

of aluminium hydroxide, it is believed that the work described in this paper adds to the evidence in favor of the existence of definit aluminates in the solutions obtained by dissolving aluminium hydroxide in alkalis.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, No. 217.]

**THE WEIGHT OF A FALLING DROP AND THE LAWS OF TATE. XII.
THE DROP WEIGHTS OF CERTAIN ORGANIC LIQUIDS
AND THE SURFACE TENSIONS AND CAPILLARY
CONSTANTS CALCULATED FROM THEM.¹**

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Received July 24, 1913.

Three tips were used in the course of this investigation, the benzene constants of which are given in the following table:²

CALIBRATION OF THE TIPS WITH BENZENE.				
Tip.	<i>t</i> .	<i>w</i> = wt. 1 drop (mg.).	<i>w</i> (<i>M/d</i>) ^{2/3} .	<i>K_B</i> .
1	30	29.307	587.86	2.3282
2	30	28.484	571.35	2.2628
3	30	28.464	570.91	2.2610

The density of benzene at 30° is 0.86824. *K_B* is calculated from the relationship

$$K_B = w(M/d)^{2/3} / (288.5 - 30 - 6),$$

where 288.5 is the critical temperature of benzene, and 6 is a constant.³

Since the surface tension is related to the weight of a falling drop according to the equation

$$\gamma = w \times 2.1148 / K_B;$$

and the capillary constant (*a*², the height of ascension of a liquid in a tube of 1 mm. radius) is related to the drop volume (*i. e.*, the drop weight *w*, divided by the density, *d*) according to the equation

$$a^2 = 0.1837 \times 2.3502 / K_B \times w/d;$$

it is now possible for us to calculate the constants by which the drop weight of any liquid must always be multiplied in order to give the surface tension of that liquid in dynes per centimeter at that temperature; and the constants by which drop volumes can be transformed into capillary

¹ For other papers of this series see THIS JOURNAL, 30, 360-72, 1055-68; 33, 349-62, 643-57, 657-72, 672-84, 1042-60, 1060-71, 1275-90, 1713-27; 35, 1249-1262.

² In order to save space, only the means of several determinations of the drop weight will be given here, although in the actual work at least three determinations each of the 30 and of the blank of 5, were made, the differences never amounting to more than a few tenths of a milligram on these weights.

³ For details of the calibration see THIS JOURNAL, 33, 1714-16.

constants. From the results in the above table the constants for the three tips employed are found to be

$$\left. \begin{aligned} \gamma_1 &= 0.9083 \times w \\ a_1^2 &= 0.1854 \times w/d \end{aligned} \right\} \text{Tip I.}$$

$$\left. \begin{aligned} \gamma_2 &= 0.9346 \times w \\ a_2^2 &= 0.1908 \times w/d \end{aligned} \right\} \text{Tip II.}$$

$$\left. \begin{aligned} \gamma_3 &= 0.9353 \times w \\ a_3^2 &= 0.1909 \times w/d \end{aligned} \right\} \text{Tip III.}$$

For all the liquids below, the calculated critical temperatures, t_c , are given as found from the equation

$$t_c = \frac{w(M/d)^{2/3}}{K_B} + t_o + 6,$$

where w is the drop weight and d the density of the liquid at the temperature of observation, t_o , and M is the formula weight of the substance. It is from these values that we can determine whether or not the liquid is non-associated or not, for it has been shown by Morgan¹ that "a constant value of the calculated t_c at all temperatures of observation indicates that the substance is non-associated."

1. Methyl-Propyl Ketone, $\text{CH}_3\text{COC}_3\text{H}_7$ ($M = 86.08$).

This preparation was from Hoffman and Kropff, the densities being specially determined in this laboratory by Miss C. A. Francis. Tip I.

t .	w .	d .	$w(M/d)^{2/3}$.	t_c calculated.
0°	28.608	0.8261	633.27	278.0
30.0	25.196	0.7977	571.37	281.4
53.5	22.553	0.7745	521.32	283.4

These results for w lead to the relationship

$$w = 29.598 - 0.1130t$$

from which we find (page 1505)

$$\gamma_t = 25.976 - 0.1026t.$$

The relationship of the drop volume, w/d , to the temperature is found to be

$$w/d = 34.637 - 0.1027t$$

from which (page 1505)

$$a_t^2 = 6.423 - 0.01904t.$$

The values of surface tension (and the critical temperatures calculated from them) as found by aid of the above equation for γ are compared in the table below with results found by aid of capillary rise by Renard and Guye² and by Ramsay and Shields,³ the results which are extrapolated

¹ THIS JOURNAL, 33, 649.

² Jour. chim. phys., 5, 81 (1907).

³ Z. physik. Chem., 12, 433 (1893).

being placed in parentheses. The k value used to calculate the t_c^{\prime} from capillary rise is 2.1148.¹

COMPARISON OF VALUES.

t	γ (M. and S.)	γ (R. and G.)	γ (R. and S.)	t_c (M. and S.)	t_c (R. and G.)	t_c (R. and S.)
13.0	24.65	25.38	278.1	...
16.7	24.27	24.98	25.39	275.0	...	288.3
27.1	23.20	23.86	279.9	...
42.5	21.60	22.19	280.1	...
46.4	21.22	21.75	22.16	278.7	...	289.9
56.2	(20.22)	20.71	281.8	...
78.4	(17.94)	18.49	18.75	280.7	...	290.8
79.9	(17.78)	18.34	283.9	...
93.1	(16.43)	17.00	284.9	...

