rials. Both the nitrogen and the oxygen containing liquids, however, swell these roasted materials with assumption in each case of their characteristic complex configurations. The glycols and glycol derivatives can then be washed out with water, regenerating the natural mineral.

"Dead burned" materials (about 700 or 800°) have not been observed to swell with any of the agents employed.

Acknowledgment.—The author is indebted to Dr. M. J. Copley of the Eastern Regional Research Laboratory, who suggested the probable existence of associations between clays and the types of liquids employed, and who furnished the various polyamines and glycol derivatives.

Summary

The association of a number of polyfunctional saturated aliphatic chains with montmorillonite surfaces gives evidence of augmented attraction of the nature of a C—H · · · O bond between methylene groups and the oxygen surfaces of the clay.

The same oxygen surfaces exercise a lesser but similar influence on some aromatic rings.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MANITOBA]

The System Aniline–Phenol–Water

BY A. N. CAMPBELL

An exhaustive treatment of the equilibrium of three liquids, both with and without the formation of two (or three) layers, has been given by F. A. H. Schreinemakers in the *Z. physik. Chem.*, between 1897 and 1903. In **23**, 649 (1897), he discusses the equilibrium of two liquid layers; in **25**, 305 (1898), the occurrence of a solid phase in the above equilibrium; in **29**, 577 (1899), the system aniline–phenol–water; in **30**, 460 (1899), the occurrence of solid phases in the system aniline–phenol–water; in **35**, 459 (1900), the vapor pressures of binary and ternary liquid mixtures of aniline–phenol–water; in **36**, 257 (1901), he gives a theoretical discussion of the vapor pressures of ternary mixtures; in **36**, 413, 710 (1901), and **37**, 129 (1901), further theory, including the distillation curves; in **38**, 227 (1901), the occurrence of three liquid layers; in **43**, 671 (1903), some concluding remarks.

Schreinemakers' experimental work on the ystem aniline–phenol–water (except the vapor pressure) was done by the method of Alexejeff, that is, mixtures of known composition were made up and the temperature of homogeneity observed. This isobaric method becomes indirect when applied to the investigation of isotherms and there is serious objection to it wherever the curvature of the isotherm is great. Thus, for example, Schreinemakers finds for the critical composition at 95°: 69.9% water, 26.6% phenol, 3.5% aniline, whereas, I find by direct analysis of equilibrium layers, at 96.7°, 59.8% water, 35.5% phenol, and 4.7% aniline. The slope of the tie-lines leaves little doubt as to the general correctness of my result, and this therefore illustrates the danger of the method used by Schreinemakers. He was probably forced to use this method through lack of an analytical method. I found an excellent analytical procedure in the conductimetric method and have determined the isotherms directly by analysis of equilibrium layers. In addition, I have also investigated the equilibrium with solid phases, and the conditions of the various eutectics. Finally, I have investigated the vapor pressures over the whole field of the diagram at different temperatures and, in some typical cases, found the composition of the vapor given off by boiling mixtures.

The Component Binary Systems

These are phenol–water, aniline–water, and aniline–phenol. The system water–phenol is too well known,[1] to require discussion, except to point out that it has been found[2] that in the stable system a solid hydrate of phenol makes its appearance, but this hydrate is never observed under ordinary circumstances.

The data on the system aniline–water are due to Alexejeff[3] who determined the mutual solubility curve; no compound is formed.

The equilibrium data for aniline–phenol are due to Schreinemakers[4] although the existence of a compound 1 aniline:1 phenol, had previously frequently been observed.[5]

The compound has a congruent melting point and there are therefore two eutectics.

Experimental Details

The analytical method was the conductimetric, which is recommended for this purpose by Kolthoff[6]; the attainable accuracy is for both substances about 0.5% of the total quantity estimated.

Samples of 20–30 g. were made up to 2 liters and 500-cc. portions titrated with normal acid and normal alkali.

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(1) Rothmund, *Z. physik. Chem.*, **26**, 443 (1898); Timmermans, *ibid.*, **58**, 184 (1907); *J. Chem. Phys.*, **20**, 491 (1923); Hill and Malisoff, THIS JOURNAL, **48**, 918 (1926); Campbell and Campbell, *ibid.*, **59**, 2481 (1937).

(2) Rhodes and Markley, *J. Phys. Chem.*, **25**, 530 (1921).

(3) Alexejeff, *Ann. Phys. Chem.*, **28**, 305 (1886).

(4) Schreinemakers, *Z. physik. Chem.*, **29**, 577 (1899).

(5) Hübner, *Ann.*, **210**, 342 (1881); Dale and Schorlemmer, *J. Chem. Soc.*, **43**, 185 (1883); Dyson, *ibid.*, **43**, 466 (1883); Mylius, *Ber.*, **19**, 1002 (1886).

