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

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The probable values of the normal K relative to that of benzene. Before closing this series of the viscosity study,⁽¹⁾ we will consult as much as available data found in the literature in order to have the probable values of the normal K.

Mixtures adopted here are (1) those the viscosity curves of which are convex or quite rarely concave towards the composition axis, and (2) these both component K's of which in accord with Ishikawa's theory have already been known, although they indicate viscosity maxima or minima.

The following notations will be used:

K signifies the ratio of the characteristic constant (ka) of component 2 to that of component 1 in formula (1) for chemically indifferent mixtures:

$$\eta = \frac{\eta_1}{1 + K \frac{z_m}{1 - z_m}} + \frac{\eta_2}{1 + \frac{1}{K} \frac{1 - z_m}{z_m}} \tag{1}.$$

This normal case is simply denoted by the symbol n.

In the course of the calculation we have met with cases in which K's slightly vary as concentration, and either of the extrapolated values of K at $z_m = 0$ or $z_m = 1$ if taken much differs from the probable value of the normal K. Such anomaly is observed in the following mixtures: Acetone—i-propyl alcohol, carbon tetrachloride—tetrachloroethane, &c. However, further tests for these mixtures prove that they must be classified into the following case.

K' and K'' denote the ratios of the characteristic constant (ka) of component 2 to that of component 1 and that of component 1 to that of component 2 respectively, more or less differing from K and 1/K in formula (1) or K'K'' > 1 as a result of anomalous changes in molecular association:

⁽¹⁾ This Bulletin, **4** (1929), 5, 25, 149, 288; **5** (1930), 47, 117; **8** (1933), 280, 293; **9** (1934), 155; **10** (1935), 153, 248; **11** (1936), 8.

$$\eta = \frac{\eta_1}{1 + K' \frac{z_m}{1 - z_m}} + \frac{\eta_2}{1 + K'' \frac{1 - z_m}{z_m}}$$
(2).

This formula for anomalous change in association on mixing holds true for the concentration range between the two extremities close to $z_m = 0$ and $z_m = 1$, where the numbers of molecules of one component become quite enough to change its original association into some other associations statistically at extremely low concentration and at extremely high concentration diluted with the other component. This anomalous case is abbreviated by the symbol a.

For the case in which the association degree of a component varies as dilution with the other, the extrapolated value of K at $z_m = 0$ or $z_m = 1$ gives the normal K for the mixture. The mixtures of phenol, guaiacol, or benzyl benzoate with benzene or toluene in which the former components suffer molecular dissociation are examples of this case. The formulation of the viscosity—composition curves of such mixtures cannot be generally done, since the decreasing rate of the association degree with dilution depends upon its own peculiarity of the associated component against the solventing action of the other component, yet a particular case can be solved with a particular means, say, taking K or its reciprocal at each composition for test whether they are in a linear relationship with composition or not. This variable case (3) is briefly denoted by the symbol v, and both extrapolated values at $z_m = 0$ and $z_m = 1$ are written thus: e.g. 0.087-0.227 for C_6H_6 (1)— C_6H_5OH (2).

The mixture phenol—dimethylaniline is considered as one more example of the case. The viscosity—composition curves observed by Bramley at the temperatures between 10° and 180° C. are sinuous nature as seen from Fig. 1 in which the points are the observed viscosities. Simply judging from the curves, one may imagine, as Bramley does, that the mixture appears to have a compound, but the freezing-point curve consists of two branches only, the eutectic temperature being found to be -36.0° C. according to Bramley. Once when we take, however, K as ordinate and z_m as abscissa, we readily see that the points at each temperature lie on a straight line. This fact shows that there occurs the molecular dissociation of phenol but no molecular compound just as the freezing-point diagram requires. The curves in Fig. 1 are traced on thus calculated viscosities (see Table 1).

⁽²⁾ A. Bramley, J. Chem. Soc., 109 (1916), 469.

Table 1. Phenol-Dimethylaniline, (Bramley).

10°C.				29.8		59.9	59.9°C.	
z _m	nobs.	ncale.	Z _m	η _{obs} .	neale.	nobs.	γicale.	
0.0000	0.2010	_	0.0000	0.0709	_	0.02530	_	
0.0571	0.1964	0.1946	0.0537	0.0686	0.0687	0.02665	0.02473	
0.1173	0.1850	0.1801	0.1116	0.0648	0.0650	0.02380	0.02387	
0.1785	0.1639	0.1596	0.1726	0.06025	0.06003	0.02270	0.02274	
0.2500	0.1347	0.1327	0.2409	0.05325	0.05352	0.02100	0.02124	
0.3149	0.1094	0.1092	0.3046	0.04705	0.04721	0.01960	0.01972	
0.3815	0.0869	0.0881	0.3778	0.0393	0.04025	0.01760	0.01790	
0.4542	0.0696	0.0693	0.4452	0.0333	0.03448	0.01587	0.01627	
0.5340	0.05315	0.0535	0.5231	0.0283	0.02373	0.01428	0.01451	
0.6110	0.04185	0.0421	0.6151	0.02315	0.02335	0.01267	0.01268	
0.7115	0.03145	0.0317	0.7042	0.01936	0.01928	0.01123	0.01118	
0.7879	0.02586	0.0259	0.7960	0.01629	0.01616	0.01001	0.00992	
0.8861	0.02076	0.0207	0.9001	0.01351	0.01356	0.00878	0.00881	
1.0000	0.01654	_	1.0000	0.01173	- 1	0.00799		

 $K = 0.25 + 6.05 z_m$.

 $K = 0.50 + 3.36 z_m$. $K = 0.50 + 1.93 z_m$.

Table 2. Acetone—Phenol, (Bramley).

_	9.95°C.		20.05°C.	
z_m	nobs.	ncalc.	човь.	neale.
0.0000	0.00360	_	0.00323	_
0.0926	0.00486	0.00486	0.00429	0.00432
0.1837	0.00635	0.00636	0.00560	0.00559
0.2749	0.00868	0.00873	0.00755	0.00752
0.3761	0.01256	0.01265	0.01055	0.01061
0.4580	0.01688	0.01683	0.01379	0.01402
0.5363	0.02358	0.02338	0.01853	0.01828
0.6340	0.03670	0.03722	0.02750	0.0273
0.6982	0.0495	0.0501	0.0359	0.0357
0.7829	0.0748	0.0736	0.0497	0.0500
0.8890	0.1193	0.1194	0.0730	0.0745
1.0000	0.2010		0.1104	_

 $\begin{array}{l} K=0.063 \ (z_m=0.0\text{-}0.20) \ ; \\ K=0.0485+0.079 \ z_m \\ (z_m=0.20\text{-}0.55) \ ; \\ K=-0.026+0.228 \ z_m \\ (z_m=0.55\text{-}1.0). \end{array}$

 $\begin{array}{l} K = 0.100 \, (z_m = 0.0 \text{-} 0.20) \, ; \\ K = 0.077 + 0.120 \, z_m \\ (z_m = 0.20 \text{-} 0.55, \, ; \\ K = -0.033 + 0.316 \, z_m \\ (z_m = 0.55 \text{-} 1.0). \end{array}$

_	29.8°C.		40.1°C.		49.8°C.	
z_m	Nobs.	nealc.	nobs.	neale.	nobs.	ncalc.
0.0000	0.002950	_	0.002700	_	0.002480	_
0.0613	0.003599	0.003596	0.003279	0.003273	0.002990	0.002980
0.1302	0.004409	0.004414	0.003991	0.003987	0.003599	0.003604
0.1912	0.005212	0.005233	0.004700	0.004698	0.004219	0.004216
0.2695	0.00670	0.00656	0.005899	0.005756	0.005299	0.005133
0.3324	0.00808	0.00805	0.00711	0.00698	0.006281	0.00617
0.4179	0.01058	0.01065	0.00904	0.00908	0.00794	0.00794
0.4832	0.01319	0.01321	0.01101	0.01105	0.00950	0.00956
0.5581	0.01658	0.01682	0.01362	0.01384	0.01149	0.01175
0.6401	0.02179	0.02188	0.01742	0.01759	0.01425	0.01459
0.7213	0.02747	0.02838	0.02232	0.02219	0.01786	0.01768
0.8187	0.03922	0.03886	0.02874	0.02911	0.02247	0.02246
0.8880	0.04902	0.04873	0.03460	0.03516	0.02618	0.02615
1.0000	0.07092	_	0.04739		0.03279	_

Table 2. (Concluded)

$$K = 0.147$$
 $(z_m = 0.0-0.20)$; $K = 0.105+0.175 z_m$ $(z_m = 0.20-1.0)$.

