Variations in compound formation, solubility and ionization in systems of the general type HX : RX are all, indeed, more extreme the weaker the acidic radical X.   Hydroxides in water differ more widely than formates in formic acid, these again are more diverse than sulfates in sulfuric acid.

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COMPOUND FORMATION IN PHENOL : CRESOL MIXTURES.

BY JAMES KENDALL AND J. J. BEAVER.

It has been shown in previous articles[1] that the extent of addition compound formation in binary liquid mixtures is controlled primarily by "chemical contrast," the stability of complexes increasing uniformly with the differences in character (i. e., in the positive or negative nature of the constituent groups) of the two components.   A great number of systems of very diverse types have been carefully examined, and incidentally no fewer than 101 new compounds have been discovered.   To all of these systems the simple generalization given above is directly applicable, except to systems containing phenols.

Several times in the course of the work[2] abnormal results with phenols have been noted and tentative explanations, such as the existence of phenol in two tautomeric forms of widely different acidic strengths, proposed. Recently, Dawson and Mountford[3] have made a thorough investigation of compound formation in systems of the type phenol: cresol by the freezing-point method, obtaining definite compounds in 5 out of 6 cases.   This they considered as rather remarkable in view of the close chemical similarity of the components, and concluded that "the relations disclosed by the freezing-point diagrams are consequently not in accord with what should have been anticipated on the basis of the views advocated by Kendall." The fact that the uniform abnormality of the phenols had already been emphasized was apparently overlooked.

A similar study of phenol: cresol systems by Fox and Barker[4] leads to quite contradictory results, a stable compound being isolated in only one of the six mixtures examined.   This discrepancy is in all probability due to inadequate purification of the materials employed by Fox and Barker, and to the general inferiority of their method.   In view of the extreme care exercised by Dawson and Mountford in all details, there is no reason

[1] For a summary of results and conclusions, see Kendall, Booge and Andrews, THIS JOURNAL, **39**, 2304 (1917).

[2] Kendall, ibid., **36**, 1241 (1914); **38**, 1317 (1916); Kendall, Booge and Andrews, loc. cit., p. 2306.

[3] Dawson and Mountford, J. Chem. Soc., **113**, 923 (1918).

[4] Fox and Barker, J. Chem. Ind., **37**, 268 (1918).

to doubt the accuracy of their freezing-point data. The fact established by Fox and Barker, however, that the boiling-point curves of phenol-cresol mixtures show very little departure from the linear, is not what would be expected from systems in which addition compounds are present in appreciable quantity.

The present paper gives the results of further investigations on the physico-chemical properties of phenol-cresol mixtures, undertaken in the hope either of bringing these systems into line with the rest, or of obtaining some clue to the source of the abnormalities which they exhibit.

Conductivity Measurements.

Kendall and Gross have demonstrated, in a recent article,[5] the validity of the general rule that compound formation and ionization in solutions proceed in parallel. For several series of binary organic mixtures it has been established experimentally that an increase in compound formation in regularly accompanied by a similar increase is specific conductivity. Where the extent of compound formation was known to be minute, the conductivity was almost immeasurable; as compound formation increased in amount, the conductivity became appreciable; where combination was extensive, the conductivity was very markedly increased.

As the first line of attack in the present work, it was consequently decided to determine the specific conductivity-composition curves of phenol-cresol mixtures. The essential principles of the experimental method employed have already been described by Kendall and Gross. The specific conductivities of the pure substances and solutions here under examination proved to be so extremely small, however, that some additional refinements in technique were necessary in order to obtain the required degree of accuracy in the experimental results.

Conductivity Apparatus.—The cell finally adopted was a 6-cylinder cell of the Beans and Eastlack type,[6] with a constant of 0.001426. The electrodes consisted of concentric platinum cylinders, 1 mm. apart, sand-blasted and connected alternately. With this cell it was possible to obtain very satisfactory sound minima with solutions of conductivity 1.0×10^{-9} mhos. Platinized electrodes could not be used, since in the presence of platinum black phenol-cresol solutions rapidly turn yellow, with a measurable increase in conductivity.

The bridge employed was a 4.70-meter circular slide-wire instrument, well-grounded and carefully calibrated. The resistance coils, up to 1000 ohms, were bifilar wound; those over 1000 ohms were of the Curtis type. A Vreeland oscillator gave a pure sine-wave alternating current of 1000 cycles per second. A high-resistance telephone receiver was used. The capacity of the cell was balanced out by means of a rotary air condenser connected in parallel with the resistance coils.

Most of the measurements were carried out in a large Freas thermostat, regulated to $25° \pm 0.005°$. Many of the solutions which normally

[5] Kendall and Gross, THIS JOURNAL, **43**, 1426 (1921).

