243. *The Electrical Conductivities of Liquid Mixtures of Phenol–Aniline, Phenol–p-Toluidine, and Phenol–m-Cresol.*

By O. RHYS HOWELL and H. G. BENTLEY ROBINSON.

THE system phenol–water has been the subject of previous investigation, the densities (Howell, *Proc. Roy. Soc.*, 1932, **137**, 418), viscosities (*idem, Trans. Faraday Soc.*, 1932, **28**, 912), and electrical conductivities (Howell and Handford, *ibid.*, 1933, **29**, 640) of solutions over the whole range of miscibility having been measured at 20°, 30°, 40°, 50°, 60°, and 70°. It was found that, for each temperature, the curves of each of these properties plotted against the composition of the mixture gave no indication of the existence of phenol hemihydrate, which is clearly shown on the freezing-point curve and is readily deposited from solution. On the contrary, the constants in the equations connecting each of these properties with temperature, when plotted against the composition, exhibited marked inflexions at the concentration corresponding to equimolecular proportion of the two constituents. This was explained as due to the dual dissociation of the two substances involving the transfer of a hydrogen ion from a molecule of water to a molecule of phenol and *vice versa*:

$$\underset{\text{water-rich}}{C_6H_5O' + OH_3^{\cdot}} \rightleftharpoons C_6H_5OH + H_2O \rightleftharpoons \underset{\text{phenol-rich}}{C_6H_5OH_2^{\cdot} + OH'}$$

It was therefore deemed of interest to examine the electrical conductivities of other systems containing phenol to obtain further evidence on these points. Since measurements were to be made at only one temperature, it was necessary to choose as the second components substances which each give mixtures liquid over the whole range, at a temperature not far above the m. p. of phenol. Aniline, *p*-toluidine, and *m*-cresol all give mixtures which are liquid below 50°, and these were chosen for examination at this temperature.

The other consideration in the choice was that the substances should exhibit compound formation with phenol. Aniline forms such a compound in equimolecular proportion and so does *p*-toluidine. Since the latter is a much stronger base than the former, the choice of these two substances enabled the influence of different basicity to be determined. *m*-Cresol also forms a compound with phenol, but in the molecular proportion of 1 phenol : 2 *m*-cresol. The acidic character of the *m*-cresol and the difference in composition of the compound formed enabled these two effects to be examined.

EXPERIMENTAL.

Preparation of Materials.—Pure phenol was prepared by distilling Monsanto detached crystals in an apparatus made entirely of quartz and constructed so as to facilitate exclusion of water; only the middle third was used. It has already been shown (*loc. cit.*) that a very pure product is obtained in this way. A common stock of starting material was used, and for each preparation the rate of distillation was approximately constant at 100 c.c. per half-hour.

Aniline was purified by distilling the pure commercial product and accepting only the middle third.

p-Toluidine was purified by recrystallisation of A.R. material from alcohol; the crystals were dried on a porous tile and then in a vacuum desiccator over calcium chloride.

The *m*-cresol, which was a gift from the Monsanto Chemical Co. for which we desire to express our thanks, was further purified by cooling until about 70% had crystallised, separating the crystals and allowing them to drain in a jacketed funnel, the temperature being allowed to rise slowly from 8° to 12° so that the crystals were washed free of the lower-melting substances. The product was distilled and the middle fraction only accepted.

Preparation of Mixtures.—All mixtures were made up by weight. The cell with a temporary stopper of cork, covered with tin-foil, was weighed. Approximately the requisite amount of phenol was distilled directly into the cell, which was then stoppered, cooled, and weighed again. Approximately the calculated amount of the other constituent was then added, and the whole weighed again. The aniline or *m*-cresol was added by means of a quartz pipette. The *p*-toluidine was compressed into sticks by melting in a tube of hard Jena glass and was added in this form.

The cell was warmed until the contents were liquid and then placed in the thermostat. The ground stopper carrying the electrodes was placed in an empty flask in the thermostat to attain the temperature at the same time. After about 1½ hours, this ground stopper was substituted for the cork one, and the conductivity measured. Readings were taken as soon as possible after insertion of the electrodes, since in the presence of even grey platinum some of the mixtures undergo change, especially those containing *p*-toluidine, which rapidly darken.

