

ION PAIR ACTIVITIES IN BENTONITE SUSPENSIONS

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ABSTRACT

The thermodynamic activities of ion pairs were measured electrometrically in a series of aqueous mixtures of monoionic bentonite and the corresponding chlorides. Ion exchange membranes and Ag-AgCl electrodes were used. The lyotropic order for the various cation species varied somewhat for two different preparations. The apparent relative escaping tendencies of the various cations did not correspond to that usually assumed on the basis of related phenomena: ion exchange selectivity, electromigration velocities, flocculation values or rates, etc.

INTRODUCTION

It is well known that the properties of clay suspensions are partially determined by the species of the exchangeable cation on the clay. One might assume that this lyotropic behavior is related to some ionic factor which provisionally may be called the activity coefficient. One may wish to compare the cation activity coefficients for suspensions of a number of monoionic clays. We are uncertain regarding the correct method of evaluating the molality of adsorbed ions, so that instead of calculating activity coefficients, we can compare measured cation activities of suspensions of equivalent exchangeable cation concentration. Marshall (1941, pp. 1912-1913) has attempted to measure cation activities in various clay suspensions. He calculated a quantity, the fraction active, which corresponds to the activity coefficient. It is generally recognized that the results of measurements of single ion functions are not rigorously thermodynamic. However, cation activities are in general neither more nor less acceptable than the widely used pH concept. In studying ion pair activities rather than single ion activities the author does not intend to disparage other workers nor to enter the present controversy regarding single ion activities.

Since the use of a salt bridge in electrometric measurements introduces an element of uncertainty, it would be desirable to eliminate the salt bridge. This can be done only by adding an appropriate electrolyte, *e.g.* KCl, to a suspension of K clay and by using two reversible electrodes. Ion pair activities, *e.g.* $a_K \cdot a_{Cl}$, rather than single ion activities are measured in this manner. When the anion species is constant, while the cation species is varied, differences in the values of $a_+ \cdot a_-$ can be correlated with differences in the cation species present on the clay and presumably may represent differences in the values of a_+ .

Measurements of monocationic systems containing added electrolyte may be compared with cation exchange equilibrium measurements. In the latter case we have two electrolytes present in both phases of a Donnan system. In a dilute system the two ion pair activities can be estimated directly upon analysis of the non-colloid phase.

EXPERIMENTAL

Bentonite Suspension No. 1

A set of monoionic clays was prepared by treating electro dialyzed Wyoming bentonite with equivalent amounts of various hydroxides or carbonates. Appropriate chlorides were added in small quantities. The proportions of clay, water, cation, and chloride ions were identical; the only independent variable was the species of cation. At a pH value slightly below 7, there was present 0.965 m.e. of adsorbed ions (*i.e.* of added hydroxide) per gm. of oven-dried electro dialyzed bentonite. The clay concentration was 1.79 gm. of oven-dried electro dialyzed bentonite per 100 gm. of water, so that the exchangeable cation concentration was 17.3 m.e. per 1,000 gm. of water.

A quantity of suspension was placed in one compartment of a cell; the other compartment contained a solution of the corresponding chloride. A calibrated Sollner (1950, p. 142C) membrane was placed between the two compartments and an Ag-AgCl electrode was put in each compartment. The set up was thus, for example:

Ag, AgCl, K susp., membrane, KCl solu., AgCl, Ag

This set up was calibrated by comparison with cells of the type:

Ag, AgCl, KCl solu. (1), membrane, KCl solu. (2), AgCl, Ag

The EMF values were determined by use of a K type Leeds and Northrup potentiometer and a lamp and scale galvanometer. Current amplification was not required to obtain sensitivity somewhat better than 0.1 mv., which was about the limit of variance in the readings.

Bentonite Suspension No. 2

Another set of measurements was carried out with monoionic clays prepared from a different batch of electro dialyzed Wyoming bentonite. The adsorbed cation concentration was 0.675 m.e. per gm. of oven-dried electro dialyzed bentonite, while the clay concentration was 3.724 gm. oven-dried electro dialyzed bentonite per 100 gm. of water. The exchangeable cation concentration was 25.0 m.e. per 1,000 gm. of water.

Ag-AgCl electrodes were again used, but, for the cation sensitive "electrodes" Rohm and Haas Amberflex C-1 membranes were used. The calibration was accomplished by inter-comparison of the EMF obtained from two or more cells employing the same suspension in one compartment, but

different concentrations of chloride in the other compartment. The whole set up for any given cation species was consolidated into a unit of several compartments. Thus all the readings were taken at intervals of a few seconds merely by moving a rotary switch. The set of readings was repeated a large number of times.