As will be observed the drop-weight methods lead to slightly lower results throughout. They agree with the results of Renard and Guye, by capillary rise, however, just about as well as these do with those of Ramsay and Shields by the same method.

According to the Morgan definition of normal molecular weight in the liquid state this liquid is slightly associated by all methods. Its surface tension at 0° is practically identical with the value found by Morgan and Owen for the isomeric compound, diethyl ketone, which gives the formula $\gamma_t = 25.970 - 0.1001t$ where this gives $\gamma_t = 25.976 - 0.1026t$.

2. Paraldehyde, $C_6H_{12}O_8$ ($M = 132.1$).

This preparation from Hoffman and Kropff was first used in its original condition, then redistilled completely within four-tenths of 1°, and then recrystallized three times, but no change in its drop weight could be determined. The densities here were especially determined by Miss Francis. Tip I was used.

t	w	d	$w(M/d)^{2/3}$	t_c calculated.
15	27.838	0.99945	722.4	340.3
30	26.064	0.98423	683.1	337.9
54	23.208	0.95655	619.9	334.0

From the results of w we find here

$$w_t = 29.623 - 0.1188t$$

from which

$$\gamma_t = 27.686 - 0.1150t.$$

The change in w/d , the drop volume, with the temperature is found to be

$$v_t = w/d = 29.240 - 0.0922t$$

from which we find

$$a_t^2 = 5.578 - 0.176t.$$

The results of Ramsay and Shields at three temperatures, together

¹ See Morgan and McAfee, THIS JOURNAL, 33, 1288.

with those by drop weight from the above γ and a^2 formulas, are given in the table below for comparison.

COMPARISON OF RESULTS.					
t .	d .	γ (M. and S.).	γ (R. and S.).	a^2 (M. and S.).	a^2 (R. and S.).
15.0	0.9993	26.02	26.47	5.314	5.401
46.5	0.9881	22.53	23.42	4.760	4.830

There is one very striking point here to be considered that would indicate that the density (their values are taken from Perkin¹) employed by Ramsay and Shields at 46.5° is quite incorrect—it will be noted that it is even larger than the one we have used at 30°, while the values are practically identical at 15°. At 15° the Ramsay and Shields values of γ and a^2 are both higher than ours by 1.8%, approximately. At 46.5° their a^2 is 1.6% larger, while their γ value is 4% higher. With the capillary rise method a^2 is a direct quantity ($= \text{height} \times \text{radius of bore}$), while γ is indirect ($= \frac{1}{2} \text{height} \times \text{radius} \times \text{density}$); with the drop-weight method, on the other hand, it is γ that is direct ($= w \times \text{constant}$), and a^2 that is indirect ($= w/d \times \text{constant}$). At 15°, where the densities are practically the same, both γ and a^2 of Ramsay and Shields' differ from ours by the same percentage, and at 46.5° the a^2 value of Ramsay and Shields' (the direct value) still differs from ours by practically the same amount, but their γ value, the indirect quantity found by aid of *their* density, differs from ours by more than twice as much. In such a comparison either method *could* be at fault, but our density, in making the values a^2 and γ differ in the two sets of observations by the same amount practically at both temperatures is shown to be the correct one.

Interpolating between 30° and 54° we find that according to our results the density of the liquid at 46.5° should be 0.9653. Using this, in place of the 0.9881, to calculate the value of γ from Ramsay and Shields' height of ascension we find the value 22.88 in place of the 23.42 they give. The difference then between their value and ours (22.53) is found to be just 1.5%—a value which agrees with the comparison in the a^2 values at this temperature. Perkin gives only two densities, one at 15° based on water at 15°, the other at 25° based on water at 25°, so that the Ramsay and Shields value at 46.5° is extrapolated through 21.5°. It may be that the Ramsay and Shields liquid was not pure, which could account for the constant difference in result—there is no question of the purity of the sample we employed, however. It is quite evident from the values of t_c calculated that paraldehyde is associated, according to the Morgan definition of normal molecular weight.

3. Ethyl Nitrate, $C_2H_5NO_3$ ($M = 91.06$).

This preparation was from Hoffman and Kropff; the densities being calculated from the formula given by Walden.² The drop weights

¹ *J. Chem. Soc.*, **48**, 479.

² *Zeit. f. phys. Chem.*, **65**, 149 (1908).

found and the critical temperatures calculated for this liquid are given in the following table: Tip 2.

t .	w .	d .	$w(M/d)^{2/3}$.	t_c calculated.
0	31.733	1.1352	590.22	266.8
30	27.788	1.0931	529.95	270.2
45	25.816	1.0721	498.75	271.4

From which we find

$$w_t = 31.733 - 0.1315t$$

and

$$w/d = v_t = 27.965 - 0.08586t$$

which lead to

$$\gamma_t = 29.658 - 0.1229t$$

and

$$a_t^2 = 5.335 - 0.1638t.$$

The only values to be found in the literature for this liquid are those of Schiff¹ which lead to the very different value $a_t^2 = 5.733 (1 - 0.00281t)$.

The liquid, by the Morgan definition, is plainly associated.

