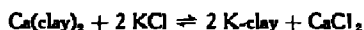


A STUDY OF Ca—K ION EXCHANGE EQUILIBRIUM WITH THE HELP OF MEMBRANE ELECTRODES

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Suitability of membrane electrodes having different mobility ratios for the same pair of cations for the determination of individual ion activities in a mixture has been demonstrated. The same procedure has been applied to the study of the clay system :



from a_{Ca} and a_{K} measurements in both the forward and backward reactions.

The features of the a_{K} curves in both the reactions are more or less similar. a_{Ca} shows a small rise which for the reverse reaction is somewhat steeper than the forward reaction. This is due to the entry of K^+ into the exchange position for Ca^{2+} in the forward reaction. For the reverse reaction, Ca^{2+} is perhaps unable to bring out the already fixed K^+ ions, and therefore Ca^{2+} ions remain in the weaker level of affinity.

The study of exchange equilibrium between Ca^{2+} and K^+ in clays by means of activity determination involves the measurement of ionic activity in a binary mixture (Marshall and Barber, *Soil Sci. Soc. Amer. Proc.*, 1950, 14, 86; McLean and Marshall, *ibid.*, 1948, 13, 179; Mitra, D. Phil. thesis, Calcutta University, 1954; Mitra and Chatterji, *J. Ind. Soc. Soil Sci.*, 1953, 1, 112). The development of clay-membrane electrodes and resin-membrane electrodes (Willie and Patnode, *J. Phys. Coll. Chem.*, 1950, 54, 204; Sinha, this *Journal*, 1953, 30, 529; Marshall and Bergman, *J. Amer. Chem. Soc.*, 1941, 63, 1911), sensitive to bivalent cations as well as to monovalent cations, has made possible the determination of individual ion activity in a mixture of two in true solution as well as in colloidal suspension (Chatterjee and Marshall, *J. Phys. Coll. Chem.*, 1950, 54, 671).

The method of measuring individual ion activity in a mixture of the two by employing clay and resin membrane electrodes has been outlined in previous communications (Bose, *J. Indian Soc. Soil Sci.*, 1955, 3, 65, 109).

The present paper is concerned with calcium—potassium reversibility, an evaluation of the 'mobility ratios' of these cations using different types of membranes, and determination of activity of each of the ions in a mixture of Ca^{2+} and K^+ ions. The exchange equilibrium reaction involving measurement of cation activities in a mixture has also been studied.

The undermentioned reaction system has been selected, for which the forward as well as the reverse reactions have been investigated :



EXPERIMENTAL

The experimental procedures regarding preparation, testing and determination of E.M.F. etc. are exactly the same as described earlier (Bose, *loc. cit.*). From the observed E.M.F. between KCl and a mixture of KCl and CaCl_2 solutions of known ionic activities, placed on the two sides of a membrane electrode, the mobility ratio is calculated from the simplified relationship :

$$E_{\text{obs}} = \frac{RT}{2F} \ln \frac{a_{\text{K}}^{\text{I}}}{a_{\text{K}}^{\text{II}} + 2 a_{\text{Ca}}^{\text{II}} \cdot \frac{U_{\text{Ca}}}{U_{\text{K}}}}$$

where E_{obs} is the observed E.M.F. in m.v., a_{K}^{I} , a_{K}^{II} and $a_{\text{Ca}}^{\text{II}}$ are the known K^+ ion and Ca^{2+} ion activities respectively, and $U_{\text{Ca}}/U_{\text{K}}$ is the mobility ratio. The calculated mobility ratios of a number of electrodes are shown in Table I.

TABLE I

Mobility ratios for different membrane electrodes.
 Inside: $a_K = 0.027$. Outside: $a_K = 0.009$; $a_{Ca} = 0.0009$.

Membranes.	*E.M.F.	U_{Ca}/U_K .	Membranes.	*E.M.F.	U_{Ca}/U_K .
A. T.C. 6 (1)	-18.5 mv	2.289	E. K.H. 5	-27.0 mv	0.230
B. P.H. 5	-20.5	1.739	F. A.H. 5	-21.0	1.616
C. I.R. (100)	-19.0	2.144	G. IONAC (200)	-19.0	2.144
D. K.C. 5	-22.5	1.233	H. T.C. 6(2)	-20.0	1.87

N.B. C and G are resin membranes; the rest are clay membranes.

