CCXXIV.—*Electrical Conductivity of Solutions in Phenol.*

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IN a previous paper (Richardson and Robertson, J., 1928, 1775) an account was given of cryoscopic and molecular-volume determinations made with solutions in phenols. The deviations from the normal values were accounted for by the theory of Hildebrand (*J. Amer. Chem. Soc.*, 1916, **38**, 1452), who ascribes deviations from ordinary freezing-point laws to intermolecular forces induced by the internal pressures and polarities of the interdiffused liquids. These effects would be expected to produce alterations in other physical properties of solutions, and with a view to investigate the nature of these changes, the conductivity method was selected.

On account of the comparatively low dielectric constant of phenol, interionic forces should also have a pronounced effect on the properties of its solutions. This influence has been taken into account in the Debye–Hückel theory and its later modifications, which have been applied with considerable success to the explanation of irregularities in the properties of solutions.

Phenol has been investigated by the conductivity method by Kraus and Kurtz (*J. Amer. Chem. Soc.*, 1922, **44**, 2463), who determined the conductivities of tetramethylammonium iodide and sodium iodide therein at 50°. The chief aim of their investigation was to ascertain the mathematical form of the conductivity curve for a solvent of dielectric constant of intermediate value. They also noticed that the dissociation of the solutes as calculated from

the conductivity was much lower than that found from the freezing-point depression results of Hartung (*Z. physikal. Chem.*, 1911, **77**, 82), who, having obtained abnormally high depressions for salts of certain weak acids, concluded that this could not be due to the electrolytic dissociation of the substances, since salts of stronger acids showed normal freezing points at the same dilution. These results were ascribed to " phenolysis," but it was shown later by Kraus that phenolysis was inappreciable in phenolic solutions of tetramethylammonium iodide. The discrepancy must therefore be accounted for in some other way. Kraus expressed the opinion that such an agreement was not to be expected even at fairly low concentrations, since any influence of interionic forces on the properties of electrolytic systems would be great in a solvent of such a low dielectric constant.

In the present investigation the conductivities of sodium acetate, aniline hydrochloride, and other electrolytes have been measured in phenol, and the effect of typically irregular non-electrolytes (ethyl malonate and toluene) on these conductivities has been examined.

Experimental.

The conventional form of Wheatstone-bridge arrangement was used. Various methods of earthing were experimented with, but in the final measurements no earth was employed. For the slide-wire arrangement an ordinary metre bridge was used with a resistance box connected at each end to act as an extension coil. A value of 1000 ohms was generally used for each of these, and the bridge adjusted until the slider reached the mid-point of the wire for a minimum. As each of the 1000-ohm coils was wound similarly, any reactance due to capacity or inductance would be equal in each coil, and so the errors would be neutralised.

For the standard resistance two boxes were employed, one a four-decade dial box, made by R. W. Paul, reading up to 10,000 ohms, and the other a Muirhead single-dial box reading in ten stages from 1000 ohms up to one megohm. By using these boxes in series it was possible to obtain any resistance up to 36,000 ohms to units. For higher resistances it was necessary to alter the ratio of the extension coils and to use a different point on the slide-wire as the point of balance. This was easily calculated, as the resistance of the slide wire was known.

A microphone hummer with a frequency of approximately 520 was used as the source of alternating current. A variable air-condenser, of the low-loss radio type, was connected across the resistance boxes to neutralise any capacity effect in the cell. The capacity required was usually very small. The telephones consisted

of a double head-set, Brown's type F, of 4000 ohms resistance. The metal head-band and the receiver cups of the telephones were connected to the slider of the bridge by a wire twisted round the telephone cord. By this means any capacity effects between the telephones or the observer and the bridge would be minimised.

With this bridge arrangement it was possible to measure resistances of 1000 ohms to about 0·1%. For higher resistances, on account of the diminished sound in the receivers, the sensitivity was less : thus at 100,000 ohms, it was about 1%. In order to detect any errors in the ratio arms or in the larger coils of the resistance boxes, a Pye laboratory standard high resistance, consisting of ten 100,000-ohm coils connected in series, was substituted for the cell in one arm of the bridge. Using this standard, the bridge was tested between 25,000 ohms and one megohm : complete agreement was obtained. The two resistance boxes used in the circuit were standardised by comparison of the various sets of coils. Agreement was again obtained within the limits of the sensitivity of the apparatus.

