

temperatures without affecting appreciably the structure of the gel as exhibited by its adsorption ability.

Summary.

It is impossible to remove all the water from the hydrogel of silicic acid by repeated immersions in anhydrous alcohol, acetone, or benzene.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY,
No. 370.]

COMPOUND FORMATION AND CONDUCTIVITY IN SYSTEMS OF THE TYPES FORMIC ACID:METAL FORMATE AND SULFURIC ACID:METAL SULFATE.

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Received June 6, 1921.

In a recent investigation¹ on systems of the types acid:ester, acid:ketone and acid:acid it has been shown that the specific conductivities of such binary mixtures increase regularly with increasing compound formation between the components. Strong support was thereby obtained for the validity of the hypothesis, formulated in earlier articles,^{2,3} that ionization in solutions is primarily dependent upon the preliminary formation of unstable solvent-solute complexes. In subsequent communications^{4,5} it has also been established that compound formation in systems of the general type $HX:RX$ increases in extent with increasing diversity in the positions of the radicals H and R in the electrode potential series. The present work continues the study of systems of this type by examining how far the parallelism between compound formation and conductivity can be traced in them. As experimental material, the two series previously investigated with respect to compound formation (metal formates in formic acid and metal sulfates in sulfuric acid) have naturally been chosen.

Very accurate determinations upon the conductivities of the alkali and alkaline earth formates in anhydrous formic acid have been carried out by Schlesinger and his co-workers,⁶ so that only a few additional data were required in this series. In the case of sulfuric acid:metal sulfate systems, the results of previous investigations proved to be much less dependable.

¹ Kendall and Gross, *THIS JOURNAL*, **43**, 1426 (1921).

² Kendall and Booge, *ibid.*, **39**, 2323 (1917).

³ Kendall and Gross, *ibid.*, **43**, 1416 (1921).

⁴ Kendall and Davidson, *ibid.*, **43**, 979 (1921).

⁵ Kendall and Adler, *ibid.*, **43**, 1470 (1921).

⁶ Schlesinger, *et. al.*, *ibid.*, **33**, 1924 (1911); **36**, 1589 (1914); **38**, 271 (1916); **41**, 72, 1921, 1934 (1919).

For correlation with these two series, we have also extensive data immediately available for a third series of precisely the same type—metal hydroxides in water. A sufficient variation in the acid radical X (from the strong acid H_2SO_4 , through the intermediate acid HCOOH , to the very weak acid HOH) is thus obtained to enable us to test the effect of changes in this radical upon the nature of the results, and to extend any generalizations deduced over the whole field $\text{HX} : \text{RX}$.

Systems of the Type, Formic Acid : Metal Formate.

Schlesinger has demonstrated that the alkali formates are extensively dissociated in formic acid solution, and that very satisfactory ionization constants can be obtained for each salt through a wide range of concentrations without the application of any viscosity correction to the conductivity data. The alkali earth formates also are highly ionized in anhydrous formic acid, and give good ionization constants throughout a somewhat more limited range if it is assumed that they behave, in moderately concentrated solutions, as uni-univalent electrolytes.⁷ It is possible that the mutual cancellation of counterbalancing factors may account for this somewhat unexpected vindication of the Ostwald dilution law in both cases, but the ionization constants for the different salts as calculated by Schlesinger can certainly be safely utilized as indicative of the order of their strengths as bases⁸ in formic acid solution, which is all that is needed for the purpose of the present investigation.

Conductivity determinations have here been carried out upon 3 salts not studied by Schlesinger, namely, barium, magnesium and lead formates. In order not to trench too deeply upon the field, no complete survey of the ionization equilibria of these salts in anhydrous formic acid has been undertaken. Only a limited concentration range has been examined in each case, and it has been assumed that within this range the three salts, like those investigated by Schlesinger, behave as uni-univalent electrolytes.

Measurements were made in a cell of the Freas type with platinized electrodes. A 3-meter Leeds and Northrup bridge was employed. Alternating current (1000 cycles per sec.) was obtained by means of a constant-speed high-frequency generator; the telephone used was tuned to the same frequency. The experiments were performed in a Freas thermostat at $25 \pm 0.01^\circ$. The formic acid used possessed a specific conductivity of 7.3 to 7.5×10^{-5} mhos, a value somewhat higher than that obtained by Schlesinger and Martin.⁹ The preparation of anhydrous acid and pure salts was carried out as described in a previous article. While no exceptional degree of accuracy is claimed for the results given below, they are probably in error by less than 0.5%.

