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.

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

BY J. LIVINGSTON R. MORGAN AND GUSTAV EGLOFF.

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 standardized[1] 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.	t.	Wt. 1 drop. (Mg.). w.	Surface tension (dynes). γ.	Constant ($= \gamma/w$).
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 $a_t^2 = 2\gamma_t/9.80 \, d_t$, 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).

From the value of the constant, 0.9389, the mean diameter of this tip is calculated[1] to be approximately 5.35 mm.

The sample of phenol used as a basis for this work was prepared especially for us[2] and was of a high order of purity. So much difficulty had been experienced in the past, however, in obtaining this substance in the pure state, considering the melting point as a criterion, that this original sample was first redistilled three times *in vacuo*, before the final recrystallization was made.

The melting point of the product so obtained was determined, with both a rising as well as a falling column, by aid of a certified thermometer; the solid and liquid phases, when stirred continuously, remaining in equilibrium for more than three hours at a constant temperature of $39.70° \pm 0.02$. This value agrees very satisfactorily with the mean of the determinations of Ladenberg,[3] $39.5°$; Guye and Tsakalatos,[4] $39.5°$; Eykman,[5] $39.6°$; Paterno and Ampola,[6] $39.6°$; Riesenfeld,[7] $39.8°$; and Block,[8] $39.9°$. As variations from this value by as much as from 7–13% are found by other observers,[9] this property should be an excellent test of purity, for it is hardly possible that any other could be as sensitive.

For use in calculating the values of specific cohesion from those of surface tension (or drop weight), careful determinations of the density of the pure phenol were made at various temperatures, employing an Ostwald-Sprengel pyknometer with stoppered limbs. The results of these measurements are given in Table II.

TABLE II.—DENSITY OF PURE PHENOL.

t	$40°$	$45°$	$50°$	$55°$	$60°$	$66°$
d	1.05794	1.05366	1.04936	1.04508	1.04077	1.03532

Application of the method of least squares to these results leads to the following linear relationship between density and temperature:

$$d_t = 1.09226 - 0.000858\ t,$$

which *between 40° and 60°* represents the experimental results to practically the fifth place of decimals.

Just as with the melting point, the densities of phenol, as determined by other investigators, vary widely among themselves, but naturally to no such extent as in the former case. The above results agree most

[1] See Morgan, *Loc. cit.*
[2] Prepared by the Hoffman and Kropff Chemical Company.
[3] *Ber.*, **43**, 202 (1910).
[4] *J. chim. phys.*, **8**, 340 (1910).
[5] *Z. physik. Chem.*, **4**, 502 (1889).
[6] *Gazz. chim.*, **27**, 481 (1897).
[7] *Z. physik. Chem.*, **41**, 1350 (1902).
[8] *Ibid.*, **78**, 397 (1912).
[9] $34–35°$ to $42.4°$.

closely with those of Worley, Thole, Hewitt and Winmill, Bolle and Guye, and Ramsay and Aston, which were taken from Kopp,[1] the difference in few cases being larger than 0.1%, which is to be considered as negligible in the calculation of specific cohesion from the surface tension.

The values of surface tension, specific cohesion, and the density used to obtain the latter from the former, as well as the γ and a^2 values given by interpolation formulas, are presented in Table III, at the various temperatures studied. Each result here is from an average of at least three measurements of drop weight, no one deviating from another by more than a few hundredths of one per cent.

TABLE III.

t.	γ ($= 0.9389\ w_t$).	γ (calc.).	d.	a^2 (from γ_t and d_t).	a^2 (calc.).
23	39.22	39.28	1.0725	7.46	7.48
30	38.56	38.54	1.0665	7.38	7.38
32	38.35	38.33	1.0658	7.34	7.35
34	38.13	38.12	1.0631	7.32	7.32
36	37.92	37.91	1.0614	7.29	7.29
38	37.68	37.70	1.0597	7.26	7.26
41	37.43	37.38	1.0571	7.23	7.22
45	36.99	36.96	1.0537	7.16	7.16
49	36.57	36.54	1.0503	7.11	7.10
55	35.90	35.91	1.0451	7.01	7.01
60	35.41	35.38	1.0408	6.94	6.94
62	35.12	35.17	1.0391	6.90	6.91
63	34.76	34.75	1.0353	6.85	6.85

Columns 2 and 3, and 5 and 6, agreeing as closely as they do, prove the interpolation formulas derived to represent the experimental results with considerable accuracy. These equations are

$$\left.\begin{aligned} \gamma_t &= 41.701 - 0.1053t \\ a_t^2 &= 7.810 - 0.0145t \end{aligned}\right\} t \text{ from } 23° \text{ to } 63°.$$

A comparison of the values of γ and a^2 interpolated or extrapolated from these equations, with those found directly by other observers, by the capillary rise method, at their temperatures, is made in Table IV.

