On the Viscosity of Binary Mixture of Liquids(1)

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Introduction

If we attempt to derive an equation which should connect the viscosity coefficient of a mixture of liquids A and B with its composition and those of its constituents, it becomes necessary, in addition, to introduce a quantity in order to take the molecular interaction of A-B type into account inasmuch as the viscosity of a mixture depends upon the mutual action of the molecules constituting it. Dolezalek,(2) at first, and then Wijk(3) introduced the quantity relating the *A*-*B* type interaction in the form of a parameter called "mutual viscosity" η_{AB} and derived their own equations having simple form, but the agreement of their equations with the experimental values seems not to be enough as will be shown below, and their definitions of η_{AB} seem to be obscure. Recently, Powell, Roseveare and Eyring(4) and Kottler(5) proposed the semi-empirical equations respectively, which involve the quantities of different type from η_{AB}, but their equations are inconvenient for numerical

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(1) The contents of this paper were read at the 1st and 2nd annual meetings of the Society in May, 1948 and in April, 1949 and were published partly in *Busseiron Kenkyu*, **11**, 20[illegible] (1948); **20**, 151 (1949) in Japanese.

(2) F. Dolezalek, *Z. phys. Chem.*, **83**, 73 (1913).

(3) A. J. A. van der Wijk, *Nature*, **138**, 845 (1936).

(4) R. E. Powell, E. Roseveare and H. Eyring, *Ind. Eng. Chem.*, **33**, 430 (1941).

(5) F. Kottler, *J. Phys. Chem.*, **47**, 277 (1943); **48**, 76 (1944).

calculation, and this is an important defect for practical use. In this paper, the authors will give the definition of η_{AB} explicitly and derive a new semi-empirical equation which has simple form and seems to be better than others.

Derivation of Equation

According to Frenkel and Eyring,(6) the viscosity coefficients, η_A and η_B, of liquids A and B are given by

$$\eta_A=(kT/v_A)\tau_A \quad \text{and} \quad \eta_B=(kT/v_B)\tau_B, \qquad (1)$$

respectively, where k is the Boltzmann constant, T the absolute temperature and v's are the volumes occupied by one molecule; the subscripts indicate the molecular species. And τ's represent the relaxation times of flow and are given by

$$\left.\begin{aligned} &\tau_A=(h/kT)\exp(\chi_A/kT)\\ \text{and} \quad &\tau_B=(h/kT)\exp(\chi_B/kT), \end{aligned}\right\}(2)$$

where h is the Planck constant and $\chi_A(\chi_B)$ is the activation free energy of flow relating only with A-A(B-B) contact of molecules. Quite similarly, the viscosity coefficient η of mixture of liquids A and B, should be given by

$$\eta=(kT/v)\tau \qquad (3)$$

$$\text{with} \quad \tau=(h/kT)\exp(\chi/kT). \qquad (4)$$

Here the letters with no subscript (τ, v and χ etc.) represent the quantities regarding the mixture.

Now, let us introduce the "mutual activation free energy of flow" χ_{AB} relating only with A-B contact of molecules in the same manner as χ_A (or χ_B) relates with A-A (or B-B) contact, and define τ_{AB} by

$$\tau_{AB}=(h/kT)\exp(\chi_{AB}/kT). \qquad (5)$$

This is the relaxation time of flow of A molecule in liquid B or *vice versa*. And τ in Eq. (3) may be given as a kind of mean of τ_A, τ_B and τ_{AB}.

If we represent the molar fractions of each component by x_A and x_B, the probabilities of occurring of A-A, B-B and A-B contacts of molecules are given by x_A^2, x_B^2 and $2x_Ax_B$ respectively under the condition of random mixing. Then assuming that τ is given by the arithmetical mean of τ's, *i. e.*,

$$\tau=x_A^2\tau_A+x_B^2\tau_B+2x_Ax_B\tau_{AB}, \qquad (6)$$

and defining the "mutual viscosity coefficient" η_{AB} by

$$\eta_{AB}=\{kT/(v_Av_B)^{1/2}\}\tau_{AB}, \qquad (7)$$

we obtain

$$\eta=x_A^2\left(\frac{v_A}{v}\right)\eta_A+x_B^2\left(\frac{v_B}{v}\right)\eta_B+2x_Ax_B\left(\frac{v_Av_B}{v^2}\right)^{1/2}\eta_{AB}, \qquad (8)$$

