TABLE V.

Solvent.	K.	ϵ.	$K\epsilon$.	Observer.
		KI.		
Water	0.412	80.0	33.0	Ostwald
Ethyl alcohol	1.67	21.7	36.2	Walden
Acetonitrile	1.45	35.8	51.9	Walden
		$LiNO_3$.		
Water	0.478	80.0	38.2	Ostwald
Methyl alcohol	1.174	32.5	38.2	Jones and Lindsay[1]
50 per cent. methyl alcohol	0.632	57.4[2]	36.3	Jones and Lindsay

Table V gives a few results for two inorganic salts. In the case of potassium iodide, $K\varepsilon$ has nearly the same value for water and ethyl alcohol, but for acetonitrile as solvent, the value of $K\varepsilon$ is abnormally large. For lithium nitrate the product $K\varepsilon$ is the same for both water and methyl alcohol. In 50 per cent. methyl alcohol, one might, at first thought, expect K to be the mean of the values for water and methyl alcohol separately. This mean is 0.826 for lithium nitrate. If, however, the product $K\varepsilon$ has the same value for the mixed solvents as for each separately, ε being the mean of the separate values,[3] then K should be 0.679; the actual value is 0.632.

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THE VISCOSITY OF NON-AQUEOUS SOLUTIONS OF POTASSIUM IODIDE.

BY FREDERICK H. GETMAN.

Received April 22, 1908.

The study of aqueous solutions of certain electrolytes exhibiting negative viscosity has led to the view that the cations are the effective agents in lowering the viscosity of the solvent while the anions and the undissociated molecules invariably tend to increase it.[4]

It seemed desirable to test this theory by working with non-aqueous solutions in which the degree of ionization is known to be less than in water. Fortunately, potassium iodide, which exhibits negative viscosity to a marked degree in dilute aqueous solutions, is quite soluble in a number of organic solvents of relatively low dissociating power.

The solvents employed in this investigation were methyl alcohol, ethyl alcohol, ethylene glycol, glycerol, furfural, acetone and pyridine. These were obtained either from Kahlbaum or Merck, special precautions being taken to insure their purity and the absence of moisture.

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[1] *Amer. Chem. J.*, **28**, 329.

[2] Drude, *Z. physik. Chem.*, **23**, 300.

[3] Drude, *Loc. cit.*

[4] Getman, *Jour. chim. phys.*, **5**, 344 (1907); Getman, THIS JOURNAL, **30**, 721 (1908).

The potassium iodide used was obtained from Kahlbaum and was known to be of the highest purity.

The viscosity measurements were made by the well-known method of Poiseuille-Ostwald, the exact mode of procedure having been outlined in earlier papers.

The solutions were made up on the percentage basis, p in the following tables denoting the number of grams of potassium iodide in 100 cc. of solution.

In addition to giving the density of the solutions $d_{(25°/4°)}$, and the absolute viscosity, η, the last column of the tables gives the ratio, r, of the absolute viscosity of the solutions to the absolute viscosity of the solvent.

All measurements were made at 25°.

TABLE I.

KI in CH_3OH.

p.	d.	η.	r.
0.000	0.78835	0.005441	1.000
0.704	0.79397	0.005545	1.019
2.406	0.80844	0.005835	1.072
5.491	0.83515	0.006327	1.163
7.694	0.85403	0.006670	1.226
10.790	0.88068	0.007133	1.311

TABLE II.

KI in C_2H_5OH.

p.	d.	η.	r.
0.000	0.78684	0.01081	1.000
0.211	0.78875	0.01090	1.008
0.421	0.79039	0.01101	1.018
0.596	0.79268	0.01113	1.029
0.841	0.79353	0.01126	1.041
1.100	0.79583	0.01133	1.048

TABLE III.

KI in $C_2H_4(OH)_2$.

p.	d.	η.	r.
0.000	1.1097	0.17330	1.000
4.641	1.1411	0.17671	1.019
9.922	1.1782	0.18243	1.052
15.471	1.2140	0.18644	1.076
19.844	1.2433	0.19040	1.098

TABLE IV.

