

Since the dissociation of Fe_2O_3 results in the formation of a solid solution, the pressure of oxygen and the composition of the solid phase depend upon the relation of the weight of the charge to the volume of the space into which the oxygen dissociates. This fact accounts for the variety and uncertainty of results heretofore obtained in experiments on the dissociation pressure of Fe_2O_3 .

WASHINGTON, D. C.

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY.]

THE VISCOSITY OF CERTAIN ALCOHOLIC SOLUTIONS.

By O. F. TOWER.

Received February 22, 1916.

About a year ago the author, in collaboration with Dr. Germann,¹ published the results of a series of determinations of the vapor pressures of solutions of three typical solutes in methyl and ethyl alcohols. It has seemed worth while to investigate in addition some of the other physical properties of such solutions. The electrical conductivity of those that are conductors have already been measured, so in this paper the results of viscosity determinations are given, together with a general discussion of the relations existing between the viscosity and other physical properties of such solutions.

The solutes were the same as those employed in the vapor-pressure determinations, *viz.*, lithium chloride, potassium iodide and benzil; and in addition urea, since vapor pressures of solutions of this substance in ethyl alcohol have recently been published.² The urea used was a pure preparation and was further purified by two crystallizations from hot absolute alcohol; the other solutes were from samples which had been purified for the vapor tension work. They were all preserved after purification in a vacuum desiccator. The alcohols were purified by allowing "C. P." preparations to stand in contact with quick-lime for a year, after which they were distilled on to anhydrous copper sulfate and remained in contact with it for somewhat over a week. After this they were fractionated *in vacuo* in an apparatus like that described in the previous paper, and were then distilled, still *in vacuo*, on to weighed quantities of the solute. The solutions thus obtained were transferred to the viscosimeter by means of an apparatus essentially the same as that employed by Thorpe and Roger³ for the same purpose, and were therefore in contact with ordinary air only for the moment they were being transferred from the distilling apparatus. In the viscosimeter they were in contact only with air which had been dried over phosphorus pentoxide.

¹ THIS JOURNAL, 36, 2449 (1914).

² Price, *J. Chem. Soc.*, 107, 188 (1915).

³ *Phil. Trans.*, (A) 185, 415 (1894).

The viscosimeter used was a modified form of the Bingham apparatus (see Fig. 1). It had two vertical capillary tubes about 5 cm. long, one in each arm of the instrument, instead of one horizontal, removable capillary as in the apparatus employed by Bingham and White.¹ Its total capacity

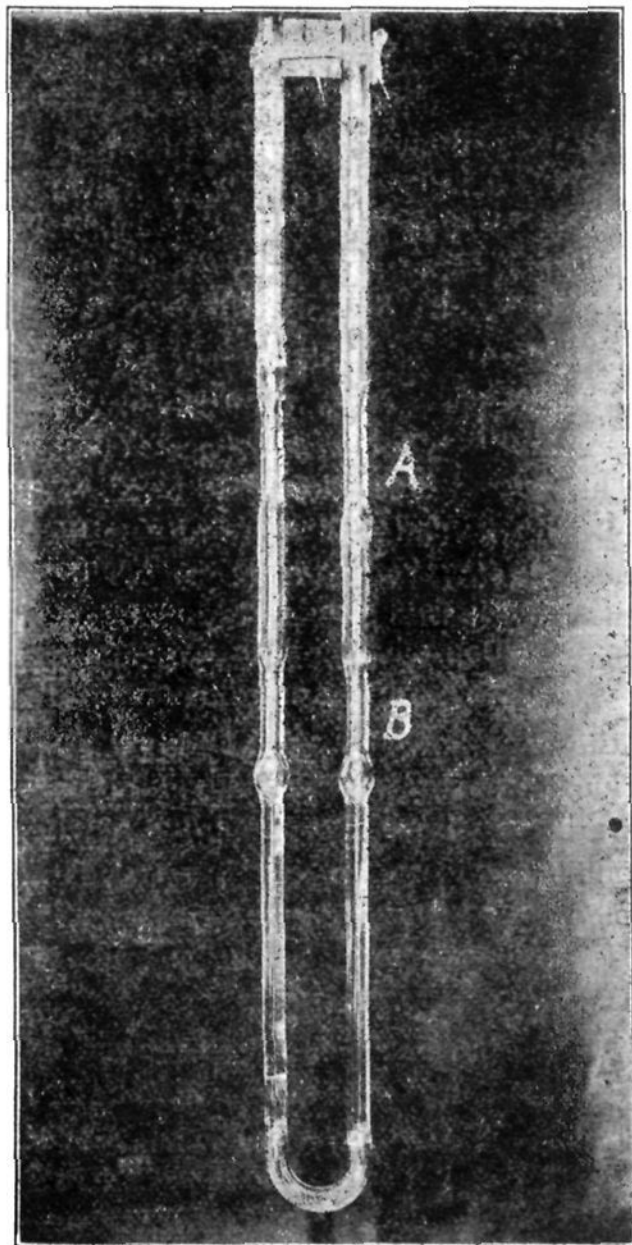


Fig. 1.