from Eqs. (1), (3), (6) and (7). If d be the density and w the weight fraction, we can obtain easily

$$x_Av_A/v=w_Ad/d_A \quad \text{and} \quad x_Bv_B/v=w_Bd/d_B. \qquad (9)$$

For the practical purposes, we can put

$$x_Av_A/v=\varphi_A \quad \text{and} \quad x_Bv_B/v=\varphi_B, \qquad (10)$$

where φ's are the volume fractions, and obtain

$$\eta=x_A\varphi_A\eta_A+x_B\varphi_B\eta_B+2(x_Ax_B\varphi_A\varphi_B)^{1/2}\eta_{AB}, \qquad (11)$$

since the volume change on mixing can be neglected in general. Although Eq. (11) appears to be rather similar to the Dolezalek equation,

$$\eta=x_A^2\eta_A+x_B^2\eta_B+2x_Ax_B\eta_{AB}, \qquad (12)$$

it must be noticed that the agreement of the former with the experiments is considerably better than that of the latter as will be shown in the following section.

It is well-known that, if we use the harmonic oscillator model of liquids,(7) we can get the relations of the following type;

$$\left.\begin{aligned} &\tau=(1/\nu)\exp(\mathcal{E}/kT),\\ &\tau_A=(1/\nu_A)\exp(\mathcal{E}_A/kT)\\ \text{and} \quad &\tau_{AB}=(1/\nu_{AB}\nu_{BA})^{1/2}\exp(\mathcal{E}_{AB}/kT),\\ &\text{etc.,} \end{aligned}\right\}(13)$$

where $\mathcal{E}$'s are the activation energies of flow and ν's are the frequencies of lattice vibration and ν_{AB} (or ν_{BA}) represents the frequency of A (or B) molecule surrounded by B (or A) molecules only. Then (1), (3) and (7) with (13) become

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(6) J. Frenkel, "Kinetic Theory of Liquids," Oxford, 1947, Chap IV, § 2; S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," New York, 1941, Chap. IX.

(7) See, for example, R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Cambridge, 1939, p. 319.

$$\left.\begin{aligned} \eta &= (kT/v\nu)\exp(\mathcal{E}/kT), \\ \eta_A &= (kT/v_A\nu_A)\exp(\mathcal{E}_A/kT) \\ \text{and}\quad \eta_{AB} &= \{kT/(v_A v_B \nu_{AB}\nu_{BA})^{1/2}\} \\ &\quad\times\exp(\mathcal{E}_{AB}/kT). \end{aligned}\right\} \quad (14)$$

That is, the temperature dependency of η_{AB} may also satisfy the expression of Andrade's type.(8)

Comparison of η with the Experimental Values

The comparison of Eq. (11) with the experimental values of viscosity coefficient, η_{obs}, has been performed in regard to about 30 systems which are chosen from various types of mixtures as shown in Tables 1 and 2. In these tables are arranged the systems in three classes; mixtures of (A) non-polar and non-polar liquids, (B) non-polar and polar liquids and (C) polar and polar liquids, for convenience' sake. And $\bar{\varDelta}$ denotes the arithmetical mean of the absolute values of $\varDelta = (\eta_{calc} - \eta_{obs}) \times 100/\eta_{obs}$ at various compositions and max. or min. in the last column of these tables indicate that $\eta - x$ curve has a maximum or minimum. The unit of η_{AB} is "centi-poise" and the values of η of all systems except B-2, 4 and C-7 are adopted from "International Critical Tables," Vol. V. Some of the results of calculation are plotted in Figures 1~3, where the circles (○ or ◐) and the full lines represent the observed

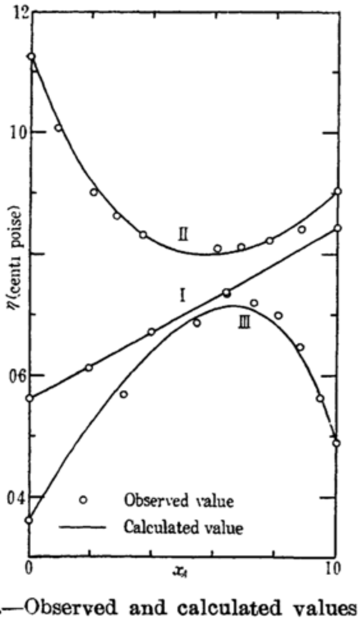

Fig. 1.—Observed and calculated values of η—1: Curve I, A = CCl_4, B = C_6H_6(30°C.); Curve II, A = CCl_4, B = CH_3COOH(25°C.); Curve III, A = H_2O, B = CH_3OH(60°C.).