KI in $C_3H_5(OH)_3$.

p.	d.	η.	r.
0.000	1.2474	4.3973	1.000
5.879	1.2828	4.1144	0.935
9.385	1.3060	3.9718	0.903
11.758	1.3168	3.8274	0.871
18.770	1.3640	3.5433	0.806

TABLE V.

KI in $C_4H_3O.COH$.

p.	d.	η.	r.
0.000	1.1539	0.01491	1.000
1.253	1.1636	0.01603	1.075
2.087	1.1699	0.01686	1.131
2.506	1.1732	0.01720	1.153
3.000	1.1722	0.01764	1.183
4.173	1.1861	0.01894	1.270

TABLE VI.

KI in $CH_3.CO.CH_3$.

p.	d.	η.	r.
0.000	0.78756	0.003124	1.000
0.437	0.79216	0.003186	1.019
0.585	0.79395	0.003215	1.029
0.874	0.79626	0.003258	1.042
1.170	0.79855	0.003300	1.056

TABLE VII.

KI in C_5H_5N.

p.	d.	η.	r.
0.000	0.97159	0.008686	1.000
0.059	0.97294	0.008791	1.012
0.119	0.97349	0.008891	1.024

The data given in Tables I to VI are plotted in Fig. 1. Owing to the slight solubility of potassium iodide in pyridine no attempt was made

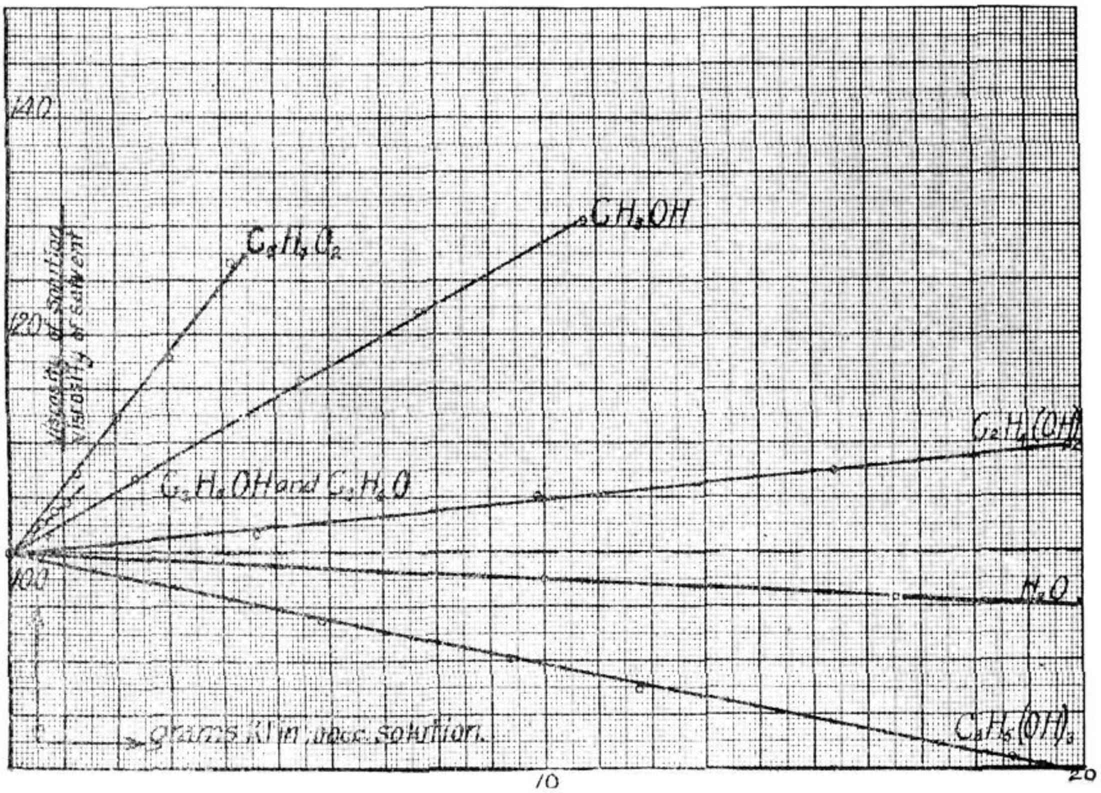

Fig. 1.

to plot the measurements recorded in Table VII. For convenience in comparing the viscosities in different solvents with the viscosity of aqueous solutions, the data for water are also plotted. The broken horizontal line is the datum line, the curves for positive and negative solutions lying above and below it respectively.