(6) Kolthoff, *Ind. Eng. Chem., Anal. Ed.*, **2**, 225–230 (1930).

respectively; for very low concentrations of aniline or phenol decinormal reagents were used. The conductivity apparatus comprised an audiofrequency oscillator or tuning fork vibrator, Wagner ground, and variable capacity in parallel with the resistance box. All these refinements are possibly unnecessary, though the Wagner ground gives a very silent end-point. The end-point was at least as clear with the tuning fork hummer as with the audio oscillator. When cell conductance is plotted against cc. of titrating fluid, two straight lines intersecting at the end-point are obtained.

In the investigations of the compositions of equilibrium liquid layers the mixture was stirred, in the thermostat, with a screw stirrer, which pulled the lower layer through the upper. After three hours of stirring, the layers were left to separate, which they never failed to do (absence of emulsification). Samples of both layers were then driven by compressed air into weighed containers, all at the temperature of the thermostat. The temperatures of investigation were 8.6, 25.4, 48.0, 66.3, 69.6 and 96.7°.

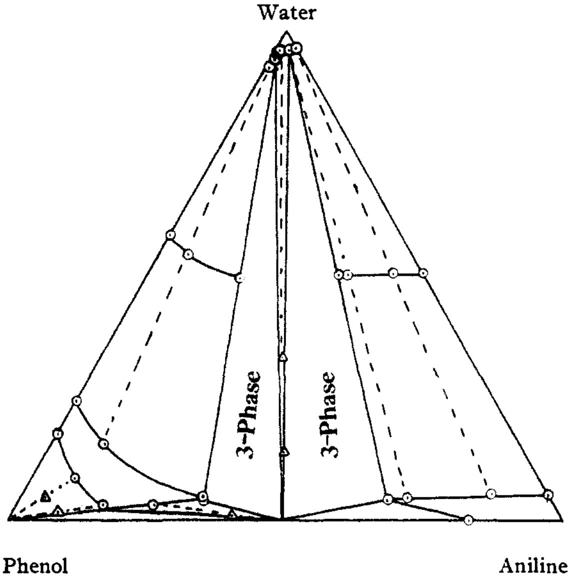

Fig. 1.—Equilibrium diagram of aniline-phenol-water at 8.6°.

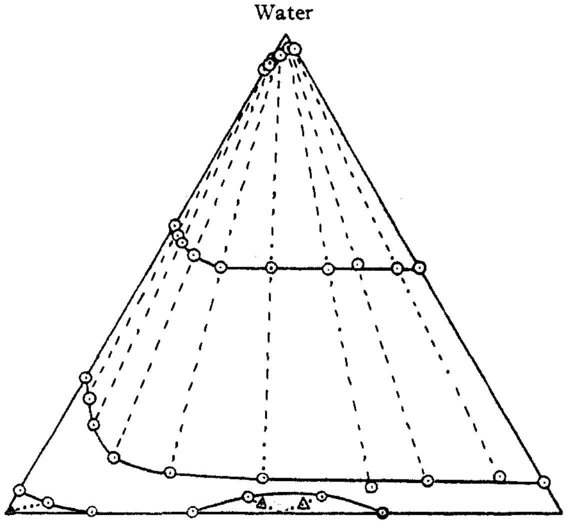

Fig. 2.—Equilibrium diagram of aniline-phenol-water at 25.4°

When plotting the results, in addition to joining congruent layers by tie-lines, the mean composition of the two layers was also plotted.

The compositions of solutions in equilibrium with solid phase were obtained by preparing such mixtures as would deposit solid phase (either compound or phenol), stirring overnight, and filtering through a sintered glass filter, under pressure and at the temperature of the thermostat: liquid and "moist residue" were analyzed.

There are two ternary eutectics in this system, *viz.*, ice, phenol, compound and ice, compound, aniline. These were determined as to temperature and composition by preparing mixtures of the approximate composition, as deduced from the known binary eutectics, and investigating by thermal analysis the temperature of eutectic solidification; a portion of the mother liquor was removed for analysis before complete solidification. The Beckmann thermometer was calibrated from the freezing point of 0.999 *N* HCl, as given by Richards and Jackson.[7]

The vapor pressure measurements were made by combining a Cottrell boiling-point apparatus with the apparatus of Ramsay and Young. The pressure in the reservoir was adjusted until the solution boiled steadily at the temperatures of the isotherms, *viz.* 96.7, 66.3, 48.0°. As the volume of solution used was large, 115 cc., the composition was not much affected by the formation of the vapor phase. except when the phenol–aniline content was large; this is never the case in the region of heterogeneity where the accuracy is good, but figures for solutions containing more than 90% phenol–aniline have only a qualitative significance. The composition was varied by taking fixed ratios of phenol to water and adding increasing quantities of aniline, *i. e.*, proceeding in a straight line across the composition diagram.