Two conductivity cells were used, one of the dip type, with a fairly high cell constant as a standard of comparison, and another, a cylindrical cell of about 20 c.c. capacity, with large horizontal disc electrodes, as a working cell. The electrodes were platinised. The standard cell was calibrated with $N/10$-potassium chloride solution, the values given by Parker and Parker (*J. Amer. Chem. Soc.*, 1924, **46**, 330) being used. The working cell was compared with the standard cell at intervals throughout the investigation.

The measurements with phenol solutions were carried out in an oil thermostat kept at $50° \pm 0·05°$. Oil has the advantage of having a much lower dielectric constant than water, and also is a good insulator, so that any capacity effects between the cell and the walls of the thermostat are thus greatly reduced and eddy currents eliminated. There is the additional advantage that no water vapour is given off by the bath to contaminate the phenol.

The phenol used was redistilled through an 8-bulb fractionating column surrounded by two concentric tubes packed with cotton-wool to keep it above the freezing point and allow the distillation to be carried out under constant conditions of temperature. After distillation, the liquid was cooled in a stoppered bottle, and the last unsolidified portion poured off. The remainder was redistilled shortly before use. The b. p. of the phenol was constant within 0·1°, and the freezing point of a typical sample was 40·55°.

The other materials used were the best available samples and were specially purified. The solids were carefully dried and the liquids fractionated before use. The hydrogen chloride solutions were

made by passing the dry gas into phenol and were analysed volumetrically before and after the conductivity measurements. The sodium phenoxide solution was prepared by dissolving a known weight of sodium in phenol containing 30% of alcohol in a current of hydrogen and subsequently distilling off the alcohol.

For the less soluble substances or for the greater dilutions, a solution was prepared by dissolving a weighed quantity of the

FIG. 1.
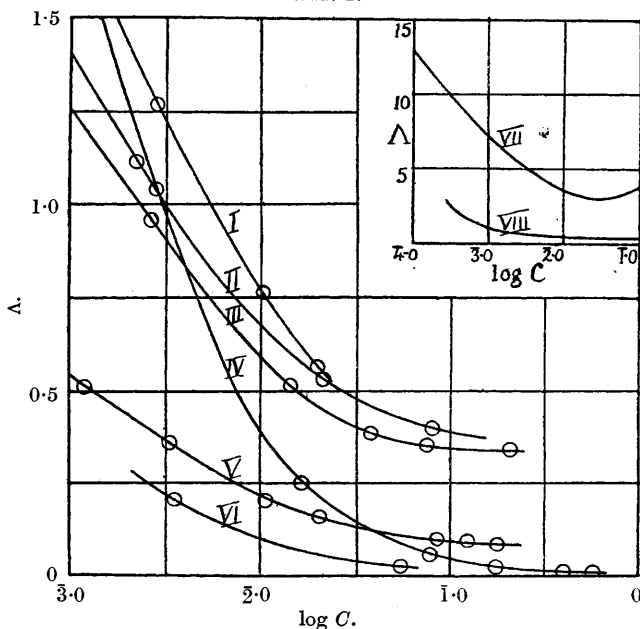
I. *Sodium acetate (in phenol and ethyl malonate).*
II. *Sodium phenoxide.*
III. *Aniline hydrochloride.*
IV. *Picric acid.*

V. *Sodium acetate.*
VI. *Hydrogen chloride.*
VII. *Tetramethylammonium iodide (Kraus).*
VIII. *Aniline hydrochloride.*

substance in a weighed quantity of phenol (usually 50—70 g.) in a flask. Sodium acetate dissolved very slowly, requiring several hours with periodic shaking to effect the solution. The flask containing the solution was left in the thermostat for 2 or 3 hours, and the required sample was then introduced into the cell and its conductivity determined 5 minutes later. The solution remaining in the flask was then weighed, an approximately equal quantity of phenol added, and the flask again weighed. This process was repeated for each dilution, and the concentration of the solution for each stage was calculated. In order to prevent any cumulative

error from becoming too great, and to guard against any contamination, a second standard solution was prepared if more than three or four dilutions were required. With liquid solutes or the more soluble substances such as picric acid, the solutions of greater concentration were prepared directly in the cell. This was closed by a glass stopper, the solute weighed therein, the required quantity of phenol added, and the cell again weighed.