These results are also presented in graphical form, as respects γ, in Fig. 1, which also includes the results of Bolle and Guye,[2] uniformly higher than all others by the same method (capillary rise); and those of Feustel,[3] by the air bubbling method, very considerably higher than the others, but of about the same temperature coefficient.

With respect to the Feustel results, it may be said that they are uniformly high for all other liquids, when compared to those obtained by capillary rise. Assuming that the method of Feustel is a correct *relative*

[1] *Ann.*, **95**, 312 (1855).
[2] *J. chim. phys.*, **3**, 38 (1905).
[3] *Ann. Phys.*, **16**, 61 (1905).

one, and standardizing it with benzene, as we do in the drop-weight method, the results for phenol, and also for several other liquids which have been studied by others, are found to be reduced to the same order as those of the others. Even relatively however, judged by the results of the surface tension of benzene, it can hardly be considered as an accurate method so far as reproducibility of result is concerned, for with that liquid large differences in value (0.1 dyne) appear at temperatures only 0.1° apart, the higher temperature in fact leading to the higher result (*viz.*, at 20.8° and 20.9° and at 57.1° and 57.2°, at which the γ values
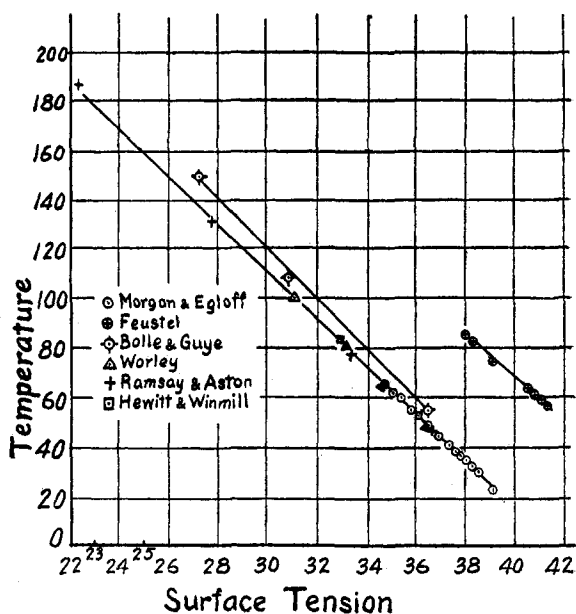

Fig. 1.

as he gives them are, respectively, 30.21, 30.31, 25.02 and 25.11 dynes).

TABLE IV.—A COMPARISON OF RESULTS.

	Surface tension, γ.				Specific cohesion, a^2.			
t.	R. & A.[1]	H. & W.[2]	W.[3]	M. & E. (calc.).	R. & A.	H. & W.	W.	M. & E. (calc.).
46.0	36.81	...	...	36.86	7.15	..	..	7.14
49.0	...	...	36.54	36.54	..	..	7.09	7.10
53.3	...	36.17	...	36.09	..	7.07	..	7.04
66.0	...	...	34.73	34.75	..	..	6.81	6.85
78.0	33.32	...	...	33.49[4]	6.71	..	..	6.69[4]
81.0	...	...	33.16	33.17[4]	..	..	6.59	6.64[4]
83.0	...	32.95	...	32.96[4]	..	6.60	..	6.61[4]
100.0	...	...	31.10	31.17[4]	..	..	6.26	6.36[4]
131.7	27.90	...	...	27.83[4]	5.88	..	..	5.90[4]
184.0	22.39	...	...	22.33[4]	4.98	..	..	5.14[4]

It will be seen from the above that the tip employed in this work, when

[1] Ramsay and Aston, *J. Chem. Soc.*, 65, 168 (1894).

[2] Hewitt and Winmill, *Ibid.*, 91, 446 (1907).

[3] Worley, *Ibid.*, 105, 267 (1914).

[4] Extrapolated above last temperature, 63°. The extrapolation in the case of a^2 is really a double one, *i. e.*, of γ, and also of d, which could account for the greater discrepancy in some values of a^2 than of γ, where but the one factor is extrapolated.

standardized by aid of the universally accepted value of the surface tension of water, also gives results for the surface tension of phenol which are in very excellent agreement with those of other observers; the values of Bolle and Guye being excluded here, since they are not in accord with the three other observers using the same method.