⁷ As dibasic organic acids do, in water solution, until ionization is very extensive.

⁸ Any salt RX in its own acid HX possesses the characteristics of a base (see Schlesinger and Calvert, *THIS JOURNAL*, **33**, 1933 (1911); Kendall, Davidson and Adler, *ibid.*, **43**, 1481 (1921)).

⁹ Schlesinger and Martin, *ibid.*, **36**, 1590 (1914).

In the following table, c denotes the concentration of the solution in gram equivalents per liter, χ is the specific conductivity in reciprocal ohms (the specific conductivity of the solvent being directly subtracted),¹⁰ λ is the equivalent conductivity, λ_0 the equivalent conductivity at infinite dilution (extrapolated according to the method employed by Schlesinger¹¹ and k the ionization constant of the salt at 25°. It will be evident, from the paucity of the data, that the values given in the last two columns are somewhat uncertain. They are to be regarded, indeed, only as indicative of the relative strengths of the three electrolytes examined.

TABLE I.
CONDUCTIVITIES OF FORMATES IN FORMIC ACID AT 25°.

Salt.	c .	χ .	λ .	λ_0 .	k .
(H. COO) ₂ Ba	0.0474	0.002575	55.59	60.3	0.515
	0.0923	0.004827	52.26		
	0.2758	0.001185	42.96		
(H. COO) ₂ Mg	0.0479	0.001683	35.14	40.6	0.266
	0.0919	0.002931	31.90		
	0.0477	0.001295	27.15		
(H. COO) ₂ Pb	0.1047	0.002387	22.80	35.2	0.124

It will be seen that the ionization constant of the barium salt is about twice as large as that of the magnesium salt, and more than four times as large as that of the lead salt.

We may now proceed to examine how compound formation varies with ionization throughout the series. In Table II below the ionization constants for the various salts and the addition compounds actually isolated from each system are listed. The last column shows the depression of the freezing point of the acid in solutions containing 5 mol % of dissolved salt.

TABLE II.
IONIZATION AND COMPOUND FORMATION. FORMATES IN FORMIC ACID SOLUTION.

Salt.	Ionization constant, 25°.	Compounds isolated (A = salt; B = acid).	ΔT (5 mol % salt). ^a
H. COO.NH ₄	1.230	AB ₂ ; AB	5.9
H. COOK	1.090	AB ₂ ; AB ₂ ; AB	6.6
H. COONa	0.810	AB ₂ ; AB	5.9
H. COOLi	0.557	4.9
(H. COO) ₂ Ba	0.515	AB	8.5
(H. COO) ₂ Ca	0.422	insoluble
(H. COO) ₂ Mg	0.266	insoluble
(H. COO) ₂ Pb	0.124	insoluble

^a The ideal freezing-point depression for formic acid containing 5 mol % solute is 3.3°.

¹⁰ Following Schlesinger's procedure. The accuracy of this method is open to serious question (as discussed in the text later), but in any case the effect is here extremely small.

¹¹ Schlesinger and Mullinix, THIS JOURNAL, 41, 74 (1919).

The rule that ionization parallels compound formation in extent is evidently generally applicable throughout the series. The strongest bases each give several compounds, the weakest bases do not show a single sample of an isolable acid salt. Two minor discrepancies in the order of compound formation (potassium giving 3 compounds to 2 of ammonium, barium one to none of lithium) may plausibly be referred to changes in the order of basic strengths with temperature. The ionization constants tabulated refer to 25° while the compounds are isolated at much lower temperatures, and Schlesinger and Coleman¹² have found that the temperature coefficient of the ionization constant in certain cases is very large.

As has been pointed out previously,¹³ however, compounds may be existent in a solution without making their appearance on the freezing-point diagram as stable solid phases. A more trustworthy method of establishing the relative extent of compound formation for the different formates in formic acid solution is fortunately available in the comparison of the depressions which they induce in the freezing point of the acid itself.¹⁴ The ideal freezing-point depression curve for formic acid¹⁵ and

