VII.—*The Viscosity of Liquid Mixtures.*

By ALBERT ERNEST DUNSTAN and ROBERT WILLIAM WILSON.

IN the two previous parts of this series, the viscosity concentration curves of various liquid mixtures have been investigated, and it has been shown that these curves could be divided into three classes :

(i) Those approximately obeying the law of mixtures, being concave to the axis of percentage composition, and having the greatest divergence from normal at some point of simple molecular concentration.

(ii) Those exhibiting definite maxima at points corresponding with mixtures of simple molecular composition. Nearly all experimental work in this class has been done with aqueous solutions, and a great volume of evidence points to the conclusion that in such mixtures the formation of hydrates is always existent, producing groups of complexes in dynamic equilibrium even when definite compounds cannot actually be isolated.

(iii) Those exhibiting minima which also are to be found at points of simple molecular composition.

In general, these liquid pairs which are made up of unimolecular non-associating components give viscosity concentration curves which, although frequently near the normal, yet sometimes diverge considerably from it.

In the present communication, a brief account is given of certain empirical relationships which hold good for these viscosity concentration curves (*Zeit. physikal. Chem.*, 1906, **56**, 370), and further

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experimental results in the shape of a curve for mixtures of water and sulphuric acid are adduced.

It has been laid down in previous papers that increase in the viscosity coefficients implied increase in the masses of the colliding slipping particles whether they be simple molecules or loosely held complexes. Whereas, on the one hand, carbon disulphide, ether, the paraffins and other simple unimolecular liquids are mobile, the alcohols and acids are more viscous, glycol and glycerol notably so, whilst the comparatively enormous molecular masses of the jellies and colloids attain an almost infinite viscosity.

A decrease in viscosity similarly may imply a decrease in complexity or the disintegration of the molecular groupings in solution, and this phenomenon is sometimes observed even when a more viscous compound is added to one of less viscosity.

The experimental data in this work have been obtained in the same manner as in previous papers. The sulphuric acid was kindly supplied in considerable quantity by Dr. Messel, to whom we are glad of this opportunity of expressing our gratitude.

The two specimens of this acid which we obtained were of special purity. The strength was determined by titration of the diluted acid, by conversion into barium sulphate, and from the density, using Pickering's tables (Trans., 1890, **57**, 64).

Analysis of the first specimen :

$$\left.\begin{array}{lll}\text{By density} \ldots\ldots\ldots & H_2SO_4 = 99{\cdot}5 & \text{per cent.} \\ \text{By titration}\ldots\ldots\ldots & H_2SO_4 = 99{\cdot}2 & ,, \\ \text{Gravimetrically} \ldots & H_2SO_4 = 99{\cdot}57 & ,, \end{array}\right\}$$

The second specimen gave as average of density determinations :

$$H_2SO_4 = 99{\cdot}924 \text{ per cent.}$$

The water used was redistilled from alkaline permanganate and kept in well-stoppered Jena flasks. A large stock of 50 per cent. acid was made, and this served for the middle determinations by addition either of water or acid. The strengths of the solutions were determined mainly by Pickering's tables of density ; frequent checks were made by titration and also by gravimetric analysis.

The following table gives the percentage composition of the solutions, the density and the viscosity coefficients. These data are plotted on the accompanying curve (Fig. 1) :

H_2SO_4 per cent.	Density.	Viscosity.	H_2SO_4 per cent.	Density.	Viscosity.
99·924	1·82714	1·06160	81·086	1·73197	0·83452
97·513	1·83171	0·85761	80·243	1·72287	0·78099
95·723	1·82986	0·83255	79·838	1·71844	0·60272
93·410	1·82348	0·84211	79·528	1·71484	0·74084
92·300	1·81930	0·85088	78·242	1·70030	0·67228
91·363	1·81476	0·87158	76·271	1·67756	0·57396
90·437	1·80982	0·88508	74·746	1·65976	0·53603
89·575	1·80525	0·95132	70·519	1·61049	0·40095
88·733	1·79985	0·91588	69·205	1·59488	0·36450
88·001	1·79522	0·92568	67·209	1·57236	0·32322
86·865	1·78650	0·93366	64·643	1·54331	0·28042
86·979	1·78737	0·93527	58·356	1·47457	0·20568
85·070	1·77160	0·94794	51·640	1·40596	0·15370
84·970	1·77074	0·92966	49·858	1·38857	0·14706
84·280	1·76447	0·92529	43·234	1·32691	0·11293
83·980	1·76069	0·91010	36·427	1·26759	0·09239
83·401	1·75588	0·90866	26·492	1·18630	0·07119
82·580	1·74750	0·89842	15·699	1·10413	0·05851
82·210	1·74384	0·86571	0	0·99717	0·00891
81·544	1·73719	0·83108			