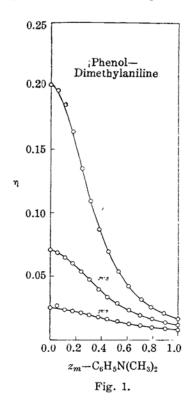
$$K = 0.198$$

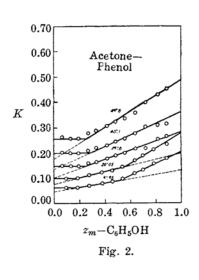
 $(z_m = 0.0-0.20)$;
 $K = 0.140+0.220 z_m$
 $(z_m = 0.20-1.0)$.

$$K = 0.257$$

 $(z_m = 0.0-0.20);$
 $K = 0.177 + 0.308 z_m$
 $(z_m = 0.20-1.0).$

Another example of this case in which K sometimes occurs to be composed of two or more sets of linear functions of z_m suggests the molecular dissociation of one component in two or more stages. For a good example the mixture of phenol (2) with acetone (1) measured by Bramley will be adopted here. Fig. 2 shows the K's plotted against the composition, in which we make distinct classifications of the points in three sets of straight lines at 10° and 20°C., and in two sets at 30° and higher temperatures. In Table 2 $\eta_{\text{calc.}}$ are obtained by assuming these sets of linear relationship of K with composition. As judged from the numerical values of the cutting points of the elongations of these sets of lines at each temperature at phenol-pure axis, the degradation of phenol-associated molecules is well explained if we assume that the phenol in its pure state consists mainly of trimol at low temperatures and of dimol at high temperatures; that is, of the three sets at low temperatures the first phenol-rich set indicates the coexistence of trimol and dimol, the second the coexistence of dimol and monomol, and the third the existence of monomol only, whereas at higher temperatures the first set at phenol-rich solutions shows the coexistence of dimol and monomol, and the second the existence of monomol only, all in equilibrium with acetone molecules. The above elucidation, though it indicates no appreciable presence of a molecular compound, yet the presence of dynamic equilibrium of dimol and monomol whose relative





amounts to each other are nearly independent of temperature, is affirmative to the melting-point diagram observed by Schmidlin and Lang⁽³⁾ which records a greatly dissociated molecular compound (CH₃)₂CO·2C₆H₅OH melting at 15°C.

 ν_1 and ν_2 signify the molecular numbers of components 1 and 2 in the molecular compound in accord with formula (4):

$$\eta = \frac{\eta_1}{1 + K \frac{z_m}{1 - z_m}} + \frac{\eta_2}{1 + \frac{1}{K} \frac{1 - z_m}{z_m}} + C_0 (\eta_1^{\vee_1} \eta_2^{\vee_2})^{\frac{m}{\vee_1 + \vee_2}} (1 - z_m)^{\vee_1} z_m^{\vee_2}$$
(4),

where C_0 and m are constants independent of the temperature and concentration. This case in which a compound occurs is denoted by the symbol c (ν_1 : ν_2).

⁽³⁾ J. Schmidlin and R. Lang, Ber., 43 (1910), 2812.

An interesting system for case (4) is the water—pyridine mixture. The solvation viscosity $\delta = \eta - \eta_0$ of this mixture at 0° and 25°C. appears to consist of two terms up to 30 mol % pyridine, i.e. it is not simply proportional to $(1-z_m)^3 z_m$ or $(1-z_m)^2 z_m$, but it corresponds to the sum of some or other

Table 3. Water--Pyridine, (Hartley, Thomas, and Applebey).

0°C.

z_m	η	γ_0	6	Scale.	ncalc.
0.0000 0.0236 0.0564 0.0872 0.1306 0.1847 0.2483 0.2713 0.2985 0.3462 0.4780 0.5789 0.6746 0.8159 0.9117 1.0000	0.01778 0.02448 0.03218 0.03840 0.04548 0.05147 0.05562 0.05560 0.05416 0.04905 0.04262 0.03298 0.01729 0.01463 0.01821	0.01765 0.01747 0.01730 0.01707 0.01679 0.01635 0.01621 0.01598 0.01564 0.01535 0.01489 0.01446 0.01385 0.01346	0.00683 1471 2110 2841 3468 3875 3927 3939 3818 3341 2727 1809 952 344 117		0.05564 0.05586 0.05404 0.04873 0.04301

K = 1.19.

25°C.

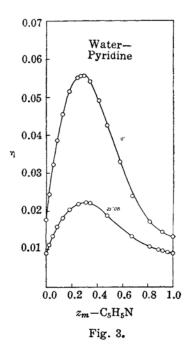
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	z_m	η	γ_0	δ	Scale.	γicalc.
0.9186 0.00942 0.00885 57 64 0.0094	0.0240 0.0515 0.0890 0.1312 0.1840 0.2522 0.3127 0.3450 0.4780 0.6730 0.8126 0.8864 0.9186	0.01116 0.01336 0.01598 0.01598 0.02032 0.02187 0.02225 0.02186 0.01894 0.01350 0.01064 0.00979 0.00942	0.00890 0.00890 0.00889 0.00889 0.00889 0.00888 0.00887 0.00887 0.00886 0.00886	446 708 944 1143 1298 1337 1298 1007 463 178 93 57	446 705 936 1142 1293 1334 1318 994 447 180 10.1	0.01112 0.01336 0.01595 0.01825 0.02031 0.02182 0.02222 0.02206 0.01881 0.01334 0.01066 0.00978 0.00949

K = 1.19.

multiples of these concentration factors, which phenomenon undoubtedly shows the coexistence of $C_5H_5N\cdot 3H_2O$ and $C_5H_5N\cdot 2H_2O$ in solution for the concentration range. For higher concentrations up to more than 90 mol % pyridine a set of hydrates $C_5H_5N\cdot 3H_2O$ and $C_5H_5N\cdot H_2O$ exists, of which the former greatly predominates, but the dihydrate disappears.

Baud⁽⁴⁾ has determined the freezing points of the system but found no decisive hydrates owing to the existence of hidden maxima. He also points

out that the volume contraction maximum occurs at 30 mol % pyridine corresponding to C5H5N·2.3H2O, whereas Pariselle(5) has observed that the density maxima at 17° and 25°C, correspond to C5H5N·3H2O and C₅H₅N·3.3H₂O respectively. However, if we consider the volume contraction per gram at 0°, 25°, and 50°C. from the density measurements done by Faust, (6) the points of maximum at these temperatures nearly lie at the same composition probably corresponding to $C_5H_5N\cdot 2.3H_2O$. These results may be fairly understood from the present study that the two hydrates C₅H₅N·3H₂O and C₅H₅N·2H₂O coexist in solution, and the former is more stable than the latter as clearly recognized from the concentration ranges of their existence (see Table 3) and also from the amounts of m, the stability coefficient, of these compounds, m of the former being estimated to be 2.4 up to 30 mol % and 1.8 up to more



than 90 mol % or in the mean 2.1, while m of the latter to be 1.6 between 0 and 30 mol %.

Fig. 3 shows how the theoretical and observed viscosities compare graphically.

It rarely happens that anomalous change occurs in association and thence follows a further chemical change to form a molecular compound. For such a case, the formula in combination of formula (2) with the second term of formula (4) may suffice to express the nature of the viscosity—composition curve. Mixtures as that of formamide with *i*-butyl alcohol or with *i*-amyl

⁽⁴⁾ E. Baud, Bull. soc. chim., [4], 5 (1909), 1022.

⁽⁵⁾ Pariselle, Compt. rend., 172 (1921), 673.

⁽⁶⁾ O. Faust, Z. physik. Chem., 79 (1912), 104.

alcohol where both a maximum and a minimum display themselves at low temperatures belong to this case:

$$\eta = \frac{\eta_1}{1 + K' \frac{z_m}{1 - z_m}} + \frac{\eta_2}{1 + K'' \frac{1 - z_m}{z_m}} + C_0 (\eta_1^{\vee_1} \eta_2^{\vee_2})^{\frac{m}{\vee_1 + \vee_2}} (1 - z_m)^{\vee_1} z_m^{\vee_2}$$
 (5).

The calculation by this formula which appears to be difficult will become easy, if we remember that K' or K'' is often nearly equivalent to K or its reciprocal as in the mixtures of higher alcohols with benzene, together with the presupposition for the values ν_1 and ν_2 from the position of a maximum point in the actual curve. For example, the mixture of i-amyl alcohol (1) and formamide (2) as determined by Drucker and Kassel will be considered in the following. Since K of formamide is 0.34 and that of i-amyl alcohol is nearly 0.30 as supposed from K (0.29) of γ -amyl alcohol, the probable value for K in this mixture may be nearly 1.17 at an extremity. From the maximum points of the viscosity curves at 0° and 76.5° C., the case for which $\nu_1 = 1$ and $\nu_2 = 2$ is highly probable. After a few trials we have the following equations which are good enough to represent the nature of the curves:

$$\eta = \frac{0.0883}{1 + 1.77 \frac{z_m}{1 - z_m}} + \frac{0.0755}{1 + 1.1 \frac{1 - z_m}{z_m}} + 0.287(1 - z_m)z_m^2 \quad \text{at} \quad 0^{\circ}\text{C.},$$

$$\eta = \frac{0.00951}{1 + 1.1 \frac{z_m}{1 - z_m}} + \frac{0.01255}{1 + 1.1 \frac{1 - z_m}{z_m}} + 0.0128(1 - z_m)z_m^2 \quad \text{at} \quad 76.5^{\circ}\text{C}.$$

The calculated viscosities show no functional divergence from the observed viscosities as seen from Table 4 and also Fig. 4 in which the curves are drawn with the calculated values.