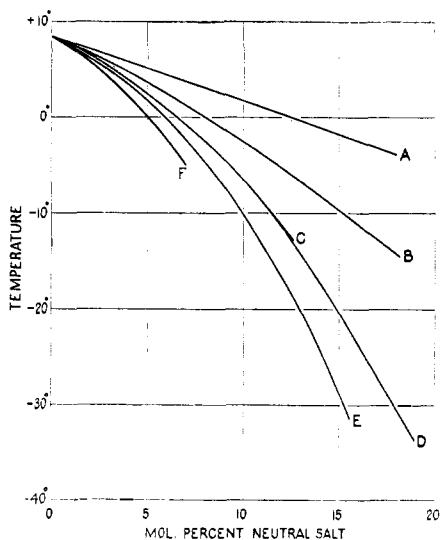


Fig. 1.—Freezing-point depression curves. Formic acid as solvent. A = ideal curve; B = lithium formate; C = sodium formate; D = ammonium formate; E = potassium formate; F = barium formate.

¹² Schlesinger and Coleman, *THIS JOURNAL*, **38**, 278 (1916).

¹³ Kendall, Booge and Andrews, *ibid.*, **39**, 2308 (1917).

¹⁴ Compare Kendall and Booge, *ibid.*, **38**, 1730 (1916).

¹⁵ Q (the molar heat of fusion) is taken as 2420 cal. (Berthelot, *Compt. rend.*, **78**, 716 (1874)).

the experimental curves obtained on addition of the various salts are shown in the accompanying diagram. The depressions for a single fixed concentration of salt (5 mol %) are also compared in Table II (p. 1848).

For the uni-univalent salts, the deviations from the ideal curve fall in the order $K > (NH_4 \text{ or } Na) > Li$, corresponding with the order of stability and complexity in compound formation. The extensive ionization of the salts in formic acid solution, of course, accounts for a great part of the abnormally large depressions obtained, but the data at the higher concentrations show clearly the additional effect of actual removal of solvent by compound formation. Thus the potassium salt gives twice the normal depression at 5 mol % concentration, while at 15 mol % the depression is nearly 4 times that calculated from the ideal curve. Compound formation in this case must be very extensive, as is evidenced not only by the compounds definitely isolated but by the transference-number data of Schlesinger and Bunting.¹⁶ With the other uni-univalent salts the effect is appreciably smaller, particularly in the case of lithium. In view of the position of this metal at the head of the electrode potential series, indeed, the comparative weakness of its formate as a base and its corresponding inability to form isolable acid salts cannot be allowed to pass without comment, although no adequate explanation can be adduced at present.¹⁷

Of the 4 remaining salts of the type $(H.CO_2)_2Me''$, only those of barium and calcium are sufficiently soluble to give reliable comparable data. The freezing-point depression curve for the barium salt (see Curve F on the diagram; the calcium salt practically duplicates this curve up to 1.5 mol %) is more abnormal even than that for the potassium salt. Thus the observed depression for a solution of 5 mol % concentration is 8.5° , compared with a calculated value of 3.3° . In view of this, it appears very improbable that Schlesinger's assumption that the alkaline earth formates behave, in moderately concentrated solutions, as uni-univalent electrolytes can be valid, since only by assuming a compound of truly enormous complexity could the position of the barium curve be accounted for on this basis. If we admit that the salt can give 3 ions by dissociation, however, the observed depressions are just about what might be expected.

Systems of the Type Sulfuric Acid : Metal Sulfate.

The same experimental procedure was employed as in the case of formic acid systems, except that sulfuric acid of minimum conductivity was made up directly in the cell (by gradual addition of acid slightly under 100%

¹⁶ Schlesinger and Bunting, *THIS JOURNAL*, **41**, 1934 (1919).

¹⁷ The question will be taken up in a later article, in connection with the atomic volume factor.

to acid slightly over 100%) in order to avoid contamination with atmospheric moisture during transfer. The specific conductivity of the acid so prepared varied from 0.01035 to 0.01050 reciprocal ohm at 25°. Lichty¹⁸ in a very careful investigation, obtained the value 0.01041; according to his conductivity-composition data, the acid here used contained less than 0.005 % of water.

The conductivity results for a series of sulfates at a single fixed concentration (0.04 gram equivalents per liter) in the 100% acid are presented in Table III below. In the preparation of this table, the method adopted by previous investigators for the evaluation of the specific conductivity of the salt has been followed, the specific conductivity of the pure solvent being subtracted directly from that of the solution.

TABLE III.
CONDUCTIVITIES OF SULFATES IN SULFURIC ACID AT 25°.