* Inside solution contains the negative electrode.

The mobility ratios, U_{Ca}/U_K , for different clay and resin membrane electrodes somewhat vary with the activity range of cations, and hence these have been determined within the actual range of activities obtaining in the experiments.

As reported earlier, two membranes having different mobility ratios have been used for this study. From the observed E.M.F.'s of the cell, comprising a mixture of Ca^{2+} and K^+ ions and a solution of known a_K , separated by the membrane electrodes, the following two equations may be set up:

$$E_1 = \frac{RT}{2F} \ln \frac{a_K^I}{a_K^{II} + 2 a_{Ca}^{II} \left(\frac{U_{Ca}}{U_K} \right)_1} \quad \dots \quad (1)$$

$$E_2 = \frac{RT}{2F} \ln \frac{a_K^I}{a_K^{II} + 2 a_{Ca}^{II} \left(\frac{U_{Ca}}{U_K} \right)_2} \quad \dots \quad (2)$$

With known values of E_1 , E_2 , $a_K^I \left(\frac{U_{Ca}}{U_K} \right)_1$ and $\left(\frac{U_{Ca}}{U_K} \right)_2$ the above two equations may be solved for a_K^{II} and a_{Ca}^{II} .

To ascertain the accuracy with which the procedure measures individual ion activities in a mixture, determinations have been made of the known calcium ion activity of a particular solution in presence of K^+ ions. The results are shown in Table II.

TABLE II

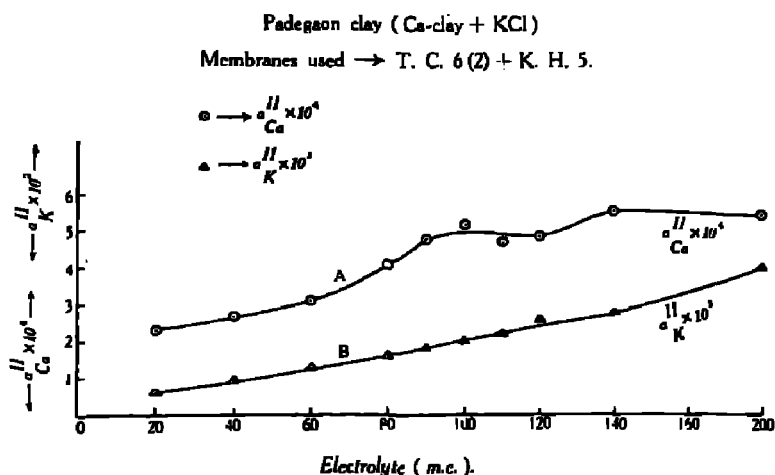
Individual ion activities in a mixture of Ca^{2+} and K^+ ions.
 Inside: $a_K = 0.027$. Outside: $a_K = 0.009$; $a_{Ca} = 0.0009$.

Membranes.	U_{Ca}/U_K .	*E.M.F.	Calculated: outside.	
			a_{Ca} .	a_K .
A. T.C. 6(1)	2.289	-34.75 mv	(H-E)-0.0009	0.0032
B. P.H. 5	1.739	-38.50	(A-E)-0.0008	0.0032
C. I.R. (100)	2.144	-41.00	(F-E)-0.0010	0.0031
D. K.C. 5	1.233	-38.50	(D-E)-0.0012	0.0031
E. K.H. 5	0.230	-51.50	(A-B)-0.0009	..
F. A.H. 5	1.660	-37.25
G. IONAC (200)	2.144	-40.00
H. T.C. 6(2)	1.870	-35.50

* Inside solution contains negative electrodes.

For the purpose of the study, K-clay and Ca-clay were prepared by adding respectively calculated amounts of KOH and CaO to electrolysed H-clay (montmorillonite) isolated from the Padegaon black cotton soil. The mixtures were kept for completion of reaction in stoppered bottles for more than one week with occasional shaking.