This procedure, which is practically an identical standardization of the tip from accepted values of the surface tension of the liquids forming the two extremes, and differing widely, enables us to lay very great stress upon the results obtained for mixtures of the two liquids, which in all cases lie between these extremes in value.

Surface Tension and Specific Cohesion of Water Mixtures.

The mixtures studied below were made up in the following manner, the water being a specially purified sample which was also employed in standardizing the tip: To a weighed amount of the one constituent in a "non-sol" vessel, a sufficient amount of the other was added to give the approximate concentration desired, the actual weight being found by weighing the stoppered vessel. The drop weights in each case were then determined as soon as possible, the vessels being kept in darkness to avoid possible decomposition. Precautions were also taken in transferring the solutions to the supply vessel of the apparatus, to minimize possible loss by evaporation, and absorption of moisture or other impurities from the air, the liquid being cooled to a low temperature just before the transfer. As the whole operation required less than a minute, any change in concentration taking place was negligible.

The values of γ and a^2 found at the various concentrations and temperatures studied, together with the density values[1] employed to calculate the one from the other are given in Table V.

TABLE V.—SURFACE TENSION AND SPECIFIC COHESION OF PHENOL-WATER MIXTURES.

$\%$ = grams phenol per 100 g. of mixture.

	$\% = 0.$		$\% = 0.534.$			$\% = 0.770.$		
$t.$	$\gamma.$	$a^2.$	$\gamma.$	$d.$	$a^2.$	$\gamma.$	$d.$	$a^2.$
0°	75.87	15.49	68.23	...	...	64.77	...	...
20	72.69	14.87	66.13	1.0010	13.50	63.23	1.0010	12.90
30	71.03	14.57	65.19	0.9974	13.32	62.51	0.9986	12.75
35	70.19	14.42	64.77	0.9965	13.27	62.14	0.9976	12.68
40	69.33	14.28	64.30	0.9955	13.20	61.83	0.9968	12.65
45	68.47	14.13	63.79	0.9934	13.13	61.40	0.9936	12.60
50	67.59	13.98	63.27	0.9897	13.06	60.99	0.9905	12.57
55	66.69	13.83	62.80	0.9862	12.98	60.64	0.9882	12.52
60	65.80	13.67	62.30	0.9827	12.92	60.27	0.9862	12.48
65	64.88	13.52	61.82	0.9792	12.85	59.89	0.9841	12.43

[1] These densities are found from interpolation formulas derived from the results of Worley (*l. c.*) for concentrations from 0.5 to 6.25%, and from Friedlander (*Z. physik. Chem.*, 38, 385 (1901)), for those from 9.54 to 100%.

TABLE V (Continued).

t.	% = 0.970 γ.	d.	a².	% = 1.47 γ.	d.	a².	% = 3.48 γ.	d.	a².
0°	62.31	....	...	...	....	...	...	....	..
20	61.02	1.0010	12.46	...	....	...	...	....	..
30	60.27	0.9975	12.36	56.23	1.0000	11.49	46.11	1.0000	9.40
35	60.08	0.9970	12.28	56.08	0.9984	11.46	46.00	0.9986	9.38
40	59.74	0.9965	12.23	55.89	0.9974	11.43	45.91	0.9970	9.36
45	59.44	0.9938	12.20	55.68	0.9954	11.40	45.85	0.9952	9.34
50	59.15	0.9911	12.16	55.44	0.9936	11.38	45.76	0.9940	9.32
55	58.80	0.9904	12.12	55.25	0.9918	11.35	45.65	0.9923	9.30
60	58.47	0.9897	12.05	55.03	0.9901	11.32	45.57	0.9907	9.28
65	58.16	0.9890	11.98	54.78	0.9884	11.30	45.48	0.9890	9.26

t.	% = 4.53 γ.	d.	a².	% = 8.74 γ.	d.	a².	% = 58.6 γ.
25	...	....	...	...	....	...	...
30	43.14	1.0012	8.78	...	....	...	...
35	43.07	1.0006	8.76	37.22	1.0016	7.63	...
40	42.95	1.0000	8.75	37.09	0.9994	7.57	...
45	42.82	0.9978	8.73	36.89	0.9975	7.53	...
50	42.67	0.9955	8.70	36.72	0.9956	7.50	...
55	42.54	0.9937	8.68	36.53	0.9940	7.47	...
60	42.36	0.9920	8.66	36.35	0.9925	7.43	35.25
65	42.28	0.9903	8.64	36.11	0.9910	7.39	34.96