In the distillation experiments small samples of condensed vapor phase and of boiling liquid (upper or lower layer) were simultaneously withdrawn from a large volume (2000 to 500 cc.) of boiling mixture. Because of the notorious difficulty of establishing equilibrium between two boiling liquid layers, a screw stirrer was enclosed in the distilling flask and this continuously drew the lower layer up through the upper in a violent stream. The boiling temperatures were also read but these were not of great significance, because of a superheating effect of 1–3°.

Experimental Results

TABLE I

COMPOSITIONS OF LIQUID LAYERS IN EQUILIBRIUM; ALL COMPOSITIONS IN WEIGHT PER CENT.

1. ISOTHERMS: EQUILIBRIUM LIQUID LAYERS

Aqueous layer			Aniline or phenolic layer		
Aniline	Phenol	Water	Aniline	Phenol	Water
		Temp., 8.6°			
3.4	0.00	96.6	95.2	0.00	4.8
3.1	0.4	96.5	84.5	10.2	5.3
2.6	1.1	96.3	69.7	25.7	4.6
0.4	6.8	92.8	9.7	75.0	15.3
0.8	4.4	94.8	32.7	62.5	4.8
0.00	6.9	93.1	0.00	75.6	24.4
1.0[a]	4.4	94.6	33.1	63.0	3.9
2.9[a]	0.9	96.2	66.5	29.3	4.2

[a] Three phase equilibrium: two liquids in equilibrium with compound.

		Temp., 25.4°			
3.6	0.00	96.4	93.8	0.00	6.2
3.4	0.2	96.4	85.0	8.4	6.6
2.5	0.7	96.8	72.5	21.0	6.5

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(7) Richards and Jackson, *Z. physik. Chem.*, **56**, 364 (1906).

TABLE I (*Continued*)

Aqueous layer			Aniline or phenolic layer		
Aniline	Phenol	Water	Aniline	Phenol	Water
2.1	1.2	96.7	62.7	31.7	5.6
1.3	3.3	95.4	42.5	50.4	7.1
0.8	4.7	94.5	25.3	66.2	8.5
0.4	6.1	93.5	13.2	72.8	14.0
0.2	6.5	93.3	6.5	75.0	18.5
Trace	7.4	92.6	2.9	73.2	23.9
0.00[b]	8.4	91.6	0.00	71.3	28.7
[b] Hill and Malisoff, ref. 1.					
Temp., 48.0°					
4.1	0.00	95.9	93.8	0.00	6.2
3.8	0.3	95.9	85.0	8.8	6.2
3.0	1.1	95.9	68.0	26.5	5.5
2.6	1.4	96.0	67.8	27.2	5.0
1.8	3.4	94.8	44.2	47.2	8.6
1.7	5.2	93.1	31.7	59.0	9.3
0.9	7.4	91.7	14.7	69.0	16.3
0.3	8.7	91.0	6.2	68.5	25.3
0.00	12.4	87.6	0.00	63.0	37.0
Temp., 66.3°					
4.9	0.0	95.1	92.8	0.0	7.2
4.0	0.6	95.4	82.0	9.8	8.2
3.6	1.2	95.2	72.5	17.9	9.6
2.7	2.0	95.3	59.5	29.8	10.7
2.7	2.8	94.5	55.3	33.0	11.7
2.0	4.5	93.5	37.9	48.7	13.4
1.5	5.3	93.2	30.9	53.7	15.4
1.1	7.1	91.8	17.5	60.2	22.3
0.7	10.8	88.5	8.7	61.3	30.0
.5	14.9	84.6	3.1	58.0	38.9
.3	15.8	83.9	1.5	55.8	42.7
.3	17.8	81.9	0.9	52.0	47.1
.3	19.9	79.8	.5	49.5	50.0
Trace	19.6	80.4	.4	49.0	50.6
0.00	19.5	80.5	.00	48.9	51.1
Temp., 69.6°					
0.9	10.1	89.0	8.9	63.7	27.4
.6	12.2	87.2	4.2	61.5	34.3
.4	15.4	84.2	2.5	58.1	39.4
.3	17.8	81.9	1.3	54.2	44.5
.3	20.4	79.3	0.7	51.3	48.0
.3	19.6	80.1	.5	51.3	48.2
.3	24.9	74.8	.4	45.2	44.4
Critical solution (extpd.)			.3	35.0	64.7
Temp., 96.7°					
7.0	0.0	93.0	89.5	0.00	10.5
6.8[c]	0.5	92.7	68.9	17.3	13.8
5.0	2.5	92.5	57.4	28.2	14.4
3.6	4.0	92.4	45.0	37.9	17.1
2.7	6.7	90.6	39.3	41.5	19.2
2.6	8.6	88.8	29.6	48.2	22.2
2.2	13.6	84.2	15.3	52.4	32.3
2.3	21.8	76.9	7.0	49.2	43.8
Critical solution (extpd.)			4.7	35.5	59.8

[c] At this temperature and for this concentration the layers interchange positions, the aniline layer becoming the lighter, but the layers revert to their former positions with increasing phenol, and decreasing aniline, content.