while in operation was 5 cc. It stood in a water bath with glass sides of about 10 liters capacity, whose temperature could easily be maintained within 0.1° of the desired temperature, usually 15° . Each arm of the viscosimeter was connected with an outlet of a four-way stopcock. The other outlets of the stopcock connected with the external air and with an air chamber, respectively. The air in the chamber was maintained at constant pressure by means of a column of water equivalent to 47 mm. of mercury. A large tube containing phosphorus pentoxide separated the air in contact with the water column from the main air chamber. In carrying out an experiment the liquid in the instrument was driven from A to B (see Fig. 1) or *vice versa* by means of the constant air pressure, the time being measured with a stop-watch.

The apparatus was calibrated by using specially purified water, whose viscosity at 15° was assumed to be 0.01136, which is the average of the

results of Thorpe and Roger² and of Bingham and White.³ To illustrate the slight variations observed in the time of flow, one set of the results with water are given in Table I.

¹ *Z. physik. Chem.*, **80**, 684 (1912).

² *Loc. cit.*

³ *Ibid.*, Hosking's value at this temperature is 0.01142, *Phil. Mag.*, [6] **18**, 260 (1909). This seems to be too high.

TABLE I.

Emptying.		Filling.	
Min.	Sec.	Min.	Sec.
5	33	5	28
5	32.5	5	29
5	33	5	29
5	32	5	28.5
5	33.5	5	28
5	33	5	28.5
Average.....5		5	28.5

Average both sides, 5 min., 30.7 sec. = 330.7 sec.

Since the driving force due to the weight of the liquid was negligible in comparison with the pressure exerted by the water column,¹ we have for any two liquids, $\eta/\eta' = t/t'$, in which η and η' are the viscosities and t and t' are the times of flow of the two liquids, respectively. For water at 15°, $\eta' = 0.01138$, and $t' = 330.7$ sec. (see Table I); therefore for any other liquid $\eta = \eta'/t' t = 0.0003435 t$, which is the equation used in calculating the viscosities in all of the following work.

The viscosity of methyl and ethyl alcohols has been previously determined, as well as that of mixtures of these alcohols with water for every 5 or 10% change of concentration up to pure water.² These results have been plotted in curves showing the variation in the viscosity with increasing quantities of water. However, no determinations have been made between the viscosity of pure alcohol and that of a mixture containing about 5 or 10% of water. This is a portion of the curve which it is very desirable to know as accurately as possible, and hence I have determined not only the viscosity of the alcohols themselves, but also that of mix-

TABLE II.

Methyl alcohol.		Ethyl alcohol.		Temperature.	Methyl alcohol.		Observer.
% water by wt.	Viscosity. η .	% water by wt.	Viscosity. η .		% water by wt.	η .	
0.0	0.006292	0.0	0.01317	14.53°	0.0	0.006405	T. & R. ³
0.762	0.00652	0.775	0.01383	15°	0.0	0.00638	Getman (⁴)
1.230	0.00671	1.876	0.01443	15°	12.24	0.00965	"
2.477	0.00708	4.115	0.01545	...	Ethyl alcohol.		
4.653	0.00782	6.764	0.01678	13.23°	0.0	0.013573	T. & R. ³
8.103	0.00891	9.267	0.01805	15°	0.0	0.01315	B. & D. ⁵
11.210	0.00995	11.104	0.01891	15°	6.22	0.0166	V. & G. ⁶
15.142	0.01111	12.974	0.01973	15°	12.275	0.0189	"

¹ Several experiments showed this to be true.

² See for example Dunstan, *J. Chem. Soc.*, **85**, 823-4 (1904); and Getman, *J. chim. phys.*, **4**, 386 (1906).

³ Thorpe and Rodger, *loc. cit.*, pp. 530-1.

⁴ *Loc. cit.*, pp. 392 and 395. Given in the text as 10% water by volume.

⁵ Bingham and White, *loc. cit.*, p. 282.

