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NOTES

Hydrogen bonding and polywater in clay–water systems*

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IN ORDER to explain the in-depth alteration of the properties of water by clay surfaces, one of us (Low, 1961) postulated that an ordered water structure is anchored to and propagated away from these surfaces by hydrogen bonding. However, numerous i.r. studies (Serratosa, 1960; Fripiat *et al.*, 1960; Russell and Farmer, 1964; Jorgensen, 1968) have shown that the frequency of OH stretching vibrations of water in clays tends to be higher than that of bulk water (3450 cm^{-1} and 3345 cm^{-1} for antisymmetrical stretch and symmetrical stretch, respectively). As a result, it has been concluded that the hydrogen bonds in clay-adsorbed water are weaker than those in bulk water. Despite difficulties encountered in interpreting the i.r. spectrum in the 3400 cm^{-1} region (Falk and Ford, 1966), this is a reasonable conclusion because it has been demonstrated that the frequency of OH stretching vibrations decreases with the strength of hydrogen bonding (Nakamoto *et al.*, 1955; Pimentel and McClellan, 1960; Kamb, 1968; Bellamy and Pace, 1969). However, it should not be inferred that relatively weak hydrogen bonds indicate a relatively disordered structure. The high-pressure polymorphs of ice (i.e., ice II, III, IV, V, VI, VII and VIII) have longer bonds than ice I; yet they are fully hydrogen bonded and well ordered (Kamb, 1968). Moreover, since some of these polymorphs may exist as clusters in water (Marchi and Eyring, 1964; Kamb, 1968) their enhancement by the clay surface could account for the observed increases in the frequency of OH stretching vibrations.

Although it is admitted that relatively weak hydrogen bonds exist in the water in clays, it is not admitted that relatively strong hydrogen bonds are absent. In fact, there is evidence in favor of the existence of such bonds.

For many years B. V. Deryaguin and coworkers have studied the properties of water near solid surfaces. The results of these studies have been summarized in recent articles (Deryaguin, 1966(a); Deryaguin, 1966(b); Deryagin, Churaev *et al.*, 1967; Deryaguin and Churayev, 1968). In brief, they found that glass and quartz surfaces alter the properties of water condensed from the vapor phase to depths of several microns. Their findings have been confirmed by several investigators, including Willis *et al.* (1969), Bellamy *et al.* (1969) and Lippincott *et al.* (1969). The last-named investigators found that the altered water, which has been variously called anomalous water, orthowater, superwater and polywater, has an i.r. spectrum like that of no other known substance. There was no absorption band near 3400 cm^{-1}, which is typical of normal water. Instead, there was a strong absorption band near 1595 cm^{-1} and an intense doublet in the 1400 cm^{-1} region. The band near 1595 cm^{-1} was attributed to OH stretching vibrations and the doublet in the 1400 cm^{-1} region was attributed to OH deformations. Calculations showed the length of the hydrogen bond to be about 2·3 Å and the energy to be about 60–100 kcal per water formula unit. The respective values for the bonds in normal water are 2·86 Å and 4 kcal.

Now, since this kind of strong hydrogen bond has not been recognized in water until now, it is possible that its existence in clay-adsorbed water may have gone unnoticed. Of particular importance is the observation that polywater has no OH stretching frequencies in the 3400 cm^{-1} region but that the OH stretching frequency is shifted to 1595 cm^{-1}, where it would tend to be obscured by the rather broad deformation band for ordinary water at 1645 cm^{-1}. Further, the OH deformation band of polywater at about 1400 cm^{-1} could easily be obscured by small amounts of adsorbed ammonium ion, whose deformation band occurs at 1420 cm^{-1}. An absorption band at about 1420 cm^{-1} is usually observed in the spectrum of clay–water systems. Published i.r. spectra of clay–water systems which we have been able to examine do not afford the resolution or sensitivity required for positive conclusions about the existence of polywater in these systems.

Russell and Farmer (1964), in their i.r. study of the dehydration of montmorillonite and saponite, observed that, at low hydration states, the ratio of the optical density at 3415 cm^{-1} to that at 1630–1640 cm^{-1} was low compared with the same ratio at higher hydration states. This observation is relevant because formation of water having properties similar to those of polywater could result in a shift of the OH stretching frequency from about 3400 cm^{-1} to 1600 cm^{-1} with a resulting low value for the ratio of optical densities at the two frequencies.

Lippincott *et al.* (1969) obtained their unique i.r. spectrum on polywater removed from fused quartz capillaries. When they determined the spectrum of polywater in Pyrex capillaries, they noted that some normal OH stretching absorption remained. Willis *et al.* (1969) and Bellamy *et al.* (1969) also determined the i.r. spectrum of polywater and found that the only bands present were those characteristic of normal water. Hence, it appears that the observed i.r. spectrum depends on the proportions of polywater and normal water that are present and that these proportions are governed by the underlying surface. Evidently, when the proportion of polywater is relatively small, its presence is difficult to detect in the i.r. spectrum; but it still has a profound effect

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on physical properties. These concepts should be kept in mind in considering the possible existence of polywater in clay systems.