4. Nitro-Methane, CH_3NO_2 ($M = 61$).

Hoffman and Kropff preparation; densities from formula given by Walden.² Tip No. 2.

t .	w .	d .	$w(M/d)^{2/3}$.	t_c calculated.
0	41.230	1.1639	577.63	261.3
30.0	36.661	1.1227	525.07	268.2
45.1	34.361	1.1034	499.35	272.4

$$w_t = 41.230 - 0.1523t$$

$$v_t = 35.438 - 0.09403t$$

from which we find

$$\gamma_t = 38.534 - 0.1423t$$

$$a_t^2 = 6.761 - 0.01794t$$

The only results in the literature for this liquid are those of Schiff at 20° and 101° , from which Walden derives the quite different equation $a_t^2 = 7.09 (1 - 0.00277t)$. The liquid is associated.

5. Butyl Alcohol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ($M = 74.08$).

This preparation was from Kahlbaum, the densities being those of Ramsay and Shields. Tip No. 2. The drop weights at the three temperatures studied here were:

t .	w .
0	27.120
20	25.440
40	23.745

from which we find

¹ *Wied. Beib.*, 1885, 562.

² *Loc. cit.*

$$w_t = 27.122 - 0.8437t$$

which leads to

$$\gamma_t = 25.348 - 0.0788t.$$

The only densities that could be found here were those used by Ramsay and Shields, so, as they led to no simple relationship with changing temperature, we used them at the temperatures 17.4° , 45.7° , and 77.9° , which they employed, with the drop weights calculated from the above relationship, to find the drop volume. The change in drop volume with temperature was thus found to be $v_t = 32.963 - 0.07763t$ which leads to

$$a_t^2 = 6.291 - 0.0148t.$$

Below the values of γ and a^2 found in this way are compared with those of Ramsay and Shields.

COMPARISON OF VALUES.

t .	γ (M. and S.).	γ (R. and S.).	a^2 (M. and S.).	a^2 (R. and S.).
17.4	23.98	24.42	6.031	6.134
45.7	(21.74)	22.14	(5.614)	5.707
77.9	(19.21)	19.36	(5.136)	5.173

The values of t_c , using the densities as given by Ramsay and Shields, at their temperatures are given below:

t .	d .	$w(M/d)^{2/3}$.	t_c calculated.
17.4	0.8115	520.11	255.1
45.7	0.7907	(479.94)	(263.6)
77.9	0.7634	(433.93)	(275.5)

from which it will be seen that the liquid is associated.

6. Isobutyl Alcohol ($\text{CH}_3)_2\text{CHCH}_2\text{OH}$ ($M = 74.08$).

Hoffman and Kropff preparation; densities from Ramsay and Shields. Tip No. 2.

The drop weights here were found to be

t .	w .
0	25.220
30	22.806
40	21.612

from which

$$w_t = 25.218 - 0.0802t$$

and

$$\gamma_t = 23.569 - 0.025t.$$

Using the density values given below, with the drop weights calculated from the above equation, we find $v_t = 30.968 - 0.0739t$ from which

$$a_t^2 = 5.908 - 0.0141t.$$

The values of t_c are given in the following table at the temperatures for which the densities are known, the values of w being calculated from the above equation:

t .	d .	$w(M/d)^{2/3}$.	t_c calculated.
16.2	0.8038	488.03	237.9
46.4	0.7800	(447.49)	(250.1)
78.4	0.7522	(403.72)	(262.8)

The values of surface tension and capillary constant of Ramsay and Shields, and Renard and Guye are given in the following table, together with our values calculated to their temperatures.

COMPARISON OF VALUES.

t .	γ (M. and S.).	γ (R. and S.).	γ (R. and G.).	a^3 (M. and S.).	a^3 (R. and S.).	a^3 (R. and G.).
10.5	22.78	...	23.01	5.760	...	5.802
16.2	22.35	22.78	...	5.680	5.778	...
36.3	20.85	...	21.05	5.396	...	5.446
46.4	(20.09)	20.36	...	(5.254)	5.322	...
54.8	(19.46)	...	19.70	(5.136)	...	5.196
78.4	(17.69)	17.77	...	(4.803)	4.817	...

It is quite evident from the values found for t_c that this liquid, like all the other alcohols, is associated.

 7. Allyl Alcohol, $\text{CH}_2:\text{CHCH}_2\text{OH}$ ($M = 58.05$).

Again this was a special Hoffman and Kropff preparation, with densities from Ramsay and Shields. The drop weights here were found to be as follows: (Tip No. 2.)

t .	w .
0	28.355
20	26.502
40	24.656

from which

$$w_t = 28.354 - 0.0925t,$$

leading to

$$\gamma_t = 26.499 - 0.0864t.$$

The values of w calculated for the temperatures used by Ramsay and Shields, by aid of their densities (see below) leads to the drop volume relation

$$v_t = 32.692 - 0.0798t$$

which gives

$$a_t^3 = 6.237 - 0.01522t.$$

The calculated values of t_c found at the Ramsay and Shields' temperatures, with their densities, are given below.

t .	d .	$w(M/d)^{2/3}$.	t_c calculated.
14.8	0.8569	448.44	219.0
46.4	0.8287	(408.89)	(233.1)
78.4	0.7989	(379.64)	(252.1)

The values of γ and a^3 at the Ramsay and Shields' temperatures are compared with their results below.

COMPARISON OF RESULTS.

t .	γ (M. and S.).	γ (R. and S.).	a^2 (M. and S.).	a^2 (R. and S.).
14.8	25.219	25.99	6.012	6.184
46.4	(22.488)	22.82	(5.531)	5.614
78.4	(20.375)	19.70	(5.044)	5.144

The liquid from the t_c values is plainly associated.

