

On the Viscosities of Mixtures of Liquids and of Solutions

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XXIX. *On the Viscosities of Mixtures of Liquids and of Solutions.* By CHARLES H. LEES, D.Sc.*

IN recent years many determinations of the viscosities of mixtures of liquids and of solutions have been made in the endeavour to discover the law of connexion of the viscosity of a mixture with the relative amounts and viscosities of its constituents. As a result several empirical formulæ have been proposed which represent the observations with more or less accuracy. Of these formulæ, the one first used by Arrhenius in 1887, and since then by Reyer, Wagner, Lauenstein, and Kanitz, for weak salt-solutions or for mixtures of liquids when one liquid is present to the extent of 90 per cent. or more, seems to be the most valuable. According to it the viscosity η at a temperature t , of a mixture which contains in 1 c.c., v_1 c.c. of a liquid of viscosity η_1 , v_2 c.c. of one of viscosity η_2 , &c., at temperature t , is given by the equation

$$\eta = \eta_1^{v_1} \cdot \eta_2^{v_2} \cdot \eta_3^{v_3} \dots$$

or

$$\log \eta = v_1 \log \eta_1 + v_2 \log \eta_2 + v_3 \log \eta_3 + \dots$$

so long as one constituent is present to the extent of 90 per cent. or more. It is the object of the present paper to consider whether this formula can be supported on theoretical grounds, to see how far it agrees with the observed facts for mixtures generally, and if the agreement is unsatisfactory to replace it by a more suitable expression.

To arrive at a theory for mixtures of fluids which have no chemical action on each other, we may suppose the volume of a mixture to be divided into elementary volumes by, say, three series of parallel planes. Each of these elementary volumes we may suppose occupied exclusively by one constituent. The limit of the calculated viscosity of a medium so built up when the elementary parts are taken indefinitely small, may be taken as the viscosity of the mixture.

The fundamental equation of the theory of viscosity of a fluid is $F = \eta \cdot \frac{dv}{dx}$, where dv is the difference of the parallel velocities of two plane layers of fluid situated at a distance dx apart, F is the tangential force transmitted through an

* Read June 8, 1900.

area of 1 sq. cm. between the layers and parallel to them, and η is the viscosity of the fluid.

If the motion throughout the fluid is steady and parallel to the y axis, and there is no variation of it along that axis, the equation

$$\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial z^2} = 0 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

must hold throughout the fluid. At a surface of separation of two fluids of viscosities η_1 and η_2 , if there is neither chemical action nor slipping, we must have

$$v_1 = v_2 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and

$$\eta_1 \frac{\partial v_1}{\partial n} = \eta_2 \frac{\partial v_2}{\partial n} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

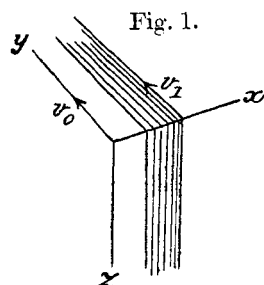
where v_1 and v_2 are the velocities close to the surface in the two fluids, and dn is an element of the normal to the surface. At a solid surface touched by a fluid there must be no relative motion of solid and fluid.

These are the necessary and sufficient conditions for the solution of any "plane" problem on the motion of viscous fluids, and the difficulty of finding a solution in any special case is a mathematical one which increases with the number of different fluids present in the space considered, and the complexity of their lines of separation. We proceed to consider a few simple stable arrangements of the fluids for which the solutions can be readily obtained.

I. Taking the velocity throughout parallel to the y axis, let us assume that it is independent of z , equal to v_0 throughout the plane $x = x_0$, and to v_1 throughout the plane $x = x_1$, and that the surfaces of separation of the various fluids present between those planes, are the planes $x = x_2, x_3$, &c.

If there are only two fluids of viscosities η_1 and η_2 present in equal volumes (fig. 1), the equations (1), (2), and (3) above, give for the viscosity η of the mixture,

$$\frac{1}{\eta} = \frac{1}{2} \left(\frac{1}{\eta_1} + \frac{1}{\eta_2} \right).$$



If each c.c. of the mixture contains v_1 c.c. of the first medium and v_2 of the second, then

$$\frac{1}{\eta} = \frac{v_1}{\eta_1} + \frac{v_2}{\eta_2}.$$

In the general case where v_1, v_2, v_3 , &c. c.c. of the constituents η_1, η_2, η_3 , &c. are present in 1 c.c. of the mixture

$$\frac{1}{\eta} = \frac{v_1}{\eta_1} + \frac{v_2}{\eta_2} + \frac{v_3}{\eta_3} + \dots$$

This result is independent of the number of layers of each constituent present. In the tables which follow it will be referred to as the "mobility formula."