[6] Beans and Eastlack, *ibid.*, **37**, 2674 (1915).

freeze at a higher temperature could be supercooled sufficiently to enable direct determinations at 25° to be made. With pure phenol and mixtures very rich in phenol, however, solidification could not be prevented in the presence of the sand-blasted electrodes, although viscosity measurements at 25° were later successfully accomplished. To complete the specific conductivity curves for phenol-cresol mixtures at 25° it was therefore necessary to perform experiments for these concentrations at higher temperatures and extrapolate the results.[7] For this purpose 2 smaller thermostats, regulated to 40° ± 0.05° and 50° ± 0.10°, respectively, were fitted up. Linear extrapolation was assumed to be valid over the small temperature range involved.[8] While this assumption is probably not strictly accurate, the values so obtained exhibit very good agreement with the direct measurements at 25°, as may be seen by referring to Fig. 1. In this diagram, the extrapolated sections of the various curves are indicated by broken lines.

Mixtures were made up by direct weighing, with the use of a Lunge pipet. The compositions as given in the tables below are accurate to within ±0.05%. The specific conductivity data themselves possess a *relative* accuracy of the order of 0.1%, but owing to the impossibility of compensating exactly for inductance and capacity effects under the conditions of experiment, no claim is made for so high a degree of accuracy in their *absolute* values.

Purification of Materials.—As in the work of Kendall and Gross, it was found that the presence of impurities in quantities insufficient to exert any appreciable influence upon the freezing point or boiling point frequently involved a very considerable change in specific conductivity. A constant specific conductivity was therefore made the final criterion of purity.

In the case of each substance used, the purest material obtainable was repeatedly fractionated from special stills of Pyrex glass.[9] A middle fraction of constant freezing point usually gave a product of constant specific conductivity after 3 to 6 additional fractionations. In view of the hygroscopic nature of the materials under study and of the marked influence exerted by traces of water upon their specific conductivities, the last fractionations and conductivity determinations were restricted entirely to cold, dry days. The sensitivity of the materials towards moisture undoubtedly constitutes the chief source of error in the whole of the experimental work, and all possible precautions were taken to minimize its effect upon the results.

[7] Compare Kendall and Gross, THIS JOURNAL, **43**, 1428 (1921).

[8] Compare Kendall and Brakeley, *ibid.*, **43**, 1830 (1921).

[9] It was found that addition of a small quantity of anhydrous powdered sodium carbonate was very beneficial in accelerating the elimination of impurities.

The System Phenol: o-Cresol.—A c. p. sample of phenol, after about 20 fractional distillations, gave a final product of specific conductivity 11.98×10^{-8} at 40° and 14.07×10^{-8} at 50°. The only previously recorded value is that of Riesenfeld,[10] 43×10^{-8} at 43°. The freezing point obtained with our material was $39.70° \pm 0.02°$, identical with that found by Morgan and Egloff[11] for a specially prepared and purified sample. Several investigators have reported considerably higher values for unpurified specimens of phenol,[12] which would appear to indicate that commercial phenol is apt to contain an impurity which *raises* its fusion point. The original material here employed, indeed, gave a freezing point higher than that of the final product.

Pure o-cresol was obtained from a c. p. product by similar continued fractionation, the final material possessing a specific conductivity of 0.127×10^{-8} at 25° and a freezing point of $30.60° \pm 0.02°$. No previous measurements of the conductivity have been made; for the freezing point the most reliable recorded value[3] is $30.45°$.

The conductivity results for the various mixtures examined at 25° are presented in Table I. The compositions of the solutions are expressed in molecular percentages throughout. The viscosity data which are appended will be discussed later.

TABLE I.

PHENOL: o-CRESOL.

Mol. % phenol.	Spec. cond. $\times 10^8$.	Viscosity.	Mol. % phenol.	Spec. cond. $\times 10^8$.	Viscosity.
0.0	0.127	0.07608	69.27	2.583	0.08645
13.43	0.375	0.07835	75.79	3.321	0.08731
19.73	0.415	0.07930	80.03	4.196	0.08757
30.00	0.612	0.08099	87.30	5.422	0.08825
38.81	0.693	0.08235	90.10	6.183	0.08851
49.10	0.885	0.08404	100.00	8.84	0.08945
62.83	1.686	0.08565			

The System Phenol : m-Cresol.—Pure m-cresol was prepared by repeated fractionation from a standard c. p. sample. The specific conductivity of the final product was 1.397×10^{-8} at 25°; its freezing point was $11.10° \pm 0.02°$. The highest value for the freezing point previously reported[13] is 10.9; no conductivity measurements are available for comparison.

[10] Riesenfeld, *Z. physik. Chem.*, **41**, 346 (1902).