The specific conductivity of the solution was calculated in the usual way, and that due to the solvent was deducted; the values given in the tables are the corrected values. The concentration (C) was calculated by using the value 1·058 for the density of phenol, and as the solutions were very dilute it was assumed that there was no appreciable variation from this value in any case. The molecular conductivity is calculated in the usual way. The values for the conductivities of a number of solutions are given in Table I. A graph of conductivities against the logarithm of the concentrations is given in Fig. 1.

TABLE I.

$C \times 10^3$.	$\kappa \times 10^6$.	Λ.	$C \times 10^3$.	$\kappa \times 10^6$.	Λ.
Sodium acetate.			Acetic acid.		
182·0	15·43	0·0847	4165	2·49	0·00060
126·6	11·47	0·0905	1582	2·49	0·00157
86·73	8·53	0·0983	1201	2·50	0·00208
20·95	3·36	0·160	466·4	1·08	0·00232
10·81	2·22	0·205	148·5	0·41	0·00276
3·37	1·21	0·359	Aniline hydrochloride.		
1·22	0·65	0·533	215·5	73·32	0·340
			78·74	28·10	0·357
Picric acid.			39·40	15·15	0·385
595·8	1·00	0·00168	15·05	7·64	0·519
413·0	2·51	0·00608	2·687	2·58	0·960
177·2	4·13	0·0234	0·4084	0·89	2·18
80·52	4·62	0·0574	Sodium phenoxide.		
17·07	4·36	0·255	83·52	33·24	0·398
2·876	2·99	1·04	22·03	11·77	0·535
0·1342	0·70	5·14	2·318	2·59	1·12
			0·4382	0·71	1·62
Hydrogen chloride.					
56·30	1·39	0·025			
3·668	0·76	0·21			

It will be seen from Fig. 1 that at the higher concentrations (0·1N) the conductivities differ greatly. Picric acid and hydrogen chloride have a very low value, whereas the salts, sodium phenoxide and aniline hydrochloride, conduct much more readily. For no substance has there been observed a minimum conductivity such as was noticed by Kraus and Kurtz for tetramethylammonium iodide in phenol, and for similar electrolytes in other solvents having a dielectric constant of the same order as that of phenol.

In determining the value of Λ_0, $1/\Lambda$ has been plotted against

$C\Lambda$ (Fig. 2), and the curve extrapolated to zero concentration. A linear graph will be given only if the solution obeys Ostwald's dilution law. It is found that while there is a wide divergence at higher concentrations, the graph becomes approximately linear at lower concentrations and so may be used for extrapolation. It is impossible to obtain accurate values for the limiting conductivity from these results, but some approximate values are :

Aniline hydrochloride, 15 ; Sodium phenoxide, 2·2 ;
Picric acid   12 ; Sodium acetate,   2.

The value obtained by Kraus and Kurtz for tetramethyl-ammonium iodide was 16·67.

FIG. 2.

$C\Lambda \times 10^3$.
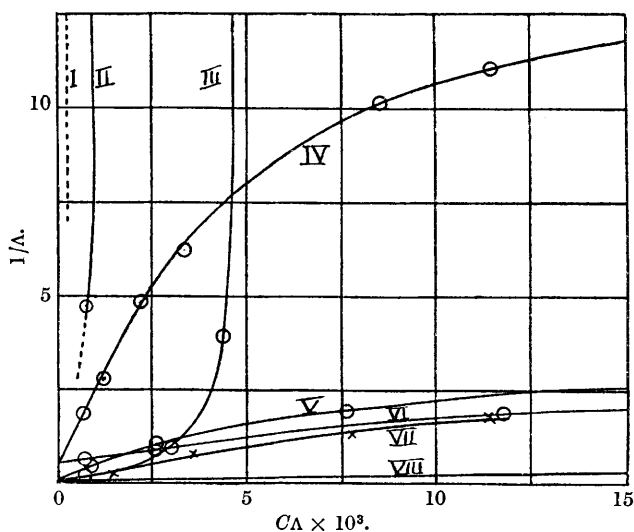
I. *Acetic acid.*   VI. *Sodium phenoxide.*
II. *Hydrogen chloride.*   VII. *Sodium acetate (in phenol and*
III. *Picric acid.*   *ethyl malonate).*
IV. *Sodium acetate.*   VIII. *Tetramethylammonium iodide*
V. *Aniline hydrochloride.*   *(Kraus).*