II. Making the same assumptions as to the velocities, but taking the planes separating the fluids as $z = z_0, z_1, z_2$, &c., if the fluids are present in equal volumes (fig. 2) we have

$$\eta = \frac{1}{2}(\eta_1 + \eta_2);$$

if 1 c.c. contains v_1 volumes of the first and v_2 of the second

$$\eta = v_1\eta_1 + v_2\eta_2,$$

and in the general case

$$\eta = v_1\eta_1 + v_2\eta_2 + v_3\eta_3 + \dots$$

A result again independent of the number of layers of each constituent present. In the following pages this will be referred to as the "viscosity formula."

III. Thirdly, let there be two systems of separating planes mutually perpendicular to each other.

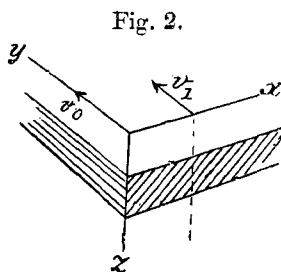
If there are two fluids of viscosities η_1, η_2 present in equal volumes, distributed as shown in fig. 3, or in fig. 4, the solution of the equations (1), (2), (3) above, for this case gives for the viscosity η

$$\log \eta = \frac{1}{2}(\log \eta_1 + \log \eta_2).$$

If 1 c.c. of the mixture contains v_1 c.c. of the η_1 and v_2 c.c. of the η_2 constituent

$$\log \eta = v_1 \log \eta_1 + v_2 \log \eta_2.$$

For a mixture containing in 1 c.c. v_1, v_2, v_3 , &c. c.c. of media



of viscosities η_1, η_2, η_3 , &c.*

$$\log \eta = v_1 \log \eta_1 + v_2 \log \eta_2 + v_3 \log \eta_3 + \dots$$

This result is independent of the number of the elementary prisms of each constituent present. In the tables which follow this will be referred to as the "logarithmic formula."

Fig. 3.

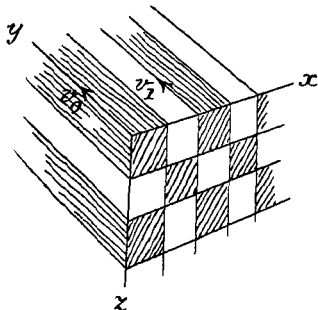
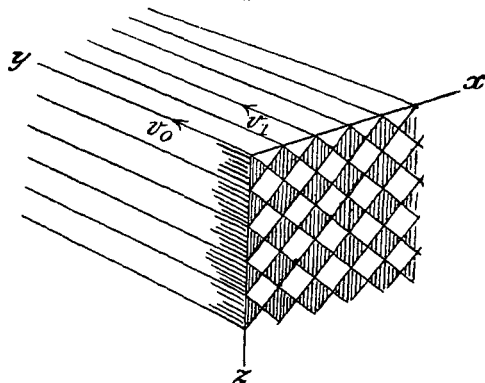


Fig. 4.



The number of mixtures of liquids, of which the viscosities have been observed and are available for comparison with the results of theory, is small, and some of them, for which the observed values of the viscosities do not fall within those of the constituents, *e.g.* mixtures of water and alcohols or certain acids †, are seen to be outside the limits of the above theory. Of the rest some, *e.g.* chloroform or carbon bisulphide and ether ‡, have points of inflection on the curve connecting viscosity and constitution, and of such singularities none of the above formulæ can take account. The conclusion may at once be drawn that the viscosity of a mixture of liquids is in general not dependent solely on the viscosities and amounts of the constituents present, but is influenced by some other action of which none of the above theories takes account. Notwithstanding this fact, it may be of use in the case of mixtures in which the action of this unknown disturbing effect appears to be least, to compare the values given by the three

* Lees, *Phil. Mag.* xlix. p. 225 (1900).

† Wijkander, *Wied. Ann. Beibl.* iii. p. 8 (1879); Thorpe & Rodger, *J. Chem. Soc.* lxxi. p. 367 (1897).