[11] Morgan and Egloff, THIS JOURNAL, **38**, 844 (1916).

[12] $42.4°$ was found for a Kahlbaum sample (Kendall and Carpenter, *ibid.*, **36**, 2498 (1914)).

[13] Kendall, THIS JOURNAL, **38**, 1315 (1916). Dawson and Mountford employed a product with f. p. 10.0°; Fox and Barker used material with a very much lower freezing point, presumably containing about 15% p-cresol (see Dawson and Mountford, Ref. 3, p. 924).

TABLE II.

PHENOL: m-CRESOL.

Mol. % phenol.	Spec. cond. × 10⁸.	Viscosity.	Mol. % phenol.	Spec. cond. × 10⁸.	Viscosity.
0.0	1.397	0.1342	63.52	4.197	0.09961
12.59	1.592	0.1250	73.25	5.094	0.09698
24.49	1.887	0.1169	81.90	5.923	0.09398
31.37	2.175	0.1131	89.21	6.810	0.09206
38.48	2.587	0.1095	93.01	7.431	0.09105
45.02	2.988	0.1070	100.00	8.84	0.08945
51.74	3.379	0.1040			

The System Phenol : p-Cresol.—The preparation of pure p-cresol from several standard c. p. samples was unsuccessfully attempted, the elimination of traces of m-cresol (which possesses almost exactly the same boiling point)[14] not being possible. Finally a satisfactory product was obtained by diazotizing pure p-toluidine[15] (f. p., 43.0°), distilling with steam, extracting the distillate with ether, and drying and fractionating the extract as described above. The specific conductivity of the final material was 1.378×10^{-8} at 25°; it gave a freezing point of 34.55 ± 0.02°. Practically the same freezing-point value was obtained in previous researches of this series;[13,12] Dawson and Mountford, in their work, used a sample with f. p. 34.15°. No previous determinations of specific conductivity are recorded in the literature.

p-Cresol was found to be much more sensitive to light than its homologs, even a carefully purified specimen turning yellow in the course of a day if kept exposed. The data here presented were obtained with the use of freshly prepared material throughout.

TABLE III.

PHENOL: p-CRESOL.

Mol. % phenol.	Spec. cond. × 10⁸.	Viscosity.	Mol. % phenol.	Spec. cond. × 10⁸.	Viscosity.
0.0	1.378	0.1474	63.85	4.972	0.1042
15.98	2.210	0.1327	75.87	5.863	0.09835
31.91	3.012	0.1218	87.83	7.151	0.09463
38.51	3.423	0.1175	100.00	8.84	0.08945
52.18	4.201	0.1099			

Systems containing Two Cresols.—In Tables IV to VI (p. 1858), the conductivity and viscosity results for binary cresol mixtures are given.

[14] The b. p. (under 760 mm. pressure) of m-cresol is 202.1°, of p-cresol, 202.5°. In the cases of phenol and p-cresol, the differences in b. p. are sufficient to permit of systematic fractionation (see Dawson and Mountford, J. Chem. Soc., **113**, 937 (1918)).

[15] The reaction was carried out in 6 molar HCl solution by slow addition of the theoretical amount of sodium nitrite, the temperature being maintained below 10° and rapid admixture being ensured by vigorous stirring. When the reaction was complete the temperature was very gradually raised to 40° and the solution allowed to stand overnight before distilling with steam.

TABLE IV.

o-CRESOL: m-CRESOL.

Mol. % o-cresol.	Spec. cond. × 10⁸.	Viscosity.
0.0	1.397	0.1342
15.37	1.134	0.1216
30.61	0.977	0.1109
35.36	0.874	0.1075
39.54	0.767	0.1050
50.60	0.633	0.09939
63.71	0.362	0.09208
76.08	0.184	0.08582
88.03	0.178	0.08086
100.00	0.127	0.07608

TABLE V.

o-CRESOL: p-CRESOL.

Mol. % o-cresol.	Spec. cond. × 10⁸.	Viscosity.
0.0	1.378	0.1474
15.47	0.726	0.1327
29.99	0.601	0.1200
35.25	0.553	0.1163
42.33	0.507	0.1103
52.56	0.410	0.1030
63.04	0.344	0.09612
75.73	0.190	0.08854
87.50	0.188	0.08209
100.00	0.127	0.07608

TABLE VI.

m-CRESOL: p-CRESOL.