Comparing water, methyl alcohol and ethyl alcohol, it will be observed that for solutions of equal concentration, the aqueous solution is the least and the ethyl alcohol solution the most viscous, while the methyl alcohol solution has a viscosity lying between the other two.

It has been pointed out by Jones,[1] in a review of the investigations of different workers on non-aqueous solvents, that the dissociating power of methyl alcohol is from one-half to two-thirds that of water, while the dissociating power of ethyl alcohol is not more than one-half that of methyl alcohol.

It will be observed that neither of the alcoholic solutions are negatively viscous and further, that the increase in viscosity is approximately in inverse proportion to the dissociating power. When we pass from monatomic to polyatomic alcohols as solvents, the viscosity decreases with increase in hydroxyl groups.

It may be noticed that the curve for water lies almost exactly midway between the curves for glycol and glycerol, the latter giving markedly negative solutions. Few or no data are available to determine whether the dissociating power increases with increase in hydroxyl groups but it is highly improbable that glycerol is a more active dissociant than methyl alcohol.[2] The explanation of this apparent exception to the proposed theory of negative viscosity must undoubtedly be found outside of the theory of electrolytic dissociation.

Furfural and acetone give positive solutions, the degree of viscosity being such as one might expect from their slight dissociating action. The curve for acetone is practically coincident with that for ethyl alcohol and their dissociating powers are not greatly different.

Pyridine dissolves potassium iodide to a limited extent only, but the solutions are positive as we might infer from our knowledge of the solvent as a dissociant.

The solvents studied, belong to several different classes of organic compounds and with the exception of glycerol, all give positive solutions. Undoubtedly the degree of association of the solvent is an important factor conditioning viscosity.

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[1] Jones, *Am. Chem. J.*, 25, 232 (1901).

[2] Since this article was written my attention was called to an article by N. Lemcke (*J. Russ. Phys. Chem. Soc.*, **37**, 1134 (1905)) on "**Electrical Conductivity and Internal Friction,**" in which he points out that the degree of dissociation of potassium chloride is greater in a mixture of glycerol and water than in pure water.

With the exception of pyridine, all of the solvents used are known to be more or less associated.

That there is some connection between the association of a solvent and its dissociating power has been pointed out by Dutoit and Aston,[1] and Dutoit and Friderich.[2]

Neither Ramsay and Shields[3] or Longinescu[4] were able to secure the necessary data for calculating the degree of association of glycerol, but its alcoholic character justifies the assumption that it is polymerized.

Dunstan[5] calls attention to the approximate constancy of the ratio, $\frac{\eta \times 10^6}{\text{molecular volume}}$, for non-associated liquids while for associated liquids the ratio varies and is almost always larger than for substances that are known to be non-associated.

Before making use of this relation as a test for the association of glycol and glycerol, it seemed desirable to calculate the ratio for a number of non-associated liquids, since Dunstan calculated it for only eight substances for which the greatest and least values were 69 and 43.

In the following tables will be found the values of the ratio for fifty non-associated liquids selected from several different classes of organic compounds.

The data required for the calculation of the ratios were obtained from the tables of Landolt and Börnstein.

TABLE VIII.

Halogen Derivatives.

Substance.	$\frac{\eta \times 10^6}{\text{Mol. Vol.}}$	Substance.	$\frac{\eta \times 10^6}{\text{Mol. Vol.}}$	Substance.	$\frac{\eta \times 10^6}{\text{Mol. Vol.}}$
C_3H_7Cl	38.0	C_2H_5Br	49.3	CH_3I	73.3
$CH_3CH.ClCH_3$	33.5	C_3H_7Br	54.1	C_2H_5I	62.5
$CH_3CH(CH_3)CH_2Cl$	40.8	$CH_3CHBrCH_3$	48.8	C_3H_7I	71.7
				CH_3CHICH_3	65.6
Mean,	37.4	Mean,	50.7	Mean,	68.3

It is apparent that the ratio approaches constancy only for a particular class of compounds and that even here if the hydrocarbon radicle be combined with an atom or group which is relatively heavy, the value of the ratio is altered. This is well illustrated in Table VIII where some of the aliphatic hydrocarbon radicles are combined with the halogens.