‡ Traube, *Ber. Chem. Ges.* xix. p. 871 (1886); Pagliani & Battelli, *Ann. R. Ist. Torino*, xiii. p. 37 (1885).

formulae with those found by experiment; and in the following Tables these observed values are compared with the values calculated from the recorded percentage compositions by weight, and the densities, on the assumption that no contraction occurs on mixing.

THORPE AND RODGER'S EXPERIMENTS*.

Carbon Tetrachloride and Benzine, at 60° C.

Per cent. Benzine.		Viscosity.						
Weight.	Volume.	Observed	Calculated.					
			Viscosity formula.	p.cent. error.	Logarithmic formula.	p.cent. error.	Mobility formula.	p.cent. error.
0	0	·00582						
22·4	34·0	503	·00517	+3	·00508	+1	·00497	-1
43·8	58·5	456	470	3	463	2	452	-1
67·7	79·2	422	431	2	425	1	420	-1
100	100	391						

Methyl Iodide and Carbon Bisulphide, at 0° C.

Per cent. Bisulphide.									
0	0	·00592							
21·6	33·2	518	·00538	+4	·00532	+3	·00526	+1	
38·8	53·4	482	504	5	498	3	490	2	
48·1	62·5	469	489	4	484	3	478	2	
68·1	79·4	449	461	3	458	4	454	1	
82·4	89·4	438	445	2	444	1	442	1	
100	100	429							

The character of the results is unaltered if the comparison is made with the values given by Thorpe and Rodger for other temperatures.

* Journ. Chem. Soc. lxxi. p. 360 (1897).

LINEBARGER'S EXPERIMENTS*.

Ethyl Ether and Benzine, at 25° C.

Per cent. Benzine.		Viscosity.						
Weight.	Volume.	Observed	Calculated.					
			Vis. formula.	p. cent. error.	Log. formula.	p. cent. error.	Mob. formula.	p. cent. error.
0	0	·00230						
28·6	25·2	282	·00323	+18	·00293	+4	·00273	-3
56·9	52·6	362	424	17	380	5	340	6
75·7	72·4	438	497	14	459	5	415	5
100	100	599						

Carbon Bisulphide and Benzine, at 25° C.

Per cent. Benzine.								
0	0	·00358						
8·9	12·2	376	·00387	+3	·00380	+1	·00377	0
34·9	43·3	416	462	4	447	0	433	-3
75·9	81·7	544	555	2	545	0	535	-2
100	100	599						

Nitrobenzine and Benzine, at 25° C.

Per cent. Benzine.								
0	0	·001834						
14·4	18·8	1417	·001602	+13	·001486	+5	·001323	-7
37·6	45·2	1017	1277	25	1104	8	950	6
80·1	84·6	681	790	16	711	4	668	2
100	100	599						

* Amer. Journ. Sc. ser. 4, vol. ii. p. 331 (1896).

Linebarger's Experiments (*continued*).

Ethyl Benzoate and Toluene, at 25° C.

Per cent. Toluene.		Viscosity.						
Weight.	Volume.	Observed	Calculated.					
			Vis. formula.	p. cent. error.	Log. formula.	p. cent. error.	Mob. formula.	p. cent. error.
0	0	·01954						
15·3	18·1	1495	·001598	+7	·001549	+4	·001324	-1
47·3	52·4	939	1223	30	995	6	822	12
76·2	79·6	679	827	22	701	3	632	7
100	100	539						

Turpentine and Toluene, at 25° C.

Per cent. Toluene.								
Weight.	Volume.	Observed	Vis. formula.	p. cent. error.	Log. formula.	p. cent. error.	Mob. formula.	p. cent. error.
0	0	·01343						
6·8	6·8	1192	·001288	+8	·001262	+6	·001219	+2
20·65	20·7	973	1177	20	1112	14	1026	5
53·7	53·8	701	911	30	822	17	745	6
75·1	75·1	607	739	21	678	12	633	4
100	100	539						

Acetic Ether and Nitrobenzine, at 25° C.