t.	% = 65.45 γ.	d.	a².	% = 70.40 γ.	d.	a².	% = 74.00 γ.	d.	a².
30	...	....	...	38.09	1.0445	7.44	38.22	1.0469	7.42
35	...	....	...	37.72	1.0407	7.40	37.83	1.0447	7.40
40	...	....	...	37.33	1.0369	7.32	37.41	1.0412	7.35
45	...	....	...	36.96	1.0331	7.25	36.99	1.0377	7.28
50	36.23	1.0244	7.23	36.53	1.0294	7.22	36.59	1.0343	7.22
55	35.93	1.0203	7.17	36.15	1.0253	7.20	36.19	1.0301	7.17
60	35.55	1.0162	7.13	35.74	1.0212	7.15	35.77	1.0260	7.13
65	35.23	1.0122	7.10	35.36	1.0171	7.08	35.38	1.0219	7.09

% = 76.60 t.	γ.	d.	a².	% = 100 pure phenol. t.	γ (calc.).	a² (calc.).
30	38.29	1.0482	7.45	0°	41.70	7.81
35	37.89	1.0452	7.40	20	39.59	7.62
40	37.50	1.0423	7.34	30	38.54	7.38
45	37.08	1.0391	7.28	35	38.02	7.29
50	39.65	1.0360	7.22	40	37.49	7.23
55	36.24	1.0322	7.15	45	36.96	7.16
60	35.83	1.0285	7.13	50	36.44	7.08
65	35.44	1.0205	7.08	55	35.91	7.01
				60	35.38	6.94
				65	34.86	6.87

The few results for the surface tension of weak water solutions of phenol given by Worley, seem to accord very satisfactorily with those interpolated, from our results given above, to his concentrations and temperatures. Naturally, the deviations here are much more considerable than in the case of pure phenol, as in fact we should expect, when the enormous

percentage change in the value of γ, due to a very small change in the concentration in solutions of just this order of concentration, is considered.

The Surface Tension of Triethylamine-Water Mixtures.

The sample of triethylamine employed here was originally of a very high order of purity, and just before being used was distilled over completely at a fixed temperature *in vacuo*.

Unfortunately, it has not been possible to calculate the values of specific cohesion (a^2) either for the pure liquid, or for its water solutions, for the densities were not determined at the time, and none can now be found in the literature.

The advantage of this liquid, when mixed with water, over phenol, is that it enabled us to extend the investigation to a point a number of degrees removed from the critical solution temperature, *on the completely miscible side*, which could not be done in the case of phenol. For, in the triethylamine case, the area of complete miscibility lies *below* a certain maximum temperature, while with phenol it lies *above* a certain minimum temperature. On the other hand, it was possible with phenol to attain a point considerably removed from the point of existence of two layers, and on the miscible side, so that a fairly complete general survey of all possible conditions is obtained from a consideration of the two systems.

The results for the surface tension of triethylamine-water mixtures are given in Table VI.

TABLE VI.—THE SURFACE TENSION OF TRIETHYLAMINE-WATER MIXTURES.

$\%$ = grams triethylamine to 100 grams of mixture.

t.	$\% = 0.$ $\gamma.$	$\% = 0.50.$ $\gamma.$	$\% = 1.00.$ $\gamma.$	$\% = 2.10.$ $\gamma.$	$\% = 2.44.$ $\gamma.$	$\% = 4.79.$ $\gamma.$
$0°$	75.87	58.21	52.49	46.07	. . .	39.61
19.2	72.82	53.23	47.42	40.25	38.71	31.78
30.0	71.03	51.47	45.01	37.39	35.96	27.18

t.	$\% = 10.00.$ $\gamma.$	$\% = 50.50.$ $\gamma.$	$\% = 75.38.$ $\gamma.$	$\% = 94.86.$ $\gamma.$	$\% = 100.$ $\gamma.$
$0°$	31.33	25.25	23.94	22.64	22.31
19.2	24.40	21.73	21.50	20.67	20.53
30.0	. . .	. . .	. . .	19.56	. . .

Discussion of Results.

Up to the present, liquids which mutually dissolve to a limited extent at some one temperature, and which in some cases ultimately mix in all proportions, have been generally distinguished, using a physical property as a criterion, only by the fact that the vapor pressures exhibited by the two constituent layers are identical.[1] But when we consider either layer alone, after its removal from the system, or the system itself after the point of complete miscibility has been passed, even the vapor pressure does not enable us to distinguish it from any other type of liquid mixture.

[1] Konowalow, *Wied. Ann.*, 14, 219 (1881).