Table 1

List of the Systems Compared and the Results Obtained.—I

No.	System (Observer)	°C.	η_{AB}	$\bar{\varDelta}$, %	
A-1	$CCl_4+C_2Cl_4$ (i)	25	0.752	0.5	min.
A-2	$CCl_4+C_2H_2Cl_4$ (i)	25	0.973	0.9	
A-3	$CCl_4+C_6H_6$ (ii)	0	1.134	0.0	
		10	0.941	0.0	
		20	0.797	0.2	
		30	0.688	0.2	
		40	0.596	0.1	
		50	0.522	0.0	
		60	0.463	0.2	
A-4	$CS_2+C_6H_6$ (iii)	25	0.474	0.6	
B-1	CCl_4+CHCl_3 (iii)	25	0.589	0.7	
B-2	CCl_4+CH_3COOH(xii)	25	0.657	0.9	min.
B-3	$CCl_4+CH_3COCH_3$(iv)	0	0.538	2.8	
B-4	CCl_4+n-$C_8H_{17}OH$ (xii)	25	1.112	3.7	
B-5	$CS_2+CH_3COCH_3$(v)	−13	0.450	0.2	min.
		−10	0.445	0.2	min.
		0	0.416	0.4	min.
		15	0.389	0.0	
		35	0.326	0.2	
B-6	$CS_2+C_2H_5OH$ (vi)	25	0.510	2.9	
B-7	$CS_2+C_6H_5CH_3$ (iii)	25	0.442	0.9	
B-8	$C_2H_2Cl_4+C_6H_5NO_2$ (vii)	5	3.41	1.4	max.
		76.5	0.958	0.7	
B-9	$C_6H_6+CHCl_3$ (iii)	25	0.572	0.2	
B-10	$C_6H_6+CH_3OH$ (viii)	25	0.636	0.2	
B-11	$C_6H_6+CH_3COOH$(vi)	25	0.464	2.9	min.
B-12	$C_6H_6+C_2H_5OH$ (vi)	25	0.524	1.8	min.
	〃 (ix)	15	0.668	1.9	min.
		20	0.614	2.5	
		25	0.567	2.0	
		30	0.522	1.4	
		35	0.481	0.9	
		40	0.445	0.9	
B-13	$C_6H_6+C_6H_5OH$ (x)	20	—	—	
B-14	$C_6H_6+C_6H_5CH_2CO_2C_6H_5$ (xi)	25	—	—	
		40	0.905	6.6	
		60	0.751	2.5	
		75	0.660	1.2	

Observer of η: (i) Herz and Rathmann, (ii) Thorpe and Rodger, (iii) Linebarger, (iv) Sakhanov and Ryakhovskii, (v) Faust, (vi) Dunstan, (vii) Drucker and Kassel, (viii) Bramley, (ix) Gertman, (x) Oholm, (xi) Bingham and Sarver, (xii) Jones, Bowden, Yarnold and Jones, *J. Phys. Coll. Chem.*, **52**, 753 (1948).

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(8) E. N. da C. Andrade, *Phil. Mag.*, **17**, 497, 698 (1934).

and the calculated values respectively. For purposes of comparison, we show also in Fig. 3 the values obtained from the Dolezalek equation, (12), and the Wijk equation,⁽³⁾

$$\log \eta = x_A^2 \log \eta_A + x_B^2 \log \eta_B + 2x_A x_B \log \eta_{AB}. \qquad (15)$$