The mean value of the ratios for the three halogen derivatives are 37.4, 50.7 and 68.3, the ratio increasing with increase in the atomic weight of the halogen. The mean value for the bromine derivative is a close

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[1] *Compt. rend.*, **125**, 240 (1897).

[2] *Bull. soc. chim.* [3], **19**, 321 (1898).

[3] *Z. physik. Chem.*, **12**, 433 (1893).

[4] *J. chim. phys.*, **1**, 289 (1903).

[5] *Z. physik. Chem.*, **51**, 732 (1905).

approximation to the mean of the values for the chlorine and iodine derivatives.

TABLE IX.

Esters, Ketones and Ethers.

Substance.	$\frac{\eta \times 10^6}{\text{Mol. Vol.}}$	Substance.	$\frac{\eta \times 10^6}{\text{Mol. Vol.}}$	Substance.	$\frac{\eta \times 10^6}{\text{Mol. Vol.}}$
				(a)	
$H.COOCH_3$	54.0	CH_3COCH_3	42.1	$C_2H_5.O.C_2H_5$	21.5
$HCOOC_2H_5$	46.8	$CH_3COC_2H_5$	44.8	$CH_3.O.C_3H_7$	24.2
$HCOOC_3H_7$	49.9	$C_2H_5COC_2H_5$	41.9	$C_2H_5OC_3H_7$	25.3
CH_3COOCH_3	45.6	$CH_3COC_3H_7$	44.4	$C_3H_7OC_3H_7$	29.8
		Mean,	43.3	Mean,	25.2
				(b)	
$CH_3COOC_2H_5$	43.3			CH_3SCH_3	38.3
$CH_3COOC_3H_7$	48.9			$C_2H_5SC_2H_5$	40.3
$C_2H_5COOCH_3$	45.9			Mean,	39.3
$C_2H_5COOC_2H_5$	43.6				
$C_3H_7COOCH_3$	47.5				
$CH_3CH(CH_3)COOCH_3$	43.7				
Mean,	46.9				

TABLE X.

Esters, Ethers and Hydrocarbons.

Substance.	$\frac{\eta \times 10^6}{\text{Mol. Vol.}}$	Substance.	$\frac{\eta \times 10^6}{\text{Mol. Vol.}}$	Δ.	Substance.	$\frac{\eta \times 10^6}{\text{Mol. Vol.}}$
(a)						
$C_6H_5COOCH_3$	164.4	C_5H_{12}	19.2	4.4	C_6H_6	69.2
$C_6H_5COOC_2H_5$	165.5	C_6H_{14}	23.6		$C_6H_5CH_3$	51.5
Mean,	160.4					
(b)						
$C_6H_5OCH_3$	100.5	C_7H_{16}	26.6	3.0	$C_6H_4(CH_3)_2(o)$	58.3
$C_6H_5OC_2H_5$	101.6	C_8H_{18}	32.1	5.5	$C_6H_4(CH_3)_2(m)$	47.3
$C_6H_5OC_3H_7$	111.6	C_9H_{20}	36.0	3.9	$C_6H_4(CH_3)_2(p)$	49.3
$C_6H_4CH_3OCH_3(o)$	107.5	$C_{10}H_{22}$	40.0	4.0		
$C_6H_4CH_3OC_2H_5(o)$	102.9	$C_{11}H_{24}$	44.9	4.9		
$C_6H_4CH_3OC_2H_5(p)$	103.9					
			Mean,	4.3		
Mean,	104.7					

The mean values for the esters and ketones as given in Table IX are very nearly the same, a fact which may be attributed to the presence of the carbonyl group in each.

Table IX also shows the value of the ratio for ethers and thio-ethers, the effect of substituting sulphur for oxygen being very apparent. The following table is devoted to some ethers and esters of the aromatic series.

It will be observed that the presence of the benzene nucleus produces a marked increase in the value of the ratio.