By that criterion, then, it has passed from the one type of mixture to another, just as it has visually.

The consideration of the property-composition curves obtained from the above results (see Figs. 2 and 3), for such typical systems of this class as phenol and water, or triethylamine and water,[1] however, shows
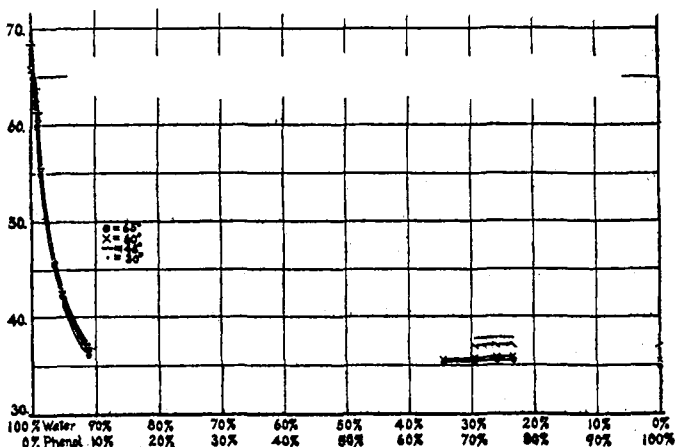

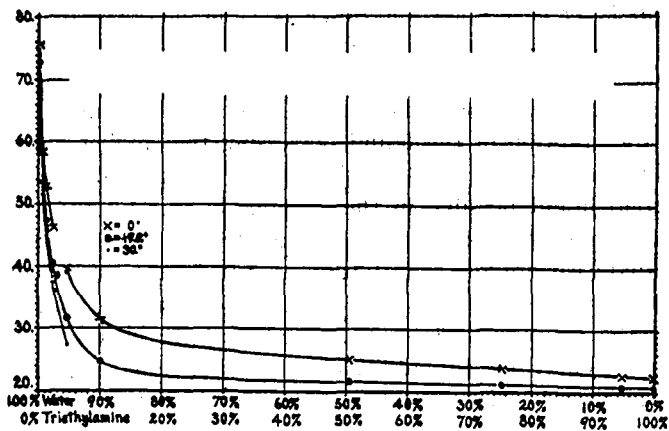
Fig. 2.—Surface tension-composition. Phenol–water.

Fig. 3.—Surface tension-composition. Triethylamine–water.

[1] A curve similar to the γ-curves above has already been given by Antonow (*J. chim. phys.*, **5**, 371 (1907)) for isobutyric acid-water mixtures, on the basis of a few capillary rise results in the more concentrated solutions. The rapid fall in the surface tension of water, due to the addition of certain other substances, has also already been noted by Whatmough (*Z. physik. Chem.*, **39**, 129 (1901), Drucker (*Ibid.*, **52**, 649 (1905)), Morgan and Neidle (THIS JOURNAL, **35**, 1860 (1913)), Worley (*Loc. cit.*) and others; but no complete or general study of such systems has ever been attempted up to the present.

The α^2-composition curve is so similar to that for γ that it is not necessary to reproduce it here.

that it is possible, with both surface tension and specific cohesion as the physical property selected, to go much farther in the characterization of such systems, not only when in two layers, but also for the one segregated layer, and even for the entire, homogeneous, system up to (or down to) a point considerably removed from the temperatures of complete miscibility.

From these property-composition curves, which certainly differ widely in form from those obtained for either γ or a^2 for any other type of liquid mixture, or from any other property-composition curve, it is to be noted, *first*, and this is apparently characteristic for all such systems, that the liquid of larger surface tension has its value enormously decreased by even small additions of the other liquid. The liquid of the smaller surface tension, on the contrary, is either infinitesimally changed, as far as its property-value is concerned, by a small addition of the other liquid, and then exhibits a constant property-value, independent of the change in concentration, even though this be large (phenol); or, there is a steady, though very small, change in the property-value with changing concentration (triethylamine). In all cases, however, the depression of the property-value of the liquid with the larger surface tension, due to the addition of the other liquid, is such that when the saturation point of the aqueous layer is reached, the property-value has been depressed to a value but slightly removed from the surface tension of the other, pure, liquid.