FIG. 1.

Percentage H_2SO_4.
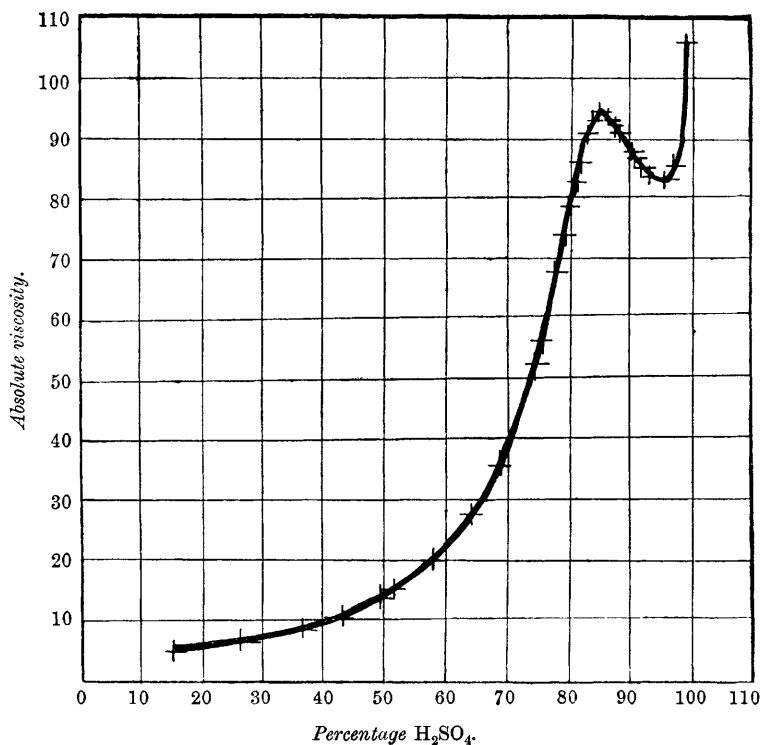
In a useful summary of work done on the question of the molecular constitution of solutions of sulphuric acid, Burt (Trans., 1904, **85**, 1351) points out that the conclusion that combination takes place in such solutions with the formation of complexes had been arrived at mainly by cryoscopic methods.

Pickering (Trans., 1890, **57**, 64, 331), in his classical investigation on this subject, brings forward indisputable evidence as to the existence of such complexes, an existence which in the case of some he proves by their actual isolation. With respect to density determinations, Pickering quotes Mendeléeff's experimental curves (*Zeit. physikal. Chem.*, 1887, **1**, 275 ; see also Crompton, Trans., 1888, **53**, 116) in which after differentiation the following hydrates were deduced : H_2SO_4,H_2O, $H_2SO_4,2H_2O$, $H_2SO_4,6H_2O$, $H_2SO_4,150H_2O$.

Pickering's own curve after a similar process afforded seventeen straight lines equivalent to a complex first curve of seventeen parabolic components, which the author considered as the density curve of seventeen hydrates in solution. From the contractions on mixing, similar discontinuous sections identical with the above were found.

He investigated Kohlrausch's conductivity curves, which gave five hydrates, and obtained the same results.

Jones (*J. Amer. Chem. Soc.*, 1894, **16**, 1), by investigating the lowering of the freezing point of acetic acid by sulphuric acid, claimed to have proved the existence of H_2SO_4,H_2O and $H_2SO_4,2H_2O$ in solution. That the former hydrate is capable of existence and isolation is no longer doubted.

