

[CONTRIBUTION FROM RUGBY SCHOOL, WARWICKSHIRE, ENGLAND]

The Association of Phenol in Different Solvents

BY FREDERICK ARTHUR PHILBRICK

The object of this work was to supplement the scanty available data on the influence of the solvent on chemical equilibrium by an examination, by the distribution method, of the association of phenol in different solvents. Kwantaro Endo¹ has shown that phenol is monomolecular in water up to at least 0.15 *M*.

The available partition data at low concentrations are not exact enough to allow the degree of association to be calculated. In amyl alcohol,² the only hydroxylic solvent hitherto investigated, phenol is monomolecular. With other solvents the partition ratio (concn. in solvent)/(concn. in water) increases more and more rapidly as the concentration in the water rises. This shows that triple or more complex molecules exist in the non-aqueous solvents at high concentrations. The present work is confined to concentrations in the water layer always below 0.10 *M* and usually below 0.05 *M*, a region which has not yet been investigated precisely. The dilute end of the curve connecting the partition ratio with the concentration in the water has always been found to be a straight line, indicating that at these concentrations the phenol in the non-aqueous layer is exclusively in single and double molecules.

Let the concentrations of single and double molecules in the non-aqueous solution be *b* and *c*, respectively, and in the aqueous layer (single molecules) be *W*. Then the distribution coefficient *P* is

$$\frac{b + 2c}{W} = P_0 + 2KP_0^2 W$$

where *P*₀ is the value of the distribution coefficient for single molecules and *K* is the association constant, *c/b*², in the non-aqueous layer. The values of *P*₀ and *K* can be determined from the linear plot of *P* against *W*. *P*₀ is not strictly equal to the distribution coefficient at infinite dilution, at which phenol would be completely ionized, but it can be calculated by extrapolating to infinite dilution the straight line connecting *P* and *W* in the concentration range examined in this work, over which ionization is negligible.

(1) Kwantaro Endo, *Bull. Chem. Soc. Japan*, 1, 25 (1926).(2) Herz and Fischer, *Ber.*, 37, 4746 (1905).

Phenol (Kahlbaum) was twice fractionally distilled and collected at 180–181° (770 mm.), then twice fractionally crystallized. The product, though kept in a desiccator in daylight, has shown no sign of darkening in six months. A stock solution was prepared and standardized by analysis; consequently it was not necessary to remove from the phenol the last traces of water.

The solvents were the best available commercial specimens, and were purified by successive fractional distillations. The carbon tetrachloride was first freed from sulfur compounds by treatment with iodine trichloride. The fractions used were collected at or between the following temperatures: toluene 110.5–111.0° (corr.); chlorobenzene 132.8° (corr.); benzene 79.5–79.7° (corr.), m. p. 4.6°; nitrobenzene 210–210.8° (755 mm.); carbon tetrachloride 76.3–76.6° (corr.).

The solutions were prepared and analyzed by weight. The stock phenol solution was mixed with water and the non-aqueous solvent in a long-necked flask, of 50- or 100-cc. capacity, in such proportions that about half the phenol was extracted from the aqueous layer. The flask was then placed in a thermostat at 25°. After standing, prolonged shaking, and complete separation into layers, some of the aqueous layer was transferred to a sealed tube to await analysis.

By the following modification of the bromate-iodide method from 3 to 10 mg. of phenol (optimum 7 mg.) can be estimated to within ±0.05%. The chief innovation is the use of carbon tetrachloride instead of starch. By dissolving the precipitate it avoids occlusion, adsorption and the difficult color conditions at the starch end-point. The use of 2 *N* acid followed by dilution before the iodine titration is also believed to be a useful improvement.

