Further Notes on the Ideal Mixture Law for Viscosity

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Six years ago the author published a paper[1] on the same subject as the above. The previous paper treated the comparison of the validity among the viscosity formulae of Kendall, Macleod, Drucker and Kassel, and Ishikawa with four examples of binary mixtures of the same crystal forms, three being the systems of AgBr-AgCl, $CdCl_2$-$CdBr_2$, and $PbBr_2$-$PbCl_2$, and one being Na-K system, but the present author has thrown some doubt since then on the result of the last pair whose K (Ishikawa's characteristic constant) takes a unique but abnormally greater value, 2.54, throughout the wide temperature range from 103.7 to 192.8°C than the values not so much different from unity for ordinary mixtures composed of like liquids. This paper is intended as a supplementary report on this subject.

Relation between the Formulae—In order to carry on further study, we must consider the relationship between these formulae. For convenience, sake we adopt the following symbols: η_1, η_2 and η signify the viscosities of component 1, 2, and the mixture respectively, φ_1, φ_2 and φ the fluidities of components 1, 2, and the mixture respectively; x_1, x_2, and x so called Macleod's free spaces of 1 cc. of components 1, 2 and the mixture respectively; a_1, a_2 and a the association degrees of component 1, 2 and the mixture respectively and z, z_m and z_v the weight, molar, and volume fraction of component 2 respectively before mixing.

1) T. Ishikawa, This Bulletin, **25**, 38 (1952).

Macleod's formula for ideal mixtures[2]:

$$\left.\begin{aligned}\eta &= \eta_1(1-z_m)\frac{x_1}{x}+\eta_2 z_m\frac{x_2}{x}\\ x &= x_1(1-z_v)+x_2 z_v\end{aligned}\right\} \quad (1)$$

Drucker and Kassel's formula[3]:

$$\varphi=\varphi_1(1-z)+\varphi_2 z \quad (2)$$

This formula can also be obtained from Macleod's relation, $\eta=K_M Ma/x$ (M is the molecular weight and K_M so called "a universal constant" according to his theory[4], and another assumable relation which becomes identical with Macleod's relation for x in Formula 1 in the case of gaseous state where $z_v=z_m$, and $a_1=a_2=a=1$:

$$\frac{x}{a}=\frac{x_1}{a_1}(1-z_m)+\frac{x_2}{a_2}z_m \quad (3)$$

Ishikawa's formula for ideal mixtures[5]:

$$\eta=\eta_1\frac{k_1a_1(1-z_m)}{k_1a_1(1-z_m)+k_2a_2z_m}+\eta_2\frac{k_2a_2z_m}{k_1a_1(1-z_m)+k_2a_2z_m} \quad (4)$$

where k_1 and k_2 denote so-called "field constants" of component 1 and 2 respectively according to his theory.

Now if we transform Formula 2 and 4 into hyperbolic forms, we obtain for Drucker and Kassel's formula, remembering $(1-z)/z=(1-z_m)M_1/z_mM_2$,

$$\frac{(1-z_m)(\eta-\eta_1)}{z_m(\eta_2-\eta)}=\frac{\varphi_2M_2}{\varphi_1M_1} \quad (5)$$

and for Ishikawa's formula,

$$\frac{(1-z_m)(\eta-\eta_1)}{z_m(\eta_2-\eta)}=\frac{k_2a_2}{k_1a_1}=K \quad (6)$$

Among 63 kinds of liquid pair which satisfy Formula 6[6], there occur four cases, for which Formula 5 holds good with nearly equal values of $\varphi_2M_2/\varphi_1M_1$ and K: trichloroethylene–pentachloroethane, ethyl propionate–propylacetate, toluene–bromobenzene and *m*-cresol–*p*-cresol (see Table I in which parentheses denote the association degrees quoted from Bingham and Spooner's table[7]).

Since each of these pairs consists of the liquids having nearly equal association degrees, i.e., $a_1=a_2$, there may undoubtedly exist the following relation, comparing Formula 6 with Formula 5:

$$\frac{k_2}{k_1}=\frac{\varphi_2M_2}{\varphi_1M_1},\ \text{or}\ K=\frac{\varphi_2M_2a_2}{\varphi_1M_1a_1} \quad (7)$$

From relation 7, it may easily be understood that the fundamental additive law for viscosity with respect to molar fraction:

$$\eta=\eta_1(1-z_m)+\eta_2z_m \quad (8)$$

is valid only for such pairs where Gartenmeister's relation, $\eta=k_GM$, k_G being a constant[8], holds good and at the same time the condition, $a_1=a_2$, is satisfied

A New Method for evaluating Association Degrees—As regards the evaluation of the association degrees of liquids, a few methods have been proposed by several investigators[9-12]. They are individually no other than deviation factors from a statistically deduced constant in some physico-chemical relation which fits normal liquids, so that for the values of highly associated liquids, there is no means among themselves for confirming whether they are probable values or not.