The results of these isotherms (except for 69.6°) are plotted in Figs. 1 to 5 inclusive.

2. Solutions in Equilibrium with Solid Phase (compound or phenol)

Solution			Nature of solid phase	Moist residue		
Aniline	Phenol	Water		Aniline	Phenol	Water
			Temp., 8.6°			
0.8	3.0	96.2	Compound	32.5	33.9	33.6
0.9	3.8	95.3	Compound	42.7	43.4	13.9
0.00[a]	82.3	17.7	Phenol			
7.9	84.0	8.1	Phenol	4.9	91.0	4.1
15.8	81.5	2.7	Phenol	8.2	90.5	1.2
24.8	72.2	3.0	Compound	39.6	59.3	1.1
83.0[b]	17.0	0.0	Compound			
[a] Campbell and Campbell, ref. 1.						
[b] Interpolated from the results of Schreinemakers.						
			Temp., 25.4°			
55.3	41.7	3.0	Compound	52.4	45.6	2.0
41.9	55.0	3.1	Compound	45.1	53.0	1.9
68.0[c]	32.0	0.0	Compound	49.7	50.3	0.0
33.5[c]	66.5	0.0	Compound	49.7	50.3	0.0
6.7	91.9	1.4	Phenol	1.0	99.0	0.00
15.5[c]	84.5	0.0	Phenol	0.0	100.0	0.0
0.0[a]	95.5	4.5	Phenol	0.0	100.0	0.0

[c] Deduced from the curve of Schreinemakers' results.

The above results are expressed graphically in Figs. 1 and 2.

3. Ternary Eutectics

Temperature, °C.	Solid phases	Composition		
		Aniline	Phenol	Water
– 0.96	Ice, phenol, compound	0.4%	5.2	94.4
–15.06	Ice, aniline, compound	89.2	8.8	2.0

4. Vapor Pressure Measurements

T, °C.	Aqueous layer		Aniline–phenol layer		P. in mm. Hg
	% Anil.	% Ph.	% Anil.	% Ph.	
I. Vapor Pressures of two liquid Systems					
96.7	2.2	18.0	12.5	52.5	702.1
96.7	2.5	13.5	16.3	51.0	702.2
96.7	2.4	11.6	22.0	51.2	702.3
96.7	2.5	7.5	32.0	46.5	705.3
96.7	4.0	4.0	48.0	36.0	711.5
96.7	4.5	2.5	62.5	24.0	713.8
96.7	5.5	1.5	71.5	16.0	714.1
96.7	6.7	0.3	76.0	12.3	715.3
96.7	7.0	Trace	81.5	7.5	716.1
96.7	7.0	Trace	83.5	5.8	716.7
96.7	7.0	0.0	89.5	0.0	719.0
66.3	0.9	12.0	8.5	63.5	205.0
66.3	0.2	13.9	17.0	61.0	205.2
66.3	1.0	7.0	17.5	60.0	205.3
66.3	1.5	6.5	27.0	56.0	205.4
66.3	1.5	5.5	35.5	51.0	205.7
66.3	2.5	2.0	48.5	39.5	206.0
66.3	3.0	1.5	65.5	24.5	206.5
66.3	4.0	0.5	73.8	17.0	206.5
66.3	3.5	1.0	79.5	12.0	206.8
66.3	4.5	Trace	85.5	7.0	206.9
66.3	4.5	Trace	86.0	6.0	207.0
48.0	0.9	7.0	10.0	70.0	85.0
48.0	1.2	5.8	16.0	69.0	85.4
48.0	1.0	5.5	19.5	67.2	85.4
48.0	1.2	5.7	25.5	64.0	85.6
48.0	1.5	3.0	34.5	56.8	85.7
48.0	2.0	2.0	49.5	43.5	85.7
48.0	3.2	0.5	80.8	13.7	85.8

TABLE I (*Concluded*)

T, °C.	Aqueous layer % Anil.	% Ph.	Aniline–phenol layer % Anil.	% Ph.	P. in mm. Hg
48.0	3.0	1.0	68.0	27.0	86.0
48.0	3.5	1.0	79.0	14.0	86.0
48.0	4.0	Trace	85.5	8.5	86.0
48.0	4.0	Trace	88.0	6.0	86.4