Weigh the phenol solution into a light 100-cc. flask, with a short neck and glass stopper, such as can be weighed on an analytical balance, then weigh in a small excess (1 to 4%) of a standard solution of potassium bromate. Add 0.1 g. of potassium bromide and then sufficient sulfuric acid to make the phenol 0.004–0.005 *M* and the acid 1.5–2.0 *N*. Stopper at once and swirl while the precipitate is forming and at intervals to coagulate it. After ten minutes (at 17°) add 0.1 g. of potassium iodide dissolved in water, swirl for sixty seconds, add from 1 to 2 cc. of carbon tetrachloride according to the quantity of phenol, swirl for about twenty seconds until most of the precipitate has dissolved, then dilute the liquid immediately with water to three or more times its volume. The remainder of the precipitate will dissolve during the titration. Titrate at once with 0.002 *M* thiosulfate, which may be added from a volume buret. Toward the end of the titration the flask is violently shaken, and at the end-point it is inverted, so that the color of the carbon tetrachloride can be observed as it collects in the neck. A similar flask containing carbon tetrachloride and water is used for comparison. In daylight the end-point can be detected to within about 0.05 cc. of 0.002 *M* thiosulfate.

This procedure is the result of 63 trial analyses under varied conditions, in addition to the analyses reported in this paper. The volumetric apparatus and the weights were all standardized. The absolute accuracy of the results of this method was not checked by direct experiment, partly because the possible sources of error have already been examined exhaustively by previous workers,³ and partly on account of the difficulty of preparing and weighing phenol with a water content of less than 0.02%. The results are independent of any small systematic error in the analyses, because the concentrations of the phenol solutions before and after distribution were measured by identical methods.

A single solution of potassium bromate served as primary standard for the whole of the work, and the 52 sub-standard solutions prepared for use in the analyses were all referred to it. The potassium bromate had been three times recrystallized and kept in a desiccator for two years before heating to constant weight at 180°. When tested as described by Kolthoff,⁴ it was found to be free from bromide. The materials used in the analyses were all tested by the usual methods and with satisfactory results. The concentration of the stock phenol solution was frequently determined in the course of the work (12 analyses), but no change could be detected in it.

One hundred and five analyses were carried out on 39 solutions, the average divergence from the mean being 0.045%. Some of the solutions in the benzene series were analyzed (in quadruplicate) by the starch method, 28 analyses of 7 solutions showing an average divergence from the mean of 0.10%. Control experiments showed that the two methods of analysis gave identical mean results, and that traces of the non-aqueous solvent dissolved in the water layer did not affect the analytical results by reaction with bromine.

Small corrections for mutual miscibility were applied to the weights of aqueous and non-aqueous layers. The solubilities used for these corrections were as given in Table I.

TABLE I

Solvent	C ₆ H ₆	C ₆ H ₅ Cl	C ₆ H ₅ NO ₂	C ₆ H ₅ CH ₃	CCl ₄
H ₂ O in solvent, g./kg.	0.70(a)	0.395(b)	1.51(b)	0.528(b)	0.072(b)
Solvent in H ₂ O, g./kg.	1.5(a)	.85(c)	2.05(a)	1.1(c)	0.83(a)

Values marked (a) from "International Critical Tables;" (b), by extrapolation from the work of Bell;⁵ (c), estimated by analogy.

The analytical results are shown in Table II.

$P_{\text{calcd.}}$ is the value of P calculated from the equation

$$P = P_0 + 2KP_0^2W$$

For values of P_0 and K see Table IV.

Table III shows the approximate concentrations (moles per liter) up to which the linear rela-

(3) Redman, Weith and Brock, *J. Ind. Eng. Chem.*, **5**, 389 (1913); Francis and Hill, *THIS JOURNAL*, **46**, 2498 (1924); Day and Taggart, *Ind. Eng. Chem.*, **20**, 545 (1928), and others.

(4) Kolthoff, "Volumetric Analysis," John Wiley and Sons, Inc., New York, 1929.

(5) R. P. Bell, *J. Chem. Soc.*, 2905 (1932).