Peculiar systems for which the viscosity maxima often display themselves as hundreds times greater than the component viscosities are also understood as special cases of formula (4).

Acetic acid—stannic chloride and ethyl formate—stannic chloride are good examples of such cases. For the former pair a molecular compound SnCl₄·3CH₃COOH is pointed out by Stranathan and Strong with the viscosity courves the maximum points of which exactly correspond to this molecular ratio, probably independent of temperature. For the latter pair a molecular compound SnCl₄·2HCO₂C₂H₅ has been confirmed by Kurnakow from the measurements of the viscosities at 30°, 40°, and 50°C. and of the fusion curve.

_	0°	С.	76.5°C.		
z_m	Nobs.	ncalc.	nobs.	ncalc.	
0.0000	0.0883	_	0.00951		
0.0538	0.0848	0.0848	0.00966	0.00960	
0.1783	0.0836	0.0837	0.01005	0.01008	
0.4571	0.0992	0.1008	0.01178	0.01183	
0.6633	0.1111	0.1106	0.01311	0.01295	
0.8194	0.1064	0.1053	0.01322	0.01324	
0.9441	0.0858	0.0881	0.01292	0.01292	
1.0000	0.0755	_	0.01255	_	

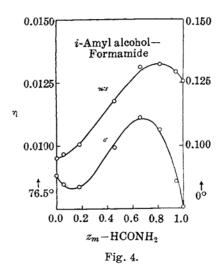
Table 4. *i*-Amyl alcohol—Formamide, (Drucker and Kassel).

Since the viscosities of both components in this type of mixtures are negligibly small as compared to the viscosity of the solution, the consideration of the true value of K is not useful for the approximate estimation of ν_1 and

 ν_2 in formula (4). In the following calculation, therefore, viscosity deviations are taken from formula (1) in which K is put as unity.

As clearly indicated in Table 5, a molecular compound SnCl₄·3CH₃COOH exists as some multiple of the simplest molecular ratio, 2-fold up to 5 mol %, 7-fold up to 17 mol %, and 14-fold for higher concentrations.

Similar phenomena are also seen from Table 6 for the mixture of ethyl formate and stannic chloride. In this mixture a molecular compound SnCl₄·2HCO₂C₂H₅ exists as a great molecule of 30-fold of the simplest ratio at concentrations up to ca 36 mol % at 30°, 40°, and 50°C.,



but exists as a greater molecule of 60-fold at the concentration range from 32 to 36 mol % at 30°C., under which temperature an enormous crystallization of this compound begins, the melting point of it, however, being at 49°C. according to the same observer.

One more molecular compound $SnCl_4 \cdot HCO_zC_2H_5$ may probably exist at ca 7-fold of the simplest ratio, though the constancy of $\delta/\{(1-z_m)z_m\}$ is not sufficiently good.

These studies suggest that the multiple number of the simplest ratio of a molecular compound at sufficiently low temperature as crystallization begins may be in close relationship with the crystal structure or probably with the dimension of the secondary structure of a crystal as judged from the magnitude of thus estimated multiple of the supposed molecular volume of the molecular compound.⁽⁷⁾

Table 5.	Acetic acid—Stannic	chloride, 25.2°C.,	(Stranathan and Strong).

z_m	η	8	$\delta/(1-z_m)^{\gamma_1}z_m^{\gamma_2}$
0.0000	0.01155		
0.0244	0.02121	0.00974	19.0 \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \
0.0520	0.04373	0.03234	16.4 \ \ 17.7 \ \ \nu_2 = 1 \times 2.
0.1084	0.1897	0.1785	1.13×10 ⁷) mean $v_1 = 3 \times 7$,
0.1719	0.963	0.952	1.13 , $1.13 \times 10^7 \text{ v}_2 = 1 \times 7.$ (1.33×10 ¹⁴)
0.2290	2.582	2.571	1.30×10^{14}
0.2527	3.034	3.023	1.44 ,,
0.2682	2.909	2.898	1.44 ,,
0.2969	2.105	2.094	1.34 " $\begin{cases} \text{mean} & v_1 = 3 \times 14, \\ 1.42 \times 10^{14} & = 1 \times 14. \end{cases}$
0.3151	1.649	1.638	1.42 ,, $v_2 = 1 \times 14$.
0.3498	0.864	0.854	1.45 ,,
0.3608	0.691	0.681	1.57 ,,
0.4111	0.4234	0.4131	(4.75 ,,)
1.0000	0.0084		

Table 6. Ethyl formate—Stannic chloride, (Kurnakow). 30°C.

z_m	η	δ	$\delta/(1-z_m)^{v_1} z_m^{v_2}$
0.00 0.25 0.30 0.32 0.335 0.36 0.50 0.75	0.06375 0.08788 0.31158 0.52286 0.57832 0.44142 0.06871 0.01526 0.00806	0.08305 0.30654 0.51773 0.57313 0.43612 0.06281 0.00828	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$

⁽⁷⁾ This Bulletin, 10 (1935), 248.

Table 6. (Concluded) 40°C.

z_m	η	õ	$\hat{c}/(1-z_m)^{\vee_1}z_m^{\vee_2}$
0.00 0.25 0.30 0.32 0.335 0.36 0.50 0.75	0.00342 0.06384 0.19034 0.27615 0.29541 0.23514 0.04952 0.01292 0.00725	0.05946 0.18577 0.27150 0.29071 0.23034 0.04419 0.00663	$ \left\{ \begin{array}{c} 2.14 \times 10^{24} \\ 1.78 \\ 2.14 \\ 2.14 \\ 2.22 \\ 2.00 \\ 7.2 \\ 8.1 \end{array} \right\} \begin{array}{c} \text{mean} & v_1 = 2 \times 30, \\ 2.05 \times 10^{24} & v_2 = 1 \times 30. \\ 2.05 \times 10^{24} & v_2 = 1 \times 30. \end{array} $

50°C.

z_m .	η	ô	$\delta/(1-z_m)^{\vee_1} z_m^{\vee_2}$
0.00 0.25 0.30 0.32 0.335 0.36 0.50 0.75	0.00311 0.04904 0.12463 0.16102 0.16758 0.14237 0.03753 0.01115 0.00668	0.04504 0.12045 0.15667 0.16327 0.13798 0.03264 0.00536	$ \begin{vmatrix} 1.62 \times 10^{24} \\ 1.15 & , \\ 1.24 & , \\ 1.24 & , \\ 1.20 & , \\ 5.3 \times 10^2 \\ 6.5 & , , \end{vmatrix} $

General Conclusions. The validity of the above formulas is acknowledged from a great deal of calculations already made (see Table 8). It may fairly be said that formula (1) deserves to be an ideal mixture law which has long been aimed at. The consideration of the viscosity deviation from the ideal mixture law in case where viscosity exhibits a maximum, which idea was introduced by Findlay⁽⁸⁾ and by Denision⁽⁹⁾ but failed owing to the lack of the true law of ideal mixtures, proves to be true in our case not only in determining the composition of a molecular compound but also in estimating its stability in solution.

The second term of formula (4) or (5) contains two factors, one being concentration function $(1-z_m)^{\nu_1}z_m^{\nu_2}$, the other main corresponding to the viscosity of a molecular compound. One may readily understand that the former is at once deduced from the law of probability by considering the

⁽⁸⁾ A. Findlay, Z. physik. Chem., 69 (1909), 203.

⁽⁹⁾ R. B. Denison, Trans. Faraday Soc., 8 (1912), 20.

number of encounter between reacting molecules, but one may throw doubt on the form of the latter in which C_0 is independent of concentration and temperature; that is, formula (4) or (5) the second term of which appears to superpose on the first term with respect to composition cannot be elucidative by the classical treatment of chemical equilibrium. If the viscosity of liquids is defined by $\frac{cm\nu}{\sigma}$ as Andrade⁽¹⁰⁾ proposes where m is a mass of a molecule, σ the distance between the centres of molecules, v the vibration frequency, and c a constant, the number of molecular encounter or collision is proportional to $\frac{\nu}{\sigma}$ which is of the order of some 10^{20} per second. Although the collision probability between ν_1 molecules of kind 1 and ν_2 molecules of kind 2 to form a molecular compound is much less than this amount, the time of such encounter may be beyond comparison with the time ordinarily required for viscosity measurements, so long as a molecular compound is only statistically recognized as such the component molecules of which are freely interchangable with the same kinds of molecules outside of its reaction sphere. Hence the fact that the viscosity of chemically reactive mixtures strictly obeys formula (4) or (5) leads to the conception that a molecular compound is not a fastcombined molecule but a molecular grouping in a statistical meaning.

Formula (4) when applied to the viscosity which exhibits a very marked maximum at low temperature may afford a clue to the study on the mechanism of crystal formation.