Mol. % m-cresol.	Specific cond. × 10⁸.	Viscosity.	Mol. % m-cresol.	Specific cond. × 10⁸.	Viscosity.
0.0	1.378	0.1474	62.38	1.551	0.1373
13.88	1.495	0.1450	67.33	1.512	0.1369
24.61	1.603	0.1432	70.71	1.449	0.1361
30.03	1.628	0.1425	73.73	1.442	0.1360
45.20	1.560	0.1400	82.67	1.378	0.1352
48.23	1.567	0.1393	91.35	1.384	0.1346
55.21	1.583	0.1385	100.00	1.397	0.1342

The specific conductivity results given in the above tables are represented graphically in Fig. 1. Curves I to III show the data for mixtures of phenol with the cresols, Curves IV to VI the data for binary cresol mixtures.

It will be immediately evident, from inspection of this diagram, that the specific conductivities of all of the solutions examined are very little
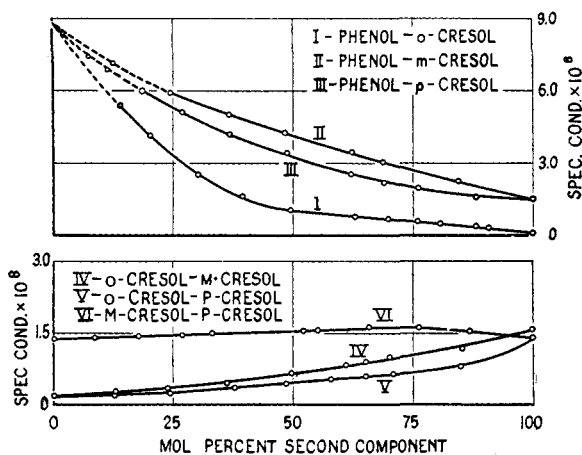

Fig. 1.—Specific conductivity-composition curves.

different from those of the pure components.[16] This type of curve, according to the predictions of Kendall and Gross,[17] is characteristic of all mixtures in which the two components are essentially similar in character. In such mixtures little or no increase in molecular complexity through compound formation is to be expected. Hence the observed conductivity of any solution should not differ significantly (if the parallelism between molecular complexity and ionization is accepted) from that obtained by linear extrapolation from the specific conductivities of its components.

The conductivity results here obtained are therefore in apparent contradiction with the freezing-point results of Dawson and Mountford, and in agreement with the generalizations formulated in previous papers of this series. This discrepancy will be discussed more fully below, after the work on some other physical properties of phenol-cresol mixtures has been described. The investigation of the viscosity-composition curves of these systems was chosen as the second line of attack in the present work, in view of the marked effect of changes in molecular complexity upon the viscosity.

Viscosity Measurements.

Viscosity curves for binary liquid mixtures fall, in general, into three distinct types.[18] The ideal curve, given by solutions in which no interactions at all take place on mixtures of the components, is not linear but appreciably sagged. Where compound formation occurs on admixture, the viscosity (owing to the production of more viscous complexes) is abnormally high; if compound formation is extensive the curve may even exhibit a *maximum*. Where disassociation of an associated component takes place on admixture, the viscosity (owing to the production of less viscous molecules) is abnormally low; if disassociation is extensive the curve may even exhibit a *minimum.* In certain cases both compound formation and disassociation effects may be existent, producing a curve of a "pseudo-ideal" type.[19] A brief consideration of the chemical character of the components will suffice, however, to enable us to distinguish such a system from one which is truly ideal. Usually, also, one effect will predominate sufficiently to give a curve quite distinct from the normal type.

It was hoped, therefore, that a study of the viscosity curves of phenol: cresol systems would either make possible a decision between the apparently conflicting conclusions drawn from freezing-point and conductivity measurements, or indicate a means of reconciliation.

[16] The curve for the system *m*-cresol : *p*-cresol differs slightly from the 5 others, exhibiting an exceedingly small flat maximum, but in view of the extremely small conductivities given by this system throughout, no special significance is attached to this fact.

[17] Kendall and Gross, THIS JOURNAL, **43**, 1420 (1921).

[18] See Kendall and Monroe, *ibid.*, **43**, 115 (1921).

[19] Compare Kendall and Brakeley, *ibid.*, **43**, 1831 (1921).

The apparatus used for the determination of viscosities was of the Bingham type,[20] the experimental procedure being essentially as described in previous work.[21]

Very extensive investigations have recently been carried out by Bramley[22] on the viscosity of systems of the general type phenol : aniline. The viscosities and densities obtained by us for phenol and the cresols may be compared with the results of Bramley by reference to the following table. Density data by Dawson and Mountford are also included.

	Phenol.	o-Cresol.	m-Cresol.	p-Cresol.
$\eta_{25°}$ (Bramley)	0.0883	0.07620	0.1240	0.1413
(Kendall and Beaver)	0.08945	0.07608	0.1342	0.1474
d_t^{25} (Bramley)	1.0710	1.0440	1.0293	1.029
(D. and M.)	1.0710	1.0415	1.0295	1.0295
(K. and B.)	1.0708	1.0414	1.0298	1.0295

It will be seen that the agreement is not all that could be expected in every case. In view, however, of the extremely careful methods of purification employed in the present work, we believe our values to be more reliable.