TABLE II

L Moles phenol per kg. solvent satd. with water	W Moles phenol per kg. water satd. with solvent	$P_{\text{obs.}}$ L/W	$P_{\text{calcd.}}$	$P_{\text{obs.}} - P_{\text{calcd.}}$
TOLUENE				
0.016112	0.007774	2.073	2.074	-0.001
.019607	.009401	2.086	2.084	+ .002
.026849	.012757	2.105	2.104	+ .001
.034165	.016097	2.122	2.124	- .002
.039380	.018423	2.138	2.138	.000
.046325	.021472	2.158	2.156	+ .002
.055418	.025558	2.168		
.064533	.029680	2.174		
.065166	.029993	2.173		
.082642	.037494	2.204		
.084097	.038216	2.200		
.10198	.045637	2.235		
CHLOROBENZENE				
0.012488	0.009440	1.323	1.323	0.000
.026927	.019995	1.347	1.348	- .001
.041888	.030639	1.367	1.374	- .007
.057309	.040929	1.400	1.399	+ .001
.073533	.051607	1.425	1.425	.000
.091994	.063281	1.454	1.453	+ .001
.11332	.076382	1.484	1.485	- .001
.13304	.088135	1.510		
BENZENE				
0.023053	0.008883	2.595	2.600	-0.005
.023553	.009038	2.606	2.601	+ .005
.029444	.011258	2.615	2.616	- .001
.045160	.017002	2.656	2.653	+ .003
.062336	.023156	2.692	2.693	- .001
.083148	.030347	2.740	2.740	.000
.10153	.036554	2.778	2.780	- .002
.12403	.043889	2.826	2.828	- .002
.14206	.049520	2.869	2.865	+ .004
NITROBENZENE				
0.051988	0.006841	7.600	7.602	-0.002
.079958	.010391	7.695	7.694	+ .001
.10663	.013706	7.780	7.780	.000
(.12185	.015607	7.807	7.828	- .021)
.16246	.020426	7.953	7.952	+ .001
.20078	.024910	8.060		
.24111	.029554	8.158		
.28197	.034349	8.209		

tion is obeyed. In nitrobenzene and toluene the measurements were taken beyond this point, and it is remarkable that the curves bend unmistakably toward the axis of W . This inflexion has not

TABLE III

Solvent	Concn. in water, M	Concn. in solvent, M	Double molecules, M
C ₆ H ₅ CH ₃	0.020	0.040	0.0012
C ₆ H ₅ Cl	.08	.13	.008
	(or more?)	(or more?)	(or more?)
C ₆ H ₆	> .05	> .125	> .007
C ₆ H ₅ NO ₂	.022	.21	.007

been observed previously. To make sure that it is genuine the measurements in toluene were carried into the region in which P again begins to increase rapidly with W . The results, which in-

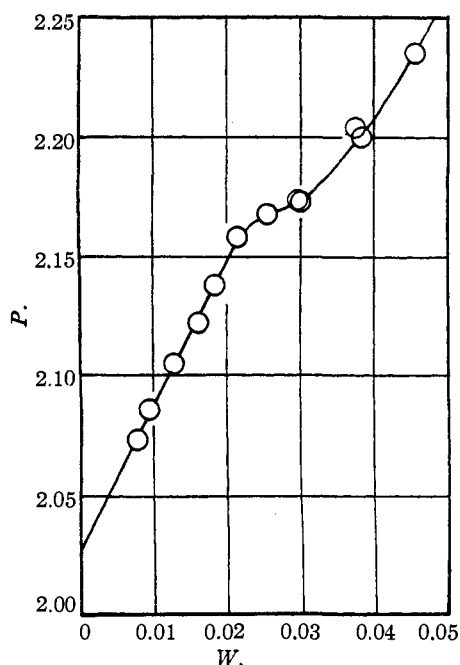


Fig. 1.—The distribution of phenol between toluene and water.

clude three independent series of measurements, are shown in Fig. 1. In Fig. 2 are shown the results for benzene, together with the dilute points of Philip and Clark,⁶ Rothmund and Wilsmore,⁶ and Kwantaro Endo.¹ These have been converted from volume to weight units with the help of the density data of Swearingen.⁷