On the other hand, if relation 7 is applied to evaluate the association degrees of liquids, it is convenient to ascertain their values, since for three ideal mixtures, A—B, B—C, and C—A, there exists the known relation:

$$\frac{k_Aa_A}{k_Ba_B}=\frac{k_Aa_A}{k_Ca_C}\cdot\frac{k_Ca_C}{k_Ba_B},\quad \text{hence}$$

$$\frac{\varphi_AM_Aa_A}{\varphi_BM_Ba_B}=\frac{\varphi_AM_Aa_A}{\varphi_CM_Ca_C}\cdot\frac{\varphi_CM_Ca_C}{\varphi_BM_Ba_B}.$$

Macleod assigned *n*-octane as a standard liquid having $a=1$ to determine K_M, and with thus obtained $K_M=4.62\times10^{-6}$, he evaluated the association degrees of 28 kinds of liquid. However, the values of highly associated liquids such as *iso*-propyl, *n*-butyl, and *iso*-butyl alcohol seem to be doubtful. Macleod at first proposed a relation, ηx^4=a constant[13], but replaced it two years later with the above quoted relation, $\eta=K_MMa/x$. Since A in the former relationship depends mainly upon the amount of molecular association, A being nearly unity for most of the normal

2) D. B. Macleod, *Trans. Faraday Soc.*, **20**, 348 (1924).
3) K. Drucker and R. Kassel, *Z. physik. Chem.*, **76**, 367 (1911).
4) D. B. Macleod, *Trans. Faraday Soc.*, **21**, 162 (1925).
5) T. Ishikawa, This Bulletin, **4**, 5 (1929).
6) T. Ishikawa and T. Baba, This Bulletin, **11**, 64 (1936).
7) E. C. Bingham and L. W. Spooner, *Physics*, **4**, 387 (1933).
8) R. Gartenmeister, *Z. physik. Chem.*, **6**, 524 (1890).
9) W. Ramsay and J. Shields, *J. Chem. Soc.*, **63**, 1089 (1893); *Phil. Trans.*, A. **184**, 647 (1893); *Z. physik. Chem.*, **12**, 433 (1893).
10) J. Traube, *Ber.*, **28**, 3292 (1895); **30**, 273 (1897).
11) D. B. Macleod, *Trans. Faraday Soc.*, **20**, 348 (1924); **21**, 162 (1925).
12) E. C. Bingham and J. P. Harrison, *Z. physik. Chem.*, **66**, 1 (1909); E. C. Bingham and L. W. Spooner, *Physics*, **4**, 387 (1933).
13) D. B. Macleod, *Trans. Faraday Soc.*, **19**, 6 (1923).

TABLE I

CASES OF EQUAL MAGNITUDE OF K AND $\varphi_2M_2/\varphi_1M_1$

Component 1	Component 2	t°C	K	$\varphi_2M_2/\varphi_1M_1$	Observers
C_2Cl_3H (0.99～1.02)	C_2Cl_5H (1.02～1.05)	25	0.40	0.389	Herz and Rathman (1913)
$C_2H_5COOC_2H_5$ (1.13～1.20)	$CH_3COOC_3H_7$ (1.16～1.21)	20 40	0.87 0.98	0.922 0.934	Unkovskaja and Volova (1925)
$C_6H_5CH_3$ (1.16～1.14)	C_6H_5Br (1.19～1.05)	20 35	0.86 0.85	0.866 0.878	Yajnik, Bhalla, Talwar and Soofi (1925)
m-$CH_3C_6H_4OH$ (1.81～1.60)	p-$CH_3C_6H_4OH$ (1.82～1.62)	25	0.90	0.910	Kendall and Beaver (1921)

TABLE II

COMPARISON OF TWO VALUES OF ASSOCIATION DEGREES DUE TO MACLEOD

Substance	x(0°C)	A	x^A	$(x)_{A=1}$	a'	a	a'/a
CH_3OH	0.1037	1.5595	0.0291	0.0580	1.99	3.20	0.62
C_2H_5OH	0.09215	1.948	0.00961	0.0450	4.68	3.75	1.25
n-C_3H_7OH	0.0333	1.3237	0.0110	0.0233	2.12	3.26	0.65
iso-C_3H_7OH	0.0559	2.104	0.00231	0.0252	10.9	4.14	2.63
n-C_4H_9OH	0.0563	2.085	0.00248	0.0248	10.0	3.77	2.65
iso-C_4H_9OH	0.0964	3.405	0.000347	0.0243	70.0	5.71	12.26

liquids, there may exist the equality: $x^A=(x)_{A=1}/a'$, where a' is the association degree when x^A can fortunately be reduced to $(x)_{A=1}$. The actual estimation of $(x)_{A=1}$ appears to be too difficult to obtain concordant values of a' with his obtained values of a, as clearly recognized from a'/a in Table II.