The relative accuracy of the viscosity data presented in Tables I to VI above is $\pm 0.2\%$. With the apparatus employed, a somewhat higher degree of precision is attainable for most substances, but the temperature coefficient of viscosity of the liquids here examined is extremely high, approximately 10% per degree.[22] Very accurate density determinations are not necessary for the evaluation of viscosities with the Bingham type of instrument.[23] Consequently, after it had been found for each system that the density of an approximately equimolecular mixture was, within error limits, identical with that calculated from the densities of its components, it was assumed that no appreciable contraction occurred on admixture in any case,[24] and the densities for the remaining solutions were obtained by linear interpolation from the specific volume-weight composition curves.

The viscosity results for the 6 systems are reproduced in graphic form in the accompanying diagram Fig. 2. From inspection of the curves, it is again immediately evident that no appreciable change in average molecular complexity occurs on admixture in any system. The curves are apparently very near to the ideal type.

[20] Bingham, J. Ind. Eng. Chem., 6, 233 (1914); Bingham, Schlesinger and Coleman, THIS JOURNAL, 38, 27 (1916).

[21] Kendall and Monroe, ibid., 39, 1787 (1917).

[22] Bramley, J. Chem. Soc., 109, 434 (1916).

[23] The density enters into the working formula only in a correction factor (approximately 1% of the total).

[24] This assumption is in agreement with the actual density determinations carried out by Fox and Barker (J. Soc. Chem. Ind., 36, 845 (1917)) with less pure materials.

When it is remembered, however, that we have independent evidence from other physical properties[25] that phenol and the cresols are highly
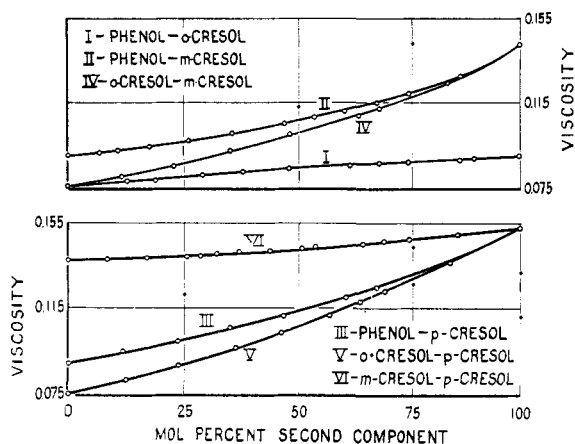

Fig. 2.—Viscosity-composition curves.

associated liquids in the pure state, it follows that this approximation to the normal type of curve must be due to the mutual compensation of the two opposing effects discussed above—compound formation and disassociation. Neither effect is here predominant; combination between the compounds appears to be practically counterbalanced by mutual depolymerization, leaving the average molecular complexity substantially unchanged.

To obtain confirmation of this point of view, a third line of attack was formulated, namely, the determination of the molecular weights of the pure substances, and the average molecular weights of certain of their binary mixtures, in an inert solvent.

Molecular Weight Determinations.

The freezing point of a pure liquid, on addition of an ideal solute, will be depressed according to the equation[26] $ln\ x = (-Q/RT_o) . (\Delta T/T)$ (where x is the mol fraction of solvent in the solution, Q the mol heat of fusion of the solvent, T_o and T the absolute freezing points of the pure solvent and the solution respectively, ΔT the freezing-point depression, and R, 1.9852). If the solute is not ideal but associated, its average molecular weight in any solution of known composition can be calculated from the above equation[27] by substituting the experimentally determined value for ΔT and solving for x.

[25] See Turner, "Molecular Association," 1915; also references in text later.

[26] Roozeboom, "Heterogene Gleichgewichte," 2, 273 (1904).

[27] Compare Washburn and Read, THIS JOURNAL, 41, 729 (1919). The error involved in the application of the simpler Raoult equation to the determination of molecular weights at high concentrations of solute is quite considerable.

As a suitable solvent, benzene was selected. The ideal freezing-point depression curve for this liquid has already been indicated in a previous article.[21] The benzene employed in the present work was very carefully prepared by repeated fractionation of a thiophene-free sample, dried over sodium. It possessed, within error limits, the same physical constants as noted in the preceding reference.

To determine the freezing-point depression of benzene on addition of phenol and its homologs the standard Beckmann apparatus and method were used. The thermometer was calibrated at the Bureau of Standards. Supercooling was limited to between 0.1° and 0.2°. For the depressions tabulated below the accuracy claimed is about 0.01°.

TABLE VII.

FREEZING-POINT DEPRESSION DATA.

Phenol.