Per cent. Nitrobenzine.								
Weight.	Volume.	Observed	Vis. formula.	p. cent. error.	Log. formula.	p. cent. error.	Mob. formula.	p. cent. error.
0	0	·00434						
22·9	18·1	582	·00687	+18	·00562	-3	·00504	-13
56·1	48·8	889	1117	26	875	2	692	22
75·5	69·7	1204	1410	17	1183	2	928	15
100	100	1834						

Linebarger's Experiments (*continued*).
Carbon Bisulphide and Toluene, at 25° C.

Per cent. Toluene.		Viscosity.						
Weight.	Volume.	Observed	Calculated.					
			Vis. formula.	p. cent. error.	Log. formula.	p. cent. error.	Mob. formula.	p. cent. error.
0	0	·00358						
7·3	10·3	370	·00377	+2	·00373	+1	·00372	+1
40·0	48·5	417	447	7	438	5	429	3
63·2	71·5	469	489	4	481	3	472	1
100	100	541						

Carbon Bisulphide and Ether, at 25° C.

Per. cent. Ether.									
0	0	·00358							
13·1	21·1	338	·00331	-2	·00326	-4	·00321	-5	
34·4	48·2	306	296	3	289	6	282	8	
62·8	75·0	269	262	3	257	5	253	6	
100	100	230							

Chloroform and Carbon Tetrachloride, at 25° C.

Per cent. Carb. Tetrachl.									
0	0	·00540							
19·3	18·2	569	·00602	+6	·00590	+4	·00581	+2	
57·3	55·6	659	731	11	710	8	690	5	
81·2	80·1	761	815	7	800	5	787	3	
100	100	883							

Several mixtures of liquids having nearly equal viscosities were investigated by Linebarger, but are not given here, as the differences between the values calculated by the three formulæ are in such cases too small to warrant conclusions as to the relative merits of the three being drawn.

WIJKANDER'S EXPERIMENTS *.

Benzine and Aniline, at 25° C.

Per cent. Aniline.		Viscosity.							
Weight.	Volume.	Observed	Calculated.						
			Vis. formula.	p. cent. error.	Log. formula.	p. cent. error.	Mob. formula.	p. cent. error.	
0	0	·0065							
20	17·6	84	·0132	+57	·0091	+8	·0076	-9	
50	46·1	138	241	75	158	14	107	22	
80	77·4	271	361	33	289	7	193	29	
100	100	447							

Ether and Alcohol, at 25° C.

Per cent. Alcohol.									
0	0	·00258							
25	23·7	360	·00499	+39	·00377	+5	·00317	-12	
50	48·3	537	749	39	558	4	420	22	
75	73·7	824	1009	22	838	7	625	24	
100	100	1275							

Ether and Carbon Bisulphide, at 25° C.

Per cent. Carb. bisulph.									
0	0	·00258							
12·5	7·5	269	·00266	-1	·00265	-1	·00264	-2	
25	16·1	276	276	0	274	1	271	2	
50	36·5	299	299	0	294	2	290	3	
66·7	53·5	320	318	-1	313	2	308	4	
100	100	370							

* Wied. Ann. Bd. iii. p. 8 (1879).

Wijkander's Experiments (*continued*)

Benzine and Alcohol, at 25° C.

P. cent. Alcohol.		Viscosity.						
Weight.	Vol.	Obs.	Calculated.					
			Vis. forml.	p. cent. error.	Log. forml.	p. cent. error.	Mob. forml.	p. cent. error.
0		·00641						
50	53·0	832	·00977	+17	·00923	+11	·00870	-5
100		1275						

An examination of these tables shows that no one of the three formulæ represents correctly the variation of the viscosity with constitution in every case. The most unsatisfactory of the three is that which makes the viscosity a linear function of the constitution, and of the other two that which makes the logarithm of the viscosity follow the linear law seems somewhat less unsatisfactory than the one which makes the mobility follow that law. In general the observed viscosity is less than that given by the logarithmic and greater than that given by the mobility law, *i. e.* the constitution shown in fig. 3 or 4 gives too great, and that in fig. 1 too small a value for the viscosity. If the observed values for different mixtures divided the interval between these two calculated values in some fairly constant ratio, it would have justified the conclusion that the viscosity of a mixture was a definite function of the amounts and viscosities of the constituents present, but it will be seen from the tables that the observed values are to be found in a different part of the interval for each mixture, and for some even outside it. Hence, even in mixtures of liquids which are generally understood to have no chemical action on each other, *i. e.* to be physical mixtures purely, there is some interaction of the liquids which prevents the viscosity of the mixture being a

function of the amounts and viscosities of its constituents only.