Table 2

List of the Systems Compared and the Results Obtained.—II

No.	System (Observer)	°C.	η_{AB}	$\bar{\Delta}$, %	
C-1	H_2O+CH_3OH (i)	0~30	—	—	max.
		40	1.510	5.1	
		50	1.232	4.2	
		60	0.997	2.1	
C-2	$H_2O+C_2H_5OH$ (ii)	0~40	—	—	max.
		45	1.940	7.0	
		50	1.721	6.3	
		55	1.532	5.6	
		60	1.370	5.1	
		65	1.230	4.7	
		70	1.108	4.5	
		75	1.000	4.3	
C-3	$H_2O+C_3H_7OH$ (iii)	20	5.31	6.5	max.
		25	4.50	6.0	
		30	3.82	5.2	
C-4	$H_2O+C_3H_5(OH)_3$		—	—	
C-5	$CHCl_3+C_2H_5OC_2H_5$ (iv)	0	0.626	3.8	
		10	0.543	3.4	
		20	0.474	2.9	
		30	0.418	2.5	
C-6	$CHCl_2F+CH_3COCH_3$ (v)	0	0.562	1.2	max.
C-7	$CH_3OH+C_2H_5OH$ (vi)	25	0.730	0.6	
		35	0.626	0.5	
		45	0.546	0.2	
		55	0.484	0.4	
C-8	$C_2H_5OC_2H_5$ $+C_6H_5OC_6H_5$ (vii)		—	—	
C-9	i-$C_5H_{11}OH$ $+HCONH_2$ (viii)	0	13.20	7.6	max.
		76.5	1.560	2.3	
C-10	i-$C_5H_{11}OH$ $+C_6H_5NO_2$ (viii)	0	1.650	6.4	min.
		80	0.503	1.2	
C-11	i-$C_5H_{11}OH+C_6H_5N(C_2H_5)_2$ (viii)	0	2.77	6.1	min.
		76.5	0.559	1.2	
C-12	$C_6H_5CH_3+C_6H_5CO_2C_2H_5$ (ix)	25	0.782	1.2	

Observer of η: (i) Traube, (ii) Bingham and Jackson, (iii) Dunstan and Thole, (iv) Thorpe and Rodger, (v) Lacher, Walden and Park, *J. Am. Chem. Soc.*, **71**, 3026 (1949), (vi) Bingham, White, Thomas and Cadwell, (vii) Kendall and Wright, (viii) Drucker and Kassel, (ix) Kendall and Monroe.

It is nothing but the illustration of the satisfactory agreement of our equation (11) with the experimental values, that $\bar{\Delta}$ of almost all the systems is less than a small percentage. It must be noticed that $\bar{\Delta}$ of the mixture

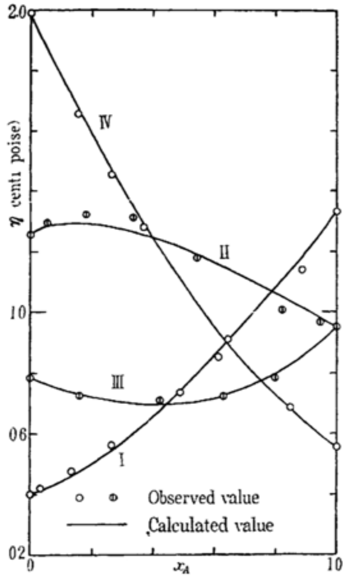

Fig. 2.—Observed and calculated values of η—2: Curve I, A=CCl_4, B=CH_3COCH_3 (0°C.); Curve II, A=i-$C_5H_{11}OH$, B=$HCONH_2$ (76.5°C.); Curve III, A=i-$C_5H_{11}OH$, B=$C_6H_5N(C_2H_5)_2$ (76.5°C.); Curve IV, A=$C_6H_5CH_3$, B=$C_6H_5CO_2C_2H_5$ (25°C.).

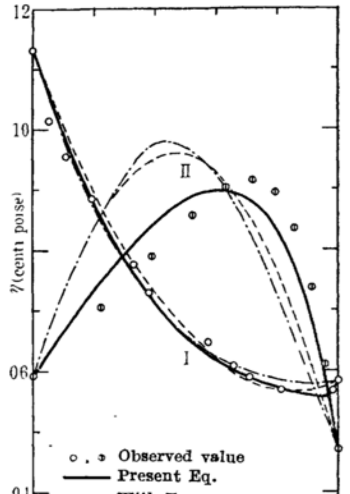

Fig. 3.—Observed and calculated values of η—3: Curve I, A=C_6H_6, B=C_2H_5OH(25°C.); Curve II, A=H_2O, B=C_2H_5OH(60°C.).

composed of liquids strongly associated becomes also less than a small percentage at a higher temperature (*cf.* Systs. C-1, 2 and 9∼11). Consequently, the equation presented here seems to be better than the equation of either Dolezalek or of Wijk. However, our equation, as well as others, seems not to be applicable to the mixture in which the difference between η_A and η_B is very remarkable (for example, the mixture of water and glycerine).