Apparatus.—The cell, which was of quartz with platinum electrodes, was the one used for the determination of the conductivity of solutions in the phenol–water system (Howell and Handford, *loc. cit.*).

Since its constant varies slightly with the volume of liquid, this was determined with a series of different volumes of $N/50$-potassium chloride solution, and a curve (cell constant against volume) was plotted. In making measurements with the mixtures, the volume present was calculated from the weight and density, and the corresponding value of the cell constant was read from the curve and applied in the calculation of the conductivity.

After each solution had been measured, the cell was thoroughly washed several times with warm water, and finally with conductivity water prepared in the still already described (*loc. cit.*). It was then dried in an air-oven at 110—120° for 40 minutes, and cooled in a desiccator over phosphoric oxide.

The electrical arrangement was also essentially similar to that used previously, except that since the Tinsley bridge was no longer available, a metre wire had to be used. The Wagner earthing device consisted of a second wire lying parallel to the bridge wire, and continuous contact with each divided in the same ratio was secured by means of two small rollers mounted on a slider. The bridge reading was taken by means of a fine line engraved on a piece of celluloid also mounted on the slider.

Owing to the relatively low resistance of the bridge wires, it was necessary to provide for a larger input, and a new oscillator was constructed having eight valves in parallel in the second stage. A more sensitive amplifier was also employed. We desire to express our thanks to Mr. C. Handford for his kindness in designing these instruments.

It was found more convenient to revert to the use of telephones instead of the loud-speaker for these measurements.

All determinations were made in a thermostat filled with water covered with a layer of oil and heated by gas from a governed supply. The temperature was 50° ± 0·01° throughout.

Results.—The compositions and conductivities of the mixtures of phenol–aniline, –*p*-toluidine, and –*m*-cresol are given in Tables I, II, and III respectively, where *C* is the percentage by weight of phenol in the mixture. The conductivity is plotted against composition for the water and the *m*-cresol mixture in Fig. 1 and for the aniline and the *p*-toluidine mixture in Fig. 2. The curve for phenol–water is given at 70° since the mixtures are not completely miscible over the whole range at 50°.

TABLE I.

Phenol–Aniline.

C.	$\kappa \times 10^6$.	*C.*	$\kappa \times 10^6$.	*C.*	$\kappa \times 10^6$.	*C.*	$\kappa \times 10^6$.
0	0·034	41·24	0·143	69·14	0·366	90·31	0·380
5·52	0·037	45·34	0·180	72·46	0·389	93·14	0·337
12·84	0·046	47·96	0·194	77·87	0·409	96·33	0·171
19·86	0·065	52·75	0·232	82·32	0·416	98·87	0·093
31·48	0·094	55·18	0·260	82·59	0·418	100	0·021
32·82	0·096	60·68	0·304	86·66	0·406	—	—
35·96	0·114	65·22	0·334				

TABLE II.

*Phenol–*p*-Toluidine.*

0	0·037	36·20	0·153	62·18	0·467	90·09	0·660
11·66	0·056	38·17	0·163	65·26	0·507	92·51	0·612
21·11	0·077	49·12	0·271	71·37	0·597	93·87	0·576
26·21	0·096	49·23	0·283	75·16	0·631	96·34	0·465
29·67	0·105	51·73	0·307	75·65	0·637	98·03	0·344
31·21	0·107	52·78	0·317	83·32	0·690	99·13	0·252
32·39	0·122	58·78	0·403	83·97	0·695	99·43	0·187
33·76	0·132	59·90	0·415	85·40	0·699	100	0·021

TABLE III.

*Phenol–*m*-Cresol.*

0	0·259	29·67	0·283	57·50	0·256	79·86	0·168
5·40	0·262	36·28	0·283	62·58	0·253	83·70	0·155
11·70	0·263	40·08	0·271	67·47	0·225	89·39	0·106
17·03	0·279	46·43	0·267	70·65	0·216	94·68	0·067
24·27	0·272	51·82	0·266	76·53	0·178	100	0·021

DISCUSSION.