In those cases where the observed viscosity is less than that calculated for fig. 3 or 4, a reduction of the calculated value might be made by assuming that there is a finite slip at each surface of contact of the two constituents. The viscosity would then diminish as the size of each element of the pattern of fig. 3 or 4 was decreased, and we should have some approach to the known fact that the viscosity in general decreases as we go from liquids with larger to liquids with smaller molecules. If we may take the molecular volumes of the liquids of the preceding tables as indications of the magnitude of the component parts of the pattern of figs. 3 and 4, the tables show no evidence of this decrease of viscosity for mixtures of liquids with small molecular volumes: in fact one of the most marked cases of small viscosity is that of turpentine and toluene, both with comparatively large molecular volumes; and in neither case would it be legitimate to assume that the molecules had dissociated.

Those cases in which the observed viscosities are higher than the normal can be more easily accounted for by some kind of loose chemical combination or "association" of the two constituents. The case of acetic ether and nitrobenzine may be instanced. Here there is a contraction of .8 per cent. for a 50 per cent. by volume mixture, which shows that some action has taken place, and the viscosity is greater than in a normal mixture.

The experiments of Arrhenius*, which enabled him to establish the logarithmic law as an empirical law, were made on aqueous solutions of alcohols and other substances of concentrations not exceeding about 10 per cent., and Reyer† found that the law held for aqueous solutions of acids. From what precedes it will be seen that in these cases, if the observed value of the viscosity of a 10 per cent. mixture is used to calculate by means of the formula that of a 5 per cent. mixture, and this value compared with the one found by experiment, the range over which the law is tested is too

* Arrhenius, *Zeitsch. für phys. Chem.* i. p. 285 (1887).

† Reyer, *ibid.* ii. p. 744 (1888).

limited to furnish a sufficient test of its generality, and the deviations from it found in the above tables would not make themselves evident.

For salt-solutions in which the concentration does not exceed 10 per cent., Arrhenius *, Reyer †, Wagner ‡, Launstein §, and Kanitz || have found that the logarithmic formula applies. Brückner ¶ has found that the formula which makes the viscosity a linear function of the concentration applies; and Mützel ** uses a formula which introduces an additional unknown constant for each mixture.

It is therefore necessary to turn to stronger solutions for a comparative test of the three formulæ corresponding to the three models of a mixture represented at the beginning of this paper. The only available observations are those of Burkhard quoted in Landolt and Bornstein's Tabellen (2nd edition, p. 294) ††.

Sugar Solution at 20° C.

P. cent. Sugar.			Specific Viscosity.							
Weight.	Vol.	p. cent. of 30 % Sol.	Obs.	Calculated.						
				Vis. forml.	p. cent. error.	Log. forml.	p. cent. error.	Mob. forml.	p. cent. error.	
0	0	0	1.0							
5	3.2	15.1	1.15	1.31	+14	1.18	+3	1.11	-4	
10	6.5	30.6	1.33	1.63	23	1.41	6	1.26	5	
15	9.9	46.5	1.56	1.96	26	1.68	8	1.46	6	
20	13.5	63.4	1.89	2.31	22	2.04	8	1.75	7	
25	17.2	80.8	2.35	2.67	14	2.47	5	2.20	6	
30	21.3	100	3.07							

* *Loc. cit.*

† *Loc. cit.*

‡ *Zeitsch. für phys. Chem.* v. p. 31 (1890).

§ *Ibid.* ix. p. 417 (1892).

|| *Ibid.* xxii. p. 336 (1897).

¶ *Ann. der. Phys.* xlii. p. 287 (1891).

** *Ibid.* xliii. p. 15 (1891).

†† Since this was written the observations of Hosking have been published (*Phil. Mag.* xlix. p. 274, 1900) and are considered pp. 475, 476.

As was found in the case of most of the mixtures of liquids, the linear viscosity law gives much too high, the logarithmic law somewhat too high, and the mobility law somewhat too low values for the viscosity.

The failure of the three formulæ deduced theoretically on the assumption that the constituents of a mixture are distributed as shown in figs. 1, 2, 3, and 4 respectively, to express the results of observations, leads one to attempt to find an empirical formula capable of so doing. As the deviations from the three formulæ are found to be different in different mixtures, it is evident that any such formula will involve an additional constant depending on the particular mixture considered.

