The historical development of the valency rule (often referred to as the Schulze-Hardy rule) in the coagulation of negatively charged hydrophobic colloidal systems emphasized the general similarity of such systems with regard to the action of polyvalent cations. Viewed solely in this way, the possibility of separating complex mixtures of clay minerals by selective coagulation of individual members appeared remote. However, study of the electrochemistry of the clays in relation to their crystal structures has revealed differences of considerable magnitude.

(a) The fundamental mechanisms of ionization for the various clay minerals may be widely different. Thus, the montmorillonite and illite clays have predominantly a well defined chemical mechanism dependent upon the lattice charge induced by atomic proxying. The kaolinite family ionizes probably by a less clearly defined process at the edges of the sheets (lattice termination) and perhaps also by ionic adsorption processes in the planar surfaces.

(b) In the montmorillonite series itself the site of the lattice charge (outer silica layer or central alumina layer) is of great importance in determining the extent of ionization (2). Thus typical beidellites (main charge on silica layers) ionize to a much smaller extent than typical montmorillonites (main charge on central alumina layer).

(c) The magnitude of the charge per unit surface exposed is probably also of great importance. This is expressed by the cation exchange capacities for the different clay minerals of the montmorillonite series. Comparisons with other clays are difficult since the specific surfaces are seldom known with any accuracy.

(d) A general consideration of the ionization of surfaces in which, as in the case of the clays, dissociation is only partial, leads to a new type of valency rule. If the fraction active (f) be defined as the ratio of the cationic activity to the total cationic concentration, then in absence of disturbing factors (differing cationic hydrations, geometrical relationships to particular surfaces, multiple mechanisms, steric effects, etc.) a simple rule connects the value of the valency of the cation (z) to the valency of the cation (f) (3). If f is the fraction active with a monovalent cation then that with a polyvalent cation of valency n will be \( f_z^n \). Hence in the comparison of different surfaces characterized by \( f_{z1} \) and \( f_{zn} \) cations, the ratio of their fractions active with monovalent cations will be \( (f_{z1}/f_{zn})^n \). This ratio rapidly becomes wider as n increases. Hence differences in ionization between surfaces rapidly increase with the valency of the cation which balances the charge. This rule, of course, relates directly to ionization and not directly to coagulation, but one of the major factors in determining the zeta potential of colloidal particles and hence their coagulation is the extent of surface ionization. Thus the chances of achieving separations are much improved in the presence of polyvalent cations. The perspective afforded by this rule was, however, not attained until the experimental work was practically completed.

Cataphoresis of Hydrogen and Sodium Clays

Using the type of cell perfected by Abramson (1), we have determined the cataphoretic velocities of freshly electrodialyzed clays and of the same clays with additions of sodium hydroxide. Table 1 presents the results for comparable degrees of saturation with sodium. (In the case of halloysite two potassium figures are given, ...