Mutual Activation Energy of Flow

If we plot $\log \eta_{AB}$ against $1/T$, a straight line will be obtained according to the definition of η_{AB}, (7) or (14). The demand for this linearity is, indeed, satisfied by our results of calculation and, accordingly, we can estimate the value of $\mathcal{E}_{AB}$ from the slope of this straight line. The values of $\mathcal{E}_{AB}$ thus obtained are tabulated in Table 3. As is expected, $\mathcal{E}_{AB}$ is approximately equal to $(\mathcal{E}_A+\mathcal{E}_B)/2$ in such systems as carbon tetrachloride+benzene or methyl alcohol+ethyl alcohol which are regarded as the so-called "ideal solutions." But in the mixture of water and alcohols, $\mathcal{E}_{AB}$ is remarkably larger than $\mathcal{E}_A$ or $\mathcal{E}_B$; $\mathcal{E}$ of pure components of these systems being 3.30 kcal./mole for water, 2.51 for methyl alcohol and 3.52 for ethyl alcohol at about 60°C. This result may be related closely with the strong affinity of alcohols with water and with the remarkable volume contraction which results on mixing. In Table 3, the values of χ_{AB} calculated from (7) with (5) or

$$\chi_{AB}=kT\ln\{(v_A v_B)^{1/2}\eta_{AB}/h\} \tag{16}$$

are also tabulated.

Table 3

Mutual Activation Energy of Flow.

Syst. No.*	ε_{AB}†	χ_{AB}(°C.)**	λ_{AB}	$\frac{\lambda_{AB}}{\varepsilon_{AB}}$	$\frac{\lambda_{AB}}{\chi_{AB}}$
A-3	2.69	3.13 (60)	7.75	2.9	2.48
4	—	2.66 (25)	6.50	—	2.44
B-5	1.19	2.47 (35)	6.62	5.6	2.68
7	—	2.67 (25)	6.70	—	2.51
8	3.46	—	—	—	—
9	—	2.86 (25)	7.75	—	2.71
12	2.90	2.75 (40)	8.73	3.0	3.12‡
14	1.98	—	—	—	—
C-1	4.52	2.82 (60)	9.81	2.2	3.48‡
2	4.88	3.08 (75)	10.22	2.1	3.32‡
3	5.18	—	—	—	—
5	2.20	2.76 (30)	7.00	3.2	2.54
7	2.65	2.99 (55)	9.50	3.6	3.51‡
9	5.31	—	—	—	—
10	2.86	—	—	—	—
11	3.98	—	—	—	—

* System No. is given in Tables 1 and 2.

** Temperatures at which χ_{AB} was calculated are put in parentheses.

† The unit of energies is kcal./mole.

‡ Compare with the values; $\lambda/\chi=4.98(H_2O)$, $3.78(CH_3OH)$ and $3.34(C_2H_5OH)$ at about 60°C.

Further, the empirical relations of $\mathcal{E}$ and χ of pure liquid with its heat of vaporization, λ, proposed by Eyring seem to hold good for $\mathcal{E}_{AB}$ and χ_{AB}, too, as shown in the table: that is,

$$\lambda_{AB}/\mathcal{E}_{AB}=3\sim4 \quad \text{and} \quad \lambda_{AB}/\chi_{AB}\doteqdot2.5, \tag{17}$$

where λ_{AB} denote the "mutual heat of vaporization" and it can be obtained from the equations of vapor pressure P of binary liquid mixture,

$$P=x_A\varphi_A P_A+x_B\varphi_B P_B + 2(x_A x_B\varphi_A\varphi_B)^{1/2}P_{AB} \tag{18}$$

with $P_{AB}=\text{constant}\times\exp(-\lambda_{AB}/kT)$.

In addition, the linearity of the $\log\eta_{AB}$ against $1/T$ is very useful for practical purposes, because we can calculate η_{AB} at any temperature so far as the values are known, at least, at two temperatures.