The present author, taking the association degrees of n-hexane and carbon tetrachloride as unity, has calculated those of 27 kinds of liquid, each being taken as a possible mean value as stated above (see Table III in which the values obtained by other investigators are also tabullated for reference).

Interpretation for the Abnormal Value of Na—K System—Quite recently Sakai[14] made experiments on the absorption spectra of mixed fused salts and led to the supposition that the great shift of absorption edge to long wave-length side with the rise of temperature may be the degradation of molecular association of component salts in the systems of $PbCl_2$—$PbBr_2$, $CdBr_2$—CdI_2, $CdCl_2$—CdI_2, and $PbCl_2$—$CdCl_2$.

Now we shall return to the pairs $PbBr_2$—$PbCl_2$, $CdCl_2$—$CdBr_2$ AgBr—AgCl, and Na—K.

For $PbBr_2(1)$—$PbCl_2(2)$ system at 510°C, $K=0.33$ and

$$\frac{\varphi_2M_2}{\varphi_1M_1}=\frac{\eta_1M_2}{\eta_2M_1}=\frac{0.0354\times278.12}{0.0495\times367.04}=0.542,$$

$$\therefore\quad \frac{a_1}{a_2}=\frac{0.542}{0.33}=1.64.$$

N.B. The melting points and latent heats of fusion of $PbBr_2$ and $PbCl_2$ are 490°C and 4.530 kcal./g-mol., and 498°C and 5.136 kcal./g-mol. respectively.[15]

For $CdCl_2(1)$—$CdBr_2(2)$ system at 600°C, $K=0.82$ and

$$\frac{\varphi_2M_2}{\varphi_1M_1}=\frac{0.0232\times272.24}{0.0258\times183.32}=1.348,$$

$$\therefore\quad \frac{a_1}{a_2}=\frac{1.348}{0.82}=1.64.$$

For AgBr(1)—AgCl(2) system at 500°C, $K=1.21$ and

$$\frac{\varphi_2M_2}{\varphi_1M_1}=\frac{0.0284\times143.34}{0.0207\times187.80}=1.047,$$

$$\therefore\quad \frac{a_2}{a_1}=\frac{1.21}{1.047}=1.16.$$

N.B. The melting points and latent heats of fusion of AgBr and AgCl are 430°C and 2.365 kcal./g-mol., and 455°C and 3.058 kcal./g-mol. respectively.[15]

For Na(1)—K(2) system at 103.7～192.8°C, K and $\varphi_2M_2/\varphi_1M_1$ are as follows:

°C	103.7	121.5	147.0	167.4	192.8	mean
K	2.61	2.54	2.45	2.51	2.55	2.54
$\varphi_2M_2/\varphi_1M_1$	2.724	2.678	2.638	2.599	2.581	2.644
a_1/a_2	1.043	1.054	1.077	1.035	1.012	1.04

N.B. The melting points and latent heats of fusion of Na and K are 97.7°C and 0.621 kcal/g-atom, and 63°C and 0.508 kcal./g-atom respectively[16].

14) K. Sakai, *J. Chem. Soc. Japan, Pure Chem. Sec,* (*Nippon Kagaku Zassi*), **78**, 1108 (1957).

15) Quoted from International Critical Tables, V. pp. 131—135.

16) Quoted from F. Henning, Wärmetechnische Richtwerte, pp. 14—15.