The form of the curves in Fig. 2 shows much more clearly the difference between the two types of solute. Sodium phenoxide and aniline hydrochloride conform comparatively closely, even at high concentrations, to the linear form required by the mass-action law. Sodium acetate shows a considerably greater divergence at the same concentrations, but at a fairly low concentration it also approaches the linear form. Picric acid and hydrogen chloride show quite a different type of curve and approach the form required by the mass-action law only at extremely low concentrations ; acetic

acid has been investigated only at high concentrations, but the results indicate that it belongs to the same class as these two compounds. The direction of bending of the curves indicates that with the salts conductivity increases more slowly than required by the mass-action law, whilst the acids show the opposite effect.

A further series of experiments has been performed to find the effect of the addition of certain non-electrolytes. Toluene and ethyl malonate were selected as being typically abnormal (compare Richardson and Robertson, *loc. cit.*). The effect of adding successive quantities of these substances to a solution of sodium acetate or aniline hydrochloride in phenol has been observed, and the results are given in Tables II, III, and IV. 20 C.c. of the solution of the electrolyte were transferred to the cell and the conductivity determined; successive quantities of 1 c.c. each of the substance to be

TABLE II.

Aniline hydrochloride solution.

C.c. added.	$C \times 10^3$	Ethyl malonate. $\kappa \times 10^6$.	Λ.	Toluene. $\kappa \times 10^6$.	Λ.	Phenol. $\kappa \times 10^6$.	Λ.
0	199	72·8	0·366	72·8	0·366	72·8	0·366
1	189	78·2	0·413	58·3	0·308	70·8	0·370
2	181	81·3	0·450	46·9	0·259	67·5	0·372
3	173	83·2	0·481	37·4	0·217	64·6	0·373
4	166	83·4	0·504	30·8	0·186	61·8	0·373
5	159	83·0	0·521	24·0	0·155	59·4	0·374
6	153	82·4	0·538	—	—	—	—

TABLE III.

Aniline hydrochloride solution, with addition of ethyl malonate.

C.c. added ...	0	1	2	3	4	5	6	7	8
$C \times 10^3$	117	111	105	101	97	93	89	86	83
$\kappa \times 10^6$	45·4	49·8	51·8	53·0	53·8	54·1	53·8	52·9	51·8
Λ	0·388	0·448	0·493	0·525	0·555	0·585	0·605	0·615	0·624

TABLE IV.

Sodium acetate solution.

C.c. added.	$C \times 10^3$.	Ethyl malonate. $\kappa \times 10^6$.	Λ.	Methyl acetate. $\kappa \times 10^6$.	Λ.	Toluene. $\kappa \times 10^6$.	Λ.
0	101	8·92	0·088	8·92	0·088	8·92	0·088
1	96	30·4	0·317	14·5	0·151	7·26	0·076
2	92	41·2	0·448	18·1	0·196	5·85	0·064
3	88	48·4	0·550	20·9	0·237	4·61	0·052
4	84	52·8	0·600	23·1	0·275	3·61	0·043
5	81	56·2	0·694	24·6	0·303	3·00	0·038
6	78	58·2	0·746	25·7	0·329	2·48	0·032
7	75	59·6	0·794	26·4	0·352	1·76	0·023
8	72	60·0	0·834	26·8	0·372	1·45	0·020
9	70	60·1	0·859	27·1	0·387	—	—
10	67	58·5	0·873	27·0	0·403	—	—
11	65	52·6	0·809	26·7	0·411	—	—
12	63	—	—	26·6	0·421	—	—

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investigated were then added, and the conductivity was determined after each addition, the concentration of the original solute being calculated from the ratio in which it was thus diluted. A control experiment was performed by adding successive quantities of phenol. All volumes were measured at 50°.