Activation Energy of Flow of Mixture

We can obtain the activation energy of flow of mixture $\mathcal{E}$ from η_{obs} by

$$\mathcal{E}_{obs}=\left\{\frac{\partial\ln(\eta_{obs}v/T)}{\partial(1/kT)}\right\}_{x_A}. \tag{19}$$

On the other hand, substituting (11) for (19) and performing the differentiation, we obtain the following expression for $\mathcal{E}$ after some rewritings;

$$\mathcal{E}_{calc}=y_{AA}\mathcal{E}_A+y_{BB}\mathcal{E}_B+y_{AB}\mathcal{E}_{AB}, \tag{20a}$$

$$\left.\begin{aligned} \text{with}\quad & y_{AA}=x_A\varphi_A\eta_A/\eta_{calc},\\ & y_{BB}=x_B\varphi_B\eta_B/\eta_{calc}\\ \text{and}\quad & y_{AB}=2(x_A x_B\varphi_A\varphi_B)^{1/2}\eta_{AB}/\eta_{calc}.\end{aligned}\right\} \tag{20b}$$

Here y's are regarded as the occurring probabilities of molecular contacts of the indicated

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(9) Eq. (18) will be published in future. As will be shown in our later paper, the value of λ_{AB} obtained from Eq. (18) agrees with the one estimated from the heat of mixing.

types. The comparison of ε_{calc} with ε_{obs} is given in Fig. 4. Here the mixture of carbon tetrachloride and benzene and that of water and ethyl alcohol are chosen as the examples of the ideal cases and non-ideal respectively. In this figure, the values calculated from the Wijk equation, (15) or

$$\varepsilon = x_A^2\varepsilon_A + x_B^2\varepsilon_B + 2x_Ax_B\varepsilon_{AB}, \qquad (21)$$

are also plotted for comparison's sake. Though in the former example, either (20) or (21) agree with ε_{obs} satisfactorily. In the latter, (21) used by Wijk does not agree with ε_{obs} even if the values of ε_{AB} were adjusted in any way. On the contrary, (20) agrees with ε_{obs} satisfactorily, if we adjust ε_{AB} so that ε_{calc} may agree with ε_{obs}. Though the values of ε_{AB} thus determined, 5.30 kcal./mole, is slightly different from that of ε_{AB} in Table 3, 4.88 kcal./mole, the inconsistency in this degree will be acceptable in such non-ideal systems as this example.

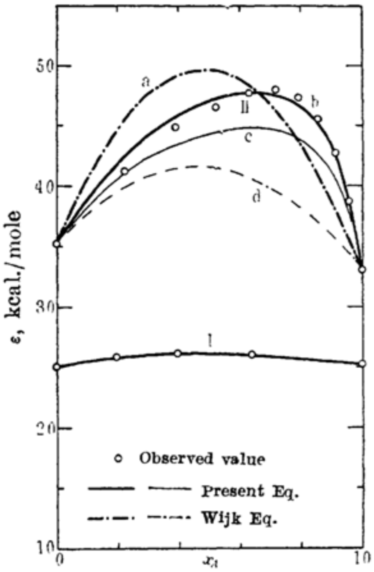

Fig. 4.—Observed and calculated values of ε: Curve I, A = CCl_4, B = C_6H_6, $\varepsilon_{AB} = 2.69$ kcal./mole; Curve II, A = H_2O, B = C_2H_5OH (at about 60°C.), ε_{AB} = ,(a); 6.50 (b), 5.30 (c and d) 4.88 kcal./mole.

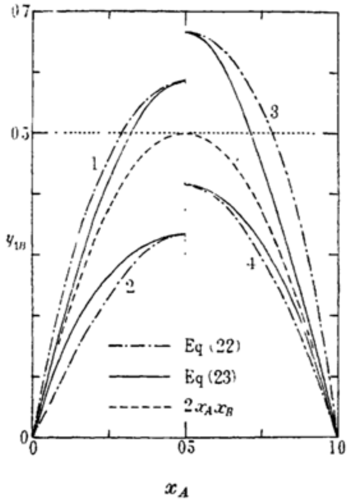

Fig. 5.—Occurring probabilities of A-B contact, y_{AB}: $\tau_A/\tau_{AB} = \tau_B/\tau_{AB} = 1/\sqrt{2}$ (curve 1); 2 (curve 2); 1/2 (curve 3); $\sqrt{2}$ (curve 4). Eq. (23) nearly coincides with the Bethe-Fowler-Takagi approximation.