Formula (1) is also valid for ideal solutions of solids in liquids.

For a strong electrolyte solution (i) where there occurs no solvation or hydration, the viscosity difference (η^{**}) between the observed specific viscosity (η^{*}) and the viscosity caused by the inter-ionic forces according to the Falkenhagen-Vernon theory⁽¹¹⁾ obeys formula (1) as expressed in specific quantity:

$$\eta^{**} = 1 + \frac{(H-1)Kz_m}{1 - z_m + Kz_m}$$
or
$$\eta^* = 1 + A\sqrt{\frac{1000sz_m}{M_1 + (M_2 - M_1)z_m}} + \frac{(H-1)Kz_m}{1 - z_m + Kz_m}$$
or
$$\eta^* = 1 + A\sqrt{c} + \frac{(H-1)KM_1c}{1000s + (KM_1 - M_2)c}$$
(6),

⁽¹⁰⁾ E. N. Da C. Andrade, Nature, 128 (1931), 835; Phil. Mag., 17 (1934), 497.

⁽¹¹⁾ H. Falkenhagen and E. L. Vernon, Phil. Mag., 14 (1932), 537.

in which H is the specific solutional viscosity of the solute, the viscosity of solvent being taken as unity, s the density of the solution at concentration c (g. mol/litre soln.), M_1 and M_2 the formal molecular weights of the solvent and the solute, and A the Falkenhagen—Vernon constant.

For a strong electrolyte solution (ii) where there forms a solvated or hydrated compound, formula (2) for which the Falkenhagen—Vernon effect is taken into account holds true for concentrations up to saturation:

$$\eta^{**} = 1 + \frac{(H-1)Kz_m}{1 - z_m + Kz_m} + C^*(1 - z_m)^{\nu_1} z_m^{\nu_2}$$
 (7)

where C^* is a constant independent of concentration.

The solutional viscosity of a solid in a liquid in accord with formulas (1), (6), and (7) is the viscosity probably due to the block of a secondary structure in accordance with the secondary structure theory on crystals when the substance is an organic non-electrolyte or is the viscosity due to the ionic pair when the substance is an ionic crystal.

At very dilute solutions where the solvation or hydration, though it happens, is not appreciable and the Falkenhagen-Dole-Vernon equation holds, formula (6) or (7) becomes

$$\eta^* = 1 + A\sqrt{c} + \frac{(H-1)KM_1}{1000s_1}c\tag{8},$$

whence it readily follows that the theoretically as yet unknown factor B of the Falkenhagen—Dole—Vernon equation is defined by

$$B = \frac{(H-1)KM_1}{1000s_1} .$$

Quite recently Sulston has made careful measurements on the temperature variation of B for aqueous solutions of KCl and K₂SO₄. As we have had for KCl H_{18} =0.9471, H_{25} =0.9765, and K=40.39 and this K may be regarded to keep constancy for higher temperatures, we can estimate the

Table 7. The Solutional Viscosity of KCl.

В	η	ncalc.
-0.0330	0.01003	0.01003
-0.0140	0.00874	0.00874
+0.0090	0.00731	0.00731
+0.0400	0.00540	0.00539
+0.0506	0.00472	0.00471
+0.0545	0.00442	0.00442
+0.0561	0.00415	0.00416
+0.0613	0.00392	0.00392
+0.0654	0.00371	0.00370
	$\begin{array}{c} -0.0330 \\ -0.0140 \\ +0.0090 \\ +0.0400 \\ +0.0506 \\ +0.0545 \\ +0.0561 \\ +0.0613 \end{array}$	$\begin{array}{ccccc} -0.0330 & 0.01003 \\ -0.0140 & 0.00874 \\ +0.0090 & 0.00731 \\ +0.0400 & 0.00540 \\ +0.0506 & 0.00472 \\ +0.0545 & 0.00442 \\ +0.0561 & 0.00415 \\ +0.0613 & 0.00392 \\ \end{array}$

⁽¹²⁾ W. J. Sulston, Proc. Phys. Soc., 47 (1935), 657.

Table 8. I. Mixture.

Component 1	Component 2	t°C.	K	Remarks	Observer
Benzene	Toluene	25	1.23	n	Linebarger
	Diphenyl		0.30	n	Kendall and Monroe
	Naphthalene	25	0.49	n	,,
	Chloroform	25	(1.81)	n	Linebarger
	Carbon tetrachloride	0	1.08	n	1
	,,	10	0.99	n	
	,,	20	0.96	n	
	,,	30	0.94		Thorpe and
	,,	40	0.88	n	Rodger
	,,	50	0.83	n	
	,,	60	0.79	n	
	,,	70	0.81	n)
	Ethylene dichloride	0	K'1.13, K''1.30	a)
	,,	19.4	K'1.00, K''1.37	a	Faust
	,,	50	K'0.72, K"1.66	a	j
	Bromobenzene	18.2	1.06	n)
	,,	30	1.10	n	Yajnik and coworkers
	,,	40	1.07	n	coworkers
	Nitrobenzene	25	0.49	n	Linebarger
	m-Nitrotoluene	15	0.40	n) _
	,,	30	0.44	n	Dessart
	Methyl alcohol	25	K'0.62, K''1.60	a	Fischler
	Ethyl alcohol	25	K'1.75, K''1.45	a	Dunstan
	n-Propyl alcohol	25	K'1.70, K''2.25	a	
	1-Amyl alcohol	30	K'1.71, K''3.36	a	Bhide and
	Phenol	20	0.087-0.23	v	Watson Bramley
	,,	25	0.12-0.32	v	Swearingen
	m-Cresol	60	0.27	n	Piatti
	Guaiacol	30	0.17 - 0.29	v	Puschin and
	Ether	25	2.28	n	Pinter Linebarger
		10	2.35	n)
	,,	20	2.20	n	I. C. T.
	"	30	2.07	n	[
	Anisol	0	0.83	n	`
	,,	10	0.80	n	1
	"	20	0.84	n	
		30	0.84	n	Piatti
	**	40	0.89	n	1
1	,,	10	0.00	**	•

I. Mixture. (Continued)

Component 1	Component 2	t°C.	K	Remarks	Observer
Benzene	Anisol	50	0.94	n	ı
	,,	60	0.97	n)
	Acetone	10	1.87	n)
	,,	20	1.79	n	I. C. T.
	,,	30	1.66	n	J
	,,	25	1.70	n	Fischler
	Acetophenone	16	0.65	n	I. C. T.
	Acetic acid	25	K'0.71, K''3.11	a	Dunstan
	Ethyl acetate	25	2.01	n	,,
	Ethyl benzoate	25	0.69	n	Kendall and Monro
	Benzyl benzoate	25	0.31-0.50	v	,,
	,,	5	0.20-0.38	v	1.
	,,	15	0.25-0.47	v	
	,,	25	0.31-0.53	v	Bingham and Sarver
	,,	40	0.37-0.61	v	}
	"	60	0.48-0.74	v)
	m-Toluidine	15	0.18	n) p
	,,	30	0.24	n	Dessart
	Pyridine	25	(0.76)	c(1:2)	Dunstan, Thol and Hun
	Quinoline	25	0.46	n	I. C. T.
	Carbon bisulphide	25	0.91	n	Linebarger
}	Sulphur chloride	15.5	0.78	n) D. C1:
	,,	20	0.78	n	De Carli
	Stannic chloride	25	K'0.86, K''2.08	a)
	,,	70	K'0.95, K''1.68	a	Kurnakow

Mixture.

Observer	Bingham, White, Thomas and Cadwell Tab. internat.,	I. C. T. Dessart ''.	::	::	Bingham, White, Thomas and Cadwell	Linebarger Kendall and Monroe ", Yajnik and coworkers
Remarks	88888		444	auuu	4444	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2
(ka) of comp. 1 rel. to (ka) of benzene	1.48)	1.58 mean 1.41 1.52	1.00 mean 0.97 0.99	1.14 mean 1.14 1.14	1.13 1.20 1.28 1.32	1.23 1.25 1.26 1.26
K	0.74 0.79 0.84 0.87 0.33 mean	0.30) mean 0.30 mean 0.31 0.31 0.28 mean 0.29 0.29 0.19 mean 0.20 0.20	0.36) mean 0.46) 0.41 0.33 mean 0.32) 0.33	0.30 mean 0.41 0.36 0.26 mean 0.29 0.28	1.35 1.27 1.19 1.15	0.81 0.24 0.38 1.02 1.02 1.02
t°C.	32 82 82 82 82 82 82 82 82 83 83 84 84 84 84 84 84 84 84 84 84 84 84 84	323323222	15 30 30 30	30 30 30	82 82 82 82 82 82 82 82 82 82 82 82 82 8	2028 22 22
Component 2	n-Decane "" Nitrobenzene	m-Nitrotoluene m -Toluidine m	m-Nitrotoluene m-Toluidine	m-Nitrotoluene m-Toluidine	n-Hexane ",	Benzene Diphenyl Naphthalene Chlorobenzene ",
Component 1	n-Hexane		Cyclohexane	Methyl cyclohexane	n-Decane	Toluene

