CCXLI.—*Chemical Action at an Interface: The Production of Acidity in Neutral Salt Solutions.*

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THE frequently noticed development of acidity in neutral salt solutions in the presence of material from which no detectable quantity of acid can be extracted by pure water can be accounted for by assuming (1) a simple chemical interaction between the salt and a definite acid or mixture of acids, (2) a preferential absorption of the base of the salt, or (3) an exchange between the kations of the salt and hydrogen ions previously adsorbed by the material (Mukherjee, *J. Indian Chem. Soc.*, 1925, **2**, 191). The second explanation assumes the selective adsorption of hydroxyl ions from water, and can evidently be employed, alternatively with the third, to account for acidity produced by materials which are not regarded as actual or potential acids.

The first, or " chemical," theory has been objected to on the ground that, if the materials dealt with contain acids, the latter must be both insoluble, since the water extracts are neutral, and strong, in that they are able to decompose salts of the strong mineral acids; but no acids of this character are known. The purpose of this paper is to show that the effects observed with materials of complex and undetermined composition may also be observed with a simple insoluble weak acid; that these effects may properly be regarded as arising from an ordinary chemical interaction of the ionic type, qualified by the circumstance that one of the ions is non-diffusible; and that their occurrence is a logical consequence of the " surface dissociation " theory. This theory was developed by Pauli in connexion with colloidal suspensions, and advocated by McBain in the case of electrokinetic phenomena, and it does not require the assumption of selective adsorption.

If the molecules in the surface of an insoluble acid in contact with water are imagined to undergo dissociation, and if the hydrogen ions so produced are osmotically active and have a range of movement determined by the electrostatic field due to the residual acid anions on the surface, such a system is separated from the external liquid by an imaginary envelope which marks the extreme range of movement of the hydrogen ions, and is equivalent to a membrane permeable by any ions except the acid anions embedded in the surface of the insoluble acid. When the external liquid is pure water, this, on separation from the insoluble acid, should not have acquired hydrogen ions from the latter, since they are electrostatically tethered to its surface; but if a neutral salt is present in the water, an exchange should take place between some of the hydrogen ions within the envelope and an electrically equivalent number of kations in the external liquid. On the foregoing assumptions, a solution of a neutral salt in contact with, *e.g.*, stearic acid, should become acid, and the total acid present should increase with increase of the volume of solution per unit surface of the solid, in consequence of the progressive dissociation of the molecules in the surface; or alternatively, if this ratio is kept constant, the acidity should vary directly with the concentration of the salt within the limits denoted by the principle of "membrane equilibrium." The experiments with stearic acid described below confirm these expectations, and suggest an equally simple explanation of the results obtained by Mukherjee and his co-workers (J., 1926, 3023) in the case of hydrated silica.

EXPERIMENTAL.

Some experiments were carried out with colloidal suspensions of stearic acid in water, in order to ascertain the order of magnitude of the acidity, if any, produced in neutral solutions of potassium chloride. The stearic acid used (Kahlbaum's best) was recrystallised twice from neutral methyl alcohol. It was shown that this degree of purification furnished a material the solubility of which in water ($3{\cdot}5 \times 10^{-6}$ equiv. per litre) was not further reduced by repeated recrystallisation (compare Bowden, J., 1911, **99**, 192; Bunbury and Martin, J., 1914, **105**, 418). The acid was dispersed by dropping a dilute methyl-alcoholic solution into boiling "conductivity" water contained in a large Jena-glass flask, the methyl alcohol being removed by continued boiling. To 50 c.c. of this suspension 25 c.c. of a neutral solution of potassium chloride were added, and the mixture was either filtered through an "ashless" filter, or, if coagulation was incomplete, submitted to ultrafiltration through a collodion membrane, the first portions of the filtrate being rejected. 10 C.c. of the clear liquid were then titrated against standard sodium hydroxide, and the acidity was calculated after the value obtained by titrating the ultrafiltrate from a suspension in water alone had been subtracted. The last-named ultrafiltrate was considered to be a saturated solution of stearic acid in water, but the solubility as determined from it is probably slightly in excess of the true value, because the liquid, in spite of its apparent clarity, may have contained a few ultramicronic and amicronic particles. The true values of the acidity due to the salt action should probably therefore be rather higher than those in Table I. It is also to be observed that, although atmospheric carbon dioxide was not rigidly excluded, the solubility determination itself constituted a control experiment, so that any error due to this cause can only be a difference between two small and nearly equal errors.