⁶ Varenne and Godefroy, *Compt. rend.*, **137**, 9931 (1903). Results have been recalculated to the same units as the others in this paper.

tures of them with small quantities of water. The measurements were made at 15° , and the results are given in Table II. Results obtained by others at or near the same temperature are shown at the right. Those with methyl alcohol differ considerably from mine. This is probably due to the fact, that so-called C. P. methyl alcohol is not as pure as absolute ethyl alcohol, not because it contains more water, but because it very likely contains traces of other organic substances, from which it is freed only by repeated fractional distillation. This was insured in the sample used here by the rigorous fractioning to which the alcohols were subjected *in vacuo*.

The results of Table II have been plotted in curves, which are reproduced in Fig. 2. The viscosities of the ethyl alcohol mixtures have been

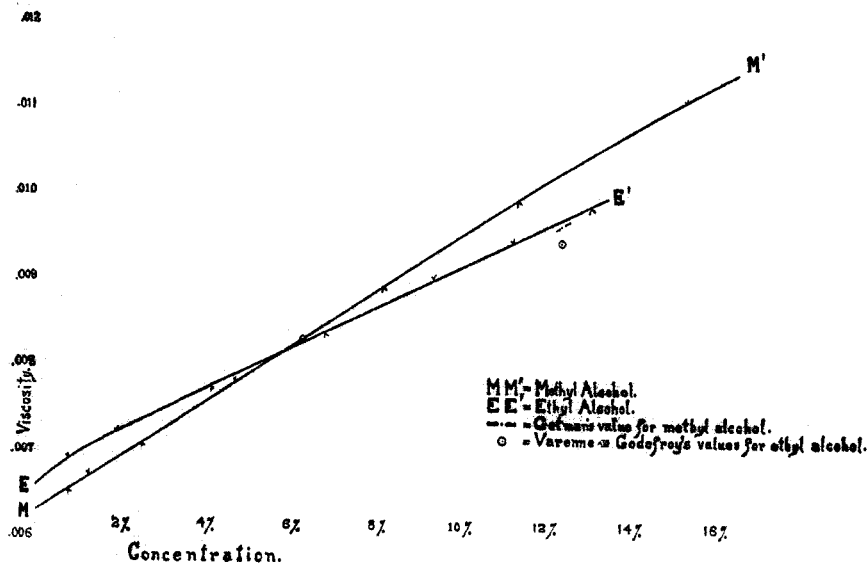


FIG. 2.

divided by two, and the numbers so obtained used as ordinates. This was done so that both curves could be shown on the same diagram. As is seen, they both approximate to straight lines, so that there is nothing exceptional in the "alcohol end" of the viscosity curves of mixtures of water with either methyl or ethyl alcohol.

The results of the viscosity measurements, which have been made at 15° (the temperature at which the vapor pressure determinations were made), are shown in Table III. The reciprocal of the viscosity is known as the fluidity. This is shown under ϕ in the last column.

Table IV gives the results using urea as solute. The measurements were made at different temperatures as indicated by the subscripts in the viscosity and fluidity columns.

TABLE III.—OBSERVATIONS AT 15°.

Solvent: Methyl Alcohol.				Solvent: Ethyl Alcohol.			
Solute: Lithium Chloride.							
Substance in 1 g. alcohol.	Mol. per mol.	η .	φ .	Substance in 1 g. alcohol.	Mol. per mol.	η .	φ .
0.06843	0.05170	0.01471	67.98	0.04516	0.04904	0.02998	33.36
0.04479	0.03386	0.01118	89.45	0.03501	0.03802	0.02486	40.23
0.02756	0.02082	0.009114	109.7	0.02093	0.02273	0.01977	50.58
0.01459	0.01102	0.007815	128.0	0.01048	0.01138	0.01643	60.86
0.01392	0.01052	0.007729	129.4	0.004824	0.005236	0.01477	67.70
0.00792	0.005983	0.007207	138.8	0.002587	0.002809	0.01405	71.17
0.00490	0.003703	0.006891	145.1				
0.002655	0.002005	0.006667	150.0				
Solute: Potassium Iodide.							
0.11694	0.02238	0.00823	121.5	0.01337	0.003709	0.01386	72.15
0.07674	0.01481	0.00768	130.2	0.00820	0.002274	0.01362	73.41
0.04574	0.00883	0.00717	139.5	0.00474	0.001315	0.01342	74.52
0.02265	0.00437	0.00674	148.4				
0.01187	0.00229	0.006565	152.3				
0.00574	0.00111	0.006465	154.7				
Solute: Benzil.							
0.04293	0.006545	0.006661	150.1	0.02039	0.004470	0.01335	74.91
0.03112	0.004745	0.006589	151.8	0.01136	0.002490	0.01328	75.30
0.01889	0.002880	0.006479	154.3	0.00682	0.001495	0.01322	75.64
0.01094	0.001668	0.006410	156.0				

TABLE IV.—UREA AS SOLUTE.