II. Mixture. (Continued)

Remarks Observer	n Yajnik and coworkers Dessart Puschin and Puschin and Puschin and Dessart Companies C	n Kendall and Monroe n	n "" n "" n "" n " ""	Kendall and Monroe n	c(1:1) Herz and Schuftan c(1:1) "
(ka) of comp. 1 rel. to (ka) of benzene	1.24 mean 1.21 1.24 1.24 1.22 1.67-1.25 1.22 1.22 1.92-1.23 (2.13?)	0.30) mean 0.30 0.30		0.49) mean 0.47) 0.48	0.21 mean 0.22 0.22 0.21, 0.45
K	0.86 mean 0.85 0.86 0.32 mean 0.36 0.34 0.18-0.24 0.57 (1.63) 0.59 mean 0.60 0.60 0.25-0.39 0.15	8.33	0.95 0.86 0.90 1.05 0.97	2.04	(3.03) (2.22) K71.72, K771.30
t _o C.	8558 8 5558	25	125 125 125 125 75	25	25,25
Component 2	Bromobenzene m-Nitrotoluene , Guaiacol Benzaldehyde Ethyl acetate Ethyl benzoate ,, Benzyl benzoate ,, Benzyl benzoate ,,	Benzene Toluene	Dibenzyl Azobenzene Benzal aniline Stilbene Azobenzene	Benzene Toluene	Methyl alcohol Ethyl alcohol n-Butyl alcohol
Component 1	Toluene	Diphenyl	Stilbene Dibenzyl	Naphthalene	Tetralin

II. Mixture. (Continued)

Observer	Sachanov and Rjachowsky	Linebarger " Thorpe and Rodger	Sachanov and Rjachowsky Tsakalotos	Thorpe and Rodger	Linebarger Herz and Rathmann Sachanov and Rjachowsky	Faust	Herz and Rathmann
Remarks	ц	$ \begin{array}{c} $	$c_0 = 0.00 \times 10^{-3}$ $c(2.1)$ $c(2.1)$ $m = 2.32$ $C_0 = 1.52 \times 10^{2}$	444444	1 8 8 B	ದವನ	u
(ka) of comp. 1 rel. to (ka) of benzene	3,38	1.82 1.79 2.02 mean	1.84	1.08 0.96 0.94 0.88 0.83 0.73	0.96 1.10, 1.68 1.08 0.91	0.77, 0.89 0.73, 1.00 0.60, 1.39	1.71
K	0.56	(0.55) 0.52 (1.13)	(0.56)	0.96 1.01 1.04 1.06 1.14 1.21 1.27	1.94 K71.44, K70.94 K71.05, K71.44 1.75 0.74	K'1.30, K''1.13 K'1.37, K''1.00 K'1.66, K''0.72	0.41
€°C.	0	880588	8 0 084	01888886	22 0 22 22	0 19.4 50	22
Component 2	Acetone	Benzene Carbon tetrachloride Ether ",	Phenetol Acetone	Benzene "" "" "" "" "" ""	Chloroform Tetrachloroethylene Tetrachloroethane Acetone Acetophenone	Benzene ",	Pentachloroethane
Component 1	Methylene chloride	Chloroform		Carbon tetrachloride		Ethylene dichloride	Trichloroethylene

II. Mixture. (Continued)

Observer	Herz and Rathmann	Sachanov and Rjachowsky	Herz and Rathmann Sachanov and Rjachowsky	Yajnik and coworkers Unkovskaja and Volova Kremann, Gugle and Meingast Bramley	Yajnik and coworkers "" Unkovskaja and Volova Kremann, Gugle and Meingast Sachanov and Rjachowsky
Remarks	æ	# H H P	пъп	4444444	44444444 >
(ka) of comp. 1 rel. to (ka) of benzene	0.99, 1.35	0.65, 1.01 1.12) mean 1.20 1.16 1.80-1.02	1.34-0.64	1.27 mean 1.27 $\left\{ \begin{array}{l} 1.27 \\ 1.27 \end{array} \right\}$ 2.80-1.25	1.08 mean 1.06 mean 1.07 1.07
K	K'0.94, K''1.44	K'1.44, K'/1.05 2.22 0.86 1.05-1.85	2.44 1.85-3.85 1.48	0.98 mean 0.97 mean 0.98 0.98 0.78 mean 0.83 mean 0.85 0.84 0.93	0.94 mean 0.91 mean 0.93 0.93 0.93 1.16 mean 1.18 1.17 1.28 1.21 mean 1.21 mean 1.21 mean 1.22 1.08 1.08
t°C.	22	25 0 0	25 0 25	256 266 266 267 267 267 267 267 267 267 26	18.2 30 40 40 20 35 20 40 60 64 64
Component 2	Carbon tetrachloride	Carbon tetrachloride Ether Phenetol Acetone	Trichloroethylene Ether Phenetol	Toluene " Bromobenzene ", ", Phenol"	Benzene " Toluene Chlorobenzene " " Acetone
Component 1	Tetrachloroethylene	Tetrachloroethane	Pentachloroethane	Chlorobenzene	Bromobenzene

II. Mixture. (Continued)

Observer	Thorpe and Rodger	Yajnik and coworkers Sachanov and Rjachowsky	Wagner	
Remarks	ਬਬਬਬਬ	44 H	ct.	$\begin{bmatrix} & & & & & & & & & & & & & & & & & & &$
(ka) of comp. 1 rel. to (ka) of benzene	0.50 0.58 0.66 0.68	$\frac{2.21}{2.19}$ mean $\frac{2.20}{2.19}$	0.39, 1.09	0.50 0.47 mean 0.49 0.49 0.22, 0.58 0.24, 0.54 0.24, 0.51 0.24, 0.51 0.27, 0.57 0.22, 0.72 0.48-0.27
K	1.89 1.64 1.64 1.45 1.39) (0.29) 0.47	K'1.27, K"2.23	3.03 mean 3.03 3.03 3.23 mean 3.23 mean 3.23 3.26 2.06 K''1.48 K'1.65 K''1.48 K'1.55 K''1.45 K'1.57 K''1.41 K'1.37 K''1.41 K'1.37 K''1.41 K'1.37 K''1.41 K'1.37 K''1.41 K'1.37 K''1.41 1.61-2.89 1.61-2.89 1.61-2.89 (1.70) (1.70)
t°C.	001088	20 45 0	1	8 1 15 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2
Component 2	Carbon bisulphide "" "" ""	Methyl alcohol ". Phenetol	Ethyl alcohol	n-Hexane "" Benzene Methyl alcohol "Butyl alcohol "," i-Butyl alcohol "Butyl alcohol "Sulphur chloride Stannic chloride Stannic bromide ","
Component 1	Methyl iodide	Ethyl iodide	Nitromethane	Nitrobenzene

II. Mixture. (Continued)

	1						
Observer	Dessart	Wagner	Beck ",	Traube	1. C. T.		Davis, Hughes
Remarks		ದ	ппп	$m = 2.00$ $C_0 = 9.2 \times 10^2$	$c(3:1) m = 2.00 C_0 = 1.55 \times 10^3 & & & & & & \\ c(2:1) m = 1.83 C_0 = 4.08 \times 10^2 $	$c(3:1) \\ m = 2.00 \\ C_0 = 1.31 \times 10^3$	c(4:1, 8:1, 2:1) c(5:1) c(4:1)
(ka) of comp. 1 rel. to (ka) of benzene	0.43 0.40 0.39 (mean 0.42 0.42)	0.53, 1.58		0.68	0.70	0.68	0.64
K	3.578 mean 3.45 3.51 2.78 mean 2.17 2.48 3.33 mean 2.44 2.89 2.50 mean 2.27 2.39 3.13 mean 2.78 2.96	K'0.92, K"2.00	1.16 1.03 1.03	(0.96)	(0.70)	(0.60)	(2.97) (2.58)
t°C.	30 30 30 30 30 30 30 30 30 30	1.	125 75 76	88488	36268860 36268860	ន្តនេះ	308
Component 2	n-Hexane Cyclohexane Methyl cyclohexane Benzene Toluene	Ethyl alcohol	Stilbene Dibenzyl Benzal aniline	Methyl alcohol ", ",	Ethyl alcohol "" "" "" "" "" ""	n-Propyl alcohol	Acetone
Component 1	m-Nitrotoluene	Cyanobenzene	Azobenzene	Water			