Now, let us examine the physical meaning of the assumption (6) used in order to derive Eq. (11). For that, it seems to be simplest to examine the meaning of y's which have been given by (20b). Substituting (1), (3), (6) and (7) into (20b), we obtain

$$\left.\begin{aligned} &y_{AA} = x_A^2\tau_A/(x_A^2\tau_A + x_B^2\tau_B \\ &\qquad + 2x_Ax_B\tau_{AB}) = x_A^2\tau_A/\tau, \\ &y_{BB} = x_B^2\tau_B/\tau \\ \text{and}\quad &y_{AB} = 2x_Ax_B\tau_{AB}/\tau. \end{aligned}\right\} \qquad (22)$$

If the difference between τ_A and τ_B be not so remarkable, we can transform (22) to the following forms after some tolerable approximations:[10]

$$y_{AB} = 4x_Ax_B/(1+\beta) \quad \text{etc.,} \qquad (23a)$$

$$\text{with} \quad \beta \doteqdot [1 + 4x_Ax_B\{(\tau_A\tau_B/\tau_{AB}^2) - 1\}]^{1/2}. \qquad (23b)$$

These equations are to be compared with those of the Bethe-Fowler-Takagi (B-F-T) approximation for regular solutions.[11] That is, according to this approximation y's are, likewise, given by (23a) with

$$\beta = [1 + 4x_Ax_B\{\exp(\Delta\zeta/kT) - 1\}]^{1/2}, \qquad (24)$$

where $\Delta\zeta$ denotes the increase of the free energy in the process,

$$\text{(A-A contact)} + \text{(B-B contact)}$$
$$\rightarrow 2 \times \text{(A-B contact)}.$$

Though (23b) and (24) seem to be slightly different, both expressions of β agree with

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[10] Since the agreement of (22) with (23) is satisfactory as will be shown in Fig. 5, the rewriting from (22) to (23) seems to be reasonable.

[11] Ref. 7, p. 358; Y. Takagi, *Proc. Phys. Math. Soc. Japan*, **23**, 44 (1941).

[12] The free energies, ζ's of molecular contacts of the indicated types are given by

$$\zeta_{AA} = (2\lambda_A/z) - (6kT/z)\ln \nu_A + (3kT/z)\ln(kT/2\pi m_A) \text{ etc.,}$$

so far as the harmonic oscillator model of liquids is used (See, Ref. 7, p. 324). Since the last terms in the right hand side of these formulae are canceled in $\Delta\zeta = \zeta_{AA} + \zeta_{BB} - 2\zeta_{AB}$, we can obtain Eq. (25).

each other as shown in the followings. Using the harmonic oscillator model of liquids, we can put(2)

$$\exp\left(\frac{\Delta\zeta}{kT}\right)=\left(\frac{\nu_{AB}\nu_{BA}}{\nu_A\nu_B}\right)^{6/z} \exp\left\{\frac{\lambda_A+\lambda_B-2\lambda_{AB}}{kT}\left(\frac{2}{z}\right)\right\}, \quad (25)$$

where z is the number of the nearest neighbors. Then, using $z \fallingdotseq 8$, the result obtained by the x-ray diffraction, and the Eyring relation (17), we obtain

$$\exp\left(\frac{\Delta\zeta}{kT}\right)\fallingdotseq\left(\frac{\nu_{AB}\nu_{BA}}{\nu_A\nu_B}\right)^{3/4}\exp\left\{\frac{\varepsilon_A+\varepsilon_B-2\varepsilon_{AB}}{kT}\right\} \fallingdotseq \frac{\tau_A\tau_B}{\tau_{AB}^2}, \quad (26)$$

from (25) and (13), for $\nu_{AB}\nu_{BA}/\nu_A\nu_B \fallingdotseq 1$ in general. Accordingly, it can be concluded that (23), nearly, coincides with the B-F-T approximation. In Fig. 5, we show the values of y_{AB} calculated from (22) and (23) and the value of $2x_Ax_B$ for some values of τ's. In conclusion, our treatment involving (22) corresponds to the B-F-T approximation. From the fact mentioned here, the reason becomes obvious why Eq. (11) corresponding to (22) is better, as shown in before, than the Wijk equation corresponding to (21) or to the Bragg-Williams approximation. Furthermore, it will be one of the strong points of (22) in comparison with (21) that the effect of the difference between the sizes of constituent molecules is tacitly taken into consideration by the weight factor, τ's, having the values which are parallel with the molecular sizes in general.

Summary

A new semi-empirical equation for the viscosity coefficient of binary mixture of liquids, Eq. (11), has been derived and we have reached the conclusion that the assumption used in order to derive our equation corresponds to the Bethe-Fowler-Takagi approximation for regular assembly qualitatively. The equations for η and ε have been compared with the experimental values and satisfactory results have been obtained.

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