The steepness of the curve showing the effect, on the surface tension of water, of the addition of the liquid possessing the smaller value, will be seen from the above to depend mainly upon the magnitude of the amount of the second liquid possible in the aqueous layer, and the γ values of water and the other constituent at that temperature. Granting, for example, that two liquids, each forming a two-layer system with water, have identical surface tensions, the one being soluble to 1% and the other to 10% in the aqueous layer, it is evident that the general trend of the γ-composition curve for the addition of the first liquid to water will be steeper than that for the second to water, for in both cases the surface tension of water will have to be depressed to practically the same value, within a few per cent. at most; the one through a distance on the axis of abscissas equal to 1, the other distributed through an interval of 10. If the effect of concentration upon the surface tension were uniform, it would be possible thus to predict, with some degree of accuracy, the actual curve that would be found; and even as it is, this would be possible on the small scale of the curves. The numerical results, however, show this to depend. perhaps, somewhat upon the nature of the liquid—at least we can go no farther, at present.

With phenol-water mixtures, it was not possible to work at a tempera-

ture above the critical solution point. For triethylamine-water mixtures, however, sets of results are given at 0°, about 18.5° on the miscible side, and at 30° about 11.5 on the immiscible side of the critical solution point. The farther a system is removed from its critical point on the immiscible side, the more the above properties are accentuated in every respect. The more it is removed from that point, on the miscible side, the smaller is the effect of the second liquid on the water, and the greater the effect of the water upon it—in other words, the more the system approaches what is probably the most common type of property-composition curve for the surface tension of liquid mixtures.

The results show apparently that phenol reacts differently when water is added to it in small quantities at 60° and 65° from the way it does at 30° and 45°; for in the latter case the pure phenol has a slightly higher value, and in the former a slightly lower value, than the system produced; the values of γ for the phenol solutions of water being equally independent, however, of changes in concentration through the range investigated.

When the above, evident, properties of such liquid systems, from the point of view of surface tension or specific cohesion, are considered in connection with the curves showing the variation in the deviation of the observed results of γ or a^2 (from those calculated from the law of mixtures)[1] with the percentage composition, a plausible explanation of the generally observed fact of a large change in the surface tension, due to a small addition of a substance to water is offered. Denison[2] has shown in this connection and from theoretical reasoning, that, when a compound is formed by the chemical interaction of the constituents of a mixture, the maximum deviation of a physical property of that system from the value calculated from the law of mixtures, must appear at that composition of the liquid system which corresponds to the composition of the substance found.

In Figs. 4, 5, 6, 7, and 8 are presented deviation curves for γ and a^2 from the above results, as well as those for density and viscosity for phenol-water mixtures,[3] and that for γ from our results for triethylamine and water. It is plain that the maximum deviation, as far as the γ and a^2 values are concerned, lies at a composition equal to 8.74 g. of phenol in 100 g. of the mixture, and that the corresponding point for triethylamine and water lies at a 10% concentration. The density and viscosity deviation curves at least enable us to fix a maximum for phenol-water mixtures

[1] See Morgan, THIS JOURNAL, 38, 555–568 (1916).

[2] Trans. Faraday Soc., 8, 20 and 35 (1912).

[3] These values for viscosity were obtained from the work of Friedlander (Z. physik. Chem., 68, 32 (1909), and Scarpa (Cim., 6, 277 (1904)), the values for density being from the same source as those above.

somewhere between 5 and 10%, but the data are not sufficient in this region to settle the point more definitely. These values, however, can be considered, as far as they go, as nothing if not confirmatory of the surface tension and specific cohesion maxima. Taking the maximum deviation for phenol–water systems at 8.74%, and that for triethylamine-
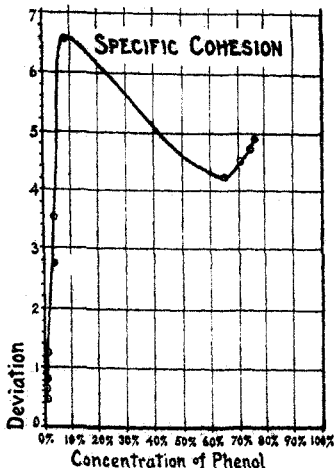
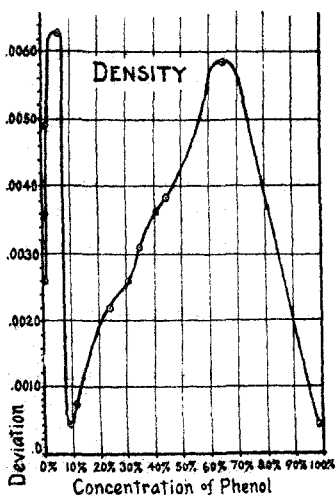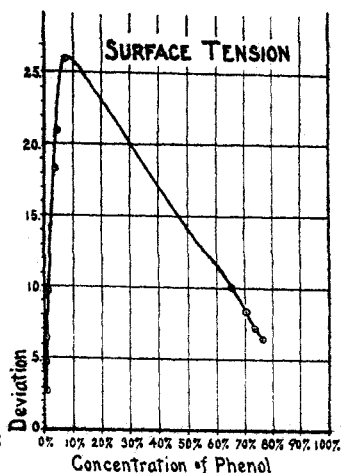Fig. 4 (65°).   Fig. 5 (65°).

