ACTIVATION AND CLARIFYING PROPERTIES OF FULLER'S EARTH.

PART IV. EQUILIBRIUM IN THE IONIC EXCHANGES IN FULLER'S EARTH.

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INTRODUCTION.

In the course of our work on the activation of fuller's earths obtained from different parts of India (This *Journal*, 1938, **20A**, 111–118 and 119–123) we have shown that the pH of the solution of sodium chloride treated with the earths varied in the inverse proportion with the change in the Lovibond units of colour removed from groundnut and safflower oils. The decolourising action of these earths and their activation by acids are thus directly related to the exchangeable hydrogen contained in them. The cation of the zeolite is replaced by the hydrogen ion during the process of activation by acids, the hydrogen in turn being replaced by sodium ion when treated with salt solution.

It is difficult to define exactly the nature of the reaction that takes place between the replaceable hydrogen of the earth and the colouring matter removed by it from non-aqueous media such as oils. We have suggested (Kulkarni and Jatkar, *Current Science,* 1936, **5**, 18) that in aqueous media, if adsorption is to be of little account, the ionic behaviour in processes like activation, salt-treatment, clarification of juices, etc., will be governed mainly by the law of mass action. We have therefore considered it necessary to examine the suggestion experimentally by studying base-exchange relationships between fuller's earth and salt solutions.

In the case of soils and clays, base-exchange reactions have been the subject of numerous investigations during the past few years. All these researches have been ably summarised by Wiegner (*J. Soc. Chem. Ind.,* 1931, **50**, 65T) and more recently by Jenny (*Jour. Physical Chem.,* 1932, **36**, 2217). In most of these, the similarity between the exchange equilibria and those governed by the law of mass action has been emphasised and equations have been developed on the basis of various assumptions (*cf.* Ganssen, *Centr. Mineral Geol.,* 1913, 699 and 728; Wiegner and Jenny, *Kolloid-Z.,* 1927, **42**,

268; and Vageler and Woltersdorf, *Z. Pfl. Dung. Bodenk,* 1930, **A15** and **16,** 329 and 184). Most of the formulæ suggested are applicable to colloidal reactions and cover, in addition to the mass-law reactions, any ionic adsorption that may occur in the system. Marshall and Gupta *(J. Soc. Chem. Ind.,* 1933, **52,** 432T) found that none of the formulæ was satisfactory in the sufficiently wide range of concentrations studied by them. Moreover, as remarked by us, the applicability of such formulæ involves very complicated experimental procedure, with the result that the accuracy of the equilibrium constants calculated therefrom becomes unreliable. In our experiments, therefore, we have tried to make the systems as simple as possible, by using very low concentrations of the reactants and assuming the simple exchange reaction represented diagrammatically as follows:

$$\boxed{}\text{-}H^{\cdot} + Na^{\cdot} \rightleftharpoons \boxed{}\text{-}Na^{\cdot} + H^{\cdot},$$
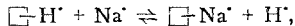
where the squares indicate the molecules, particles or crystal lattices of the activated earth, more or less uniformly distributed throughout the volume of the aqueous system and therefore acting as a reactant with a definite concentration. As the reaction consists in the simple replacement of the H$^{\cdot}$ ions by the Na$^{\cdot}$ ions from the salt solution, the equilibrium constant K can be calculated from:

$$K = \frac{[\boxed{}\text{-}Na^{\cdot}]\,[H^{\cdot}]}{[\boxed{}\text{-}H^{\cdot} - \boxed{}\text{-}Na^{\cdot}]\,[Na^{\cdot} - H^{\cdot}]}$$

$$= \frac{[H^{\cdot}]^{2}}{[\boxed{}^{3}H^{\cdot} - H^{\cdot}]\,[Na^{\cdot} - H^{\cdot}]} \qquad \cdots \qquad \cdots \quad (1)$$

With regard to the methods of measurements of the various ionic concentrations, potentiometric methods have been used both by Marshall and Gupta *(loc. cit.)* and Jenny *(loc. cit.).* We found that a conductivity method was far simpler for systems at low concentrations. For high concentration, however, the conductivity method failed and potentiometric methods were used.

EXPERIMENTAL.

The decolorisation of the oil was studied by treating the oil with an increasing concentration of the earth. A sample of safflower oil used in Part III of this series (This *Journal,* 1938, **20A,** 119–123) was treated with activated Jodhpur earth in increasing proportions

and the bleaching and the corresponding pH values of the normal sodium chloride solution were measured in the manner described previously.