Mol % Solute	0.97	1.81	3.17	4.50	6.38	7.92			
ΔT, °C.	0.398	0.711	1.190	1.621	2.221	2.635			

o-Cresol.

Mol % Solute	0.88	1.86	2.84	3.81	4.71	5.95	7.53		
ΔT, °C.	0.591	1.170	1.752	2.257	2.728	3.341	4.082		

m-Cresol.

Mol % Solute	0.67	1.54	2.00	3.10	4.33	5.43	6.01		
ΔT, °C.	0.439	0.925	1.161	1.711	2.161	2.584	2.843		

p-Cresol.

Mol % Solute	0.95	2.01	3.18	4.54	5.70	7.10	8.68	10.33	
ΔT, °C.	0.590	1.180	1.691	2.225	2.625	3.102	3.569	4.065	

1 Phenol + 1 o-Cresol.

Mol % Solute	1.15	2.33	3.64	5.07	6.65	7.79	9.46		
ΔT, °C.	0.602	1.180	1.774	2.383	2.998	3.444	4.060		

1 Phenol + 2 m-Cresol.

Mol % Solute	0.66	1.71	2.78	4.04	5.70	7.25	8.70	10.24	11.74
ΔT, °C.	0.380	0.908	1.396	1.905	2.490	2.987	3.409	3.890	4.347

1 o-Cresol + 2 p-Cresol.

Mol % Solute	0.91	2.02	3.02	4.11	5.34	6.72	8.59		
ΔT, °C.	0.590	1.218	1.727	2.239	2.743	3.275	3.953		

The positions of three of the resultant freezing-point depression curves (those for phenol, for o-cresol, and for an equimolecular mixture of phenol and o-cresol) with respect to the ideal are shown in Fig. 3. Phenol is evidently far from being monomolecular in benzene solution, the abnormally small depressions obtained pointing towards very extensive association. The curve for o-cresol, on the other hand, is very much closer to the ideal curve, indicating that this substance is far less highly associated in benzene solution.[28] The equimolecular mixture, finally, gives

[29] Hildebrand, (THIS JOURNAL, **38**, 1452 (1916)) has shown that it is dangerous to ascribe deviations from the ideal curve to differences in molecular complexity when the solutes possess very divergent internal pressures. In view of the essential similarity in character of phenol and the cresols, however, the comparisons here made between

a curve which falls almost exactly midway between those of its two components. In other words, the average molecular complexity is practically unchanged by admixture.
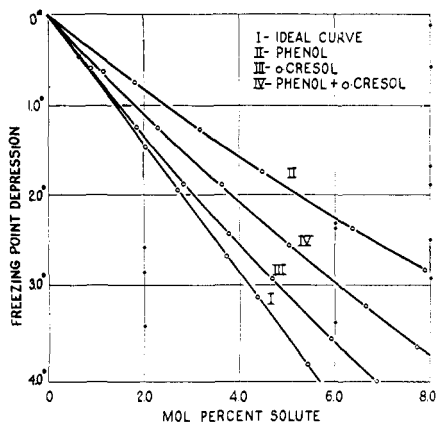

Fig. 3.—Freezing-point depression curves
in benzine.

Precisely the same behavior is exhibited by the remaining results presented in Table VII (p. 1862). Each of the two mixtures tested (phenol and m-cresol in molecular proportions 1 to 2; o-cresol and p-cresol in the molecular proportions 1 to 2) corresponds to a definite compound isolated by Dawson and Mountford. The freezing-point depression curve in each case is found to occupy a position intermediate between the curves of the respective components, and nearer to that component which is present in excess.

If these phenol-cresol compounds were true *addition compounds* (their formation involving an increase in molecular complexity) entirely different results would have been obtained. Even although dissociation of such compounds into their simpler components would be greatly favored by the dilution of the mixture with a large excess of solvent benzene, we should still find appreciable combination indicated by abnormally small freezing-point depressions. Thus, to cite an instance, which will be taken up in detail in a subsequent communication, the freezing point of a solution of ethyl acetate in benzene is practically unchanged on addition of an equimolecular amount of trichloro-acetic acid,[29] showing that the acid-ester addition compound formed is only very slightly broken up into its components in benzene solution. A similar, but much less decided in-

their association factors are valid, even although the absolute values, as given later, may not be altogether correct.

[29] In a previous article (Kendall and Booge, This JOURNAL, **38**, 1712 (1916)) it has been shown that these two substances form a stable equimolecular addition compound, melting at $-27.5°$.

crease in molecular complexity on admixture in benzene solution is exhibited by ethyl acetate and acetic acid. In the cases here studied, however, the freezing-point depression curves resemble the viscosity curves in indicating that hardly any change in average ·molecular complexity occurs in phenol-cresol mixtures; any compound formation between the components must therefore be compensated for by simultaneous depolymerization

In order to obtain a definite idea with regard to the relative molecular complexities in the different solutions examined in this article, the following table may be consulted. As an arbitrary fixed concentration for comparing the various systems, 5 mol % solute has been selected. Specific-conductivity and viscosity data are added for convenience of reference in the subsequent discussion.