Table IV shows the conversion to volume units of concentration. D_0 and k are the values of P_0 and K after converting the concentrations to moles per liter of solvent in both layers, and are derived from P_0 and K as follows

$$D_0 = \frac{d}{0.99706} P_0 \text{ and } k = \frac{K}{d}$$

d being the density of the pure solvent and 0.99706 the density of water, both at 25°. The dielectric

Solvent	P_0	K	d	D_0	k	
$C_6H_5CH_3$	2.39	2.0276	0.7289	0.86181	1.7525	0.843
C_6H_5Cl	5.94	1.2997	.7163	1.1019	1.4363	.648
C_6H_6	2.28	2.5425	.5034	0.87344	2.2273	.575
$C_6H_5NO_2$	36	7.4238	.2355	1.1983	8.9224	.196
CCl_4	2.24	0.3141	?	1.5843	0.4991	?

(6) Philip and Clark, *J. Chem. Soc.*, **127**, 1274 (1925); Rothmund and Wilsmore, *Z. physik. Chem.*, **40**, 611 (1902).

(7) Swearingen, *J. Phys. Chem.*, **32**, 785, 1346 (1928).

constant ϵ is also given for reference. Both d and ϵ are from the "International Critical Tables." The change in density due to the mutual solubility of water and the solvent has been neglected.

The attempt to estimate K in carbon tetrachloride was a failure, and the percentage change in P in this solvent is probably too small for the method to give satisfactory results. Eight solutions were examined between $W = 0.014$ and $W = 0.063$. The values of P varied erratically about a mean value of 0.3141, the average divergence from this mean being ± 0.0010 . These results do not justify any conclusion as to the value of K , but P_0 should not be in error by more than 1%.

It is advisable to note that the concentration of dissolved water is of the same order as the phenol concentration, the two highest water solubilities being 0.084 M in nitrobenzene and 0.039 M in benzene. This dissolved water may affect both D_0 and k , but the close concordance between the results and the law of mass action makes it improbable that the mutual solubility is appreciably affected by small concentrations of phenol, though the inflexion observed at higher concentrations may be attributed to an increased solubility of the solvent in water.

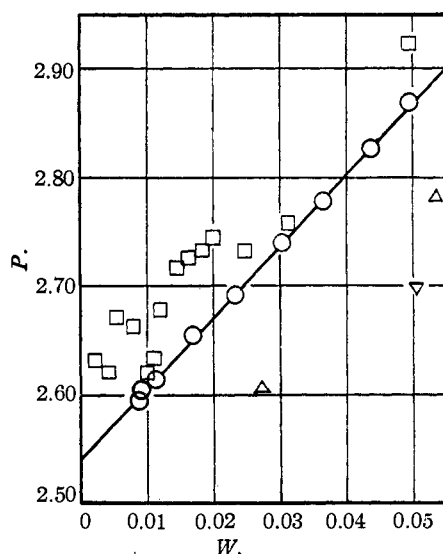
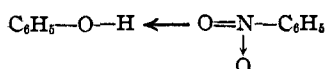


Fig. 2.—The distribution of phenol between benzene and water. \circ , Present work; \square , Philip and Clark; \triangle , Rothmund and Wilsmore; ∇ , Kwantaro Endo.

The extent of the association studied in this work does not exceed 13%, and the results do not allow us to distinguish between dipole association and the formation of a definite coordinate link

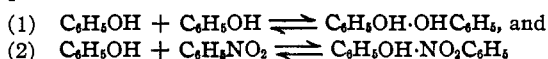
between molecules. The latter hypothesis is adopted in the discussion which follows.