II. Vapor Pressure of Homogeneous Systems

T, °C.	Ratio. Ph/water	% Anil.	P. in mm. Hg
96.7	1:9	90	674
96.7	2:8	90	653
96.7	3:7	90	613
96.7	4:6	90	576
96.7	5:5	80	688
96.7	5:5	90	525
96.7	Critical solution (4.66% aniline 35.5% phenol)	..	702
96.7	6:4	10	699
96.7	6:4	80	639
96.7	6:4	90	423
96.7	7:3	10	690
96.7	7:3	20	696
96.7	7:3	30	702
96.7	7:3	40	706
96.7	7:3	50	693
96.7	7:3	60	680
96.7	7:3	70	635
96.7	7:3	80	517
96.7	7:3	90	335
			Cm.
96.7	8:2[a]	10	64
96.7	8:2	20	64
96.7	8:2	30	65
96.7	8:2	40	63
96.7	8:2	50	61
96.7	8:2	60	59
96.7	8:2	70	51
96.7	8:2	80	40
96.7	8:2	90	23
96.7	9:1	10	46
96.7	9:1	20	48
96.7	9:1	30	44
96.7	9:1	40	40
96.7	9:1	50	36
96.7	9:1	60	33
96.7	9:1	70	28
96.7	9:1	80	21
96.7	9:1	90	13
			Mm.
66.3	4:6	90	158
66.3	5:5	90	145
66.3	6:4	90	106
66.3	7:3	80	162
66.3	7:3	90	68
			Cm.
66.3	8:2	10	19
66.3	8:2	20	19
66.3	8:2	30	19
66.3	8:2	40	20
66.3	8:2	50	19
66.3	8:2	60	18
66.3	8:2	70	15
66.3	8.2	80	11
66.3	8:2	90	9
66.3	9:1	10	14
66.3	9:1	20	14
66.3	9:1	30	13
66.3	9:1	40	11
66.3	9:1	50	10
66.3	9:1	60	9
66.3	9:1	70	8
66.3	9:1	80	5
66.3	9:1	90	3
48.0	7:3	90	3.3
48.0	8:2	10	8
48.0	8:2	80	5
48.0	8:2	90	4
48.0	9:1	10	6
48.0	9:1	20	6
48.0	9:1	30	6
48.0	9:1	40	5
48.0	9:1	50	5
48.0	9:1	60	5
48.0	9:1	70	4
48.0	9:1	80	3

[a] For solutions containing 80% and more phenol, the vapor pressures have been rounded off to the nearest cm., since, as stated in the introduction, the accuracy is low in that region.

The results for the 96.7° isotherm are expressed, in a qualitative manner, in Fig. 6; the arrows indicate the direction of increasing vapor pressure.

5. Distillation Experiments

Equilibrium compositions, %

Boiler: Upper layer Aniline	Boiler: Upper layer Phenol	Boiler: Lower layer Aniline	Boiler: Lower layer Phenol	Distillate Aniline	Distillate Phenol	Boiling point, °C.
4.1	4.9	42.5	40.0	15.0	3.9	99.4
3.5	5.5	43.5	39.0	10.0	6.4	99.8
2.5	6.5	39.0	41.5	9.3	7.3	101.4
2.5	8.5	29.5	48.2	7.2	7.8	100.3
2.5	11.0	22.0	51.5	4.5	9.6	101.5
2.3	11.0	22.0	51.5	2.5	10.0	100.9
2.5	12.5	18.0	52.0	2.5	10.4	100.8
Homogeneous		21.5	74.5	6.0	15.9	112
Critical solution		4.7	35.5	2.2	10.3	100.7
Homogeneous		5.5	51.9	2.4	11.4	101.1
Homogeneous		6.9	64.9	1.8	17.1	103.6
Homogeneous		11.7	88.0	7.0	92.9	178

The above results are expressed graphically in Fig. 7, the full curve expressing liquid composition and the dotted curve vapor composition. Tie-lines, indicating conjugate liquid and vapor, have been omitted to avoid unduly complicating the diagram.

Discussion of Results

Equilibrium Diagrams.—The most interesting isotherm is that for 8.6° (Fig. 1), for here the region of stable existence of solid compound intersects the region of two liquid layers. The diagram shows, and it has been verified experi-

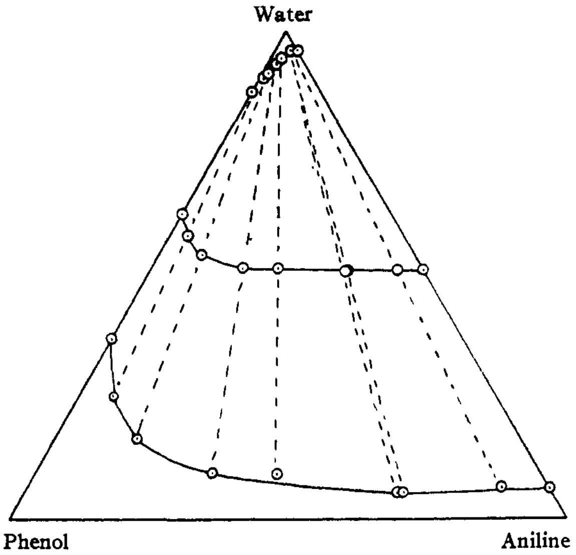

Fig. 3.—Equilibrium diagram of aniline–phenol–water at 48.0°.