TABLE I.

Earth %	Lovibond Change	pH Original Earth	Lovibond Change	pH Activated Earth
1	7·4	7·60	11·3	3·11
2	8·5	7·65	11·7	2·92
3	11·1	7·72	12·1	2·80
4	11·7	7·75	12·1	2·73
5	11·7	7·77	12·1	2·67
6	11·7	7·80	12·1	2·63

These results show that there remains a certain amount of colour (0.7 Lovibond unit) in the oil which cannot be removed by increasing the percentage of earth used, showing that an equilibrium has been reached. With the activated earth, decrease in pH is shown with increase of the percentage of the earth, but in the case of the original earth the increasing amount of free alkali contained in the earth more than counterbalances the hydrogen ion concentration released, thus showing an increase in pH. It is interesting to note that the product of Lovibond change and pH of the salt solution treated with 1–3% of the activated earths is 34–35 in agreement with the results obtained in Part III.

Exchangeability of hydrogen with varying concentrations of sodium chloride solutions was studied quantitatively by potentiometric and conductometric methods.

(1) *Potentiometric method.*—That the exchangeability of hydrogen proceeds according to some form of mass law is shown by the progressive exchangeability of hydrogen with increasing concentration of the sodium chloride solution. The progressivity is seen from the following results :—

TABLE II.

NaCl solution	pH 3% earth	NaCl solution	pH 3% earth
·02 N	3·13	4 N	2·45
1 N	2·91	5 N	2·32
2 N	2·70	6 N	2·26
3 N	2·58	..	..

Concentrations higher than 6N could not be tried owing to the limited solubility of sodium chloride.

When allowance is made for the effect of neutral salt on the activity of hydrogen ion, these results show that even with a saturated solution of sodium chloride, the limit of exchangeability of hydrogen is not easily reached, showing that the basic crystal has far more affinity for hydrogen than for any other base. Hydrogen thus appears to be tenaciously held on to the lattice and is difficult to be displaced. Even on boiling the earth with concentrated salt solution, the hydrogen could not be completely displaced by sodium.

On the assumption that a solution of 6 Normal sodium chloride effects almost complete removal of the exchangeable hydrogen ion we obtain 6×10^{-3} as the approximate value of the equilibrium constant in equation (1) when 3% fuller's earth is used in 0.02 and 6 Normal sodium chloride solutions. The results with different concentrations of sodium chloride are, however, very discordant, due to adsorption factors and certain experimental errors.

The above results are in agreement with the peculiar behaviour of hydrogn ion in ionic exchange observed by Jenny (*loc. cit.*). It may be mentioned that while Jenny (*loc. cit.*) used in his experiments highly dispersed soil clay, we used the coarser portion of fuller's earth without prejudice to the decolourising efficiency.

(2) *Conductivity method.*—The method consisted in treating samples of activated earth with salt solutions of different concentrations and measuring the concentration of the liberated H· ion from conductivity measurements. The activated earth was freed from acids and other electrolytes by boiling the earth with distilled water and then washing with conductivity water and drying at 110° C. In a blank

experiment, 1 gram of the dried earth was shaken with 100 c.c. of conductivity water in a stoppered Jena glass bottle and the mixture kept overnight in a thermostat at $(30 \pm 0.01)°$ C. and the specific conductivity of the mixture was measured by the Leeds-Northrup outfit using a calibrated resistance box. This gave the specific conductivity due to any residual ions that might have remained after washing. Further samples of the earth were then treated in an identical manner with different solutions of sodium chloride and the conductivities of the mixtures found. From each of these specific conductivities, that of the blank was subtracted, so as to get the conductivity, only due to the ions partaking in the reaction.