TABLE VIII.

ASSOCIATION OF PHENOL, ETC., IN BENZENE SOLUTION.

(Solute concentration = 5 mol %.)

	ΔT.	Mol. Wt.	Average mol. complexity.	Spec. cond. $\times 10^8$ .25°.	Viscosity 25°.
Phenol	1.780	178.4	1.897	8.84	0.08945
o-Cresol	2.861	125.1	1.157	0.127	0.07608
m-Cresol	2.450	146.9	1.358	1.397	0.1342
p-Cresol	2.400	150.2	1.390	1.378	0.1474
1 Phenol + 1 o-Cresol	2.342	144.5	1.427	0.979	0.08415
1 Phenol + 2 m-Cresol	2.258	153.2	1.482	2.230	0.1121
1 o-Cresol + 2 p-Cresol	2.613	137.6	1.274	0.570	0.1177

The results are in good agreement with those of previous investigators[30] in indicating that phenol is much more highly associated than the cresols. The specific conductivity of phenol, it will be noted, is also considerably greater than the values obtained for the cresols, a point in exact accordance with the work of Kendall and Gross[31] in which a parallelism between specific conductivity and molecular complexity in a series of liquids of similar type was predicted.

o-Cresol is much less associated than its two isomers, all of the physical properties of which are strikingly similar. In line with this, the specific conductivities of m-cresol and p-cresol are much higher than that for o-cresol. The influence of a larger association factor is also evident in the relative viscosity values.

With regard to the behavior of the three binary mixtures tested, nothing needs to be added here to what has been said in the discussion above.

[30] Beckmann, Z. physik. Chem., 2, 725 (1888); Auwers, ibid., 12, 689 (1893); Mascarelli and Benati, Gazz. chim. ital., [2] 37, 527 (1907); [2] 39, 642 (1909); Hewitt and Winmill, J. Chem. Soc., 91, 441 (1907).

[31] Kendall and Gross, THIS JOURNAL, 43, 1418 (1921).

General Conclusions.

The following experimental facts have been established with regard to phenol-cresol mixtures: (*a*) 5 out of 6 of the possible binary systems give isolable compounds by the freezing-point method; (*b*) no significant changes in specific conductivity occur on admixture in any case; (*c*) the viscosity-composition curves are all "pseudo-ideal" in type; (*d*) the freezing-point depression curves given by binary mixtures in benzene solution are intermediate between the curves found for the pure components. The conclusions drawn from these several facts are not all in harmony with one another, as has been remarked upon at various places in the text above. It remains for us to examine whether a rational reconciliation can be effected now between the various results and the general hypothesis correlating chemical contrast, compound formation and conductivity in solutions developed in previous articles of this series, or whether the whole behavior of systems containing phenols must continue to be classed as "abnormal."

On careful consideration of the problem, it appears that an extension to these solutions of the views presented by Kendall and Gross[32] regarding conductivity and molecular complexity in pure associated liquids and in binary mixtures of the same supplies a complete explanation of all the points in dispute.

Phenol and its homologs, as already shown, are highly associated in the liquid state. The association of phenol, in particular, has been critically investigated by Yamanoto,[33] the conclusion reached being that the main equilibrium is represented by the equation,

$$3 (C_6H_5OH) \rightleftharpoons (C_6H_5OH)_3.$$
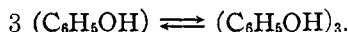
Determinations of the molecular weight of phenol in various organic solvents by other workers, however, indicate that still more complex molecular types are also existent. The attractive forces between simple molecules, inducing the formation of larger molecular aggregates in the liquid, must consequently be very pronounced; in other words, the substance is markedly "polar." The same applies, to somewhat less degree, to the three cresols.

Now it has been noted by Kendall and Gross that in a solution containing two highly associated components of similar character, compounds of the general type $(AB)_x . (CD)_y$ are undoubtedly formed in quantity. The average molecular complexity of such a mixture, however, (and hence its specific conductivity also) will not differ greatly from that of its pure components, since extensive disassociation of these is also involved. The complexes here existent are to be regarded, indeed, not as *addition* but

[32] Kendall and Gross, THIS JOURNAL, **43**, 1420 (1921).