8. Formic Acid, HCOOH ($M = 46.02$).

The sample used here was from Kahlbaum, afterwards purified very carefully by distilling over sulfuric acid and recrystallizing several times until it gave a constant melting point. The impurity here, owing to the hygroscopic nature of the acid, would be likely to be water, which would increase the drop weight and surface tension considerably. The sample we used, however, may be considered pure. The densities here were from Garner, Sexton and Parker.¹ The drop weights (Tip No. 2) are as follows:

t .	w .
20	38.856
25	38.304
30	37.772

from which

$$w_t = 41.053 - 0.1097t$$

and

$$\gamma_t = 38.368 - 0.1025t.$$

Employing the densities given below with the values of w from the equation, we find

$$v_t = 33.016 - 0.0587t$$

from which

$$a_t^2 = 6.299 - 0.0112t.$$

The values of t_c calculated here, which show this liquid to be associated are

t .	d .	$w(M/d)^{2/3}$.	t_c calculated.
16.8	1.207	444.19	219.1
46.4	1.170	(415.94)	(236.2)
79.8	1.129	(382.56)	(254.9)

Walden finds from Ramsay and Shields' values the equations

$$\gamma_t = 39.35 - 0.1091t$$

and

$$a_t^2 = 6.633 - 0.01339t$$

the larger value of which would tend to show the presence of water in their sample. It must be remembered here that the drop-weight values in certain cases (always easily recognized, due to very small drop volume

¹ *Am. Chem. J.*, 46, 236 (1911).

and viscous nature, see Morgan and Cann,¹ *could* conceivably be too high, but *never* too low.

9. Propionic Acid, C_2H_5COOH ($M = 74.05$).

Kahlbaum preparation, densities from Ramsay and Shields, Tip No. 2.

t .	w .
10	28.608
20	27.532
30	26.505
40	25.488
50	24.560
60	23.574

from which we find

$$w_t = 29.742 - 0.1142t + 0.000196t^2$$

leading to

$$\gamma_t = 27.797 - 0.1067t + 0.000183t^2.$$

The drop volumes calculated at the three Ramsay and Shields temperatures, using their densities, give the relationship

$$v_t = 28.848 - 0.06863t$$

from which

$$a_t^2 = 5.504 - 0.01309t.$$

The values of t_c calculated at these three temperatures of observation are:

t .	d .	$w(M/d)^{2/3}$.	t_c calculated.
16.6	1.0060	490.04	239.2
46.4	0.9710	447.20	250.0
79.6	0.9354	(403.72)	(264.4)

showing that this liquid as are all other acids is associated.

The values of γ and a^2 are compared with Ramsay and Shields' in the following table:

COMPARISON OF VALUES.

t .	γ (M. and S.).	γ (R. and S.).	a^2 (M. and S.).	γ (R. and S.).
16.6	26.076	26.57	5.287	5.381
46.4	23.242	23.54	4.897	4.902
79.6	(20.466)	20.36	(4.459)	4.437

Schiff gives values of a^2 at 0° and 140.7° which are respectively, 5.832 and 3.725, where ours would be 5.504 and 3.663, the latter extrapolated through 80.7° . Rodenbeck² gives 6.055 at 14° compared with our 5.32 and the Ramsay and Shields' of about 5.42, all of which shows how the values of a^2 and of γ can differ when all are determined by capillary rise, but by different observers.

¹ THIS JOURNAL, 33, 1066.

² Dissertation, Bonn, 1879.

10. Butyric Acid, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ ($M = 88.06$).

This was a Kahlbaum preparation and the densities were those used by Ramsay and Shields. The drop weights (Tip No. 2) at the five temperatures of observation were:

t .	w .
0	29.695
30	26.664
40	25.690
50	24.738
60	23.806

from which

$$w_t = 29.705 - 0.10495t + 0.0001117t^2.$$

Using the densities employed by Ramsay and Shields and given below, with drop weights calculated from the above equation, we find the equation for the variation of drop volume with the temperature to be:

$$v_t = 29.988 - 0.07213t + 0.00000846t^2$$

from which, with that for w_t , we find

$$\gamma_t = 27.762 - 0.0981t + 0.000104t^2$$

$$a_t^2 = 5.721 - 0.01376t + 0.0000016t^2.$$

A comparison of these values with those found by Ramsay and Shields, as well as the critical temperatures calculated from the values of γ_t are given below:

COMPARISON OF VALUES.				
	γ (M. and S.).	γ (R. and S.).	a^2 (M. and S.).	a^2 (R. and S.).
15.0	26.436	26.74	5.518	5.600
46.5	23.372	23.75	5.081	5.258
78.6	(20.697)	20.97	(4.650)	4.702

VALUES OF t_c CALCULATED

t .	d .	$w(M/d)^2/3$.	t_c calculated.
15.0	0.9734	566.95	271.5
46.5	0.9412	511.73	278.6
78.6	0.9086	(452.87)	(284.7)

The liquid is plainly associated.