Solvent: Methyl Alcohol.								
Substance in 1 g. alcohol.	Mol. per mol.	η_{25}° .	φ_{25}° .	η_{40}° .	φ_{40}° .			
0.09154	0.04882	0.006690	149.5	0.005493	182.1			
0.06110	0.03258	0.006435	155.4	0.005155	194.0			
0.04335	0.02312	0.006183	161.7	0.004964	201.5			
0.02986	0.01592	0.005968	167.6	0.004819	207.5			
0.01567	0.008355	0.005771	173.3	0.004663	214.5			
0.008693	0.004636	0.005665	176.5	0.004558	219.4			
Pure alcohol.....		0.005523	181.1	0.004460	224.2			
Solvent: Ethyl Alcohol.								
Substance in 1 g. alcohol.	Mol. per mol.	η_{25}° .	φ_{25}° .	η_{50}° .	φ_{50}° .	Mol. per mol.	η_{40}° .	φ_{40}° .
0.04749	0.03641	0.01243	80.5	0.007762	128.8	0.04875	0.009595	104.2
0.03163	0.02435	0.01195	83.7	0.007535	132.7	0.03804	0.009323	107.2
0.01432	0.01098	0.01140	87.7	0.007301	137.0	0.03005	0.009124	109.6
0.007395	0.00567	0.01121	89.2	0.007164	139.6	0.01836	0.008842	113.1
						0.01095	0.008647	115.7
						0.006659	0.008542	117.1
						0.003712	0.008430	118.6
Pure alcohol.....	0.01098	91.1	0.007040	142.1			0.008382	119.3

In order to ascertain how the viscosity of these solutions varies with change of temperature, the following measurements were made at the temperatures indicated by the subscripts (Table V):

TABLE V.
Potassium Iodide in Methyl Alcohol.

Substance in 1 g. alcohol.	Mol. per mol.	η_{25}° .	φ_{25}° .	η_{40}° .	φ_{40}° .
0.09772	0.01885	0.006767	147.8	0.005443	183.7
0.07039	0.01358	0.006450	155.0	0.005207	192.0
0.03593	0.006933	0.006018	166.2	0.004864	205.6
0.01786	0.003445	0.005782	173.0	0.004661	214.6

Benzil in Methyl Alcohol.

Substance in 1 g. alcohol.	Mol. per mol.	η_{40}° .	φ_{40}° .
0.05477	0.00835	0.004880	204.9
0.03337	0.00509	0.004727	211.5
0.02010	0.003065	0.004624	216.3
0.01074	0.001637	0.004552	219.7

Benzil in Ethyl Alcohol.

Substance in 1 g. alcohol.	Mol. per mol.	η_{40}° .	φ_{40}° .
0.04717	0.01934	0.008723	114.6
0.03824	0.008383	0.008659	115.5
0.02574	0.005642	0.008566	116.7
0.01206	0.002644	0.008472	118.0

The variation of the viscosity with the concentration of those solutions of which the measurements were made at 15° and of the urea solutions at 40° is shown in the form of curves in Fig. 3.

These curves show that each solute affects the viscosity of both alcohols in a very similar manner. The steepness of the curve depends obviously on the solvation of the solute. Lithium chloride combines to a considerable extent with the alcohols and its curves are therefore the most inclined, potassium iodide which combines to a less extent gives curves of intermediate slope, while the curves of benzil and urea which do not combine with the solvent to any extent are quite flat. Of course also, in the case of the first two solutes besides combination with the solvent, ionization takes place, which renders interpretation of the results more difficult.

According to Bousfield¹ the viscosity of a solution is proportional to the radiations of the different substances composing the solution. By radiation he denotes the average molecular radius of a given species of molecules, as, for example, those of water, in the forms of hydrol, dihydrol and trihydrol. His expression for the viscosity is then, $\eta = C_1 B_1 r_1 + C_2 B_2 r_2 + \text{etc.}$ in which $C_1, C_2, \text{etc.}$, are constants and $B_1, B_2, \text{etc.}$, are the volume fractions occupied by a set of molecules whose radiations are $r_1, r_2, \text{etc.}$, respectively. Now in aqueous solution, on account of the association of the solvent, the value of r may undergo great changes due to the action of the solute on the three kinds of water molecules. The alcohols are less associated than water, and consequently one might expect a solute to have less effect in altering the average molecular size, that is, in altering their radiations. This being the case, the change in

¹ *Phil. Trans., (A)* 206, 134 (1906), and also *J. Chem. Soc.*, 107, 1781 (1915).

viscosity of a given solution with the concentration should depend more upon the solute and its changes in solvation and ionization than upon the solvent; and this is what the curves of Fig. 3 seem to show. In aqueous solution these solutes have a very different effect upon the viscosity.