The conductivity–composition curves for phenol–aniline and phenol–*p*-toluidine are precisely similar, except that the maximum, which occurs at almost exactly the same composition for both, *viz.*, 16% of the second constituent, is considerably higher for *p*-toluidine. The curves are also remarkably similar to that for phenol–water, except that their maxima are at the phenol-rich end of the series, whereas with phenol–water it is almost exactly similarly situated at the water-rich end, *viz.*, at 16% phenol. In fact, in general form the curves for phenol–aniline and phenol–*p*-toluidine are mirror-images of the curve for phenol–water.

A striking feature of the curves (as of those for phenol–water) is the absence of any indication of the known compounds. The freezing-point curves of the system show that aniline forms a compound in equimolecular proportion with phenol (50·27% phenol), the compound existing over the range 8—79 mols.% of phenol (Schreinemakers, *Z. physikal. Chem.*, 1899, **29**, 577; Voano, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 76). Similarly, *p*-toluidine forms a compound with phenol in equimolecular proportion (46·76% phenol) existing over the range 32—75 mols.% of phenol (Kremann, *Monatsh.*, 1906, **27**, 91). The conductivity curves, however, are quite continuous for a considerable range on either side of the composition corresponding to these compounds.

It has already been pointed out that the increase in conductivity on continued addition of water to phenol begins to become appreciable only after the composition corresponding to equimolecular proportion is exceeded. In this connexion it may be noted that in discussing the conductivities of solutions of butyric acid and water, Grindley and Bury (J., 1930, 1665) point out that the conductivity does not begin to rise appreciably until the concentration of water exceeds about 15%. This is readily explained on the basis of the mechanism already suggested, since mutual ionisation involves the transfer of one hydrogen ion from one compound to the other (as for phenol and water), so that there should be little change in conductivity at the butyric acid-rich end of the series until the concentration exceeds that corresponding to equimolecular proportion (16·98% water).

FIG. 1.

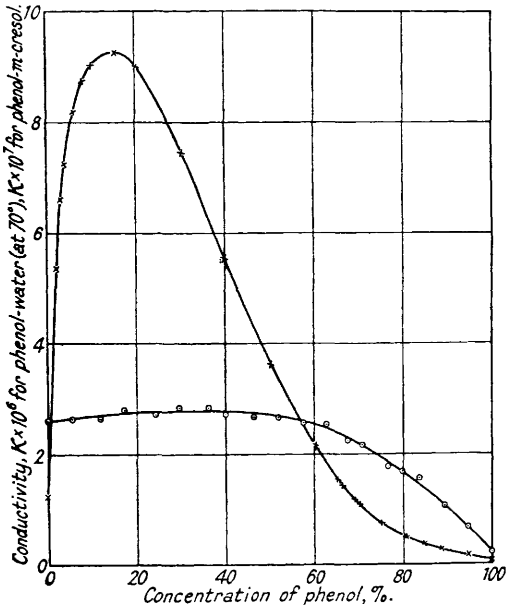
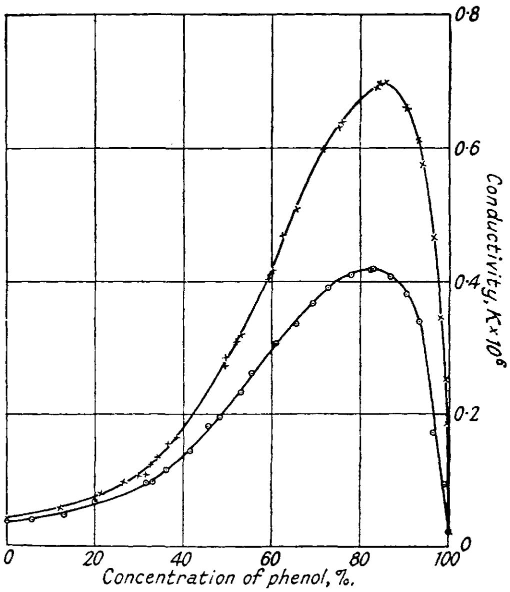


FIG. 2.