II. Mixture. (Continued)

Observer	I. C. T.)I. C. T.	Dunstan Merry and Turner Hartley, Thomas and Applebey	Fischler Herz and Schuftan Yajnik and coworkers Fischler Traube	_
Remarks	c(1:1)	$m = 1.68$ $C_0 = 1.16 \times 10^2$	n n c(3:1+2:1) c(3:1+1:1)	$c(1:1)$ n n n $c(1:2)$ $m = 2.00$ $C_0 = 9.2 \times 10^2$,
(ka) of comp. 1 rel. to (ka) of benzene	mean 0.67			0.63, 0.62 mean 0.64	_
(ka)	0.68	0.67	0.69	0.64	
K	(0.69)	(1.29)	0.28 0.48) mean 0.50) 0.49 } (1.19)	$ \begin{cases} K'1.60, K''0.62\\ (0.33) \end{cases} $ $ \begin{cases} (3.45)\\ 0.76 \end{cases} $ $ (1.04) $	_
t°C.	5555	6128888446669668	25.08 25.08	5262556856	9
Component 2	Formic acid	Acetic acid ,, ,, ,, ,, ,, ,, ,, ,, ,, ,, ,, ,, ,,	Lacti'c acid Formamide ,, Pyridine	Benzene Tetralin Ethyl iodide Nitrobenzene Water ",	•
Component 1	Water			Methyl alcohol	

II. Mixture. (Continued)

Observer	Bingham, White, Thomas and Cadwell Herz and Kuhn Baker Mardles Merry and Turner	Dunstan Herz and Schuftan Wagner " I. C. T. Bingham, White, Thomas and Cadwell Parks and Schwenck Parks and Kelley " " " Leeuw Dunstan
Remarks	n n v c(1:2)	$c(1:1)$ a a a $c(1:3)$ $m = 2.00$ $C_0 = 1.55 \times 10^3$ $m = 1.83$ $C_0 = 4.08 \times 10^2$ n
(ka) of comp. 1 rel. to (ka) of benzene	0.91-0.47	0.69, 1.75 mean 0.65-0.32 0.65-0.32 0.46, 0.85 0.61, 0.99
(ka) (ka)	0.63 0.65 0.64 0.64	0.49 0.47 0.51 0.51
K	0.78 0.84 0.86 0.91 0.91 2.33–4.55 1.60 (1.34) 0.50) mean 0.55) 0.53	K'1.45, K'/1.75 (0.45) K'2.23, K'/1.27 K'2.00, K'/0.92 (1.43) 1.28 1.19 1.16 1.10 0.88 0.78 3.30-6.60 K'1.70, K'/1.01 K'1.70, K'/0.96 (1.7) (1.7) (1.9) 3.7-6.9
t°C.	8848888888	8:81105888888888888888888888888888888888
Component 2	Ethyl alcohol "" "-Propyl alcohol Ether Phenetol Acetic acid Formamide ""	Benzene Tetralin Nitromethane Cyanobenzene Water " " " " " Methyl alcohol " " "-Propyl alcohol Ether Anisol Phenetol Acetaldehyde Acetone
Component 1	Methyl alcohol	Ethyl alcohol

II. Mixture. (Continued)

/					
Observer	Merry and Turner I. C. T. Dunstan Wagner	Dunstan Dunstan and Thole Herz and Kuhn Parks and Schwenck Trew and Watkins Baker English and Turner	Parks and Kelley Trew and Watkins Parks and Chaffee	Herz and Schuftan Swearingen and Heck Trew and Watkins ""	Wagner
Remarks		$\begin{cases} m = 2.00 \\ m = 2.00 \\ C_0 = 1.31 \times 10^3 \\ n \\ $	пгв	ಡೆ ಡೆ ಡೆ ಡೆ ಡೆ ಡೆ ಡೆ ದೆ ದೆ ದೆ	ಡ
(ka) of comp. 1 rel. to (ka) of benzene	0.48 0.51 0.48)	0.40 0.40 0.41 0.43 0.41 0.48 0.0.55 0.0.27 0.15, 0.27	0.38) mean 0.42) 0.40 0.37, 1.47	0.17, 0.38 0.33, 1.01 0.30, 0.81 0.32, 0.75 0.33, 0.75 0.35, 0.74 0.31, 0.64 0.37) mean 0.35 / 0.36	0.16, 0.50
K	0.70) mean 0.71) 0.71 0.89 2.00 2.70 K/1.82, K//1.22	K/2.25, K''1.70 $\{1.67\}$ $\{1.69\}$ $\{1.14\}$ $\{0.89\}$ $\{3.88-7.76\}$ $\{1.76\}$	1.28 0.85 K'4.76, K''0.85	K71.30, K71.72 K71.10, K71.16 K71.10, K71.66 K71.61, K71.66 K71.52, K71.53 K71.41, K71.53 K71.41, K71.50 K71.60, K71.31 1.12 1.17 0.63	K'3.16, K"1.02
t₀C.	555551	22 22 22 22 22 22 22 22 22 22 22 22 22	ន្ទន្ទន	8884886888888	
Component 2	Formamide Quino'line Carbon bisulphide Mercaptan Allyl thiocyanide	Benzene Water " Methyl alcohol Ethyl alcohol Ethyl alcohol Fether Formamide	Ethyl alcohol n-Butyl alcohol Acetone	Tetralin Dekalin Nitrobenzene "" "- "- "- "- "- "- "- "- "- "- "- "-	Nitrobenzene
Component 1	Ethyl alcohol	n-Propyl alcohol	i-Propyl alcohol	n-Butyl alcohol	i-Butyl alcohol

II. Mixture. (Continued)

Observer	Trew and Watkins English and Turner	Bhide and Watson Drucker and Kassel ". English and Turner	Trew and Watkins	Dunstan	Bramley Swearingen Bramley Kendall and Beaver ", ",
Remarks	a, c(1:2)	a a a a, c(1:2)	u	c(1:4, 1:3, 1:2)	<pre></pre>
(ka) of comp. 1 rel. to (ka) of benzene	0.23 0.17, 0.44	0.30, 1.71 0.22, 0.96 0.35, 0.78 0.19, 0.37 0.31, 0.37 0.21, 0.37	0.29	0.48	$\begin{array}{c} 4.35-11 \\ 3.13-8.3 \\ 5.44-12 \\ 0.69 \\ 0.69 \\ 0.65 \\ 0.68 \\ 0.063(z_m=0.00-0.20) \\ 0.0485+0.0792z_m(z_m=0.20-0.55) \\ 0.0485+0.0792z_m(z_m=0.50-0.55) \\ 0.0485+0.0792z_m(z_m=0.50-0.55) \\ 0.0485+0.0792z_m(z_m=0.55-1.00) \\ 0.10(z_m=0.00-0.20) \\ 0.077+0.12z_m(z_m=0.55-1.00) \\ 0.033+0.316z_m(z_m=0.55-1.00) \\ 0.147(z_m=0.00-0.20) \\ 0.105+0.175z_m(z_m=0.20-1.00) \\ 0.1987(z_m=0.00-0.20) \\ 0.140+0.22z_m(z_m=0.20-1.00) \\ 0.25-6.30 \\ 0.50-4.53 \\ 0.50-3.86 \\ \end{array}$
K	1.59 K'1.99, K''0.90	K73.36, K71.71 K72.25, K71.97 K71.41, K71.58 K71.77, K71.10 K71.10, K71.10 K71.60, K71.10	1.25	(1.43)	
toC.	25.55	30 0 0 76.5 25	23:	52	29 25 26 25 25 25 27 20.05 40.1 49.8 10 29.8 29.8
Component 2	n-Butyl alcohol Formamide	Benzene Nitrobenzene Formamide ",	n-Butyl alcohol	Water	Benzene Chlorobenzene o-Cresol m-Cresol Actone "" " " " " " " " " " " " " " " " " "
Component 1	i-Butyl alcohol	<i>i</i> -Amyl alcohol	i - γ -Methyl butyl alcohol	Allyl alcohol	Phenol

II. Mixture. (Continued)

Observer	Bramly	Kendall and Beaver	Piatti Kendall and Beaver ",		Puschin and Pinter ", ", ",
Remarks	> > > ± > > ± & & & & & & & & & & & & &	454	4 H H	455	>> n u
(ka) of comp. 1 rel. to (ka) of benzene			0.27		0.29-0.17 0.30-0.22 0.85-0.31
K	0.60-3.10 0.50-2.43 0.50-2.10 0.50-1.75 1.40 0.52-0.93 0.55-0.95 0.75 K71.65, K71.19 K71.79, K70.81 K71.66, K70.82 K71.08, K71.16 K71.08, K71.16	1.45 0.67 0.68	3.70 1.92 1.49 0.31–0.87	1.72 1.47 1.16–3.23	3.45-5.88 4.17-5.56 2.00-5.56 1.41 2.50
€C.	40.2 89.9 80.1126 1177 30 80 80 80 80 80 80	888	ទន្ទន្ទន	ន្តន្តន	88888
Component 2	Dimethyl aniline "" Diphenyl amine "," Diphenyl methyl amine "," "," ","	Phenol m-Cresol p-Cresol	Benzene Phenol o-Cresol p-Cresol	Phenol o-Cresol m-Cresol	Benzene Toluene Acetone Metbyl aniline Dimethyl aniline
Component 1	Phenol	o-Cresol	m-Cresol	p-Cresol	Guaiacol