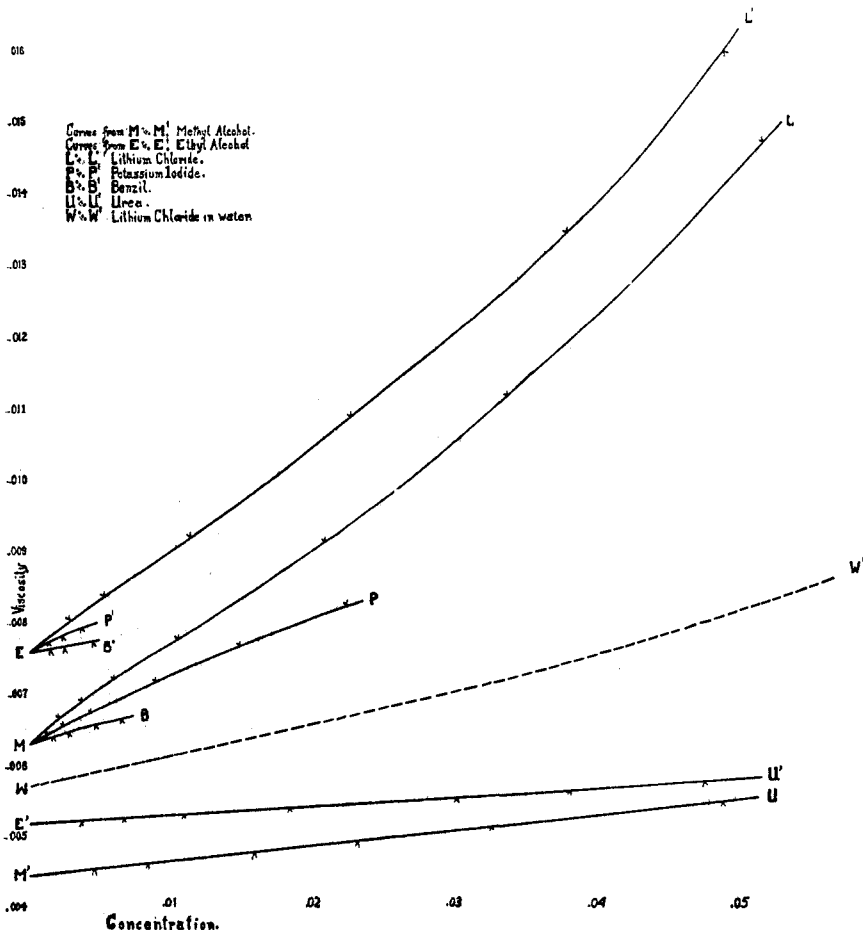


Fig. 3.—The scale of viscosities is that of the solutions in methyl alcohol. In order to show the results in ethyl alcohol solution on the same diagram, the viscosities of such solutions have been halved and then 0.001 added. This last was done so that the curves would not be superimposed upon those of the methyl alcohol solutions. For example, the viscosity of pure ethyl alcohol at 15° is 0.01317; one-half of this is 0.00659, and adding 0.001 we obtain 0.00759, which is the point E in the left-hand margin. All ordinates for the ethyl alcohol solutions were obtained in the same manner.

As is well known, potassium iodide and a number of other salts of caesium, rubidium, potassium and ammonium, when dissolved in water, yield solutions with negative viscosities, and also the viscosity curve of lithium

chloride in water¹ (shown as a dotted line in Fig. 3) is very unlike the ones here obtained when it is dissolved in alcohols.

The viscosity of a solution is a resultant of a number of forces, of which one of the principal is the same as that which determines the vapor tension. Vapor tension is due to the motion of the molecules of a liquid and the consequent escape of some of them from the surface of the liquid into the vapor state; and in general the more viscous a liquid the less is its vapor tension. The expression, $p - p_1/pc$, that is, the relative lowering of the vapor pressure divided by the concentration is a characteristic constant for solutions. It is known that the similar expression for the viscosity, *viz.*, $\eta' - \eta/\eta c^2$ is not characteristic of aqueous solutions. However, for the reasons advanced above, in the case of alcoholic solutions such an expression might be constant and might show some relation to the vapor-pressure lowering constant. To test this these two expressions have been evaluated for the alcoholic solutions considered in this paper in so far as vapor-pressure measurements are available. The results are shown in Table VI.