Salt.	Specific conductivity			Equiv. cond. of salt.
	Solution.	Solvent.	Due to salt.	
Na ₂ SO ₄	0.01206	0.01044	0.00162	40.5
BaSO ₄	0.01149	0.01038	0.00111	27.8
CaSO ₄	0.01210	0.01043	0.00167	41.8
MgSO ₄	0.01130	0.01043	0.00087	21.8
ZnSO ₄	0.01207	0.01039	0.00168	42.0
PbSO ₄	0.01237	0.01050	0.00187	46.8
Ag ₂ SO ₄	0.01208	0.01035	0.00173	43.3

Previous measurements upon the conductivities of neutral sulfates in 100% sulfuric acid have been carried out by Walden,¹⁹ Hantzsch,²⁰ Bergius²¹ and Poma.²² The results obtained are extremely discordant; thus for sodium sulfate at the concentration examined above the interpolated equivalent conductivity values of these 4 observers are 97, 31, 46 and 14, respectively. From results of this order of accuracy, it is obviously futile to attempt to draw any conclusions.

The main source of error is undoubtedly due to the solvent correction, which varies from 80 to 90% of the total conductivity. A small error in this correction will introduce a very significant error in the equivalent conductivity of the salt, and the tacit assumption that the specific conductivity of the pure solvent is unchanged on addition of neutral salt is quite as unjustified as would be the corresponding assumption that the ionization equilibrium of water is unaffected by addition of a base. If we knew the mobilities of the various ions existent in any given solution, it might be possible for us to apply more dependable solvent corrections,²³

¹⁸ Lichty, THIS JOURNAL, 30, 1841 (1908).

¹⁹ Walden, *Z. anorg. Chem.*, 29, 383 (1902).

²⁰ Hantzsch, *Z. physik. Chem.*, 61, 293 (1908).

²¹ Bergius, *ibid.*, 72, 338 (1910).

²² Poma, *J. chim. phys.*, 10, 187 (1912).

²³ Compare Kendall, THIS JOURNAL, 39, 7 (1917).

but at the present time we cannot do more than concede that all of the salts investigated give conductivity values indicating approximately the same degree of ionization at the concentration here studied. To deduce differences in the basic ionization constants of sulfates in sulfuric acid from the different equivalent conductivities given in the last column of Table III above would obviously be quite unwarranted. It may be noted here that differences in the extent of acid salt formation are also less pronounced in the sulfuric acid than in the formic acid series.⁵

In the third series for which data are available, however, (namely systems of the type water:metal hydroxide) differences in basic ionization constants and in the stability and complexity of hydrates are exceedingly great. At the head of the electrode potential series we have the strongest bases, the alkali hydroxides, each of which gives several stable hydrates. The hydroxides of all metals in the neighborhood of hydrogen are scarcely ionized at all in aqueous solution. At the foot of the series we find an increase in basic strength again becoming apparent, silver hydroxide being a moderately strong base. Solubility variations are similarly much more marked among the hydroxides than in either the formate or the sulfate series.²⁴

From the results of this and previous articles it may be concluded, therefore, that systems of the general type $HX : RX$ supply strong support for the fundamental relationships suggested between diversity of chemical character (*i. e.*, electrode potential difference between R and H), compound formation, solubility and ionization. Variations in all of these properties, however, and particularly variations in ionization, can be much more clearly traced when X is a weakly acidic radical. With hydroxides enormous differences are evident, with formates the gradations are much less steep (for example, the ionization constant of the potassium salt is only 9 times that of the lead salt), with sulfates the solvent correction error is sufficient to mask any differences in ionization entirely. The examination of intermediate series (such as cyanides, acetates or fluorides) would undoubtedly add results of great interest in this connection, but must be deferred for the present in favor of work on systems of other types.

Summary.

Conductivity measurements have been carried out for neutral formates in formic acid solution and for neutral sulfates in sulfuric acid solution. In the case of the formates, it has been possible to obtain direct confirmation for the parallelism between the extent of compound formation and ionization. For the sulfates, however, the uncertainty of the solvent correction is so great as to obscure the results.

²⁴ Compare Kendall, Davidson and Adler, *THIS JOURNAL*, **43**, 1490 (1921).

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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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF COLUMBIA UNIVERSITY, No. 371.]

COMPOUND FORMATION IN PHENOL : CRESOL MIXTURES.

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Received June 6, 1921.

It has been shown in previous articles¹ 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 work² 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 Mountford³ 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 Barker⁴ 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).