11. Isobutyric Acid, $(\text{CH}_3)_2\text{CHCOOH}$ ($M = 88.06$).

Kahlbaum's preparation, redistilled; density used by Ramsay and Shields. The drop weights were (Tip No. 2):

t .	w .
0	28.047
30	25.028
45	23.550

from which

$$w_t = 28.042 - 0.100t.$$

This formula for drop weight, with the densities used by Ramsay and Shields, leads to values of drop volume from which we derive

$$v_t = 29.183 - 0.8467t.$$

From these equations, we find

$$\gamma_t = 26.208 - 0.0935t$$

and

$$a_t^2 = 5.568 - 0.01615t.$$

The values of t_c for this liquid are:

t .	d .	$w(M/d)^{2/3}$.	t_c calculated.
16.0	0.952	540.82	261.0
46.4	0.923	(488.62)	(286.3)
78.4	0.898	(429.60)	(274.2)

which prove it to be associated.

In the table below are compared the values of γ and a^2 from the above equations with those found by Ramsay and Shields from capillary rise:

COMPARISON OF VALUES.

t .	γ (M. and S.).	γ (R. and S.).	a^2 (M. and S.).	a^2 (R. and S.).
16.0	24.702	24.99	5.299	5.350
46.4	(21.871)	22.07	(4.689)	4.873
78.4	(18.885)	19.53	(4.292)	4.431

The isobutyl arrangement in acids thus lowers the surface tension just as it does with the corresponding alcohol.

12. Isovaleric Acid, $(\text{CH}_2)_2\text{CHCH}_2\text{COOH}$ ($M = 102.08$).

This Kahlbaum preparation was first redistilled. The densities again were those used by Ramsay and Shields.

The drop weights (Tip No. 2) were

t .	w .
20	26.282
30	25.382
40	24.478

which lead to

$$w_t = 28.091 - 0.09035t$$

while the drop volumes found by aid of the densities below lead to the relationship

$$v_t = 29.395 - 0.0697t.$$

From the above equations, thus, it is evident that

$$\gamma_t = 26.253 - 0.0844t$$

and

$$a_t^2 = 5.608 - 0.0133t.$$

The critical temperatures, which show this liquid to be associated are:

t .	d .	$w(M/d)^{2/3}$.	t_c calculated.
17.0	0.9428	603.74	286.5
46.5	0.9107	(555.38)	(297.9)
78.2	0.8796	(500.26)	(305.2)

The comparison with the values of Ramsay and Shields is given in the following table:

t	γ (M. and S.).	γ (R. and S.).	a^2 (M. and S.).	a^2 (R. and S.).
17.0	24.818	25.64	5.382	5.543
46.5	(22.327)	22.86	(4.990)	5.115
78.2	(19.650)	20.04	(4.568)	4.645

The differences here are somewhat greater than usual, but it is quite certain that the sample we used was pure.

13. Ortho-Toluidine $C_6H_4CH_3NH_2$ ($M = 107.08$).

This preparation was from Hoffman and Kropff and redistilled before use. The densities are those given by Dutoit and Friedrich.¹

The drop weights (Tip No. 2) were found for this liquid to be

t .	w .
0	44.805
15	42.871
30	41.180

from which we find

$$w_t = 44.797 - 0.1208t;$$

and, by use of the below densities,

$$v_t = 44.144 - 0.0849t.$$

By application of the proper constant to these relations we find

$$\gamma_t = 41.867 - 0.1129t$$

and

$$a_t^2 = 8.422 - 0.01621t.$$

The values of the t_c calculated here are found to be

t .	d .	$w(M/d)^{2/3}$.	t_c calculated.
0	1.0149	1000.25	448.2
15	1.0024	967.75	448.7
30	0.9899	934.74	449.1

It is quite evident here by the slight change in t_c that this liquid is practically non-associated. The values found by Dutoit and Friedrich together with the value of γ from our equation are given in the following table:

t .	d .	γ (M. and S.).	γ .	$\gamma(M/d)^{2/3}$.	t_c .	a^2 (M. and S.).	a^2 .
8.1	1.008	40.953	39.09	876.5	431.3	8.291	8.246
108.4	0.986	(29.629)	28.33	672.0	433.2	(6.666)	6.511
208.5	0.839	(18.327)	18.33	465.9	436.2	(5.044)	4.655

Although the values for γ do not agree at all well here (the value of γ we have calculated is extrapolated through 178.5° and means little) it is quite evident here that the difference of 5° in the value of t_c could well be

¹ *Arch. des Sci. Phys. et Nat.*, [4] 9, 105 (1900).

accounted for by inaccuracy in the density values which are only carried out to three places any way. Other liquids which are associated, through such an interval (200°) of observation temperature show many times that difference in t_c . We may conclude then, that all observations show this liquid to be non-associated (practically) by the Morgan definition.

14. Para-Toluidine, $C_6H_4CH_3NH_2$. ($M = 107.08$.)

Preparation of Hoffman and Kropff; densities from Dutoit and Friedrich. The values of drop weight (Tip No. 3) and of the t_c calculated for this liquid, at the only two temperatures studied, are given in the following table:

t .	d .	w .	$w(M/d)^{2/3}$.	t_c calculated.
50	0.9612	35.984	832.93	424.4
60	0.9528	34.996	814.97	426.4

from which it is evident that this liquid is associated. From the above w and d values we find

$$w_t = 40.924 - 0.0988t$$

and

$$v_t = 40.934 - 0.0701t$$

from which

$$\gamma_t = 38.277 - 0.0924t$$

and

$$a_t^2 = 7.816 - 0.01338t.$$

The only values given by Dutoit and Friedrich are at 107° and 210.6° and are very decidedly different from ours (more than 10% lower in fact).