Pictet (*Compt. rend.*, 1894, **119**, 642) obtained, by the cryoscopic method, maximum and minimum points corresponding with H_2SO_4,H_2O, $H_2SO_4,2H_2O$, and others.

Ramsay and Shields (Trans., 1894, **65**, 179) found that the constant boiling liquid $12H_2SO_4,H_2O$ had an abnormally high molecular weight and concluded that complexes had been formed.

Graham's work (*Phil. Trans.*, 1846, *A*, 513 ; 1861, 373) on solutions of sulphuric acid and water brought out quite clearly the maximum at 85·1 per cent. of the acid corresponding with H_2SO_4,H_2O ; the remainder of the curve on both sides of this point is quite normal.

Burt's own conclusions (*loc. cit.*) drawn from his results on the vapour pressures of sulphuric acid solutions are of great interest ; he points out that :

(1) The molecular weights calculated from the vapour pressures never rise above 32·7.

(2) The molecular weights usually lie below 32·7, increase with temperature, and decrease with greater concentration.

(3) Inversion points are of frequent occurrence in the curves of

molecular weight × temperature. He concludes that complexes are formed, but finds no evidence for the existence of definite hydrates.

Knietsch (*Ber.*, 1901, **34**, 4069) made an elaborate investigation of these mixtures, using not only determinations of viscosity, but also of the melting points, conductivities, and surface tensions.

From the melting-point curve, he deduced the existence of H_2SO_4,H_2O, and H_2SO_4,SO_3 at maxima, and of $2H_2SO_4,H_2O$, $4H_2SO_4,SO_3$, and $H_2SO_4,2SO_3$ at minima.

From the conductivity numbers, he found discontinuities at points corresponding with H_2SO_4,H_2O, and $2H_2SO_4,H_2O$, and at 15 per cent. free SO_3.

The viscosity data show that the effect of adding sulphuric acid to water in gradually increasing amount is to cause an equally gradual increase in the viscosity. The first maximum point is attained at 85 per cent., that is, the "monohydrate," but it is to be noticed that the increase in the viscosity is by no means commensurate with the simple addition of H_2O to H_2SO_4 or of H_2SO_4 to H_2O.

So far as can be seen from the previous work on aqueous solutions, these maxima would more probably correspond to aggregates such as $(H_2SO_4,H_2O)_n$, where "n" may be of considerable magnitude.

As will be noticed in the sequel, a very rough approximation for the addition of CH_2 in an homologous series is 0·001 unit of viscosity. Thus toluene to xylene, methyl to ethyl iodide, hexane to heptane, ethyl bromide to propyl bromide give such increments. Larger increments are found in the alcohol and acid series, but in the case we are considering, the minimum point viscosity is 0·083255, and the maximum point 10 per cent. from it is 0·094794, whilst water is 0·00891. From this maximum, further addition of water reduces the viscosity to a minimum which is located at about 95 per cent.; after this point the viscosity again steadily increases through H_2SO_4 until the second maximum at 50 per cent. free SO_3 (Knietsch, *loc. cit.*), both maxima corresponding with the two maxima of density.

It will be noticed that in the appended curve there is a minimum point at 95 per cent. corresponding with $3H_2SO_4,H_2O$.

A similar minimum point was obtained with mixtures of benzaldehyde and alcohol and with benzene and alcohol. Such a point can be interpreted as being the final result of the fission of sulphuric acid complexes by the water, the fission being complete when the water reaches the above concentration. The addition of more water causes more complex formation until this culminates in the building up of the monohydrate, which, at any rate in solution, may be the first anhydride of ortho-sulphuric acid. The position of this well-known compound is clearly indicated at 85 per cent. No further well-marked discontinuity occurs, at any rate, of the same order as the maximum already quoted.

Possibly more delicate apparatus would indicate such complexes of the "second order." The position of sulphuric acid and its "monohydrate" on the viscosity-molecular weight curves (v.s.) indicates the high degree of association it possesses.