These results show that toluene and ethyl malonate behave in opposite ways, as would be expected from their cryoscopic behaviour : with the former, the conductivity decreases fairly rapidly in proportion to the amount added; but with the latter, the first addition produces a large increase in the conductivity, and on further addition, the specific conductivity reaches a maximum and then decreases again, the molecular conductivity increasing more slowly than with the first addition and appearing also to tend towards a maximum, if allowance is made for the effect of dilution. Methyl acetate showed an effect similar to that of ethyl malonate, but not quite so pronounced.

In order to discover if this effect extended to low concentrations of the electrolyte, a further determination was carried out using a fixed proportion of ethyl malonate to phenol and varying the amount of the electrolyte by dilution with the mixed solvent, which contained $4 \cdot 75\%$ of ethyl malonate by volume. The results of this determination are given in Table V. The figures in parentheses in the last column are the corresponding interpolated values of the conductivity for solutions in pure phenol.

TABLE V.

Sodium acetate in phenol containing ethyl malonate.

$C \times 10^3$.	$\kappa \times 10^6$.	Λ.
20·03	11·39	0·568 (0·161)
10·19	7·81	0·767 (0·221)
2·826	3·60	1·27 (0·375)
0·3345	1·48	4·43 (0·92) (?)

The curves obtained from these results are given in Figs. 1 and 2. The value obtained for Λ_0 is approximately 13, whereas that for sodium acetate in pure phenol is 2. It was found that for the mixed solvent used in this determination the conductivity was rather less than that of pure phenol, whereas a corresponding amount of phenol in ethyl malonate had about three times the conductivity of pure phenol. The conductivity of pure ethyl malonate is very low, possibly less than one-tenth of that of phenol. As neither aniline hydrochloride nor sodium acetate is appreciably soluble in ethyl malonate, their conductivity in this solvent could not be determined.

It was decided to carry out some approximate determinations of the dielectric constants of the mixed solvents used in order to

ascertain if these differed from that of pure phenol by an amount sufficient to account for the conductivity effects observed. These measurements were made by one of us at King's College, London, under the direction of Mr. C. S. Salmon.

A heterodyne beat method of the usual type was used, the capacity of the condenser cell containing the liquid investigated being determined by connecting the cell in parallel with a standard condenser which tuned one oscillator, and observing the alteration in capacity of this standard condenser necessary to bring the circuit back into resonance with the fixed oscillator. Suitable switching devices were used to minimise any change in capacity of the wiring in this operation. The condenser cell was maintained at $50° \pm 0.1°$ by means of a paraffin bath. The mixed solutions were prepared by volume in the same way as for the conductivity determinations. The results were as follows :

Dielectric constants at 50°.

Toluene	2·3	Phenol + toluene (20 : 1)			9·95
Ethyl malonate	7·5	Phenol + ethyl malonate (20 : 1)	...		10·2
Phenol	10·3	,,	,,	,, (20 : 2) ...	10·15
		,,	,,	,, (20 : 4) ...	9·7

It will be seen that the mixed solutions conform roughly to the simple mixture law in respect of dielectric constant. In the case of both toluene and ethyl malonate the dielectric constant of the mixture is slightly lower than that of pure phenol.

An interesting effect observed during these determinations was that the dielectric losses with the phenol–ethyl malonate mixtures were much greater than with either of the pure liquids, a considerably greater in-put being required to maintain the oscillations in the circuit. These losses increased with the amount of ethyl malonate present in the mixture. The effect could not be accounted for on the assumption of an increase in the conductivity of the mixture, for it was shown that the mixtures had a lower conductivity than that of pure phenol. The losses must, therefore, be due to some action between the liquids which has no appreciable effect on either the dielectric constant or the conductivity.

Discussion.