The effect of the para arrangement is seen to reduce the surface tension, which was first observed by Feustel¹ who found in the case of the cresols, toluidines and xylenes that the ortho derivative gives the greatest surface tension while the para gives the least, the meta compound being very similar to the para.

This relationship certainly holds true for the xylenes, for it can be shown from the drop weight work of Morgan and Daghlian² that the surface tension temperature relationship from drop weight leads to

$$\gamma_t = 29.937 - 0.1031t \text{ for } \textit{ortho} \text{ xylene}$$

$$\gamma_t = 29.497 - 0.1035t \text{ for } \textit{meta} \text{ xylene}$$

$$\gamma_t = 29.262 - 0.1025t \text{ for } \textit{para} \text{ oxylene}$$

15. Formamide, $HCONH_2$. ($M = 45.02$.)

Hoffman and Kropff preparation; densities from Turner and Merry.¹ This liquid is very viscous, so that very great care was taken with the determinations. The drop weights (Tip No. 3) found are as follows:

¹ *J. Chem. Soc.*, 97, 2074 (1910).

² *THIS JOURNAL*, 33, 676 (1911).

t .	w .
0	62.340
20	60.640
40	58.950

from which

$$w_t = 62.338 - 0.0848t.$$

Using this equation and the densities given below we find

$$v_t = 54.158 - 0.0363t$$

from which, it follows:

$$\gamma_t = 58.306 - 0.7927t$$

and

$$a_t^2 = 10.341 - 0.00693t.$$

The values of t_c calculated, here, are

t .	d .	$w(M/d)^{2/3}$.	t_c .
20	1.1350	705.32	337.9
30	1.1267	698.88	345.1
45	1.1142	(689.12)	(355.8)

from which it is evident that the liquid is associated.

Below is a comparison with the results of Turner and Merry:

COMPARISON OF VALUES.

t .	γ (M. and S.).	γ (T. and M.).	a_t^2 (M. and S.).	a_t^2 (T. and M.).
20	56.721	57.35	10.39	10.30
30	55.928	56.51	10.13	10.22
45	(54.739)	55.27	(10.03)	10.11

The results of Turner and Merry, as has been observed by other workers with the capillary rise method, are always higher than any others—just as would be observed if there had been some error in the measurement of the radius of their capillary tube. What this is due to in reality, it is of course impossible to tell; here, however, we also wish to call attention to the fact that the Turner and Merry results are invariably higher than those obtained from drop weight.

16. Dimethyl Nitroso-amine, $(\text{CH}_3)_2\text{N}\cdot\text{NO}$. ($M = 74.07$.)

Hoffman and Kropff preparation; densities from Turner and Merry. The drop weights here (Tip No. 3) are

t .	w .
20	39.788
30	38.469
40	37.185

from which

$$w_t = 42.380 - 0.1300t.$$

By aid of the densities and this equation, we find

$$v_t = 41.398 - 0.0927t$$

from which

$$\gamma_t = 39.639 - 0.1216t$$

$$a_t^2 = 7.905 - 0.0177t.$$

The values of t_c here are given in the following table:

t .	d .	$w(M/d)^{2/3}$.	t_c calculated.
20	1.0059	698.86	335.1
30	0.9965	680.26	336.9
45	0.9813	(652.44)	(339.6)

and prove the liquid to be associated.

A comparison of the results with those of Turner and Merry will be found in the following table:

COMPARISON OF RESULTS.

t .	γ (M. and S.).	γ (T. and M.).	a_t^2 (M. and S.).	a_t^2 (T. and M.).
20	37.207	38.97	7.551	7.888
30	35.991	37.73	7.374	7.720
45	(34.775)	35.80	(7.108)	7.437

Here the differences from Turner and Merry's results are even greater than usual. This may be due to differences in the samples of materials used, for all the liquids in this investigation are difficult to obtain pure and then to retain them in that condition.

17. Acetophenone, $\text{CH}_3\text{COC}_6\text{H}_5$. ($M = 120.06$.)

Preparation from Hoffman and Kropff, densities as used by Dutoit and Friedrich. The drop weights (Tip No. 3) densities, drop volumes and values for t_c are given in the table below:

t .	w .	d .	v .	$w(M/d)^{2/3}$.	t_c calculated.
30	39.880	1.0195	39.117	958.14	459.7
40	38.671	1.0109	38.254	934.36	459.2
50	37.413	1.0022	37.329	909.19	458.1

from which

$$w_t = 43.626 - 0.1243t$$

and

$$v_t = 41.810 - 0.0894t$$

which leads to

$$\gamma_t = 40.805 - 0.1162t$$

and

$$a_t^2 = 7.983 - 0.0171t.$$

A comparison of these values with those by Dutoit and Friedrich is given in the following table:

t .	γ (M. and S.).	γ (D. and F.).	a_t^2 (M. and S.).	a_t^2 (D. and F.).
24.5	37.957	37.85	7.564	7.538
74.9	(32.014)	32.35	(6.702)	6.579
127.2	(26.020)	26.90	(5.808)	5.894

Guye and Perrot¹ give the value 34.43 at 54.4°, while the value extrapolated from our equation would be 34.50.