The forms of the above three formulæ :—

$$\begin{aligned}\eta &= v_1 \eta_1 + v_2 \eta_2, \\ \log \eta &= v_1 \log \eta_1 + v_2 \log \eta_2, \\ \frac{1}{\eta} &= v_1 \frac{1}{\eta_1} + v_2 \frac{1}{\eta_2},\end{aligned}$$

suggest immediately the empirical formula :—

$$\eta^n = v_1 \eta_1^n + v_2 \eta_2^n,$$

where n is a constant to be determined for each mixture. In the following tables the values of n are given and the calculated and observed values of η for various mixtures are compared*.

Carbon Tetrachloride and Benzine at 60° C. $n = -\cdot 42$.

Per cent. Benzine by volume.	Observed η .	Calculated η .
0	·00582	·00582
34·4	503	502
58·5	456	456
79·2	422	422
100	391	391

* In most of the cases which follow no attempt has been made to determine n to a greater degree of accuracy than 2 or 3 units in the second decimal place.

Ethyl Ether and Benzine at 25° C. $n = -\cdot 50$.

Per cent. Benzine by volume.	Observed η .	Calculated η .
0	·00230	·00230
25·2	282	282
52·6	362	361
72·4	438	438
100	599	599

Nitrobenzine and Benzine at 25°. $n = -\cdot 50$.

Per cent. Benzine by volume.	Observed η .	Calculated η .
0	·01834	·01834
18·8	1417	1410
45·2	1017	1020
84·6	681	689
100	599	599

Ethyl Benzoate and Toluene at 25°. $n = -\cdot 30$.

Per cent. Toluene by volume.	Observed η .	Calculated η .
0	·01954	·01954
18·1	1495	1489
52·4	939	938
79·6	679	676
100	539	539

Benzine and Aniline at 20° C. $n = -\cdot 33$.

Per cent. Aniline by volume.	Observed η .	Calculated η .
0	·0065	·0065
17·6	84	85
46·1	138	138
77·4	271	259
100	447	447

Ether and Alcohol at 20° C. $n = -\cdot 11$.

Per cent. Alcohol by volume.	Observed η .	Calculated η .
0	·00258	·00258
23·7	360	368
48·3	537	538
73·7	824	812
100	1275	1275

The success of the attempt to represent the viscosities of these mixtures by means of the formula proposed, leads to the attempt being extended to mixtures of glycerine and water, in which the range of viscosity is very great. The following results have been obtained :—

Glycerine and Water at 8°·5 C. (Schöttner) *.

$$n = -\cdot 22.$$

Per cent. Glycerine.		Viscosity.	
Weight.	Volume.	Observed.	Calculated.
0	0	·0136	·0136
49·8	43·9	·0925	·099
64·0	58·4	·222	·245
75·0	70·3	·552 †	·61
80·3	76·3	1·021	1·05
89·9	86·5	3·553	3·16
94·5	93·1	7·437	7·59
100	100	23·98 †	23·98

* *Wien. Ber.* ii. 79, p. 477 (1879).

† Calculated from Schöttner's numbers.

Glycerine and Water at 20° C. (Archbutt & Deeley)*.

$$n = -\cdot 25.$$

Per cent. Glycerine.		Per cent. of 97.5 per cent. Glycerine by volume.	Viscosity.	
By weight.	By volume.		Observed.	Calculated.
0	0	0	·0103	·0103
40.0	34.5	35.4	·038	·040
71.0	66.0	67.6	·236	·253
78.8	74.6	76.5	·498	·518
82.4	78.7	80.8	·75	·76
85.5	82.4	84.5	1.11	1.09
94.0	92.5	94.9	4.08	3.92
98.0	97.5	100	8.69	8.69

Applying the formula to the sugar and the sodium-chloride solutions investigated by Hosking†, and to the sugar solution tested by Burkhard, we have the following results:—

Sugar Solution at 0° C. (Hosking). $n = -\cdot 50.$

Per cent. Sugar.		Viscosity.	
Weight.	Volume.	Observed.	Calculated.
0	0	·0179	·0179
5	3.2	205	207
10	6.5	244	244
20	13.5	372	366
40	29.3	·1476	·1476

* 'Lubrication and Lubricants,' London, Griffin, 1900, p. 133.