SPECIFIC COHESION

Deviation

Concentration of Phenol

SURFACE TENSION

Deviation

Concentration of Phenol

DENSITY

Deviation

Concentration of Phenol

VISCOSITY

Deviation

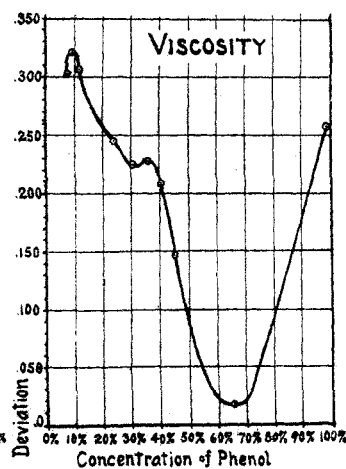Concentration of Phenol

Fig. 6 (70°).   Fig. 7 (70°).

water mixtures as 10%, the temperature not altering at all the concentration at which the maximum is exhibited, we find the compounds formed in the two cases are, respectively: $C_6H_5OH.55H_2O$ and $(C_2H_5)_3N.50H_2O$.

Granting the correctness then, of Denison's method, and the consequent truth of the existence in such systems of chemical compounds, we

see that the first addition to water of any liquid, which is mutually soluble in it, would result in the formation of the compound, and the lowering of the surface tension. Further additions, would then increase the amount of the compound present, with the consequent increase in the depression of the surface tension of the water layer, or what will ultimately be that, until when it is formed to the maximum extent, and all the water is so combined, the surface tension of the water is reduced to nearly that value for the other liquid itself. From the property-composition curves it is clear that the influence of this compound upon the surface tension of the other liquid, when dissolved in it, can be but small in any case.

We have made no attempt in this work to study the surface tensions of the two constituent, mutually saturated, layers of such systems when in equilibrium, feeling that a general survey of the same concentrations at various temperatures more important as a *first* step than the employment of a different concentration for each temperature.[1] From our
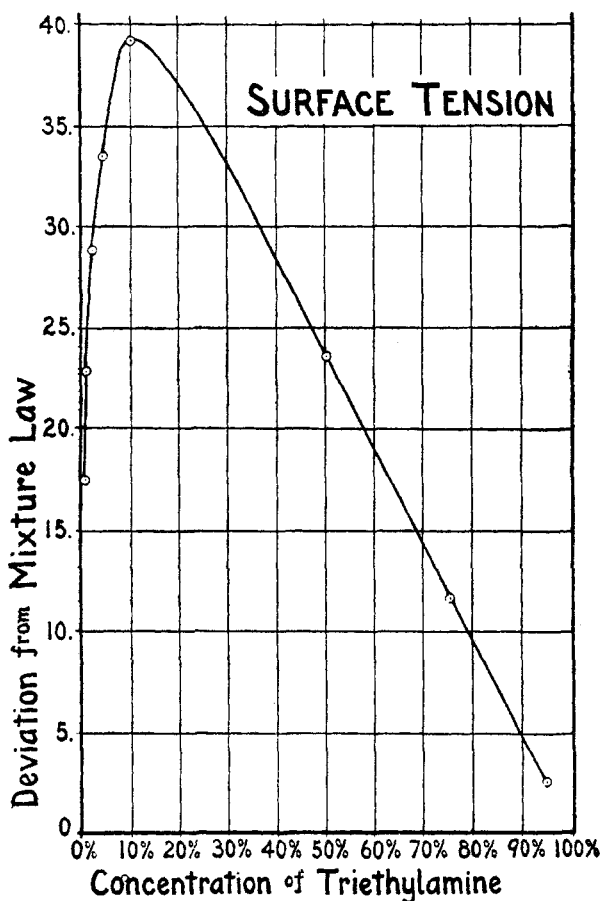

Fig. 8.

results, and the above reasoning, however, it would seem that the water layer consists simply of the compound formed, while the other layer is probably a solution of this compound in the second liquid, affecting its surface tension in the way shown in the curves—the critical solution point

[1] The question as to the surface tensions values of two co-existing layers, mutually saturated, at many temperatures, for a number of such systems is now being investigated in this laboratory and will be reported upon in the near future.

being the temperature at which the compound is soluble in the other liquid in all proportions.