Just what this decrease in the value of t_c with increased temperature of observation means is not certain—but assuredly the liquid is not to be considered as non-associated. Perhaps a decrease in t_c , as calculated, may also be taken as a sign of association just as an increase is. At any rate, in the course of this work we are collecting such data with others in the hope that ultimately we shall be able to correlate most of the properties of a liquid through its drop weight or surface tension, or its drop volume or constant of capillarity. For the present then we shall consider liquids of this type as associated—for certainly they cannot be non-associated since t_c is not independent of the temperature of observation.

18. Benzophenone, $(C_6H_5)_2CO$. (M = 182.0.)

Preparation from Eimer & Amend, three times recrystallized—densities as used by Dutoit and Friedrich. The drop weights (Tip No. 3) are

t .	w .
10	47.673
20	46.475
30	45.455
40	44.220
50	43.052
60	41.898
70	40.787

from which we find

$$w_t = 48.827 - 0.1151t.$$

By aid of the densities below, with this equation we find

$$v_t = 43418 - 0.0725t - 0.0000466t^2$$

from which we have

$$\gamma_t = 45.669 - 0.1076t$$

and

$$a_t^2 = 8.290 - 0.01384t - 0.00000891t^2$$

whereas Walden gives as the results of Dutoit and Friderich's measurements

$$\gamma_t = 45.80 - 0.1025t$$

and

$$a_t^2 = 8.37 - 0.0148t.$$

A comparison of results and the values found for t_c is given in the table below:

t .	d .	γ (M. and S.).	γ (D. and F.).	$w(M/d)^2/3$.	t_c .	a_t^2 (M. and S.).	a_t^2 (D. and F.).
33.5	1.099	42.07	42.38	1356.2	639.3	7.816	7.867
89.4	1.054	(36.05)	36.50	1195.0	623.9	(6.982)	7.060
173.9	0.986	(27.01)	28.05	934.0	593.0	(5.613)	5.801

¹ Arch. des. Sci. Phys. et Nat., 11, 225 (1901).

Guye and Perrot¹ give the value 40.08 for γ_c at 54.3°, compared with 39.83 from our equation. Here again the value for γ_c decreases with the temperature of observation. We shall therefore regard benzophenone, just as acetophenone, as associated. In this case we worked much below (39°) the solidifying point of the stable modification, 49°, to see whether the supercooled liquid would show anomalous surface tensions; but this was not found to be the case.

19. Ethyl-propyl ether, $C_2H_5OC_3H_7$. ($M = 88.09$.)

Preparation from Hoffman and Kropff; densities calculated from Dobreiner's equation for specific volume, $v = 1 + 0.0013116t + 0.0526162t^2 + 0.0715616t^3$ where the specific gravity at 0° is 0.7545. The drop weights (Tip No. 3) densities, and values of t_c are given in the following table:

t .	w .	d .	$w(M/d)^{2/3}$.	t_c calculated.
0	22.404	0.7545	535.21	242.7
20	20.112	0.7346	489.06	242.3

from which it is plain that the liquid is non-associated. The equations for w_t and v_t are

$$w_t = 22.404 - 0.1146t$$

and

$$v_t = 29.694 - 0.1159t$$

from which

$$\gamma_t = 20.955 - 0.1072t$$

and

$$a_t^2 = 5.670 - 0.02213t.$$

No results of capillary rise or surface tension are to be found in the literature.

20. Acetal, $CH_3CH(OC_2H_5)_2$. ($M = 118.11$.)

Preparation from Hoffman and Kropff. Densities from Walden's formula $d_t = 0.8461(1 - 0.001228t)$. The drop weights (Tip No. 3), drop volume and values of t_c are given in the following table:

t .	w .	d .	v .	$w(M/d)^{2/3}$.	t_c .
20	22.394	0.84402	26.518	612.36	296.83
30	21.326	0.84298	25.323	589.00	296.50
40	20.322	0.84194	24.125	565.25	295.70

While the values of t_c show a slight downward trend, it is probable that this liquid, with more carefully determined densities, would show itself to be perfectly non-associated. It is to be considered as non-associated.

The only results in the literature are those of Schiff; at 20° he finds 21.47 for γ as compared with our 20.934. It is seldom that even those observers working with the capillary rise method, can check Schiff, who simply made determinations at the freezing and boiling points of a liquid.

¹ *Loc. cit.*

21. Furfural, C_4H_3OCHO . $M = (96.032)$

This sample was from Hoffman and Kropff and was redistilled just before each determination; the densities were from Walden's formula $d_t = 1.1811(1 - 0.000895t)$. The values for this liquid (Tip No. 3) are as follows:

t .	w .	d .	v .	$w(M/d)^2/s$.	t_c .
20	44.757	1.1600	38.618	850.91	376.3
30	43.568	1.1494	37.839	831.01	367.5
40	42.150	1.1388	37.045	811.25	358.8

from which we find

$$w_t = 47.407 - 0.1305t$$

$$v_t = 40.197 - 0.07875t$$

and

$$\gamma_t = 44.341 - 0.1221t$$

$$a_t^2 = 7.675 - 0.01504t.$$

Again Schiff's values are considerably higher than those for γ and a^2 from drop weight.