It will be readily seen from what has gone before that little obedience to the mixture law can be expected from two components like sulphuric acid and water, alcohol and benzene, or, in brief, wherever we deal with associated substances, and it is because of this reciprocal action of one on the other that all attempts to investigate these effects have failed. The formula given by Lees (*Phil. Mag.*, 1901, [vi], **1**, 128), $\eta^n = v_1 \eta_1{}^n + v_2 \eta_2{}^n$, where "$n$" is a constant for the liquid pair, η, η_1, and η_2 the viscosity coefficients for the mixture, and the two components respectively, and $v_1 v_2$ the relative volume of the two components, fits in most closely with observed facts ; at the same time it should be noticed that this can scarcely be described as a mixture law which has to be qualified in each case.

Several regularities have been met with in the course of this investigation, especially in connexion with unimolecular liquids.

A. *Connexion between Molecular Weight and Angle between Tangent to Curve and Axis of Viscosity.*

In any of the previously given curves (Trans., 1904, **85**, 817 ; 1905, **87**, 11) let tangents be drawn at the point where the curve meets the viscosity axis.

Let a be the angle between the tangent and the viscosity axis.

Then a is connected with the molecular weight of the liquid in question, as follows :

TABLE I.

Solution in benzene.	Mol. wt.	a.	Product.	Solution in alcohol.	Mol. wt.	a.	Product.
Carbon tetrachloride.	154	52	7·9	Carbon disulphide.	76	128	9·73
Toluene	92	93	8·55	Mercaptan	62	148	9·17
Ethyl acetate	88	94	8·27	Acetone	58	100	5·8
Carbon disulphide	76	105	7·98	Benzene	78	48	3·72
Ethyl ether	74	102	7·55	Benzaldehyde	106	62	6·57

It is to be noticed that the last three alcoholic solutions give abnormal experimental results, in that minima or exceptionally sagged curves are shown.

If such behaviour indicates dissociation, then the associated benzaldehyde and benzene having a greater molecular mass than normal would, as shown in the sequel, give a steeper curve and a smaller angle a. In all cases examined, the viscosity concentration curves are parabolic, and can be fairly represented by

$$x = ay^2 + by + c,$$

$$\text{therefore } \frac{dx}{dy} = Ky + M,$$

hence a relation exists between the tangent of a and y, that is, the viscosity coefficient, or, as is shown here, between a and molecular weight.

B. *Connexion between Molecular Weight and Viscosity.*

The following table (Dunstan, *Zeit. physikal. Chem.*, 1905, **51**, 738) further shows the close connexion between molecular weight and viscosity, and also illustrates the great abnormality of the hydroxylated liquids (see Thorpe and Rodger, *Phil. Trans.*, 1897, **185**, *A*, 397):

Liquid.	$\eta/\text{M.V.} \times 10^6$.	Liquid.	$\eta/\text{M.V.} \times 10^6$.
Benzene	65	Water	493
Ethyl acetate	60	Methyl alcohol	138
Ethyl iodide	69	Ethyl ,,	189
Ethyl bromide	51	Propyl ,,	262
Chloroform	67	Allyl ,,	180
Acetone	43	Glycol	2750
		Benzaldehyde	143
		Acetic acid	195
		Lactic ,,	5410

A further relationship may be deduced from the viscosity concentration curves given in previous communications (*loc. cit.*).

Taking again tangents to these curves at the vertical axes and calling the angles between the curve and tangent "b" and "c" respectively, then the following statement holds good. The product of the molecular weight of each liquid with the angle "c" or "b" is constant, for the effect of liquid A on liquid B is measured by the angle "b" and *vice versâ*, the effect of B on A is measured by the angle "c":

TABLE II.

Liquid A.		$/b$.	Liquid B.		$/c$.	$\dfrac{A/c}{B/b} = K$.
Ethyl mercaptan	62	16	Ethyl alcohol	46	13	$\dfrac{806}{736} = 1\cdot09$
Toluene	92	2	Benzene	78	2	$\dfrac{184}{156} = 1\cdot18$
Carbon disulphide	76	2	Methyl iodide	142	4	$\dfrac{304}{284} = 1\cdot07$
Ethyl ether	74	12	Benzene	78	15	$\dfrac{1110}{936} = 1\cdot18$
Carbon disulphide	76	3	Benzene	78	3	$\dfrac{228}{234} = 0\cdot97$
Ethyl acetate	88	13	Benzene	78	12	$\dfrac{1056}{1014} = 1\cdot04$