FIG. 1



K-clay suspension (5 c.c.) was taken in each of 10 bottles and calculated amounts of CaCl_2 were added to each, and made up with water to 30 c.c. The contents of the bottles were allowed to equilibrate with occasional shaking for 48 hours. The mixture was set against $a_K = 0.027$ inside the membrane electrode. The E.M.F.'s for the same system were measured with the help of two clay-membrane electrodes, K.H.5 and T.C.6(2), having respectively the mobility ratios U_{Ca}/U_K equal to 0.23 and 1.87. The individual a_K and a_{Ca} were calculated by solving the simultaneous equations (1) and (2). The relevant data for the reverse reaction were obtained in an exactly similar manner. The results are recorded in Tables III and IV and graphically shown in Figs. 1 and 2.

TABLE III

Ca (clay)₂ + 2 KCl.

KCl added (m.e.)	..	20	40	60	80	90	100	110	120	140	200
Calc. activities:											
$a_{Ca}^{II} \times 10^4$..	2.3	2.7	3.1	4.1	4.8	5.2	4.7	4.8	5.5	5.4
$a_K^{II} \times 10^3$..	0.66	0.97	1.3	1.6	1.8	2.0	2.0	2.6	2.8	4.0

TABLE IV

2 K-clay + CaCl_2 .

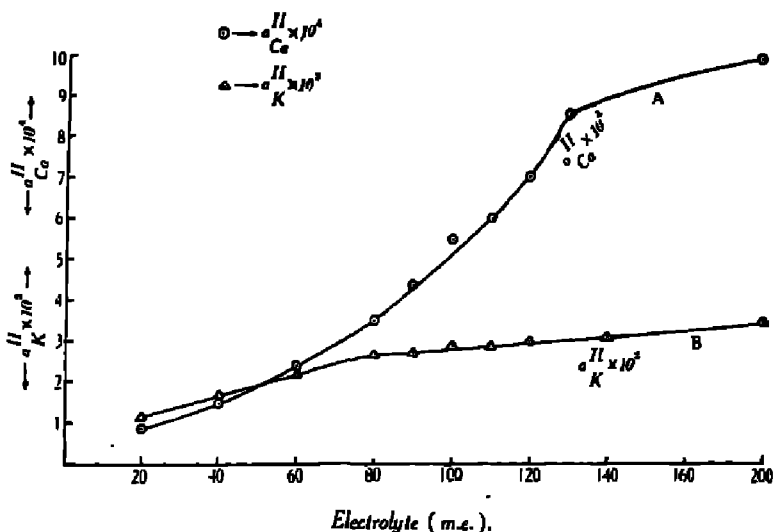
CaCl_2 added (m.e.)	..	20	40	60	80	90	100	110	120	140	200
Calc. activities:											
$a_{Ca}^{II} \times 10^4$..	0.9	1.5	2.4	3.5	4.4	5.5	6.05	7.021	8.6	9.9
$a_K^{II} \times 10^3$..	1.2	1.7	2.24	2.7	2.72	2.9	2.9	3.03	3.1	3.5

DISCUSSION

The mobility ratios of some of the electrodes (Table I) are fairly different and are therefore quite suitable for the purpose of the measurements envisaged here. The membranes actually used for the measurements reported above are K.H.5 and T.C.6(2). From the data in Table II a_{Ca} , determined in the mixtures, appears to agree well with the actual value.

FIG. 2

Padegaon clay (K-clay + CaCl₂).
Membranes used: T. C. 6 (2) + K. H. 5.



The peculiarly low activity of K^+ in both the forward and reverse reactions (Figs. 1 & 2) suggests that K^+ , which is liable to be fixed, prevents its easy exchange for Ca^{2+} . For the same reason K^+ readily replaces Ca^{2+} from Ca-clay because the process of fixation is attended with a greater loss of free energy. The Ca^{2+} ion activity, however, increases more sharply in the reverse than in the forward reaction. K^+ ions added as KCl to Ca-clay are probably 'fixed' in a less active form, and consequently these K^+ ions cannot bring the Ca^{2+} ions completely into intermicellar liquid in an active form, and hence the Ca^{2+} ion activity is low. Comparing the curves for the reverse reaction, it is to be noticed that $CaCl_2$ added to K-clay is unable to bring out the already 'fixed' K^+ ions, and therefore Ca^{2+} ions remain in the outer or the weaker level of affinity. As a result, a_{Ca} rises sharply and possesses high values, especially at higher concentrations of added $CaCl_2$.

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