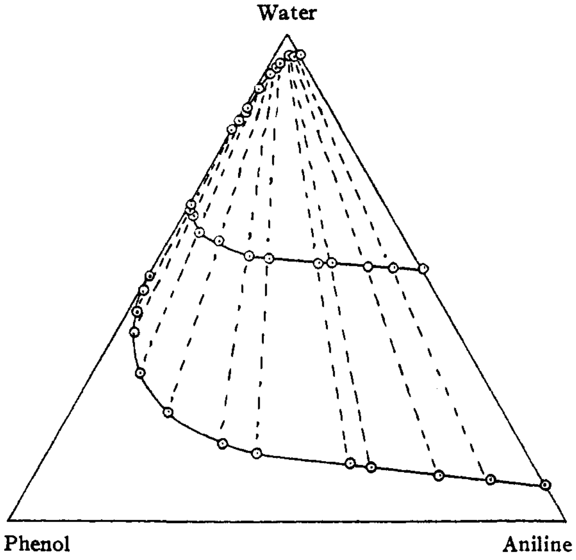

Fig. 4.—Equilibrium diagram of aniline–phenol–water at 66.3°.

mentally, that if the ratio of aniline to phenol in the system is close to the molecular ratio 1:1, solid compound can exist in equilibrium with a (very limited) range of aqueous solutions. If, however, the ratio is somewhat displaced from 1:1, invariance results with the formation of two liquid layers of constant composition in equilibrium with compound. There are two sets of such liquid layers, depending on whether the system is richer in aniline or in phenol. If the ratio is still further displaced, the compound melts completely and two liquid layers of variable compositions are left. If the system is very low in water, solid compound may exist in equilibrium with two series of single solutions rich in phenol and aniline (as distinct from the aqueous solution mentioned above). One of these solubility curves intersects the solubility curve of solid phenol, producing the invariant point: solid compound, solid phenol, solution.

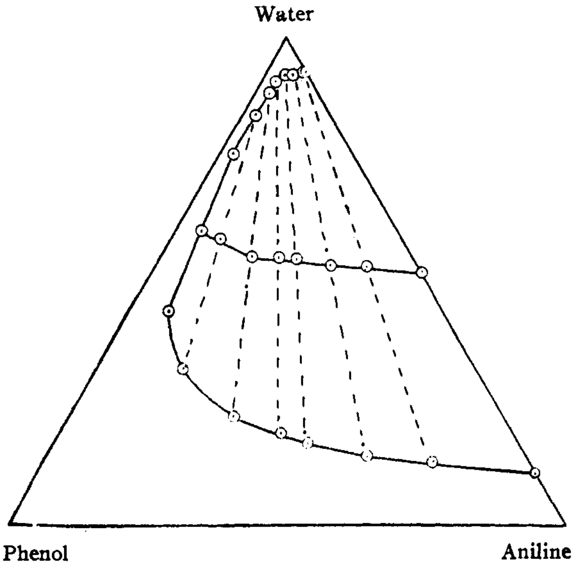

Fig. 5.—Equilibrium diagram of aniline–phenol–water at 96.7°.

At 25.4° (Fig. 2) the picture is simplified, because the region of stable existence of solid no longer intersects the region of two liquid layers, *i. e.*, the compound never melts to form two liquid layers; it can only be in equilibrium with a series of solutions rich in phenol–aniline. Neither does the solubility curve of phenol intersect this solubility curve, so that the invariant point: solid compound, solid phenol, solution, is lacking.

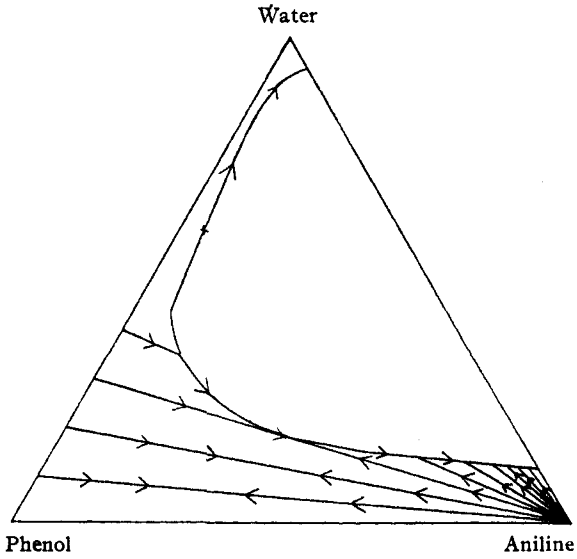

Fig. 6.—Vapor pressure isotherm for 96.7° (qualitative.) The arrows show the direction of increasing vapor pressure.