The liquids, excepting the alkali contained in the microburette, were handled in vessels coated with hard, neutral paraffin wax, and the experiments were carried out at the ordinary temperature (about 23°). The results are in Table I.

TABLE I.

50 c.c. Stearic acid suspension + 25 c.c. KCl solution.

Normality of KCl in mixture ...	0·001	0·007	0·027	0·083	0·33	0·84
Normality ($\times 10^6$) of acid due to salt action	6	7	16	26	32	49

A second series of experiments had for its object the accurate determination at the ordinary temperature of the relation between acidity and salt concentration, and between acidity and the volume of salt solution per unit surface of stearic acid. The method used was the electrical measurement of the hydrogen-ion activity of mixtures of stearic acid suspensions with neutral solutions of potassium sulphate. The hydrogen-ion activity of solutions of potassium sulphate at the three dilutions employed, when containing various known quantities of sulphuric acid, was also measured separately, and curves were drawn from which the actual quantity of sulphuric acid liberated by the suspensions could be read off. Preliminary experiments with an ordinary hydrogen electrode were discontinued on account of the unsatisfactory readings obtained, due possibly to the spoiling of the platinised surface of the electrode by particles of stearic acid. A bright platinum quinhydrone electrode gave satisfactory and reproducible results.

The quinhydrone, stearic acid, and potassium sulphate were recrystallised several times, the best-quality " conductivity " water was used, and no liquid of which the hydrogen-ion activity was to be measured was ever in contact with glass other than well-steamed Jena-glass or glass coated with neutral, hard paraffin wax. The liquid was deprived of dissolved carbon dioxide, before measurements were made, by prolonged passage of carbon dioxide-free air saturated with the vapour of the liquid under examination. A " saturated " calomel electrode was used as the second pole of the combination the *E.M.F.* of which was measured, and the combination was kept on an earthed metal sheet in a large air thermostat at 29° (the room temperature during these experiments being usually 27—28°). In order to avoid contact of the liquids with soda-glass measuring vessels, the solutions were prepared in every case by weight, not volume. The solutions of known acidity were made up by adding sulphuric acid of known strength contained in a paraffined weight-pipette to 25 g. of potassium sulphate solution of double the strength required, in a tared Jena-glass flask, the final weight being then made up to 50 g. with conductivity water. The stearic acid mixtures contained equal weights of the suspension and of the potassium sulphate solution. If coagulation occurred before dissolved carbon dioxide was removed, as it did with the $N/2$-salt solutions at all dilutions except the highest, the liquid was filtered through an " ashless " paper, and the first 10 c.c. were rejected. If coagulation occurred either not at all or only after the bubbling of air, the unfiltered liquid was used. The relative hydrogen-ion activities were calculated from the formula $\log f = (E - 0{\cdot}4536)/0{\cdot}0598$, in which E denotes the measured *E.M.F.* of the combination. The values of the hydrogen-ion activities corresponding to various concentrations of sulphuric acid in the three solutions of potassium sulphate used are in Table II. The figures are calculated on the assumption that the potential at the K_2SO_4–saturated KCl junction is zero, an assumption which does not affect their validity for the purposes of this investigation.

TABLE II.

	$N/100$·K_2SO_4.						
Conc. of H_2SO_4 ($N \times 10^6$) ...	26·80	6·77	4·97	2·02			
Relative $H^{\cdot}$ activity ($\times 10^6$)	15·45	4·45	3·57	1·62			
	$N/10$-K_2SO_4.						
Conc. of H_2SO_4 ($N \times 10^6$) ...	55·8	28·0	20·07	14·55	6·89	4·64	2·72
Relative $H^{\cdot}$ activity ($\times 10^6$)	17·42	8·38	6·72	4·58	2·47	1·73	1·19
	$N/2$-K_2SO_4.						
Conc. of H_2SO_4 ($N \times 10^6$) ...	269	145	52·8	33·66	20·79	13·06	5·94
Relative $H^{\cdot}$ activity ($\times 10^6$)	39·84	21·52	6·78	3·88	2·26	1·57	1·10