The results of the present investigation have shown that, in phenol solutions, there are certain phenomena which are difficult to explain even by taking into account interionic forces. The acids examined differ entirely from the salts in the form of their conductivity curves. There are but few examples of compounds whose conductivity increases more rapidly with dilution than is required by the mass-action law, as does that of the acids investigated. Behaviour of

this kind has been noticed for aqueous solutions of certain weak organic acids and their salts. As the viscosity of such solutions is abnormally high, the deviations are ascribed to the rapid increase of viscosity with concentration. In the present instance the lowering of conductivity is noticeable in solutions which are so dilute that any appreciable change in viscosity is unlikely. It is noteworthy, also, that the salts do not show this effect; sodium acetate giving a curve of the opposite type to that of acetic acid, whilst in water sodium formate acts in exactly the same way as formic acid.

Another remarkable effect is the large increase in conductivity observed on the addition of a non-electrolyte such as ethyl malonate to the solutions of salts, which are insoluble in such non-electrolytes. This influence has been shown for sodium acetate to persist even at extreme dilutions. The explanation is not to be sought in a decrease of viscosity consequent on the addition of the non-electrolyte. In the first place the increase in conductivity with even a small amount of ethyl malonate is abnormally great; then again the deviation shows a maximum effect. Actually both ethyl malonate and toluene reduce the viscosity of phenol, but the toluene, which *lowers* the conductivity of the solutions, causes a *greater* increase in the fluidity than the ethyl malonate.*

A consideration of the dielectric constant of the mixed solvents also fails to afford an explanation of the behaviour of the esters investigated. In the case of toluene the lowering of the dielectric constant would possibly account for the decrease in conductivity, even if the slight decrease in viscosity which it also produces is taken into account. Ethyl malonate, however, which produces a considerable *increase* in the conductivity, *also lowers* the dielectric constant of the solvent, although to a smaller extent. It certainly lowers the viscosity, but to a considerably smaller extent than toluene, so that the viscosity change would not be sufficient to neutralise the effect of the change of dielectric constant, much less to reverse it. Evidently an explanation other than that of a change of viscosity or dielectric constant must be sought.

We may now proceed to a comparison of the results of the present investigation with those obtained in the previous work on phenolic solutions (Richardson and Robertson, *loc. cit.*). It was found that toluene and ethyl malonate produced opposite changes in the molecular freezing-point depression constant. These results were accounted for on the assumption that differences in the internal pressures or polarities of the mixed liquids produce a decrease in the

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* Phenol, viscosity at 50°, 0·0323; phenol with 10% ethyl malonate, 0·0305; phenol with 10% toluene, 0·0273. We are indebted for these measurements to Mr. O. H. Keys of this laboratory (Victoria College).

intermolecular attraction and a consequent increase in the vapour pressure, with corresponding effect on the freezing point.

Toluene and phenol differ considerably in internal pressures and polarities, as estimated from molecular solution volumes and dielectric constants respectively; they show a marked decrease in the molecular depression constant with decreasing concentration. Ethyl malonate and phenol, on the other hand, have similar internal pressures and polarities; in such solutions the depression constant increases with decreasing concentration.

With regard to the electrical properties of these solutions, a decrease in the intermolecular attraction, produced, as in the case of toluene and phenol, by differences in internal pressures and dielectric constants, corresponds with decreased conductivity. Conversely, an increase in intermolecular attraction, as with ethyl malonate and phenol, corresponds with increased conductivity of the electrolyte.

It is impossible to draw any general conclusion without extending the investigation to a wider range of solutions, but the results obtained for the solutions examined appear to indicate that there is a connexion between the intermolecular attraction of the solvent molecules and the conductivity of the solute.

This effect may also account for the abnormally low conductivity of the acids investigated where they are present in high enough concentrations to affect the solvent in the same way as do the non-electrolytes examined.

Summary.

1. The conductivities of certain acids and salts in phenol solution have been determined. Considerable differences are observed in the equivalent conductivities of the various electrolytes.

2. The acids and salts investigated are found to show totally different forms of conductivity curves; the values for the acids increase much more rapidly with dilution than required by the mass-action law, whereas the salts show the opposite effect.

3. The addition of esters produces a remarkable increase in the conductivity of solutions of salts, this effect being equally pronounced even at very low concentrations of the electrolyte.

4. These results are in agreement with the cryoscopic and molecular-volume measurements of Richardson and Robertson, and it is suggested that they may be explained in the same way, *viz.*, that they are due to intermolecular forces induced by the internal pressures and polarities of the mixed liquids.

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