There is an obvious correlation between the values of D_0 and k in the several solvents. The most striking feature of the results is the low value of the association in nitrobenzene, coupled with the high distribution coefficient for single molecules between this solvent and water. The latter is about three times as great as for any solvent yet examined except amyl alcohol.² These results both indicate combination between nitrobenzene and single molecules of phenol to form the substance⁸



The different values of the association constant found in the other solvents cannot be explained by differences in the dielectric constant, but can be attributed satisfactorily to differing degrees of solvation. The association of phenol involves coördination between hydroxylic oxygen and hydroxylic hydrogen. If solvation of single phenol molecules takes place in benzene it must be due to coördination between hydroxylic oxygen and a hydrogen atom of the benzene ring. There is other evidence⁹ that the benzene molecule can form coördinate links, both in solution and in the solid state. The effect on this combination of substituents in the benzene ring can be predicted from the work of Sutton¹⁰ on the dipole moments of mono-substituted benzenes. He found that ortho- and para-directing substituents like CH_3 and Cl produced a drift of electrons into the ring. This will reduce the tendency of the nuclear hydrogen atoms to act as acceptors, and hence reduce solvation in toluene and chlorobenzene as compared with benzene, in agreement with the results of the present work.

That solvation is confined to single molecules of phenol is unlikely in view of the work of Bell¹¹ on the hydration of the chloroacetic acids. If, however, we assume that the solvation of single molecules is chiefly responsible for the variation in the association constants we can make a rough comparison of the equilibrium constants of the reactions



(8) Sidgwick and Callow, *J. Chem. Soc.*, **125**, 527 (1924).

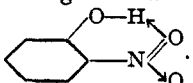
(9) Sidgwick, "The Covalent Link in Chemistry," Cornell University Press, Ithaca, N. Y., 1933, p. 135; Grace, *J. Chem. Soc.*, 594 (1931).

(10) Sutton, *Proc. Roy. Soc. (London)*, **A133**, 668 (1931).

(11) R. P. Bell, *Z. physik. Chem.*, **A150**, 20 (1930).

The former is supposed equal to the association constant in toluene (assuming that there is no solvation in this solvent), and has the value 0.843. The proportion of single molecules solvated in nitrobenzene, on the assumptions stated, can be calculated from the apparent association constant in this solvent, and is equal to $1 - (0.196/0.843)^{1/2} = 0.52$. The fraction $[\text{C}_6\text{H}_5\text{OH (solvated)}]/[\text{C}_6\text{H}_5\text{OH(not solvated)}]$ therefore has the value $0.52/(1 - 0.52) = 1.08$. This is divided by 9.74, the number of gram molecules of nitrobenzene in a liter, the resulting equilibrium constant of (2) being 0.11. This may be compared with 0.843, the equilibrium constant of (1), the comparison, though approximate, being sufficient to show that the tendency to association is probably considerably greater than the tendency to combine with nitrobenzene.

These conclusions are in entire agreement with the work of Auwers¹² on the cryoscopic behavior of substituted phenols dissolved in substituted toluenes. He found that the apparent association of the solute was increased by certain substituents in the benzene ring of the solvent but decreased by others, the order of the groups being, as has been found in the present work, CH_3 , Cl , (H) , NO_2 , OH . Groups like NO_2 which reduce association when present in the solvent increase it, as would be expected, when present in the solute. An interesting exception was provided by the ortho-substituted phenols, which do not associate when a six-membered ring can be formed, as in *o*-nitrophenol, to which Sidgwick and

Callow⁸ give the formula 

A quantitative comparison between Auwers' results and the present work is impossible because the temperature of his observations necessarily varied with the melting points of the solvents used. Moore, Shepherd and Goodall,¹³ working on the combination between aniline and substituted benzenes, likewise found the order of the substituents to be CH_3 , Cl , NO_2 .

The author is indebted to Dr. N. V. Sidgwick and Mr. R. P. Bell for suggestions in connection with the interpretation of these results.

Summary

1. The bromate-iodide method for phenol analysis has been adapted to small quantities, and the end-point has been improved.

(12) Auwers, *ibid.*, **42**, 513 (1903).

(13) Moore, Shepherd and Goodall, *J. Chem. Soc.*, 1447 (1931).

2. The distribution of phenol between water and five solvents has been studied in dilute solution at 25°.

3. In these solvents the phenol is shown to be present exclusively in single and double molecules.

4. A hitherto unreported inflexion has been observed in the curve connecting the distribution coefficient with the concentration.