The fluidity of a solution has sometimes been found to be more intimately related to certain other of its physical properties than has the viscosity. Consequently for the solutions of lithium chloride in the alcohols the numerical values of the expression $\varphi - \varphi'/\varphi c$ are given also. It is seen, however, that these values are not so constant as those under the similar expression for the viscosity, and hence space will not be consumed in giving these values for the remainder of the solutions. The vapor pressures of the lithium chloride, potassium iodide and benzil solutions are taken from the work of Tower and Germann,³ and of the urea solutions from the work of Price.⁴ In the former case the viscosities have been read off from the curves of Fig. 3, at the concentrations at which the vapor pressures were measured, and in the latter case the reverse method has been employed, that is, the vapor pressures have been taken from Price's curves at the concentrations at which the viscosities were determined. The values of the viscosity are not repeated in the following table unless they are interpolated values not previously given. The viscosity, η , of the pure alcohols will be found in the previous tables. The following are the values used for p , the vapor pressure of the pure solvents:

Methyl alcohol, 15°, 73.61 mm.	Ethyl alcohol, 40°, 134.95 mm.
Ethyl alcohol, 15°, 32.18 mm.	Ethyl alcohol, 50°, 224.8 mm.

The concentration c is expressed in mols per mol, and the temperature is 15° unless indicated otherwise by a subscript.

¹ Data from Hosking, *Phil. Mag.*, [6] 7, 472 (1904).

² In this expression η' is the viscosity of the solution and η that of the pure alcohol.

³ *Loc. cit.*, pp. 2454-5.

⁴ *Ibid.*, pp. 191-3.

TABLE VI.

Solute: Lithium Chloride.

Solvent: Methyl Alcohol.

Solvent: Ethyl Alcohol.

<i>c.</i>	<i>p'</i>	η'	$\frac{p-p'}{pc}$	$\frac{\eta'-\eta}{\eta c}$	$\frac{\varphi-\varphi'}{\varphi c}$	<i>c.</i>	<i>p'</i>	η'	$\frac{p-p'}{pc}$	$\frac{\eta'-\eta}{\eta c}$	$\frac{\varphi-\varphi'}{\varphi c}$
0.04103	67.85	0.01250	1.91	24.1	12.1	0.04156	30.385	0.02632	1.34	24.0	12.0
0.03150	69.27	0.01082	1.87	22.9	13.3	0.02268	31.0215	0.01974	1.59	22.0	14.7
0.02032	70.950	0.00905	1.78	22.1	15.0	0.01875	31.4262	0.01854	1.26	21.8	15.5
0.01298	71.870	0.00807	1.82	21.8	17.0	0.01289	31.6930	0.01687	1.18	21.8	17.0
0.00724	72.6035	0.00733	1.88	22.8	19.6	0.01024	31.8403	0.01618	1.03	22.3	18.2
0.00468	73.0229	0.00700	1.70	24.1	21.5						
0.00185	73.4652	0.00665	1.06	30.9	28.9						

Solute: Potassium Iodide.

Solvent: Methyl Alcohol.

<i>c.</i>	<i>p'</i>	η'	$\frac{p-p'}{pc}$	$\frac{\eta'-\eta}{\eta c}$	<i>c.</i>	$\frac{\eta'-\eta}{\eta c_{25}^{\circ}}$	$\frac{\eta'-\eta}{\eta c_{40}^{\circ}}$
0.02444	70.692	0.00837	1.62	13.5
0.01489	71.830	0.00769	1.62	14.9
0.00942	72.487	0.00721	1.62	15.5	0.01885	11.95	11.70
0.00630	72.812	0.00693	1.72	16.2	0.01358	12.36	12.33
0.00333	73.187	0.00665	1.73	17.2	0.006933	12.93	12.48
0.00115	73.456	0.00647	1.76	24.0	0.003445	13.61	13.08

Solute: Potassium Iodide.

Solvent: Ethyl Alcohol.