TABLE III
ASSOCIATION DEGREES OF LIQUIDS

Substance	Ramsay and Shields (16～46°C)	Traube (15°C)	Macleod (0°C)	Bingham and Spooner	This author (20～60°C)
n-C_6H_{14}	—	1.00	0.99	1.03～1.02	1.00
$CHCl_3$	0.92	1.00	1.19	1.02～1.06	1.00
CCl_4	1.01	1.00	1.12	1.09～1.00	1.00
CH_3I	—	1.30	0.90	0.98～1.05	1.00
C_2H_5I	1.01	1.19	0.92	0.99～1.04	1.24
CS_2	1.07	—	1.50	0.93～1.02	1.10 2.10
C_2H_5SH	1.04	—	—	1.05～1.10	1.29
CH_3COCH_3	1.26	1.53	1.66	1.28～1.31	1.74
C_6H_6	1.01	1.18 (16°C)	1.45	1.32～1.22	1.48
$C_6H_5CH_3$	—	1.08	1.15	1.16～1.14	1.40
C_6H_5Cl	1.03	1.00 (20°C)	—	1.10～1.12	1.84
$HCONH_2$	6.18(20～30°C)* 4.85(45～60°C)*	—	—	2.00～3.40	4.93
$C_6H_5NO_2$	0.93	1.47 (20°C)	—	1.23～1.77	1.38
$C_6H_5NH_2$	1.05	1.35 (20°C)	—	1.62～2.03	2.93
C_9H_7N (Quinoline)	0.81	—	—	1.33～1.58	2.32
$C_2H_5OC_2H_5$	0.99	1.00	1.04	1.02～1.06	1.27
CH_3COOCH_3	—	1.48 (0°C)	1.35	1.23～1.33	1.99
$CH_3COOC_2H_5$	0.99	1.25	1.16	1.20～1.25	1.85
CH_3COOH	3.62 2.13(20°C)**	1.56	2.53	1.71～1.95	3.01
H_2O	3.44(20～30°C) 1.64(20°C)**	3.06	—	—	6.79
CH_3OH	3.43 2.32(20°C)**	1.79	3.20	1.93～1.89	2.22
C_2H_5OH	2.74 1.65(20°C)**	1.67	3.75	1.98～1.90	2.44
n-C_3H_7OH	2.25	1.66	3.26	1.92～1.78	2.87
iso-C_3H_7OH	2.86	1.53	4.14	2.01～1.72	2.77
n-C_4H_9OH	1.94	—	3.77	1.85～1.63	2.57
iso-C_4H_9OH	1.95	1.54	5.61	1.95～1.63	2.25
C_6H_5OH	—	1.43 (20°C)	—	1.89～1.71	3.33

* W. E. S. Turner, E. W. Merry, *J. Chem. Soc.*, **1910**, 2069.
** W. Ramsay, *Z. physik. Chem.*, **15**, 111 (1894).

TABLE IV
K AND $\varphi_2M_2/\varphi_1M_1$ VALUES OF ISOMORPHIC COMPOUNDS

Component 1	Component 2	t°C	K	$\varphi_2M_2/\varphi_1M_1$
Stilbene ($C_6H_5CH{:}CHC_6H_5$)	Azobenzene ($C_6H_5N{:}NC_6H_5$)	125	0.862±0.013	1.831
Stilbene	Dibenzyl ($C_6H_5CH_2CH_2C_6H_5$)	125	0.951±0.006	2.361
Stilbene	Benzalaniline ($C_6H_5CH{:}NC_6H_5$)	125	0.902±0.009	2.516
Azobenzene	Dibenzyl	75	1.03 ±0.09	1.290
Azobenzene	Benzalaniline	75	1.03 ±0.02	1.372
Benzalaniline	Benzylaniline ($C_6H_5CH_2NHC_6H_5$)	75	0.992±0.006	1.531

TABLE V
ASSOCIATION DEGREES OF ISOMORPHIC COMPOUNDS AT 125°C

Compound	m.p. °C	Heat of fusion kcal./g-mol.[15]	Association degree at 125°C estimated	calculated from Eq. (1)	Eq. (2)
Benzylaniline	32	4.002	1.00	(1.25)	1.02
Benzalaniline	49	—	1.54	1.56	1.52
Dibenzyl	52	5.649	1.64	1.62	I.61
Azobenzene	68	5.280	2.05	2.02	2.07
Stilbene	124	7.215	4.24	4.27	(3.70)

As judged from Sakai's first and second experimental results summarized in two figures on single salts[17], the temperature variation of absorption edge of $PbBr_2$ is greater than that of $PbCl_2$, and that of $CdCl_2$ is greater than that of $CdBr_2$. These facts run parallel with the here-obtained association degrees, that is, the association degrees, of $PbBr_2$ and $CdCl_2$ are 1.6 times greater than those of $PbCl_2$ and $CdBr_2$ respectively.

Before entering into the study on Na—K system, we shall add two more systems of molten metals of different crystal forms, lead—tin and lead—bismuth[18].