RESULTS AND DISCUSSION

The data are reported as mean ionic activities functionally related to the molality of the Cl added. Figures 1-4 present the data. No Mg mixture was prepared with bentonite No. 1. Actually 5 different Cl concentrations with Bentonite No. 1 were studied. Only the 3 lower concentrations are plotted since the higher concentrations were electrolyte solutions relatively unaffected by the presence of clay. The complete 5 point curves are smooth, so the smoothness shown in the figures is not illusory. The outstanding characteristics are the lyotropic order shown by the alkali-bentonite No. 1 mixtures and the alkaline-earth-bentonite No. 2 mixtures. The two sets of mixtures differed widely in clay concentration and in content of adsorbed cations. Although the alkali-bentonite No. 2 curves do not exhibit the same order as the alkali-bentonite No. 1 curves, the significance of the results is similar.

It is generally known that bentonites and many other clays exhibit a fairly consistent lyotropic order in ion exchange selectivity, particle migration velocity, flocculation values or rates, and rheological phenomena. In general this order of the cations is such as to suggest that the Li ion has a high escaping tendency from the particles as compared with the Cs ion, while the other ions of the group fall in place between these two. For example, the ion exchange constant, k , involving K-Na exchanges for the simple mass action equation:

$$\frac{[K](Na)}{[Na](K)} = k$$

is often of the order of 2-5. (Bracketed terms represent adsorbed ions, terms in parentheses are ions in the non-colloid phase.)

It is apparent that these "normal" relationships do not hold for ion pair activities in general as far as the bentonite preparations used in this work are concerned. Somewhat similar results were obtained by Marshall in his studies of single ion activities.

It would be futile to speculate widely regarding the reason for the observed discrepancy between the usual lyotropic order and that shown by Marshall's and the author's results, although some very tentative suggestions may be in order. The use of three types of membranes: clay, activated collodion, and resin, leads to similar results. The membranes cannot be at fault *per se*, since measured relative activities of pure solutions of salts indicate normal behavior. Whether or not the membranes behave well with the adsorbed ions cannot be known since there are no independent tests,

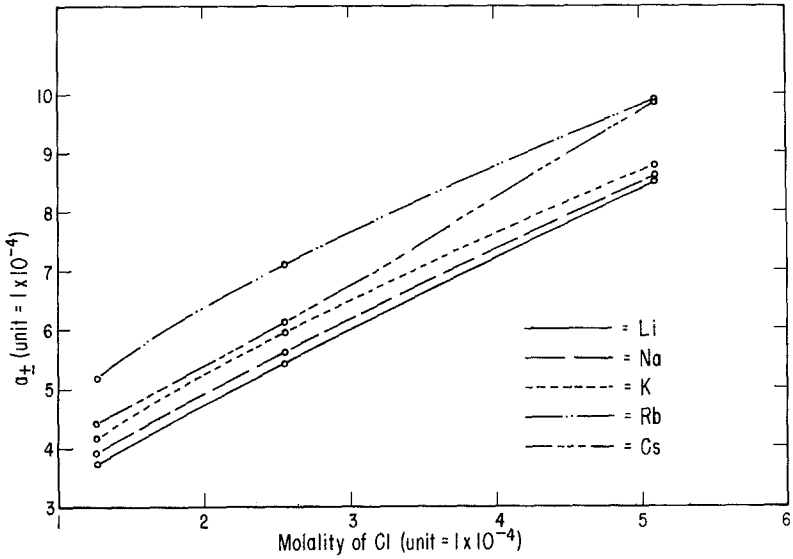


FIGURE 1.— Ion pair activities in alkali systems containing bentonite No. 1.

