On the Equilibrium in the System: Water, Phenol and Benzene.

By

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(Received July 6, 1914.)

The partition coefficient of phenol between water and benzene has been already studied by V. Rothmund and N. T. M. Wilsmore¹, but the complete state of the equilibrium of the system consisting of water, phenol and benzene has ever remained undetermined. The present paper gives an account of an investigation to determine the state of the equilibrium of this ternary mixture at 25.0°C.

Experimental Methods.

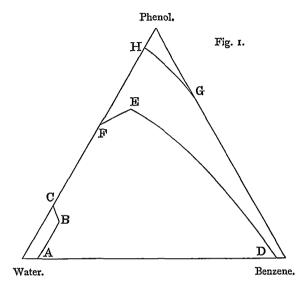
For the determination of phenol in a mixture of water and benzene, the usual method with bromine was employed, but for the analysis of the water and benzene in the mixture no chemical method was practicable. When benzene is added drop by drop to an aqueous solution of phenol and strongly shaken, constant turbidity is observed at the saturation point of benzene, and this fact was utilized in the following way. An aqueous solution of a known concentration was put in a long necked flask which was immersed in the thermostat at 25.0°C and strongly shaken by means of an electric motor. Then benzene was added drop by drop from a capillary burette until constant turbidity was observed, and from the volume of benzene added the percentage composition of the saturated solution was calculated. The saturation point of water in benzene solution of phenol was also estimated by a similar method, water instead of benzene being added.

Results.

For a graphical representation of this ternary system, equilateral triangular co-ordinates were chosen, as usual for such a ternary system,

¹ Zs. physik, Chem., 40, 611 (1902).

the angular points representing the pure components respectively. Thus the following five saturation curves, as shown in Fig. 1, were obtained:



- (1) The saturation curve of benzene in water (AB).
- (2) The saturation curve of water in benzene (DE).
- (3) The saturation curve of phenol in water (CB).
- (4) The saturation curve of water in phenol (FE).
- (5) The saturation curve of phenol in mixture of water and benzene (HG).

Curve 1 and Curve 3.

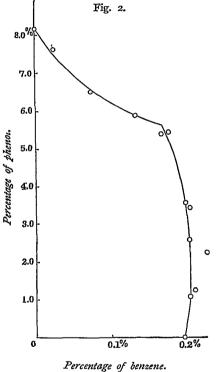
a) The system: Water and benzene.

Water.	Benzene.	Sp. gravity $\left(\frac{25.0^{\circ}\text{C}}{25.0^{\circ}\text{C}}\right)$.
99.802%	o•198 <i>%</i>	`I•0002

b) The system: Water, phenol and benzene.

Water.	Phenol.	Benzene.	Sp. gravity $\left(\frac{25 \cdot 0^{\circ} \text{C}}{25 \cdot 0^{\circ} \text{C}}\right)$.
98•737	1.059	0.204	1.0008
98.523	ì·265	0.212	1.0010
97.525 .	2.249	0.226	1.0020
97-193	2.602	0.205	1.0021
96.355	3•440	0.205	

96.275	3.526	0.199	1.00305
94•429	5-405	0•166	
94•393	5•430	0.177	
93•915	5•953	0.132	
93·409	6.516	0.075	1.0059
92•292	7 •683	0.025	100.69



c) The system: Water and phenol.

[Water. Phenol. Sp. gravity
$$\left(\frac{25 \cdot 0^{\circ} \text{C}}{25 \cdot 0^{\circ} \text{C}}\right)$$
 99.805 8.195 1.0073

The point B, the intersection of the curves CB and AB, was estimated graphically in Fig. 2, which represents the data for the curves AB and CB according to rectangular instead of triangular co-ordinates, as follows:

Water.	Benzene.	Phenol.
94•18	0.17	5•65

Curve 2.

a) The system: Water and benzene.

Water.	Benzene.	Sp. gravity $\left(\frac{25 \circ^{\circ} C}{25 \circ^{\circ} C}\right)$.
0.05	99•95	0.8764

b) The system: Water, phenol and benzene.