22. Anethole, $CH_3OC_6H_4CH:CHCH_3$. ($M = 148.09$.)

This liquid was obtained from Hoffman and Kropff; the densities from Bolle and Guye.¹ The values of w here (Tip No. 3) are as follows:

t .	w .
25	36.69
35	35.64
45	34.52

from which

$$w_t = 39.420 - 0.1087t.$$

From this and the densities below, we find

$$v_t = 38.751 - 0.0783t.$$

For γ_t and a_t^2 we therefore find

$$\gamma_t = 36.871 - 0.1016t$$

$$a_t^2 = 7.399 - 0.0149t.$$

The values of t_c , as well as a comparison of the values for γ and a^2 , from these formulas with those found by capillary rise by Renard and Guye, will be found in the following tables:

t .	w .	d .	v .	$w(M/d)^2/s$.	t_c .
8.3	38.518	1.011	38.099	1070.3	487.7
41.4	34.922	0.983	35.526	988.7	484.7
55.2	(33.423)	0.971	(34.421)	(954.1)	(483.2)

From this we find

$$w_t = 39.420 - 0.1087t$$

$$v_t = 38.751 - 0.0783t$$

¹ *Jour. chim. phys.*, 3, 39 (1905).

and
$$\gamma_t = 36.871 - 0.1016t$$

$$a_t^2 = 7.399 - 0.0149t.$$

Walden has calculated from Renard and Guye's results (from 8.3° to 224.2)

$$\gamma_t = 36.61 - 0.08639t^1$$

and

$$a_t^2 = 7.59 - 0.01503t.$$

t .	γ (M. and S.).	γ (R. and G.).	a^2 (M. and S.).	a^2 (R. and G.)
8.3	36.090	36.71	7.275	7.395
41.4	32.665	33.25	6.781	6.896
55.2	(31.263)	31.89	(6.575)	6.698

The higher value by capillary rise here may well be due to impurity—the sample we employed was as pure as it could be made, and that just before the determination. The liquid is to be considered as associated just as those others discussed above.

Summary.

The results of this investigation may be summarized as follows:

1. The drop weights of twenty-two pure organic liquids have been determined at various temperatures, and the equations giving the variation, with temperature, of the surface tension and capillary constant calculated from them.

2. The application of the Morgan definition of normal molecular weight in the liquid state, shows that only three of these liquids, *viz.*, acetal, ethyl propyl ether, and ortho toluidine are non-associated, for they are the only ones for which the calculated values of the critical temperature (t_c) were found to be constant, and independent of the temperature of observation.

3. In some of the cases it was found that t_c , as calculated, actually decreased with the temperature of observation. What this indicates is not known—but for the present, since these liquids cannot be considered as non-associated (for t_c is not constant), they are regarded as associated.

4. The liquids used in this investigation are just those which are difficult to get and to keep in a pure condition. It is thought here that in every case purity was attained—in some cases it being even necessary to redistil just before each determination. The agreement with the results of other observers is not quite as good as has been observed in the other paper of this series—and it is thought to be due to a difference in purity of the samples used.

5. Benzophenone was studied as much as 39° below its solidifying point, in order to see if the supercooled liquid showed any abnormalities; but

¹ This curve does not agree well with the lower points but does with the higher. In the table are the first three actual R. and G. results.

none were observed. The observation of Feustel that the ortho compound has always the highest surface tension, while the para gives the smallest, is borne out by our work on the toluidine—and also by the Morgan-Daghlian work on the xylenes.

LABORATORY OF PHYSICAL CHEMISTRY.

[FROM THE BIOCHEMICAL LABORATORY OF HARVARD MEDICAL SCHOOL, BOSTON.]
**THE EFFECT OF ULTRA-VIOLET LIGHT UPON THE CATALYTIC
ACTIVITY OF COLLOIDAL PLATINUM.**

BY CHESTER J. FARMER AND FREDERIC PARKER, JR.

Received July 31, 1913.

The experiments described in this paper were suggested by the results obtained in certain experiments by Bovie and Farmer. These experimenters exposed cystin to the ultra-violet light and found that hydrogen sulfide and ammonia were set free. The ammonia was determined quantitatively by the new Folin method. Hydrogen sulfide was evolved after acidifying the exposed liquid with sulfuric acid.

It is known that the catalytic action of colloidal platinum on hydrogen peroxide is destroyed by boiling the colloidal platinum solution. If heat and ultra-violet light have a similar effect, it seemed reasonable to expect that the light would destroy the catalytic activity of the colloidal platinum. Such, indeed, was found to be the case, as is described below.

Preparation of Colloidal Solution.—A solution of colloidal platinum was prepared by the Bredig method, *i. e.*, by producing an arc between platinum electrodes under distilled water.

Source of Light.—The ultra-violet light used for these experiments was obtained from mercury vapor. The lamp was loaned to us by Mr. Bovie of the Department of Plant Physiology, Harvard University. It was constructed of transparent quartz tubing 1 cm. in diameter. The lamp carried 1½ amperes of current. The voltage across the terminals was 45 volts. The arc was 10 cm. long.

Exposure of the Colloidal Platinum.—The surface of the platinum solution was directly exposed to the rays of the lamp in the following manner:

Thirty-five cc. of colloidal platinum solution were put into a shallow crystallizing dish. This dish was placed in a larger Petri dish, which contained water. In this way evaporation was reduced to a minimum, and the possibility of the destruction of the colloid by heat was guarded against. Any water lost by evaporation was replaced.

Preparation of a Dilute Hydrogen Peroxide Solution.—The hydrogen peroxide used to measure the activity of the colloidal platinum was obtained by diluting a 3% solution of Merck's hydrogen peroxide with an equal volume of distilled water. This solution was kept at a constant temperature by being immersed in running tap water.