[33] Yamanoto, *Sakurai Memorial Papers*, No. **12**, p. 33 (1908).

rather as *substitution* compounds, for disintegration and recombination of the various molecular and ionic types present will evidently result, finally, in an almost "haphazard" replacement of the different radicals by one another at all points of the original associated molecules. If the attractive forces between the constituent groups are such that a certain particular substitution complex predominates in stability, then it is only logical to expect that such a complex may be definitely isolated under suitable conditions. (*e. g.*, by freezing the solution.) The phenol-cresol compounds discovered by Dawson and Mountford are consequently not true addition compounds (as, indeed, the physical properties investigated in this article have sufficiently demonstrated) but substitution compounds formed by the replacement of part of an associated molecule by a homolog. It is very significant in this connection that *all* of the five compounds isolated by Dawson and Mountford are trimolecular, *e. g.*, 1 phenol + 2 *m*-cresol. Such complexes could evidently be readily formed from the predominating phenol complex $(C_6H_5OH)_3$ by replacement of two phenol groups. No increase in the average molecular complexity of the mixture is involved in such replacements, and the apparent contradiction between Dawson and Mountford's results and those of the present work is therefore entirely removed.

It must also be noted that mixtures of this type, if no particular substitution complex predominates in stability, will necessarily tend to give "mixed crystals" on solidification. This is here the case with one system only, phenol:*o*-cresol. A careful determination of the solidus curves would indicate, in all probability, limited formation of solid solutions in the remaining systems. Precisely analogous behavior is shown by binary mixtures of fused salts of similar character, *e. g.*, neutral salts of the alkali metals.[34] Thus potassium sulfate gives a continuous series of solid solutions with sodium sulfate and with potassium chromate. Lithium sulfate and potassium fluoride, on the other hand, form stable equimolecular compounds with potassium sulfate. These latter systems are evidently identical in character with the five compound-producing phenol-cresol mixtures here examined.

Summary.

By repeated fractionation, very pure samples of phenol and the three cresols have been prepared, and their chief physical constants determined. The specific conductivity and viscosity curves for phenol-cresol mixtures have been carefully investigated; freezing-point depression curves for phenol, the cresols, and various binary mixtures in benzene solution have also been constructed. Without exception, the results indicate that no increase in molecular complexity occurs on admixture. This is in agree-

[34] Landolt-Börnstein, "Tabellen," **1912**, p. 611–37.

ment with the views correlating addition compound formation with diversity in character of the components developed in previous articles of this series. It is apparently in disagreement, however, with the fact that Dawson and Mountford succeeded in isolating definite compounds from phenol-cresol mixtures in five out of six systems.

A brief consideration of the equilibria existent in binary mixtures of associated liquids has shown that the compounds obtained by Dawson and Mountford are to be regarded as substitution rather than as addition compounds. Under this view, no conflict exists between the results of Dawson and Mountford and those of the present work; both fall directly into line with the general theory.

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SOME PHYSICAL PROPERTIES OF AQUEOUS SOLUTIONS OF CERTAIN PYRIDINE BASES.

BY WILLIAM JACOB JONES AND JOHN BAMBER SPEAKMAN.

The physical properties of mixtures of pyridine and water have been the subject of a number of investigations.[1] The optical and thermal constants of pyridine and the mono methylpyridines have been determined by Constam and White.[2] More aqueous solutions of the higher homologs of pyridine have not been examined up to the present with the exception of 3 and 4 methylpyridines and 2,6-dimethylpyridine, studied by Flaschner.[3] In the present article are given measurements of densities and other physical characteristics of aqueous solutions of some of these higher homologs.

Preparation of Materials.

The bases used had been purified by the methods described elsewhere.[4] On account of their hygroscopicity they were redistilled before use from solid sodium hydroxide, in an apparatus previously dried by the passage of air dried with sulfuric acid, and the receiver was protected from the external air by a calcium chloride tube. They were then preserved in desiccators kept in the dark. The aqueous solutions were made up by weight with conductivity water in the type of weighing bottle recommended by Hartley, Thomas and Applebey, having its stopper fitting over the outside of the neck.

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[1] "Absorption by Electric Waves," Bredig, Z. Elektrochem. 7, 767 (1901); "Densities and Viscosities," Dunstan, Thole and Hunt, J. Chem. Soc., 91, 1718 (1907); "Densities, Viscosities and Surface Tensions," Hartley, Thomas and Applebey, ibid., 93, 538 (1908); "Refractive Indices and Partial Vapor Pressures," Zawidski, Z. physik. chem., 35, 129 (1900), "Composition of Constant Boiling Mixtures," Goldschmidt and Constam, Ber. 16, 2977 (1883).

[2] Constam and White, Am. Chem. J., 29, 1 (1903).

[3] Flaschner, J. Chem. Soc., 95, 668 (1909).

[4] Heap and Jones, THIS JOURNAL, 43, 1936 (1921).