Table III gives the results of the measurements of acidity produced by the stearic acid suspensions. The figures headed " dilution " refer to dilutions of the stock suspension which contained 2·32 g. of stearic acid per litre. Columns A, B, and C contain, respectively, the relative hydrogen-ion activities ($\times 10^6$), the concentration of acid (g.-equivs. $\times 10^6$ per kg.), and the total acid liberated (g.-equivs. $\times 10^6$ per g. of stearic acid). The figures are calculated from the mean of two or more separate measurements in each case.

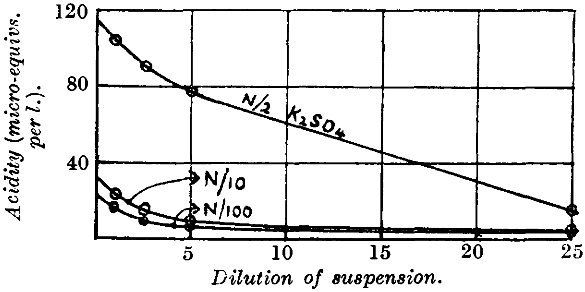
TABLE III.

	Normality of K_2SO_4 solution.								
	$N/100$.			$N/10$.			$N/2$.		
Dilution.	A.	B.	C.	A.	B.	C.	A.	B.	C.
1	10·4	16·2	13·9	7·75	23·3	20·1	15·4	105	90·6
2·5	6·52	8·8	18·9	5·14	14·8	31·9	12·8	91·5	197
5	4·98	6·0	25·8	3·35	8·5	36·6	10·6	77·6	333
25	3·88	4·14	89·6	2·12	4·4	94·8	1·98	15·8	340

The Nature of the Reaction between an Insoluble Acid and Salt Solutions.

The application of the theory of "membrane equilibrium" to the present problem is complicated by two factors which were not included in the theory as originally formulated by Donnan, *viz.*, (1) the unknown ratio of the volumes of liquid on either side of the "membrane," and (2) incomplete dissociation of the non-diffusible substance, involving the possibility of an increase in the number of diffusible ions available for exchange. In the absence of any knowledge of the magnitude of these factors, no quantitative application of the theory is possible; but an examination of the results of the experiments just described is strongly in favour of the conclusion that the reaction under discussion (and, by implication, similar reactions in which acidity is produced in neutral salt solutions) is qualitatively accounted for by the theory.

FIG. 1.



The progressive dilution of a suspension by the salt solution used is equivalent to increasing the volume of the liquid containing only diffusible ions, while maintaining constant that of the liquid containing the non-diffusible ion. If no dissociation of the surface molecules of the insoluble acid takes place, the activity of the hydrogen ions in the external liquid should decrease in an approximately linear manner with the dilution, provided that the volume of the external liquid is always a large fraction of the total volume, as it almost certainly is when the suspension is dilute. Assuming, on the other hand, that the surface molecules are initially but slightly dissociated, then if there were an unlimited supply of such molecules, which could undergo progressive dissociation, the hydrogen-ion activity in the external liquid should show little change with dilution. Under the experimental conditions the supply of surface molecules is limited, and it can be seen from Fig. 1 that, at the higher dilutions, the observations nearly correspond to these two extreme cases. Since a concentrated salt solution produces a more complete exchange of ions than do the more dilute solutions, the reserve of undissociated molecules is in the former case nearly exhausted initially, and very little further dissociation is possible as the volume is increased; on the other hand, in the dilute solutions the acid concentration is comparatively little affected by dilution. Fig. 2, showing the relation between dilution and total acid liberated, provides a striking clue to this behaviour: practically all the available acid is liberated by the strong salt solution during the early part of the dilution process (1 to 5), and further dilution (5 to 25) produces no more. With the weaker solutions, the production of acid is still in evidence even at the highest dilution.

FIG. 2.

