene are as follows: 0.97(80°), 0.86(90°), 0.78(100°), 0.71(110°), 0.65(120°), 0.59(130°), 0.54(140°) and 0.49 centipoise (at 150°).

These values have been tabulated in K. Shiba, Tables of Physical Constants (in Japanese, Iwanami, Tokyo, 1947), p. 78.