II. Mixture. (Continued)

Observer	Bramley "	Linebarger I. C. T. Thorpe and Rodger Sachanov and Rjachowsky Baker " Kendall and Wright	Piatti Baker
Remarks	$egin{array}{c} \mathbf{a} \\ \mathbf{a} \\ \mathbf{a} \\ \mathbf{a} \\ \mathbf{c}(2:1) \\ m = 2.00 \\ C_0 = 7.02{\times}10 \end{array}$	m m n n n n n $c(1:2)$ $m = 2.62$ $C_0 = 6.08 \times 10^3$ n v	සසසසසසස
(ka) of comp. 1 rel. to (ka) of benzene	0.36, 0.73 0.44, 0.74 0.44, 0.74 0.53, 0.85 0.59, 0.85 0.51 0.66	2.28 2.20 2.07 2.10 2.69 1.36 2.91 1.49 3.27 1.63 3.15 1.58	0.83 0.80 0.84 0.84 0.83 0.97 0.49, 0.89
K	K71.10, K"1.83 K"0.36, K"1.76 K"0.91, K"1.69 K"0.93, K"1.55 (1.82) (1.64) (1.64) (1.93)	$\begin{pmatrix} 0.44 \\ 0.43 \\ 0.45 \\ 0.46 \\ 0.48 \\ \end{pmatrix}$ $\begin{pmatrix} 0.89 \\ 0.26-0.54 \\ 0.22-0.43 \\ 0.15-0.30 \\ 0.18-0.26 \\ 0.48 \\ \end{pmatrix}$	1.21 1.25 1.19 1.19 1.12 1.06 1.08 K71.01, K"1.81
t₀C.	8688868	88880 0 88818	260504 260504 250504
Component 2	Aniline "" Pyridine ""	Benzene "" Chloroform "" Tetrachloroethane Pentachloroethane Methyl alcohol Ethyl alcohol Phenetol	Benzene "" "" Ethyl alcohol
Component 1	o-Nitrophenol	Ether	Anisol

II. Mixture. (Continued)

Remarks Observer	c(1:2) Sachanov and Rjachowsky n "" "" "" "" "" "" "" "" "" "" "" "" "	n Kendall and Wright	c(1:1, 1:3) Leeuw	n V n De Carli	n J. C. T. n Fischler
(ka) of comp. 1 rel. to (ka) of benzene	$ \begin{vmatrix} 1.04 \\ 1.00 \\ 1.03 \\ 1.02 \end{vmatrix} $ mean $ \begin{vmatrix} 1.04 \\ 1.03 \\ 0.51, 0.83 \end{vmatrix} $	0.56	0.83 0.92	0.71 0.86 0.67	1.87 1.79 1.66 1.70
K	0 (1.79) 0 1.16 25 0.68 26 0.68 27 0.08 25 0.08 26 0.29 10 0.29 10 0.32 20 0.37 80 0.47 80 0.54	1.85	(0.59) (0.53)	1.75 0.89-0.53 0.91 1.16	0.53 0.56 0.60 0.59
t'C.	0 0 22 0 23 23 23 0 0 0 0 0 0 0 0 0 0 0	25	081	17 3 13.2 20	8882
Component 2	Chloroform Tetrachloroethane Pentachloroethane Ethyl iodide Methyl alcohol Ethyl alcohol Ether Diphenyl ether Aniline "" ""	Phenetol	Ethyl alcohol	Toluene Sulphur chloride ",	Benzene ", ",
Component 1	Phenetol	Diphenyl ether	Acetaldehyde	Benzaldehyde	Acetone

II. Mixture. (Continued)

Observer		Sachanov and Rischowsky	,, ,, ,, ,, ,, ,, ,, ,, ,, ,, ,, ,, ,,	Davis, Hughes	Dunstan Parks and Chaffee	Bramley	Puschin and Pinter	Kendall and	Faust	I. C. T.	Sachanov and Riachowsky	Kendall and Brakeley] I. C. T.
Remarks	m = 2.32 $C_0 = 1.52 \times 10^2$	u	> >	c(1:5)	c(1:4) v a	>>>	> >	c(1:2, 1:4)	ಪ ಪ ಪ	u	u	c(1:1)	c(1:1)
(ka) of comp. 1 rel. to (ka) of benzene	1.78	1.89	2.15-1.22	1.98	3.50-1.81 0.47, 1.92	cetone	1.67-0.60	1.76	0.75, 1.10 $0.93, 1.24$ $0.67, 0.85$	0.65)	0.70 mean	129.0	0.46
K	(1.05)	0.57	0.54-0.95 $0.60-0.82$	0.34	0.39 0.14-0.27 K'0.85, K''4.76	See Phenol-Acetone	0.18-0.50	(0.49)	K'1.27, K''1.16 K'1.02, K''1.31 K'1.42, K''0.89	1.54	1.35	(1.28)	(1.45)
<i>t</i> °C.	084	0	00	0	ន្តនន្ត	20.05 20.05 29.8 40.1	30.0	22	$\begin{array}{c} -13 \\ -10 \\ 0 \end{array}$	16	22	25	55 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8
Component 2	Chloroform ",	Carbon tetrachloride	Tetrachloroethane Bromobenzene	Water	Ethyl alcohol i-Propyl alcohol	Phenoi	Guaiacol	Acetic acid	Carbon bisulphide	Benzene	Carbon tetrachloride	Acetic acid	Water ", ", ", ", ", ", ", ", ", ", ", ", ",
Component 1	Acetone									Acetophenone			Formic acid

II. Mixture. (Continued)

Observer	Davis and Jones Merry and Turner	Dunstan)I. C. T.	Mardles Kendail and	brakeley ", Davis and Jones	Kendall and Brakeley ",	Swearingen and Heck
Remarks	e(1:1)	ಡ	$m = 1.68$ $C_0 = 1.16 \times 10^2$	c(2:1) c(2:1, 4:1)	c(1:1) c(1:1)	n n c(1:2) c(1:1)	m = 1.44 $C_0 = 1.4 \times 10$ & (5.1) m = 2.00 $C_0 = 3.44 \times 10^3$
(ka) of comp. 1 rel. to (ka) of benzene	0.46 mean 0.48 0.47	0.32.0.71	0.86	0.85	0.86 0.86 0.89	0.85	0.85
K	(1.87)	K/3.11, K'/0.71	(0.78)	(0.75)	(0.78)	0.49 2.33 0.89	(0.93)
₽°C.	5888	8488888	545566888888888888888888888888888888888	22 23	858	8888	43858
Component 2	Acetic acid Formamide	Benzene Water ",		Methyl alcohol Acetone	Acetophenone Formic acid	Trichloroacetic acid Ethyl acetate Ethyl benzoate Pyridine	
Component 1	Formic acid	Acetic acid					

II. Mixture. (Continued)

Observer	Stranathan and Strong	Tsakalotos Yajnik and coworkers	Dunstan	Kendall and Brakeley	Merry and Turner ", " English and Turner ", " Drucker and Kassel Merry and Turner Kurnakow
Remarks	7, 8×14 7, 1×14	$c(3:1) \\ c(3:1) \\ m = 1.60 \\ C_0 = 1.60 \times 10^2$	п	ц	n n n n a, c(2:1) a, c(2:1) a, c(2:1) a, c(2:1) c(1:1) c(1:1) c(1:1) x60, 1x7 x7
(ka) of comp. 1 rel. to (ka) of benzene	Polym. $v_1 = 3 \times 2, 3 \times 7, 3 \times 14$ $v_2 = 1 \times 2, 1 \times 7, 1 \times 14$	1.32 1.52 1.98	0.19	0,42	0.33 mean n 0.35 0.34 mean n 0.35 0.34 a, c(2 0.26, 0.78 a, c(2 0.26, 0.46 a, c(2 0.26, 0.19 0.28) $0.26, 0.19$ a, c(2 0.26, 0.19 a, c(2 0.33) $0.26, 0.19$ c(1:1 $v_1 = 2 \times 30, 2 \times 60, 1 \times 7$ $v_2 = 1 \times 30, 1 \times 7$ $v_3 = 2 \times 30, 1 \times 7$ $v_4 = 2 \times 30, 1 \times 7$
K		(0.60) (0.60) (0.52) (0.40)	3.57	2.04	2.08 mean 2.00 2.04 2.00 2.04 2.00 mean 1.82 1.91 1.43 mean 1.41 1.42 K70.80, K77.30 K71.10, K71.10, K71.10
t°C.	25.2	20 18.2 30 40	25	25	25
Component 2	Stannic chloride	Pyridine ","	Water	Acetic acid	Water Methyl alcohol Ethyl alcohol i-Propyl alcohol i-Butyl alcohol i-Amyl alcohol i-Amyl alcohol i." Formic acid " Stannic chloride
Component 1	Acetic acid	n-Butyric acid	Lactic acid	Trichloroacetic acid	Formamide Ethyl formate