5. The association constant of phenol in four of the solvents has been calculated.

6. Differences in the association constants are attributed to solvation of single molecules of phenol.

7. Substituents in the benzene ring of the solvent reduce (or increase) solvation in the following order: CH₃, Cl, (H), NO₂, OH.

8. This is shown to be in agreement with previous work, and is accounted for by a consideration of the mechanism of solvation and association.

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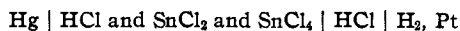
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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF WASHINGTON]

The Stannous-Stannic Oxidation-Reduction Potential

By C. S. HUEY AND H. V. TARTAR

Although the stannous-stannic electrode potential has been determined by Forbes and Bartlett¹ it was considered advisable to redetermine this constant, and extend the data over a wider range of acid concentration by a more accurate method developed since that time by Popoff and Kunz.² The electromotive force of cells of the following type was measured



The treatment of these data is essentially the same as that by Popoff and Kunz.

Apparatus and Reagents

Two 150-cc. Pyrex flasks were used as electrode vessels, with proper fittings for gas inlet and outlet, electrode and flowing junction. Stock solutions were stored in Pyrex bottles and under carbon dioxide. The potential was read to ± 0.01 mv. The temperatures used were 15, 25, and 35 $\pm 0.03^\circ$.

All reagents were of very pure materials. A "C. P. Analyzed" grade of tin was used. The hydrochloric acid was distilled. The water was conductivity water redistilled from alkaline permanganate. A good quality of mercury was thoroughly washed with dilute nitric acid containing mercurous nitrate, dried and distilled *in vacuo*.

Analytical Methods

Total Tin.—The gravimetric method in which the tin is precipitated with ammonia as the hydroxide³ was found to be very satisfactory.

Ratio of Stannous to Stannic Tin.—This determination was made using a modification of the iodimetric method.³ The stannous tin was first titrated and then the total

tin was determined after reduction to the stannous condition. It was found necessary that the starch indicator be oxygen-free and that the time for reduction be extended to one hour for solutions in which the concentration of hydrochloric acid was less than 0.5 *M*.

Chlorides.—Volhard's method was used for the determination of chlorides. Sufficient nitric acid was added to make the solution 3 *N* with respect to this reagent at the end of the precipitation with silver nitrate. This accomplished the oxidation of the tin to the stannic form, thus preventing any reduction of the silver by the stannous ion, and also prevented the hydrolysis of stannic nitrate. The solubility of the silver chloride in this concentration of nitric acid was found to be not great enough to interfere with the reliability of the method.

Choice of Electrode Material

Several electrode materials were tried in the hope that at least two could be found that would be inert toward the potential, and thus afford comparison. Copper, gold, bismuth and platinum (bright and black) failed to give steady and reproducible potentials. Silver electrodes proved more promising and were tested exhaustively. Electrodes were made by coating silver wire with fine crystals electrolytically deposited and by covering the wire with spongy silver made from a coating of the carbonate decomposed at 445°.⁴ The latter gave potentials that were quite steady, but they were not reproducible; the variations with a given solution covered a range of 100 mv. These results, in general, confirm the observations of previous investigators.⁵

Small quantities of various potential mediators⁶ were tried, such as ferric chloride with the platinum electrode and silver nitrate with the silver electrode. In no case was the behavior of the electrode improved by this means.

The mercury electrode alone was found to give repro-

(1) Forbes and Bartlett, *THIS JOURNAL*, **36**, 2030 (1914); **37**, 1201 (1915).

(2) Popoff and Kunz, *ibid.*, **51**, 382 (1929).

(3) Hillebrand and Lundell, "Applied Inorganic Analysis," J. Wiley and Sons, Inc., New York, 1929, p. 239.

(4) Lewis, *THIS JOURNAL*, **28**, 158 (1906).

(5) For a review of this literature, see Forbes and Bartlett, *ibid.*, **36**, 2030 (1914).

(6) Goard and Rideal, *Trans. Faraday Soc.*, **19**, 740 (1924).