† Phil. Mag. xlix. p. 286 (1900).

DR. C. H. LEES ON THE VISCOSITIES OF
Sugar Solution at 40° C. $n = -\cdot 50$ (Hosking).

Per cent. Sugar.		Viscosity.	
Weight.	Volume.	Observed.	Calculated.
0	0	·00657	·00657
5	3·2	732	742
10	6·5	843	848
20	13·3	1180	1170
40	29·3	3132	3132

Sugar Solution at 80° C. $n = -\cdot 50$.

0	0	·00360	·00360
5	3·2	399	400
10	6·5	448	448
20	13·5	586	588
40	29·3	1238	1238

Sodium Chloride Solution at 0° C. (Hosking). $n = -\cdot 3\cdot 0$.

Per cent. Sodium Chloride.		Viscosity.	
Weight.	Volume.	Observed.	Calculated.
0	0	·0179	·0179
5	2·44	186	189
10	5·03	204	204
20	10·64	267	267

Sodium Chloride Solution at 40° C. $n = -\cdot 33$.

0	0	·00657	·00657
5	2·44	725	724
10	5·03	802	805
20	10·64	1025	1025

Sodium Chloride Solution at 80° C. $n = \cdot 25$.

0	0	·00360	·00360
5	2·44	399	402
10	5·03	455	451
20	10·64	571	571

Sugar Solution at 20° C. (Burkhard).

$$n = -\cdot 50.$$

Per cent. Sugar.		Per. cent of 30 per cent. Solution.	Viscosity.	
Weight.	Volume.		Observed.	Calculated.
0	0	0	1.0	1.0
5	3.2	15.1	1.15	1.14
10	6.5	30.6	1.33	1.33
15	9.9	46.5	1.56	1.56
20	13.5	63.4	1.89	1.89
25	17.2	80.8	2.35	2.34
30	21.3	100	3.07	3.07

The agreement between the calculated and experimental values in all the above cases is sufficient to justify the use of the empirical formula

$$\left(\frac{1}{\eta}\right)^m = v_1 \left(\frac{1}{\eta_1}\right)^m + v_2 \left(\frac{1}{\eta_2}\right)^m$$

as, at any rate, a first approximation towards a representation of the viscosity of a physical mixture in terms of the viscosities and natures of its constituents. Like other empirical formulæ, it will in time be replaced by a formula founded on theory and capable of including cases in which the liquids, owing to some chemical action on each other, give rise to mixtures having viscosities outside the limits of those of their constituents.

Since a liquid at temperature t may be regarded as produced by a mixture of suitable amounts of the liquid at temperatures 0 and t_1 respectively, the above formula for the viscosities of mixtures should be capable of expressing the variation of the viscosity of a liquid with temperature.

If 1 c.c. of a mixture at temperature t is supposed to result from mixing v_0 c.c. of liquid at 0° C. and v_1 c.c. of liquid at t_1 ° C., $t = v_1 t_1$; and if the viscosity is η_0 at 0° C., η at t ° C., and η_1 at t_1 ° C., then

$$\begin{aligned}
 \left(\frac{1}{\eta}\right)^m &= v_0 \left(\frac{1}{\eta_0}\right)^m + v_1 \left(\frac{1}{\eta_1}\right)^m \\
 &= \left(\frac{1}{\eta_0}\right)^m + \left\{ \left(\frac{1}{\eta_1}\right)^m - \left(\frac{1}{\eta_0}\right)^m \right\} \frac{t}{t_1} \\
 &= \left(\frac{1}{\eta_0}\right)^m \{1 + \alpha t\},
 \end{aligned}$$

where

$$\alpha = \frac{1}{t_1} \left\{ \left(\frac{\eta_0}{\eta_1}\right)^m - 1 \right\}.$$

Hence

$$\eta = \frac{\eta_0}{(1 + \alpha t)^{\frac{1}{m}}},$$

an empirical formula proposed by Slotte*, and found by him, and more extensively by Thorpe and Rodger†, to be applicable to all liquids on which experiments have been made.

The values of m for most of the mixtures mentioned in the preceding tables vary between .20 and .50; and Thorpe and Rodger have found its values in Slotte's temperature-variation formula to lie between .22 and .3 for alcohols, and to be about .6 for water, benzine, ether, and chloroform. In the following table (p. 479) the values found suitable for expressing the viscosity of a mixture in terms of the viscosities of its constituents, are compared with those found best for expressing the variation of the viscosity of each constituent with temperature.