C. *Relation between Molecular Weight and Viscosity of Series of Compounds.*

An important connexion between these quantities is evidenced when they are plotted as in Fig. 2, log. viscosity against molecular weight. It will be seen that the various members of a chemical series lie on the same curve. The viscosity-molecular weight curves are parabolic. The

Fig. 2.
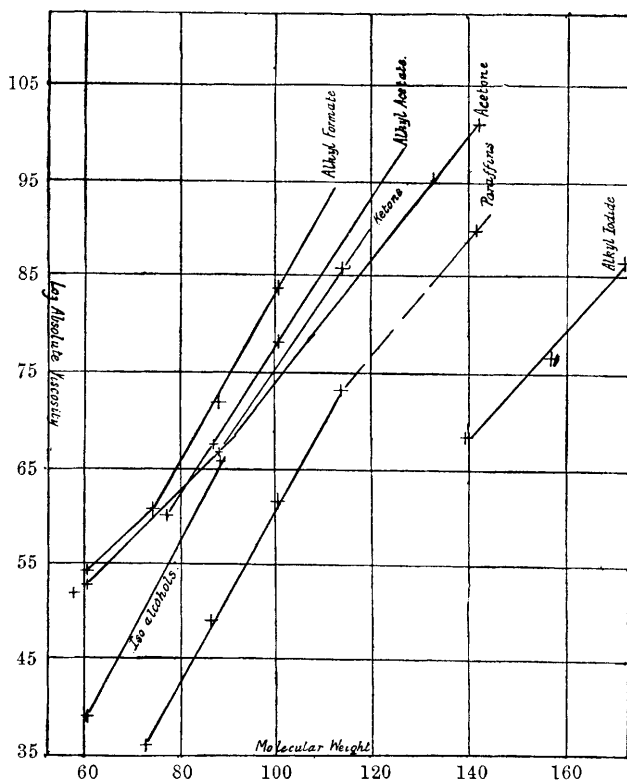
simple esters lie closely together, and there is a similar proximity between the symmetrical and asymmetrical ketones. Chloroform is placed near the paraffins. The paraffins investigated by Thorpe and Rodger lie almost on a straight line; other available determinations show a considerable want of agreement with these and with themselves.

It is to be noticed that the first members of each series diverge more or less from the logarithmic line and behave as though they had a

larger molecular weight than normal (see also, for this association of the early members of homologous series, Ramsay and Shields, Trans., 1893, **53**, 1101).

Benzene also occupies an anomalous position, giving evidence of considerable association (nearly 110 mol. wt.).

Fig. 3 shows the logarithmic curves for the acids and alcohols. The two curves are very similar and indicate the same inconsistent behaviour of the earliest members ; from the points given by water and formic acid the curves follow almost parallel to each other. A con-

FIG. 3.
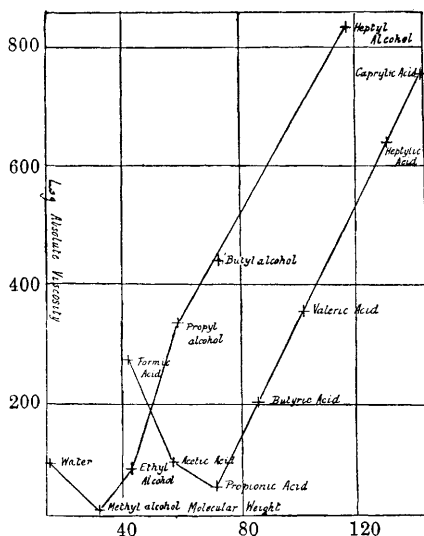
sideration of these curves will show that water behaves as a liquid of molecular weight nearly 50, that is, $(H_2O)_3$, and formic acid nearly 100, that is, $(H \cdot CO_2 H)_2$, assuming that the other members are normal. Hence we may deduce the general law :

$$\gamma = A + B \log. \eta,$$

where γ is the molecular weight, A and B are constants depending on the particular series to which the liquid belongs, and η is the viscosity coefficient.

It will be noticed that B, which measures the slope of the curves, is almost the same in the various series, and has therefore a general nature, A being the specific constant for each family.

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