<i>c.</i>	<i>p'</i>	η'	$\frac{p-p'}{pc}$	$\frac{\eta'-\eta}{\eta c}$	<i>c.</i>	$\frac{\eta'-\eta}{\eta c_{40}^{\circ}}$
0.00463	31.9903	0.01399	1.27	13.5
0.00275	32.0673	0.01372	1.27	15.2
0.00170	32.1172	0.01355	1.15	17.0

Solute: Benzil.

Solvent: Methyl Alcohol.

0.00558	73.278	0.00662	0.81	9.4	0.00835	11.3
0.00479	73.290	0.006595	0.91	10.1	0.00509	11.8
0.00315	73.418	0.006505	0.83	10.8	0.003065	12.0
0.00161	73.510	0.00640	0.84	10.9	0.001637	12.6

Solute: Benzil.

Solvent: Ethyl Alcohol.

0.00619	31.992	0.01339	0.99	2.70	0.01034	3.94
0.00338	32.061	0.01332	1.09	3.37	0.008383	3.94
0.00175	32.121	0.01325	1.05	3.47	0.005642	3.89
...	0.002644	4.06

Solute: Urea.

Solvent: Methyl Alcohol.

Solvent: Ethyl Alcohol.

<i>c.</i>	$\frac{\eta'-\eta}{\eta c_{25}^{\circ}}$	$\frac{\eta'-\eta}{\eta c_{40}^{\circ}}$	<i>c.</i>	p'_{40}°	$\frac{p-p'}{pc_{40}^{\circ}}$	$\frac{\eta'-\eta}{\eta c_{40}^{\circ}}$	<i>c.</i>	$\frac{\eta'-\eta}{\eta c_{25}^{\circ}}$	p'_{50}°	$\frac{p-p'}{pc_{50}^{\circ}}$	$\frac{\eta'-\eta}{\eta c_{50}^{\circ}}$
0.04882	4.33	4.74	0.04875	126.8	1.24	2.97
0.03258	5.07	4.78	0.03804	128.6	1.24	2.95	0.03641	3.63	214.5	1.26	2.81
0.02312	5.17	4.89	0.03005	130.3	1.23	2.95	0.02425	3.64	217.74	1.27	2.90
0.01592	5.06	5.06	0.01836	132.2	1.10	2.99	0.01098	3.48	221.81	1.21	3.38
0.008355	5.38	5.45	0.01095	133.5	0.98	2.89	0.00567	3.69	222.84	1.50	3.11
0.004636	5.55	4.74	0.00666	2.87

Considering first the observations at 15°, it is seen that the value of the expression $\eta' - \eta/\eta c$ is a constant for any one substance within the limits of error of the measurements. To avoid frequent circumlocution this will be termed the "viscosity constant," and for the same reason the expression $p - p'/pc$ will be known as the "vapor-pressure constant." The former does not vary much with the nature of the alcohol except in the case of benzil, where it has a much greater value in methyl alcohol than in ethyl. In connection with the calculations of the molecular weights from the lowering of the vapor pressure it was remarked: "The molecular weight of benzil in ethyl alcohol seems to be normal, while in methyl alcohol it seems to be associated with one or two molecules of the solvent."¹ This would account for the abnormally large value of benzil's viscosity constant in methyl alcohol (it is not only much larger than that of benzil in ethyl alcohol, but also than that of urea in either of the alcohols), for the more a solute combines with the solvent the greater is this constant. This is shown by its large value in the lithium chloride solutions. In the potassium iodide solutions the value is smaller, but still considerably greater than in the non-solvated urea solutions. The vapor-pressure constant varies in the same order with the solvation of the solute, but to a much less degree. There is therefore only the most general sort of a parallelism between the two constants.

The values of these constants at other temperatures than 15° illustrates the effect of change of temperature upon them. As is well known, Babo's law states that the relative lowering of the vapor pressure of a solution at any given concentration is independent of the temperature, and this has recently been confirmed by Price, that is the expression $p - p'/pc$ would be constant at different temperatures, which is seen to be true. As to the viscosity constant, it shows but little variation with the temperature. As far as these results are concerned it is apparently constant for moderate changes of temperature. However, the data here are too meagre to warrant a sweeping statement.

In a recent paper by Jones and associates,² the opinion is expressed that the negative viscosity exhibited by some salts of caesium, rubidium, potassium and ammonium in certain solvents depends, among other things, on the association of the solvent. No negative viscosities were found for any of the solutions of these salts in formamid, and they therefore conclude that this is due to a certain extent to the high association of this solvent. It is, however, so far as has been investigated, only in water and glycerol of the pure solvents that these salts yield negative viscosities. No such negative viscosities have been observed in pure

¹ Tower and Germann, *loc. cit.*, p. 2456.