II. Mixture. (Continued)

Remarks Observer	v Unkovskaja n and Volova	n Kremann, Gugl	n Chadwell	n Linebarger Kendall and Brakeley Chadwell Kendall and Wright V I. C. T.	n Kremann, Gugl n and Meingast v Unkovskaja n yolova	y u y u	n Kendall and Monroe Linebarger n Kendall and Monroe (2:1) Kendall and Brakeley v Kendall and Wright	v Kendall and Monroe
Rem				44 4 47			c(2	
(ka) of comp. 1	(ka) or benzene		2.16	2.00) mean 2.03 2.03 2.05 2.03 2.17-1.26 2.31-1.58			0.69 0.73 0.76 0.96-0.81	0.50-0.31
K	1.24-0.99 1.08	1.00	0.94	0.50 (0.61) 0.42 1.06 0.22-0.38 0.13-0.19	1.00 0.93 1.47–0.96 1.02	1.01-0.81 0.93 0.68-1.04 0.98	1.45 1.70 mean 1.60 1.69 (1.12) 0.50-0.59	2.00-3.23
t°C.	20	12 64	25	8888889	112 20 40 40	8484	88888	25
Component 2	Ethyl propionate	Propyl acetate	Ethyl acetate	Benzene Toluene Acetic acid Methyl acetate Benzyl benzoate Aniline	Amyl formate Ethyl propionate	i-Butyl formate Propyl "cetate",	Benzene Toluene " Acetic acid Benzyl benzoate	Benzene
Component 1	i-Butyl formate	Amyl formate	Methyl acetate	Ethyl acetate	Propyl acetate	Ethyl propionate	Ethyl benzoate	Benzyl benzoate

II. Mixture. (Continued)

Observer	Bingham and Sarver Kendall and Monroe Kendall and Wright	Bramley	Puschin and Pinter	Bramley Puschin and Pinter
Remarks	>>>>>>	%%%%12111111	u	>>>>>
(ka) of comp. 1 rel. to (ka) of benzene	0.38-0.20 0.47-0.25 0.53-0.31 0.61-0.37 0.74-0.48 0.77-0.45 0.43-0.37	0.30 0.33 0.38 0.40 0.39–0.26		
K	2.63-5.00 2.18-4.00 1.89-3.23 1.64-2.70 1.36-2.70 2.66-4.08 2.63-4.55 1.70-2.00	K71.83, K"1.10 K71.76, K"0.96 K71.63, K"0.91 K71.55, K"0.93 8.45 8.12 2.72 2.54 2.43 2.11 1.86 5.26-7.69	0.71	0.16-4.0 0.22-2.0 0.26-2.0 0.32-1.7 0.41-2.0 0.51-2.0 0.71
t₀C.	252468 2525 2525 2525 2525 2525 2525 2525 25	50000000000000000000000000000000000000	8	10 20 29.8 40.2 59.9 80 126 177
Component 2	Benzene "" "' Toluene Ethyl acetate Ethyl benzoate	o-Nitrophenol "" Phenetol "" "" Ethyl acetate	Guaiacol	Phenol
Component 1	Benzyl benzoate	Aniline	Methyl aniline	Dimethyl anıline

II. Mixture. (Continued)

Observer	Bramley		Beck "		Dessart "" "" "" "" "" ""	Dunstan, Thole and Hunt Hartley, Thomas and Applebey Bramley
Remarks	> h u	त त त त त त	444	u	**************	c(2:1) c(1:3+1:2) c(1:3+1:1) c(1:2) m = 2.00 $C_0 = 7.02 \times 10$
(ka) of comp. 1 rel. to (ka) of benzene					0.30 mean 0.31 0.31 (0.18?) (0.24?) (0.26?)	0.76 0.80
×	1.08–1.92 1.05–1.82 1.33	K71.15, K"1.65 K71.19, K"1.44 K70.81, K"1.79 K70.92, K"1.66 K71.16, K"1.08 K71.20, K"0.91	1.11 0.97 0.99	1.01	5.26) mean 5.00) 5.13 3.03) mean 3.13 3.08 3.85) mean 3.45 3.65 5.56 4.17 6.67 4.76	(1.32) (0.84) (0.55) (0.65) (0.74)
t°C.	30 40 81	8.6 80 80 80 80 80	125 75 75	75	80 80 80 80 80 80 80 80 80 80 80 80 80 8	25.08 30 30 40 60
Component 2	Phenol	Phenol "" "" "" "" "" "" "" "" "" "" "" "" ""	Stilbene Azobenzene Benzyl aniline	Benzal aniline	n-Hexane Cyclohexane Methyl cyclohexane Benzene Toluene	Benzene Water o-Nitrophenol ","
Component 1	Diphenyl amine	Diphenyl methyl amine	Benzal aniline	Benzyl aniline	m-Toluidine	Pyridine

II. Mixture. (Continued)

Observer	Swearingen and Heck Tsakalotos Yajnik and coworkers	I. C. T.	Linebarger Thorpe and Rodger Dunstan Faust	Dunstan	Wagner	$\left. iggr \} ight.$ Arpi $\left. iggr \} ight.$ ",
Remarks	$c(1:1)$ $m = 1.44$ $C_0 = 1.4 \times 10$ & $c(1:5)$ $m = 2.00$ $C_0 = 3.44 \times 10^3$ $c(1:3)$ $c(1:3)$ $m = 1.60$ $C_0 = 1.6 \times 10^2$	uu	日日日日日日 成 8 8	п	ಡ	8888
(ka) of comp. 1 rel. to (ka) of benzene	08.0	0.46) mean 0.44) 0.45	0.91 mean 0.95 0.98	1.32	0.40, 0.89	
K	$ \begin{cases} (0.84) \\ (1.08) \\ (1.67) \\ (1.67) \\ (1.67) \\ (1.92) \\ (2.50) \end{cases} $	2.17 1.12	1.10 0.63 0.61 0.61 0.69 0.75 K71.16, K771.27 K71.31, K771.02 K70.89, K771.42	0.37	K'1.22, K"1.82	1.15 1.03 2.6 1.6
t₀C.	80 45 55 65 75 80 80 40 40	25 25	20 0 0 20 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	22	1	400 500 400 500
Component 2	o-Nitrophenol Acetic acid "" "" Butyric acid ""	Benzene Ethyl alcohol	Benzene Methyl iodide " " " Ethyl alcohol Acetone "	Ethyl alcohol	Ethyl alcohol	Tin Bismuth ",
Component 1	Pyridine	Quinoline	Carbon bisulphide	Mercaptan	Allyl thiocyanide	Lead

II. Mixture. (Concluded)

Observer	Arpi		De Carli	Kurnakow De Carli Stranathan and Strong Kurnakow	} De Carli
Remarks	пп	пп	uu>>>uu	$m = 2.00$ $m = 2.00$ $C_0 = 1.31 \times 10^2$ $T, 1 \times 14$ $T, 3 \times 14$ $\times 60, 1 \times 7$ $\times 60, 1 \times 7$ $\times 7$	c(1:1)
(ka) of comp. 1 rel. to (ka) of benzene			0.78) mean 0.78) 0.78 1.40-0.79 0.59-0.79	$\begin{array}{c} 0.48, 0.86 \\ 0.66 \\ 0.60, 0.95 \\ 0.83 \\ 0.83 \\ 0.99 \\ 0.98 \\ 0.98 \\ 0.98 \\ 0.99$	0.49
K	0.87 0.97	0.38 0.63	1.28 1.28 0.35-0.62 0.83-0.62 1.89-1.12 1.10 0.86	K72.08, K770.86 K71.68, K770.95 (0.74) (0.59)	(1.00)
toC.	400	400	15.5 20 3 20 3 3 13.2 20	25 115 25 25 25 30 40 60	40
Component 2	Lead ",	Lead ",	Benzene Nitrobenzene Benzaldehyde ",	Benzene Nitrobenzene " Acetic acid Ethyl formate " "	Nitrobenzene ",
Component 1	Tin	Bismuth	Sulphur chloride	Stannic chloride	Stannic bromide

Literature for the adopted mixtures in Table 8.

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solutional viscosity or the viscosity of ionic pair of KCl. Column 3 in Table 7 shows thus estimated solutional viscosities, the viscosities of water at the corresponding temperatures being adopted from Internat. Crit. Tables, V.

By simple calculation, we see that these viscosity values are quite sufficiently expressed by the quadratic equation:

$$\eta_t = \frac{0.01533}{1 + 0.02730t + 0.0001141t^2} \ .$$

The fact that the equation of this type has been proved by Thorpe and Rodger⁽¹³⁾ to reproduce very closely the viscosity of numerous organic liquids without molecular complexity, and further that the magnitudes of these here obtained coefficients also are reasonably acceptable as compared with those for such liquids as ethylene chloride, carbon tetrachloride, and acid anhydrides, draws the conclusion that the solutional state of an electrolyte which is composed of its ionic pairs behave, as would be expected, like a liquid containing no molecular aggregates.

In conjunction with our study hitherto made some inquiry about the characteristic constant K along quite different lines, which we earnestly hope, may afford a clue to unvail the mysterious nature of liquids.

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⁽¹³⁾ T. E. Thorpe and J. W. Rodger, Phil. Trans., A, 185 (1894), 397.