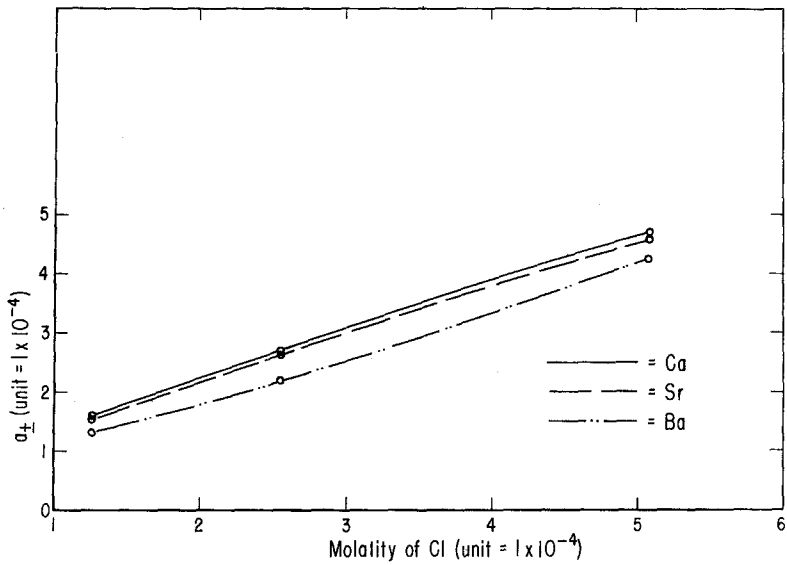


FIGURE 2.— Ion pair activities in alkaline-earth ion systems containing bentonite No. 1.

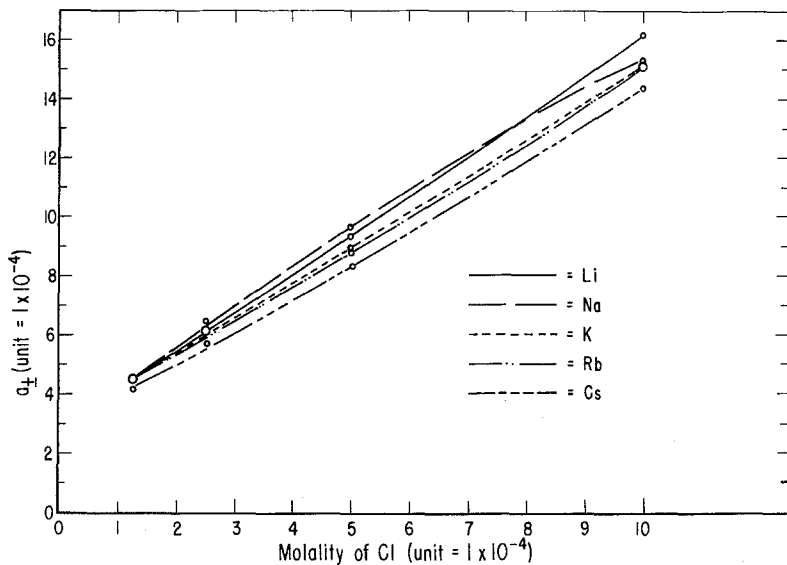


FIGURE 3.—Ion pair activities in alkali ion systems containing bentonite No. 2.

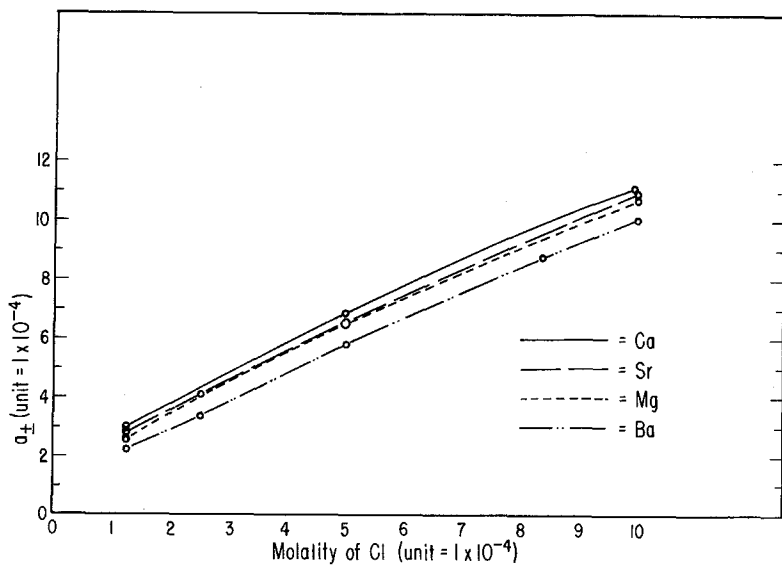


FIGURE 4.—Ion pair activities in alkaline-earth systems containing bentonite No. 2.

unless the usual lyotropic order of the cations is in a sense such a test.

It is possible, perhaps, to assume that a fraction of the "adsorbed" ions are so truly adsorbed that they are positionally unavailable to "react" with a membrane electrode and that the lyotropic order is different from that of the "freer" ions, which presumably follow the usual order.

REFERENCES

- Marshall, C. E. (1941) *The electrochemical properties of mineral membranes*: Jour. Amer. Chem. Soc., vol. 63, pp. 1911-1916.
- Sollner, K. (1950) *Recent advances in the electrochemistry of membranes of high ionic selectivity*: Jour. Electrochem. Soc., vol. 97, pp. 139C-151C.