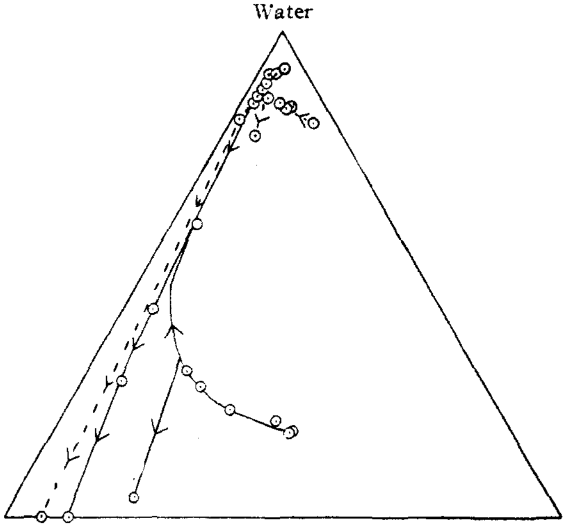

Fig. 7.—Composition of liquid and of vapor during distillation.

The isotherms for temperatures higher than 8.6° show the increasing mutual solubility of aniline and water in the presence of phenol. It is remarkable that the isotherm for 66.3° did not show complete miscibility of phenol and water, though the accepted figure for the critical solution temperature of phenol–water[1] is below this. A higher temperature had previously been found by Campbell and Campbell[1] though, at the time, we had preferred Hill's result because of his well-known accuracy. A repetition of the determination in the present case, using carefully purified phenol, showed that phenol and water are not miscible in all proportions at 66.3°; the compositions of the equilibrium layers are given in the tables of results. Hill's figure for the critical composition appears to be correct.

At 69.6° phenol and water are completely miscible, but as little as 0.30% aniline is sufficient to cause separation of two layers. At 96.7° the critical solution has moved well into the triangular area, corresponding to an aniline content of 4.66%; this solution, however, does not have the minimum content of aniline, since a number of heterogeneous mixtures exist containing only 2.5% aniline in the aqueous layer. On the whole there is good agreement between my figures and those obtained by Schreinemakers by an indirect method, except in the region of critical solution where the discrepancy is large.

On all the isotherms the mean compositions of the layers have been plotted (law of the rectilinear diameter). It appears that, except for solutions low in aniline, the plot is a straight line, usually parallel to the base of the triangle (constant water content). As the critical composition is approached, the line curves upwards in the direction of decreased phenol content.

The ice, phenol, compound eutectic lies close to the binary eutectic phenol–water, with only 0.4% aniline. The ternary eutectic, aniline, compound, ice, at −15.06° and containing 8.8% phenol is to be compared with the binary eutectic aniline–water at −11.85° and containing 2.7% water as against 2.0% in the ternary. The binary eutectic, aniline–compound, lies at −12° and 92% aniline (Schreinemakers).

The temperature of the ice, phenol, compound eutectic (−0.96°) is incompatible with that previously given by Campbell and Campbell[8] for the binary eutectic ice–phenol, *viz.*, −1.3°. Repetition of the phenol–ice binary eutectic inclines me to believe that this temperature should really be −0.85°, but, for the present, all that can be said is that both eutectics lie at about −1°.

Vapor Pressure Measurements.—Figure 6 shows the nature of these results for 96.7°. In the area of heterogeneity (two liquid layers), the vapor pressure rises continuously from that of the critical solution to that of aniline–water. The total increase in pressure amounts only to 17 mm., and, in general, this area represents a slightly inclined plateau of high pressure on the pressure composition diagram. The first completely homogeneous series of solutions is that in which phenol : water = 7:3, and in this series a maximum vapor pressure with increasing aniline content occurs at about 40% aniline, where the curve approaches closest to the area of heterogeneity. A similar maximum occurs on the other homogeneous curves but with increasing phenol content it appears to become less in amount, and to be displaced toward increasing phenol content; it is possible that the maximum has entirely disappeared in the binary system: phenol–aniline. This prediction is borne out by the suggestion of Ewell, Harrison and Berg[9] that this system would show a minimum in vapor pressure.

Distillation Experiments.[10]—The results of the vapor pressure measurements are confirmed by the distillation experiments, as far as alteration of composition during distillation is concerned but, whereas it was natural to suppose that in the high pressure heterogeneous area the vapor would be principally composed of water and aniline, it was found that the ratio of phenol to aniline in the vapor is high and, over a certain range, phenol predominates over aniline. In the heterogeneous area, the vapor is richer in aniline than the aqueous layer, poorer than the heavy layer, while its phenol content is not greatly different from that of the aqueous layer and less than that of the heavy layer. Hence, on distillation, the compositions of the liquid layers approach that of the critical solution, the bulk of the

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(8) Campbell and Campbell, This Journal, **59**, 2481 (1937).