Table X gives similar data for some hydrocarbons of both series. It will be observed that there is no constant for the aliphatic hydrocarbons but that the addition of a CH_2 group increases the ratio by about 4.3. With the aromatic hydrocarbons there appears to be no well-defined relation between successive members of the series. Undoubtedly the relative positions of the aliphatic substituents in the benzene ring is a disturbing factor.

Inspection of the oregoing tables shows conclusively that the relation of Dunstan is nothing more than an approximation which holds only within very narrow limits.

Owing to the impossibility of applying to glycol and glycerol the well-known methods for determining the degree of association of liquids, we feel warranted in making use of the ratio of viscosity to molecular volume In the following table is given the value of this ratio for the different solvents used:

TABLE XI.

Substance.	$\frac{\eta \times 10^6}{\text{Mol. Vol.}}$
H_2O	495.0
CH_3OH	134.0
C_2H_5OH	185.1
$C_2H_4(OH)_2$	3105.7
$C_3H_5(OH)_3$	59664.7
$C_5H_4O_2$	179.2
$CH_3.CO.CH_3$	42.1
C_5H_5N	106.3

The extremely large values of the ratios for glycol and glycerol may be interpreted as indicating association.

If one of the factors conditioning negative viscosity is association and if the ratio of viscosity to molecular volume affords a rough measure of the degree of the association of the solvent, then we would infer that both glycol and glycerol should act similarly to water and yield negative solutions.

As a matter of fact glycerol gives more negative solutions than water, while glycol gives positive solutions.

It must be remembered, however, that the ratio of viscosity to molecular volume is but an approximate measure of association and that the presence of two or more hydroxyl groups exerts a marked influence in raising the value of the ratio, so that in all probability glycol is less, and glycerol more associated than water.

Summary of Results.

(1) The viscosities of solutions of potassium iodide in methyl alcohol, ethyl alcohol, ethylene glycol, glycerol, furfural, acetone and pyridine have been measured. With the exception of the glycerol solutions, all exhibit positive viscosity.

(2) The negative viscosity of the glycerol solutions is attributed to the association of the solvent.

(3) The value of the ratio of absolute viscosity to molecular volume has been calculated for fifty non-associated organic liquids. This ratio is approximately constant for members of the same class of compounds in the same series.

(4) By means of this ratio it has been inferred that the degree of association of glycerol must exceed that of water.

(5) The results of the measurements on non-aqueous solutions confirm the conclusions drawn from previous investigations, that the cations of an electrolyte and the association of the solvent are factors causing negative viscosity.

COLUMBIA UNIVERSITY, NEW YORK CITY,
April, 1908.

THE CHARACTER OF THE COMPOUND FORMED BY THE ADDITION OF AMMONIA TO ETHYL-PHOSPHO-PLATINO-CHLORIDE.

BY CHAS. H. HERTY AND R. O. E. DAVIS.

Received March 23, 1908.

By heating together phosphorus pentachloride and spongy platinum, Baudrimont[1] obtained the phospho-platino-chloride $PtCl_2.PCl_3$. Later Schützenberger[2] prepared the compound $PtCl_2.2PCl_3$ by treating Baudrimont's salt with phosphorus trichloride and he studied the various derivatives of these two substances.

The apparent analogy of these compounds to those of platinous chloride with ammonia led one of us (Herty) in 1901 to investigate them further by physico-chemical methods, in order to determine whether the analogy was real and therefore whether they conformed to Werner's[3] extension of the valence hypothesis. If so, various possibilities of isomerism at once suggested themselves.

These views, in abstract form, were presented to the committee in charge of the C. M. Warren Research Fund and a grant was made for the purchase of platinum. Work was begun at once, but unfortunately a call to another field made impossible the completion of the investigation. The platinum was recovered, sold, and the grant returned.

Later, Rosenheim[4] published the results of an investigation covering practically the same ground. He found that the analogy was real and succeeded in obtaining numerous isomers. With the stable ethoxy derivatives, molecular weight determinations, both ebullioscopic and

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[1] *Ann. chim. phys.* [4], 2, 47.

[2] *Bull. soc. chim.* [2], 17, 482; 18, 101, 148.

[3] *Z. anorg. Chem.*, 3, 267.

[4] *Ibid.*, 37, 394; 43, 34.