Water.	Phenol.	Benzene.	Sp. gravity $\left(\frac{25 \cdot 0^{\circ} \text{C}}{25 \cdot 0^{\circ} \text{C}}\right)$.
0.24	4•78	94.98	0.8818
o•81	1 <i>7</i> •36	81.83	იფირრ

1. 63	21.15	77-22	0.9142
1.80	26.48	71•72	
2.18	28·01	69•81	0.9280
5.05	44•39	50.56	0•9629
8.07	55·80	36•13	0.9891
14•49	69•18	16.33	1.0256
17.72	71•46	10.82	1.0354

Curve 4.

a) The system: Water and phenol.

Water.	Phenol.
70.71	29.29

b) The system: Water, phenol and benzene.

Water.	Phenol.	Benzene.
26•75	1.62	71.63
23.83	2.60	73·57

The point E, the intersection of the curves DE and EF was estimated in triangular co-ordinates. Its composition was found as follows:

Water.	Benzene.	Phenol.
22.5	3.0	74.5

Curve 5.

a) The system: Phenol and benzene, with phenol as a residue.

The percentage composition of phenol in the saturated solution in benzene was found as follows:

_r (81•02	TT (81·10
I \begin{cases} 81.02 \\ 80.97 \end{cases}	II \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \
Mean 81.03	81.10
Phenol.	Benzene.
81 . 06	18•94

b) The system: Phenol, benzene and water, with phenol as a residue.

The percentage compositions of phenol in two different mixtures of water and benzene with phenol as a residue were found as follows:

Phenol.	Water.	Benzene.	
92.31	3•62	4.07	
89•78	2.30	7.92	

c) The system: Water and phenol, with a phenol as a residue.

Phenol.	Water.
95.14	4.86

Determination of the Conjugate Points.

The results of the research of the partition of phenol in water and benzene by V. Rothmund and N. T. M. Wilsmore were as follows:

Phenol in aqueous layer. (Mol. concentration).	Phenol in benzene layer, (Mol. concentration).
0.5299	6-487
0•4853	5 • 735
0.4523	5.040
0∙3688	3 •046
0.3660	2•978
0.2847	1.512
0.2578	1.254
0.1816	ი∙638
0.1013	0.279
0.0532	0.129
0.0272	0.062

The experimental data for curve 2 were recalculated in molar concentration using the values of specific gravities of those mixtures. Then the composition of the conjugate solutions were estimated graphically by making use of the data of Rothmund and Wilsmore and the percentage compositions of these conjugate solutions were recalculated by help of their specific gravities.

Phenol. (Weight percentage.) (Mol. concentration.)		Lower layer. Phenol. (Mol. concentration). (Weight percentage.)		
17•36	1.666	0•297	2.80	
21.15	2•047	0.320	3.01	
28.01	2.754	0•356	3.35	
44•39	4.528	0.4325	4.07	
55•80	5•846	0.487	4.58	

The Complete Equilibrium of the System.

Upper layer.		Lower layer.			
Phenol.	Benzene.	Water.	Phenol.	Benzene.	Water.
0	99.95	0.05	0	0.198	99•802
4•78	94.98	0•24	1.43	O•2I	98•36
17.36	81.83	0.81	2.80	0.21	96•99
21-15	77.22	1.63	3.01	0.21	96.77
28.01	69.81	2-18	3.35	0.21	96•44
44•39	50•56	5.08	4.07	0•19	95•74
55 · 80	36∙13	8.07	4.58	0.19	95-23
74•5	3.0	22•5	5•65	0.17	94•18
70·71	0	29•29	8.195	0	91.805

Saturated Solutions with solid phenol as residue.

Phenol.	Benzene.	Water.
81.06	18.94	0
89•78	7.92	2.30
92•31	4.07	3.62
95•14	0	4.86

The above data are plotted in Fig. 3 which represents completely the equilibrium state of the ternary system in question at 25.0°C.