For both cases, Ishikawa's formula holds strictly good (deviations are at most ±1 in the last cipher of absolute viscosity values), giving for Pb(1)—Sn(2) system $K=1.15$(400°C) and 1.03(500°C), $\varphi_2M_2/\varphi_1M_1=0.926$(400°C) and 0.897(500°C); and for Pb(1)—Bi(2) system $K=2.60$(400°C) and 1.58(500°C), $\varphi_2M_2/\varphi_1M_1=1.323$(400°C) and 1.263(500°C), whence we obtain $a_2/a_1=1.24$ (400°C) and 1.16(500°C) for the former pair, and $a_2/a_1=1.97$(400°C) and 1.25(500°C) for the latter pair.

N.B. The melting points and latent heats of fusion of lead, tin, and bismuth are 327.4°C and 1.18 kcal./g·atom, 231.9°C and 1.66 kcal./g·atom, and 271.0°C and 2.72 kcal/g·atom respectively.[16]

In regards to metals, the atomic complexity of bismuth degrades greatly from 1.97 to 1.25; that of tin degrades slightly from 1.24 to 1.16 both for 100° temperature interval, whereas sodium and potassium, judging from the constancy of a_1/a_2 throughout the temperature range, 103.7~192.8°C, may undoubtedly be monoatomic, or else greatly similar in atomic complexity against temperature change, and hence the constant, $K=2.54$ for the pair composed of these metals, is not abnormal, but is typically normal just as the pair of pentachloroethane(1)—trichloroethylene(2) ($K=1/0.40=2.5$) in Table I.

Examples for elucidating the Degradation of Molecular Complexity—The six cases of ideal mixtures[19] composed of isomorphic and greatly similar compounds in chemical constitution as shown in Table IV are those which nearly satisfy the additive law, i.e., $K=1$, but their corresponding $\varphi_2M_2/\varphi_1M_1$ takes something other than unity. This discrepancy, however, would be elucidated in the following way.

From K values of five pairs except the last, the already mentioned condition for three ideal mixtures composed of three kinds of liquids are calculated as follows:

$$0.862\times\frac{1}{0.951}\times1.03=0.933,$$

$$0.902\times\frac{1}{0.862}\times\frac{1}{1.03}=1.016.$$

These values approach nearer to unity, if we take the probable errors of K into account, and therefore the condition is fairly satisfied in spite of a wide temperature difference, 50°, taken in the viscosity measurements.

Since these isomorphic compounds have, according to the observer, equal viscosity values at the temperature of 1° above their melting points (viscosity values relative to that of water at 4°C are 1.3909±0.0037 or ±0.265% deviations from the mean), the molten state at their melting points should be in equal molecular association. Assuming then that the association degree of benzylaniline having the lowest melting point among them is unity at 75°C, the association values of benzalaniline, dibenzyl, and azobenzene have been found from the pairs at 75°C to be 1.54, 1.64, and 2.05 respectively, and by applying these values to the pairs at 125°C the association degree of stilbene has been estimated to be 4.35, 4.07, 4.30 or the mean 4.24.

17) K. Sakai, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **78**, 138, 306 (1957).
18) R. Arpi, *Z. Metallographie*, **5**, 142 (1914).
19) K. Beck, *Z. physik. Chem.*, **48**, 652 (1904).

These values in the reverse order in Table V are presumably regarded to be the association degrees of any one of these compounds at temperatures of 1°, 57°, 73°, 76°, and 93° above its melting point (temperature differences of each melting point from 125°C). If it be really so, there should exist some simple functional relationship between the association values and their corresponding temperature differences. Taking logarithms of the association values, a, as ordinate and the temperature differences, Δt, as abscissas, we can easily find that a linear relaiton

$$\log a = 0.6365 - 0.00582\,\Delta t \qquad \text{(i)}$$

nearly holds except the lowest value. Next taking a as ordinate and Δt as abscissa, the following simplest relation

$$a = 3.73 - 0.0291\,\Delta t \qquad \text{(ii)}$$

holds except the highest value. Judging from these two trials, it is highly probable that the molecular association of these compounds degrades at first rapidly (logarithmically) in the neighborhood of the melting point, but then gradually with the rise of temperature.

Summary

In the previous paper on the same subject the author made an erroneous explanation on the result of Na—K system.

Comparison of Ishikawa's formula with Drucker and Kassel's formula leads to the new relation, $K = \varphi_2 M_2 a_2 / \varphi_1 M_1 a_1$, from which the association degrees of 27 kinds of liquid have been evaluated.

By the use of this relation, the abnormally high value of K of Na—K system has been proved to be normal.

Two systems of different crystal forms, Pb—Sn and Pb—Bi, and six systems composed of isomorphic compounds, benzylaniline, benzalaniline, dibenzyl, azobenzene, and stilbene are added for elucidating the degradation of atomic or molecular complexity with rise of temperature.

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