(9) Ewell, Harrison and Berg, *Ind. Eng. Chem.*, **36**, 873 (1944).

(10) Somewhat similar work on the same system, though not so extensive, was carried out by Schreinemakers at 57.3° (*Z. physik. Chem.*, **35**, 459 (1900)) and he obtains a figure very similar to mine (Fig. 6, p. 478, *loc. cit.*).

aqueous layer becoming less. In most cases the aqueous layer will disappear before the critical composition is reached and then the distillation curves undergo a sharp change. The composition of the liquid (heavy layer) now moves along a practically straight line, joining the point at which the solution left the heterogeneous area and the apex of the triangle, toward the base of the triangle; the composition of distillate (vapor phase) follows along what is practically the same straight line but with much higher water content (see the first point marked "homogeneous" in Table V). If the composition of the heterogeneous mixture is such that the critical composition is reached without exhaustion of the aqueous layer, the behavior is qualitatively the same. The composition of the boiler liquid turns sharply downwards toward the base of the triangle and eventually only anhydrous phenol–aniline is left. The vapor composition curve passes out of the area of heterogeneity some time before the liquid mixture has become homogeneous, the aniline content of the vapor falling as low as 1.8% at one point. The last point in Table V, referring to a system from which all the water had distilled, shows a composition of vapor very close to that of liquid.

The existence of a maximum vapor pressure on the curves below the heterogeneous area might be thought to determine the direction of the distillation curves to the left or the right, but while this is true in a binary system it is not necessarily so in a ternary system. It must be remembered that the system represented by the base line, *viz.*, phenol–aniline, is one of low vapor pressure and all mixtures rapidly arrive on it, after leaving the heterogeneous area.

From a practical point of view, it is of some importance to observe that almost any heterogeneous mixture of phenol, aniline and water, will, on being submitted to distillation, give rise to an eventual residue free from water and, usually, richer in phenol than aniline. The distillate will be at first rich in aniline, poor in phenol, but its composition will change during distillation, the aniline content falling to a minimum of 1.8% (after which it will rise again) and the phenol content rising progressively.

Summary

The following have been investigated experimentally for the system phenol–aniline–water:

1. The isotherms for 8.6, 25.4, 48.0, 66.3, 69.6 (partially) and 96.7°. The investigations include, besides the mutual solubility curves, the equilibria with solid phases, where solid phases exist.
2. The ternary eutectics.
3. The vapor pressure isotherms for 96.7, 66.3 and 48.0°.
4. The distillation curves.

The above data are discussed.

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The Surface Tensions of Calcium Chloride Solutions at 25° Measured by their Maximum Bubble Pressures

BY H. L. CUPPLES

The surface tensions of calcium chloride solutions have been determined by a number of observers.[1] As calcium chloride is very soluble in water, it is possible to measure large values of the surface tension of the solution minus that of the pure solvent ($\Delta\gamma$), and a comparison of measurements by different methods affords an excellent test of the precision and comparability of the respective methods when applied to aqueous solutions of high surface tension. Harkins and Gilbert used the drop-weight method according to the directions of Harkins and Brown.[2] Belton[3] measured the surface tension of calcium chloride solutions by the method of maximum bubble pressure, but his results cover only a minor fraction of the available range of concentrations. It was considered to be of much interest to measure the surface tensions of these solutions by the method of maximum bubble pressure, and to compare the results with those obtained by Harkins and Gilbert and other investigators.

Experimental

The determination of surface tension by measuring the minimum pressure required to blow a bubble from the bottom of a tube extending vertically downward to or below the surface of a liquid, named by Sugden[4] the "method of maximum bubble pressure," was first suggested by Simon.[5] It was developed by Cantor[6] and by Jaeger.[7] Important and fundamental improvements were made by Sugden.[4] The theory and application of the method is described by Adam.[8]

These observations were made by the Sugden meth of maximum bubble pressure, using a capillary tip

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[1] W. D. Harkins and E. C. Gilbert, THIS JOURNAL, **48**, 604–607 (1926).

[2] W. D. Harkins and F. E. Brown, *ibid.*, **41**, 499–524 (1919).

[3] J. W. Belton, *Trans. Faraday Soc.*, **32**, 1717–1721 (1936).

[4] S. Sugden, (a) *J. Chem. Soc.*, **121**, 858–866 (1922); (b) **125**, 27–31 (1924).

[5] M. Simon, *Ann. chim. phys.*, [3] **32**, 5–41 (1851).

[6] M. Cantor, *Ann. der Phys. u. Chem.*, **47**, 399–423 (1892).

[7] F. M. Jaeger, *Z. anorg. allgem. Chem.*, **101**, 1–214 (1917).

[8] N. K. Adam, "The Physics and Chemistry of Surfaces," ed. 3, Oxford University Press, London, 1941, pp. 11, 372–376.