As the reaction consists of simple replacement and liberation of the more mobile hydrogen ions by the sodium ions, resulting in an increased conductivity of the mixture, the liberated H-ion concentration was calculated by the formula:

$$X = \frac{(l_2 - l_1)\ 1000}{U_H - U_{Na}}, \qquad \cdot\cdot \qquad \cdot\cdot \quad (2)$$

where U_H and U_{Na} are the mobilities of the hydrogen ion and sodium ion respectively, l_1 and l_2 are the specific conductivities of original and resulting salt solutions and X is the concentration of hydrogen ion in gram equivalents per litre, liberated by the addition of the earth. The mixture law of conductivities has been assumed for the dilute concentrations used. The mobilities of H˙ and Na˙ at 30° C. were graphically extrapolated from values at different temperatures as given in *Landolt-Börnstein Tables,* and found to be 375 and 55 respectively in the usual units. As the hydrogen-ion concentrations so calculated were of the order of 10^{-4} gm. equivalents per litre, their thermodynamic activities were considered to be identical with the concentrations, considering that the mean activity of H˙ at 0.001 N is about 0.98 (25° C.). The mean activity of Na˙ at different concentrations of sodium chloride solutions, was calculated from the activity coefficients given by Lewis and Randall (*Thermodynamics,* p. 344, McGraw-Hill, 1923). In the final calculation of the equilibrium constant, as $[\boxdot\text{-}H˙]$ in equation (1) is great compared to $[H˙]$ the factor $[\boxdot\text{-}H - H˙]$ was considered constant, so that equation (1) became

$$K = \frac{H˙^2}{Na˙ - H˙} \qquad \cdot\cdot \qquad \cdot\cdot \qquad \cdot\cdot \quad (3)$$

The following Table III gives the results obtained when various salt solutions were treated with 1% earth. The specific conductivity of the blank mixture was found to be 2.852×10^{-5} r.ohms.

TABLE III.

Salt concentration	Mean activity of Na ion $\times 10^4$	Sp. cond. of the salt solution $\times 10^5$	Sp. cond. of the mixture $\times 10^5$	$l_2 - l_1$ $\times 10^5$	Calculated H $\times 10^4$	K $\times 10^4$
0·02 N	178·4	253·24	270·18	14·09	4·403	0·111
0·01 N	92·2	129·50	143·55	10·19	3·156	0·112
0·005 N	48·3	66·60	77·53	8·08	2·526	0·100
0·003 N	28·8	44·56	53·28	5·87	1·833	0·124
0·0025 N	23·1	34·17	41·94	4·82	1·507	0·100
0·002 N	19·3	27·30	34·28	4·13	1·306	0·116

A similar set of experiments with solutions containing 2% earth gave the following results (Table IV). The specific conductivity of the blank mixture was found to be 5.160×10^{-5} r.ohms.

TABLE IV.

Salt concentration	Observed sp. cond. of the mixture with 2% earth $\times 10^5$	$l_2 - l_1$ $\times 10^5$	Calculated H $\times 10^4$	K $\times 10^4$
0·02 N	278·43	20·0	6·26	0·23
0·01 N	151·14	16·5	5·15	0·31
0·005 N	83·88	12·1	3·79	0·32
0·003 N	59·54	8·9	2·79	0·30
0·0025 N	49·62	7·5	2·34	0·26
0·002 N	39·47	7·0	2·19	0·28

The average values of the equilibrium constants in Tables I and II are 1.1×10^{-5} and 3.0×10^{-5} respectively. The values of the constants thus obtained are more concordant than those given by

previous workers. This constancy also proves that the adsorption effects have been reduced to a minimum by the use of low concentrations of the earth and the salt, and that the ionic exchange is stoichiometric.

The low value of the equilibrium constant is in harmony with the findings given in the earlier part of the paper that hydrogen ion is replaced with great difficulty. It also follows that hydrogen ion should be most effective in replacing other cations in the fuller's earths even in moderate concentrations, as found by Jenny (*loc. cit.*) in the case of soils. A high concentration of acid, however, is employed for activation, as this assists in dissolving the metallic constituents and by breaking up the fuller's earth increases the effective surface of the product obtained.

SUMMARY.

The limit of hydrogen ion exchangeability by sodium ion in fuller's earth has been measured by potentiometric methods in concentrated solutions and conductivity method in dilute solutions of sodium chloride. Concordant results were obtained for the value of the equilibrium constant for the base-exchange reaction in the latter experiments. The effects due to adsorption were minimised by rejecting the colloidal portions of the earth.

A similar limit was found in the decolorisation of a vegetable oil using different amounts of fuller's earth.

The value of the equilibrium constant obtained for the exchange of sodium ion by hydrogen ion shows that the latter even in small concentrations should be most effective in replacing other ions. In actual practice, acid of high concentrations is employed for activation as it breaks up the fuller's earth and thereby increases the effective surface.

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