It is evident from the conductivity–composition curve for phenol–aniline that the increase in conductivity begins to become appreciable, not at equimolecular proportion of the two compounds, as in the instances already discussed, but at 1 phenol : 2 aniline (33·57% phenol). Consequently, it appears that ionisation of these substances at the aniline-rich end of the series occurs as follows :

$$2C_6H_5{\cdot}NH_2 + C_6H_5{\cdot}OH \rightleftharpoons 2C_6H_5{\cdot}NH' + C_6H_5{\cdot}OH_3^{\cdot\cdot}$$

and at the phenol-rich end, the transfer of a hydrogen ion from phenol to aniline occurs, forming the active $C_6H_5{\cdot}NH_3^{\cdot}$ ion and yielding a better-conducting solution :

$$C_6H_5{\cdot}NH_2 + C_6H_5{\cdot}OH \rightleftharpoons C_6H_5{\cdot}NH_3^{\cdot} + C_6H_5{\cdot}O'$$

[cf. Franklin's suggestion (*Amer. Chem. J.*, 1912, **47**, 285; *J. Amer. Chem. Soc.*, 1924, **46**, 2137) that ammonia ionises thus : $NH_3 + NH_3 \rightleftharpoons NH_4^{\cdot} + NH_2'$].

In the system phenol–*p*-toluidine also, it is seen from the curve that the conductivity begins to increase rapidly only after the concentration of phenol exceeds that corresponding to the composition 1 phenol : 2 *p*-toluidine (30·52% phenol), and a precisely similar mechanism is suggested for the ionisation in this system.

It has already been noted that the maxima in the phenol–aniline and phenol–*p*-toluidine curves occur at approximately the same concentration, *viz.*, 16% of phenol, and that in the phenol–water system at 16% of water. The conductivity curves for water–hydrochloric acid (Howell, J., 1927, 2843) and for water–butyric acid (Grindley and Bury, *loc. cit.*) also show maxima at about 16% of acid. Grindley and Bury point out that the freezing-point and the contraction curve of the system water–butyric acid exhibit abrupt changes of slope at this same concentration. They regard this as evidence of micelle formation, but do not attribute the maximum on the conductivity curve to the same cause. In the systems phenol–aniline and phenol–*p*-toluidine there is no reason to suppose that micelle formation occurs, and the maximum on the conductivity curve cannot be due to this effect.

At the maxima, the two substances aniline and *p*-toluidine exist under very nearly identical conditions. The temperature and solvent are identical and the concentration is almost the same. Hence, if the scheme of ionisation already suggested is correct, the conductivities at the maxima should be a measure of the extent to which hydrogen ion has been transferred from the phenol to the bases, and therefore of the relative basicity of these bases. The conductivities at the maxima are $0{\cdot}698 \times 10^{-6}$ and $0{\cdot}418 \times 10^{-6}$ for *p*-toluidine and aniline respectively, and the ratio 1·67.

The dissociation constants of aniline and *p*-toluidine calculated from the degree of hydrolysis of their salts, determined by different observers using different methods at various temperatures (usually 18°, 20°, or 25°), are given below, together with the relative basicity calculated on the assumption that $\alpha = \sqrt{K_b}$

Observers.	1.	2.	3.	4.	5.	6.	7.	8.
10^{10} . K_b, aniline	—	4·1	17	5·7	5·3	5·2	3·0	5·4
10^{10} . K_b, *p*-toluidine ...	—	13·2	36	20	11·3	22	10	13
Relative basicity	1·6	1·8	1·5	1·9	1·5	2·1	1·8	1·6
								Mean 1·7

References.—(1) Lellmann and Görtz, *Annalen*, 1893, **121**, 247; (2) Bredig, *Z. physikal. Chem.*, 1894, **13**, 191, 322; (3) Walker and Aston, J., 1895, **67**, 576; (4) Löwenhertz, *Z. physikal. Chem.*, 1898, **25**, 385; (5) Farmer and Warth, J., 1904, **85**, 1713; (6) Denison and Steele, J., 1906, **89**, 999, 1386; (7) Pring, *Trans. Faraday Soc.*, 1923, **19**, 705; (8) Mitzutani, *Z. physikal. Chem.*, 1925, **116**, 350; 1926, **118**, 327.

The conductivity–composition curve of the system phenol–*m*-cresol (Fig. 1), like those for phenol–aniline and phenol–*p*-toluidine, shows no marked discontinuity at the composition corresponding to the compound formed by the two substances. In this instance, the compound, as shown by the freezing-point curve (Dawson and Mountford, J., 1918, **113**, 923; Fox and Barker, *J. Soc. Chem. Ind.*, 1918, **37**, 268), is 1 phenol : 2 *m*-cresol (30·32% phenol) existing over the range 4·8—55·2 mols.% of phenol.