Density and viscosity both show by their deviations the existence of other compounds of phenol and water, which do not appear to be possible of indication by either surface tension or specific cohesion. These are at 36% for viscosity (a faint maximum), and at 65% by density, which would correspond to the formulas $C_6H_5OH.9H_2O$ and $C_6H_5OH.3H_2O$, but the deviations in general are so small and the data so distributed, and so meager at the necessary concentrations, that, it is thought, little emphasis can be laid upon the results obtained.

The very exaggerated effect of a small amount of substance on the surface tension of water has usually been attributed to the effect of adsorption, which would cause the surface of the liquid to become more concentrated with respect to the other substance than the interior. The above reasons for this action, *viz.*, that at complete saturation the water layer *must* show a value of surface tension but little removed from that of the pure second liquid itself, which is dissolving; together with the fact that such curve types handled by the Denison deviation method must always indicate a compound at the composition of saturation, while perhaps not supplanting the theory based upon adsorption, at least would deserve a place beside it, especially as it has the advantage perhaps of enabling one from general grounds to predict approximately what will take place, even before a measurement is made.

Summary.

The results of this investigation may be very briefly summarized as follows:

I. The surface tensions have been found by the drop-weight method for a number of concentrations of the typical mutually soluble liquids, phenol and water and triethylamine and water, at temperatures both above and below the critical solution point.

II. The property-composition curves for such systems are typical, and characterized by the fact that the constituent of the lower surface tension depresses that of the other to such an extent that the maximum amount soluble in the water layer reduces the surface tension of this to a value differing but slightly from that of the other constituent, when pure. The smaller the amount necessary to saturate the water layer, the greater the effect will have to be, *i. e.*, the steeper the curve must be in all cases when the surface tensions of the second liquid are identical. On the other hand, the effect of the liquid of the larger surface tension upon that of the other is exceedingly slight, and may be independent of the concentration, or vary very slightly with it—according to the nature of the second liquid, perhaps.

III. Using the deviation of property-composition curves as a criterion

as to the possibility of a chemical combination of the constituents of the mixture, both surface tension and specific cohesion show a distinct maximum in the case of phenol at 8.74% phenol, indicating a compound of the formula $C_6H_5OH.55H_2O$, while triethylamine-water mixtures lead to a maximum at 10%, or $(C_2H_5)_3N.50H_2O$. Both density and viscosity for phenol and water, using results from the literature, confirm the above value.

The water layer of such systems must then be considered as transformed completely into a compound, the other layer being the second pure liquid containing the compound in solution, and having its surface tension but little affected thereby. The critical solution point can only be, then, the point at which the compound is completely miscible in the second liquid. As the coexisting layers of such systems in general are now being studied, the further discussion of these points must be postponed.

IV. A theory is presented which at any rate can serve as an alternative to the usual adsorption theory of the exaggerated effect upon the surface tension of water by the addition to it of other liquids.

NEW YORK. N. Y.

A REVISION OF THE ATOMIC WEIGHT OF CADMIUM.

[FOURTH PAPER.]

THE ELECTROLYTIC DETERMINATION OF CADMIUM IN CADMIUM BROMIDE.

BY GREGORY PAUL BAXTER, MERRITT ROY GROSE. AND MINER LOUIS HARTMANN.

Recently the atomic weight of cadmium has been redetermined by Baxter and Hartmann[1] in this laboratory by the electrolytic analysis of cadmium chloride. By using a glass electrolytic cell of special design it was found possible to deposit the metal in a mercury cathode directly from the solution of the salt. The results of this work fully substantiate the value for the atomic weight of cadmium previously established in the Harvard laboratory by Baxter, Hines, and Frevert[2] through comparison of the chloride and bromide of cadmium with silver. Both methods yielded the result 112.417 (Ag = 107.880). The electrolytic analysis of cadmium chloride was instigated by investigations by Perdue and Hulett,[3] Laird and Hulett,[4] and Quinn and Hulett,[5] who have recently obtained a considerably lower value,

[1] THIS JOURNAL, 37, 113 (1915); Z. anorg. Chem., 92, 53.
[2] Ibid., 27, 222 (1905); 28, 770 (1906); Ibid., 44, 158; 49, 415.
[3] J. Phys. Chem., 15, 1579 (1911).
[4] Trans. Am. Electrochem. Soc., 22, 385 (1913).
[5] J. Phys. Chem., 17, 780 (1913); THIS JOURNAL, 37, 1997 (1915).