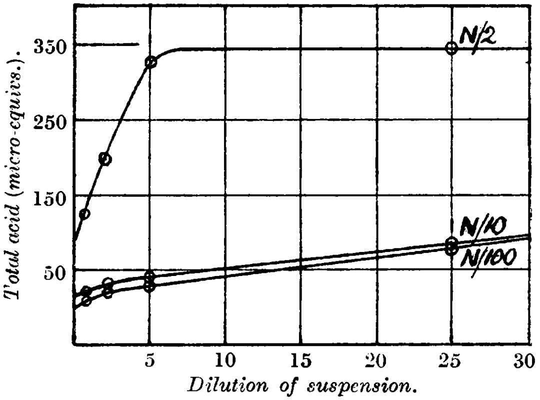
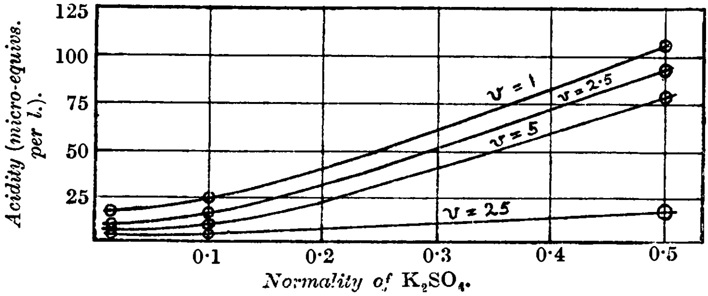


FIG. 3.



Again, the increase of acidity due to an increase in the concentration of potassium sulphate (see Fig. 3) is, at least qualitatively, predicted by the theory of membrane equilibrium. The increase is considerably greater than would be expected in a system where the number of exchangeable ions is constant, and this constitutes additional evidence of the dissociation of the surface molecules under the experimental conditions.

The Relation between Acid Concentration and Hydrogen-ion Activity.

Donnan's theory is concerned with activities rather than concentrations, but in the present experiments the activity relationships tend to be obscured by disturbing factors incidental to the method used. In the presence of an excess of potassium sulphate, any sulphuric acid liberated is present as potassium hydrogen sulphate which, itself a strong binary electrolyte, furnishes an anion which is an acid with a dissociation constant of about 10^{-2} (Drucker, *Z. physikal. Chem.*, 1920, **96**, 382). An increase in the concentration of potassium sulphate may therefore be expected to influence the hydrogen-ion activity and the acid concentration in opposite senses, because a higher concentration of the salt, whilst effecting a more complete exchange of hydrogen ions, will at the same time cause a greater proportion of them to assume an inactive condition. This is, in fact, observed, for the activity–salt concentration curves pass through a minimum except at the highest dilution of the suspension.

Although it is chiefly a matter of terminology whether the production of acid, in circumstances similar to those considered in this paper, is to be regarded as an ionic exchange or as a chemical reaction between equivalent quantities of two molecular species, the suggestion has been put forward (Mukherjee, *loc. cit.*), in the case of hydrated silica, that the production of acid is to be attributed to an exchange of *adsorbed* ions bearing no stoicheiometric relation to the number of molecules of silica associated with them. The point of view advocated here differs radically from Mukherjee's in regarding the action as taking place between quantities of the insoluble acid and the neutral salt which are in a simple stoicheiometric proportion; in other words, one is dealing with a reversible chemical change differing from the ordinary type only in its localisation at an interface. The advantages of this point of view are that it does not need to invoke any of the various types of adsorption, and is at once in harmony with accepted chemical theory and with a theory of interfacial behaviour for which there is a rapidly increasing body of evidence (see *Trans. Faraday Soc.*, 1925, **21**, 406).

Summary.

1. The production of acidity by suspensions of stearic acid has been measured in neutral solutions of potassium chloride and potassium sulphate.

2. The variation of hydrogen-ion activity and of total acid with the salt concentration and with dilution of the suspension has been

examined, and found to be consistent with the view that the observed acidity is produced by exchange of the kations of the salt with hydrogen ions formed from dissociating molecules in the surface of the insoluble acid.

3. It is considered that the production of acidity in neutral solutions of salts of strong acids in contact with an extensive surface of a weak insoluble acid is generally to be expected on the basis of accepted theory, and is capable of a simple chemical interpretation.

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