The same mechanism of ionisation is again suggested, *viz.*, the transfer of a hydrogen ion from one compound to the other :

$$\underset{m\text{-cresol-rich}}{CH_3{\cdot}C_6H_4{\cdot}O' + C_6H_5{\cdot}OH_2^{\cdot}} \rightleftharpoons CH_3{\cdot}C_6H_4{\cdot}OH + C_6H_5{\cdot}OH \rightleftharpoons \underset{\text{phenol-rich}}{CH_3{\cdot}C_6H_4{\cdot}OH_2^{\cdot} + C_6H_5{\cdot}O'}$$

In each of the systems phenol–aniline and phenol–*p*-toluidine, the two components are very different in character, the one acidic and the other basic, so that at one end of the series the transfer of hydrogen ion reaches a high value, resulting in a comparatively large increase in conductivity, and the curve shows a well-defined maximum. In the system phenol–*m*-cresol, however, the two components are very similar and differ only slightly in acidity. A number of determinations, all at 25°, have been made of the dissociation constant of phenol; the values found for $10^{10}K_a$ are : 1·3 (Walker, *Z. physikal. Chem.*, 1900, **32**, 137); 1·3 (Hantzsch, *Ber.*, 1902, **35**, 210); 1·09 (Lundén, *Z. physikal. Chem.*, 1910, **70**, 249); 1·15 (Boyd, J., 1915, **107**, 1538); 1·03 (Tiessens, *Rec. trav. chim.*, 1929, **48**, 1066). Only one, however, is available for *m*-cresol: $K_a = 9{\cdot}8 \times 10^{-11}$ (Boyd, *loc. cit.*). Boyd's two values being used, the relative acidity phenol : *m*-cresol is approximately 1·08. The tendency to transfer a hydrogen ion is therefore very little different in the two compounds, and, on the mechanism suggested, there should be no great increase in conductivity at either end of the series, so that the curve should not exhibit a pronounced maximum. Since the transfer of only one hydrogen ion is involved in both possible ionisations, the curve might be expected to consist of two branches falling away smoothly from the value for equimolecular proportion (46·53% phenol) to the values for the two pure constituents. It is seen (Fig. 1) that this is so, and that the highest conductivity is very little greater than that of the better-conducting component (*m*-cresol).

It is remarkable that in each of the four systems examined, there has been found in the liquid state an association different from that so clearly shown in the corresponding freezing-point curves. This may be conveniently summarised thus :

	Molecular association.	
System.	At the f. p.	In solution.
Phenol–aniline	1 : 1	1 : 2
Phenol–*p*-toluidine	1 : 1	1 : 2
Phenol–water	2 : 1	1 : 1
Phenol–*m*-cresol	1 : 2	1 : 1

SUMMARY.

1. The electrical conductivities of the systems phenol–aniline, -*p*-toluidine, and -*m*-cresol have been determined at 50°.

2. Each conductivity–composition curve (like that for the system phenol–water, which has been previously investigated) shows no indication of the existence of the compound which is so clearly marked on the corresponding freezing-point curve.

3. On the contrary, there is evident association in other molecular proportions.

4. At one end of the series, the conductivity increases only slowly until the composition exceeds a certain value, which for phenol–water and phenol–*m*-cresol corresponds to equimolecular proportions and for phenol–aniline and phenol–*p*-toluidine to 1 of phenol to 2 of base. This is explained by the dual ionisation of the two constituents, which consists in the transfer of hydrogen ions.

5. The curves for phenol–aniline and phenol–*p*-toluidine show pronounced maxima at approximately the same composition. Since the conditions at the maxima are practically identical, the ratio of the conductivities should be a measure of the relative basicities, and the value found is in good agreement with those obtained by measurements of the hydrolysis of the salts.

6. The curve for phenol–*m*-cresol rises gradually at both sides to a value only slightly higher than that of the better-conducting component. The two substances are so similar that the tendency to transfer a hydrogen ion is little different at either end of the series.

THE COLLEGE OF TECHNOLOGY, MANCHESTER.

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