Although in the examples of non-electrolytic mixtures and solutions there seems to be some connexion between the values of m in the formula for the temperature-variation of the viscosities of two liquids, and its value in the formula for the viscosities of mixtures of the two, the number of instances is too small to warrant a general conclusion being drawn. In the case of the electrolytic solution (NaCl) the values of m for the mixtures at different temperatures vary greatly from one another, although the values in the temperature formula are practically identical. Possibly the magnitude of the heat of

* *Ofv. Finska Vet. Soc. Förhand.* xxxii. p. 127, formula (11) (1890).

† *Phil. Trans. A.* 189. p. 96 (1897).

Liquids.	Values of m .		
	In Temperature Variation Formula.		In Mixture Formula.
Carbon Tetrachloride and Benzine	·58 *	·64 *	·49
Nitrobenzine and Benzine	·67 †	·64	·50
Ethyl Ether and Benzine.....	·68	·64	·50
Ethyl Ether and Alcohol.....	·68	·23	·11
Ethyl Benzoate and Toluene	·50 ‡	·61	·30
Glycerine and Water	·12 §	·65	·22 & ·25
40-per-cent. Sugar solution and water.	·45	·65	·50
20-per-cent. NaCl solution and water...	·66	·65	3·0 to —·25

* The numbers in these two columns, with the exception of those for nitrobenzine, ethyl benzoate, and glycerine, are taken from Thorpe and Rodger's papers.

† Calculated from observations of Pribram and Handl, *Wien. Ber.* II. lxxviii. p. 113.

‡ Calculated from observations of Rellstab, *Inaug. Diss.* Bonn, 1868.

§ Calculated from Schöttner's values, *l. c.*

|| Calculated from Hosking's values, *l. c.* The agreement between observed and calculated values may be seen from the following tables:—

40-per cent. Sugar Solution.

Temperature	Viscosity.	
	Observed.	Calculated.
0° C.	·148	·148
10	·895	·903
20	·607	·605
30	·423	·430
40	·313	·320
50	·241	·247
60	·191	·195
70	·155	·158
80	·129	·130
90	·109	·109

20-per cent. NaCl Solution.		
0	·0267	·0267
10	·197	·197
20	·154	·153
30	·124	·123
40	·102	·102
50	·87	·86
60	·74	·74
70	·65	·65
80	·57	·57
90	·51	·51

solution of NaCl places it outside the class of simple mixtures considered in what precedes.

The result of this investigation may be summed up as follows:—

(1) No one of the three theoretical formulæ (1), (2), (3) represents the viscosity of a mixture with sufficient closeness.

(2) The empirical formula $\left(\frac{1}{\eta}\right)^m = v_1 \left(\frac{1}{\eta_1}\right)^m + v_2 \left(\frac{1}{\eta_2}\right)^m$ with a suitable value for m gives a satisfactory representation.

(3) It leads also to Slotte's formula for the variation of viscosity of a liquid with temperature.

XXX. *On the Law of Cailletet and Mathias and the Critical Density.* By SYDNEY YOUNG, D.Sc., F.R.S., University College, Bristol*.

IN a very interesting paper (*Mém. de la Soc. Roy. des Sci. de Liège*, sér. 3, ii. 1899) M. E. Mathias discusses the law of the Rectilinear Diameter, discovered in 1886 by M. Cailletet and himself, and the law of the corresponding states of matter. The law of Cailletet and Mathias may be stated simply in this way:—The means of the densities of liquid and saturated vapour for any stable substance are a rectilinear function of the temperature.

It has been shown (Mathias, *Ann. de la Fac. des Sci. de Toulouse*, 1892; Young, *Phil. Mag.* Dec. 1892, p. 506) that if the generalizations of van der Waals regarding corresponding temperatures, pressures, and volumes are correct, the angular coefficient α [$D_t = D_0 + \alpha t$, where D_t and D_0 are the means of the densities at t° and 0° respectively] of the diameters of different substances should be directly proportional to their critical densities, and inversely proportional to their absolute critical temperatures; or that for any substance

$$\alpha = \text{const.} \times \frac{D_c}{T_c};$$

* Read June 22, 1900.