² *Pub. Carnegie Inst.*, 230, p. 36.

methyl or ethyl alcohol nor in acetone. The association factors of these liquids are

Formamid,	6.18	Ethyl alcohol,	2.74
Water,	3.81	Glycerol,	1.80
Methyl alcohol,	3.43	Acetone,	1.26

The phenomenon of negative viscosity in these solvents has nothing apparently in common with the order of these numbers, and until a great deal more data are at hand it will be impossible to show what the influence of the solvent is upon it.

With regard to the nature of the solute, the theory of Jones and Veazey¹ seems plausible, that is, that it is due to the large molecular volume of this component of the solution.

In the paper to which reference has just been made a number of viscosity measurements of salts in formamid at 15°, 25° and 35° are reported.² Unfortunately, the concentrations are expressed in volume normal terms and no densities are given, so that direct comparison with the results of this paper can not be made. However, values of the expression $\eta' - \eta/\eta c'$ in which c' is the volume normal concentration, can be calculated; and such values, though not exactly proportional to the values of the expression used above, will enable one to form some idea of its constancy. I have made this calculation for a number of salts at different temperatures, and find the numbers so obtained to be approximately constant for the same salt and to be smaller for salts like CsNO₃ and N(C₂H₅)₄I, which are not solvated, than for salts like NaI and LiNO₃, which probably do combine more or less with the molecules of the solvent. At different temperatures the values are usually a little less at 35° than at 15°, but this is not always the case. In these formamid solutions the viscosity was determined only at three concentrations (sometimes only two), hence the data are rather insufficient for any broad generalization. Furthermore, all of the solutes employed were electrolytes. Simpler relations might be found to hold if non-electrolytes were used. Additional information regarding the points discussed in this paper could probably be obtained by measuring the viscosity of solutions in a non-associated solvent. The author expects to take up such an investigation at an early date.

Summary.

(1) The viscosity of very pure samples of methyl and ethyl alcohols has been determined, and also that of mixtures of these substances with small proportions of water.

(2) The viscosity of solutions of a number of typical solutes in these alcohols has been measured, and the value of the expression $\eta' - \eta/\eta c'$

¹ *Am. Chem. J.*, **37**, 405 (1907).

² Jones and associates, *Pub. Carnegie Inst.*, **230**, p. 16.

has been compared with that of $p - p'/pc$, obtained from former vapor-pressure determinations.

(3) This "viscosity constant" increases with the solvation of the solute, and for the solutions here investigated seems to be almost independent of changes of temperature.

(4) So-called "negative viscosity" is discussed in the light of the results here obtained and also in the light of those obtained by Jones and associates with solutions in formamid and in other solvents.

CLEVELAND, OHIO.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, No. 261.]

THE PROPERTIES OF MIXED LIQUIDS. II. PHENOL-WATER AND TRIETHYLAMINE-WATER MIXTURES.

By J. LIVINGSTON R. MORGAN AND GUSTAV EGLOFF.

Received February 3, 1916.

The object of this paper is to report the results of the study of two typical, so-called, "mutually soluble" liquid mixtures in a large number of concentrations, and at temperatures lying both above and below the critical solution point, not only from the point of view of surface tension, but also of some other physical properties.

The tip used to determine the surface tension, by aid of the drop-weight method, was standardized¹ by the use of both benzene and water, with the following result, each drop-weight value being the mean of at least three results agreeing to within a few hundredths of one per cent.:

TABLE I.—STANDARDIZATION OF TIP.

Liquid.	<i>t</i> .	Wt. 1 drop. (Mg.). <i>w</i> .	Surface tension (dynes). γ .	Constant (= γ/w).
Benzene.....	30°	28.352	26.625	0.9391
Water.....	30°	75.680	71.033	0.9386
Average.....				0.9389

To find the surface tension of any liquid in dynes per centimeter, from the drop weight in milligrams, at the same temperature, from this tip, we have, then,

$$\gamma_{l,t} = 0.9389 \times w_{l,t}.$$

And since the specific cohesion (a^2) is related to surface tension, through the density, by the equation $a^2 = 2\gamma_t/9.80 d_t$, we have, substituting for γ , its value in terms of w ,

$$a_{l,t}^2 = 2 \times 0.9389 \times w_{l,t}/9.80 d_{l,t} = 0.1916 \times w_{l,t}/d_{l,t},$$

so that from the drop weight and the density we can also calculate the value of the specific cohesion for any liquid, at any temperature.

¹ See Morgan, THIS JOURNAL, 37, 1462 (1915).