Although our examination of the i.r. spectra of clay–water systems for evidence of polywater was inconclusive, there is indirect evidence that polywater, or a similar species of water, does exist in these systems. Consider the following points:

1. A proposed structure for polywater (Lippincott *et al.*, 1969), based on i.r. analysis, consists of a negatively charged, planar, hexagonal network of water molecules that is held together by protons or hydronium ions. NMR and other investigations of water in clays indicate that the water molecules are oriented parallel to the planar clay surfaces (Woessner and Snowden, 1969a, 1969b) and that proton dissociation is much higher than that in normal water (Ducros and Dupont, 1962; Mortland *et al.*, 1963; Touillaux *et al.*, 1968). Thus, the orientation and dissociation of water in clays are consistent with the proposed structure of polywater.
2. Polywater is birefringent (Fedyakin *et al.*, 1965; Willis *et al.*, 1969; Lippincott *et al.*, 1969). So is the water associated with clay (Derjaguin and Greene-Kelly, 1964).
3. The thermal expansion of polywater is different from that of normal water (Fedyakin, 1962; Deryagin *et al.*, 1966; Schufle and Venugopalan, 1967; Willis *et al.*, 1969). It has a lower temperature of maximum density and a greater coefficient of thermal expansion above this temperature. The same is true of water in clays (Clementz, 1969).
4. Polywater is more viscous than normal water (Deryagin and Fedyakin, 1962; Derjaguin, 1966b). The water in clay systems is also more viscous than normal water (Rosenqvist, 1955; Low, 1960; Kemper *et al.*, 1964; Low, 1968).
5. Polywater has a yield value (Deryagin and Fedyakin, 1962; Bazaron *et al.*, 1966). A yield value has also been found for water in clays (Oakes, 1960; Miller and Low, 1963; Li, 1963).
6. Polywater has a lower vapor pressure than normal water (Derjaguin, Fedjakin *et al.*, 1967). As indicated by numerous published adsorption isotherms, this is the case for water in clays as well. The reduced vapor pressure of water in clays is generally ascribed to the osmotic activity of exchangeable cations. But it could also be due, at least partly, to structural modifications.
7. Polywater freezes at a relatively low temperature (Deryagin, Churaev *et al.*, 1967; Anisimova *et al.*, 1967), as does some of the water in clay systems (e.g., Anderson and Hoekstra, 1965; Low *et al.*, 1968; Anderson, 1968). It appears that interaction of the water with the particle surfaces is a significant factor in preventing freezing in these systems (Buehrer and Rose, 1943; Kolaian and Low, 1963).
8. Some polywater remains in open capillaries at a temperature as high as 320°C (Willis *et al.*, 1969). Adsorbed water remains in clays at this temperature (Fripiat *et al.*, 1960). Since ions dehydrate at much lower temperatures, this adsorbed water cannot be attributed to the hydration of exchangeable cations.
9. Polywater is best prepared by condensation in *dry* capillaries at reduced vapor pressures (Anisimova *et al.*, 1967). It does not form to a measurable extent when the capillary is first wet inside with a film of normal water (Deryagin *et al.*, 1965; Bellamy *et al.*, 1969). When *dry* clays are exposed to water vapor, they will adsorb water until their 001 spacing is 19–20 Å (e.g., Foster *et al.*, 1955; Emerson, 1962). However, when they are brought in contact with liquid water, they will adsorb it until their 001 spacing far exceeds this value. This suggests that the water adsorbed by clays from the vapor phase, like that adsorbed by capillaries from the vapor phase, is different than water adsorbed from the liquid phase.

The only measured property of polywater and clay-adsorbed water that does not deviate from that of normal water in the same way is the density. The density of polywater is 1–1·4, depending on its purity (Deryaguin and Churayev, 1968; Lippincott *et al.*, 1969), whereas the density of clay-adsorbed water is $<1{\cdot}0$ (Anderson and Low, 1958; Bradley, 1959; Davey and Low, 1968). The difference in density may be accounted for by structural vacancies, imperfections, etc., that are present in the clay-adsorbed water as a result of its interaction with either exchangeable cations or the surface oxygens of the clay (which are arranged differently than those of Pyrex and quartz). Or it may be due to the presence in the clay-adsorbed water of less-dense species, e.g., clathrate-like species. However, these explanations are only tentative.

As already noted, we have not found conclusive evidence for the presence of polywater in clays by examining published i.r. spectra. Nevertheless, we submit in Fig. 1 i.r. evidence for stronger hydrogen bonds in clay–water systems than have previously been detected. The spectra shown are differential spectra obtained by using matched films of hydrogen-saturated specimens of an expanded muscovite (Bronson *et al.*, 1960). The spectrum (C), obtained by placing the film heated to 300°C in the reference beam and the air-dry film in the sample beam, indicates that there are absorption bands ranging in frequency from 3620 cm^{-1} down to about 1940 cm^{-1}. Assuming that the shoulder at about 3470 cm^{-1} is due to strong absorption by a perturbed OH in the heated specimen in the reference beam, there are six absorption maxima that may be attributed to OH stretching of interlayer water molecules. These occur at 3620, 3350, 3220, 2900 (small peaks at 2920 and 2850 cm^{-1} are probably due to C–H stretching of contaminating hydrocarbon), 2460 and 1940 cm^{-1}. On the basis of the relationships between O–O distance and OH stretching frequency given by Nakamoto *et al.* (1955), these frequencies correspond to the following O—O distances: 3·10 Å (3620), 2·80 Å (3350), 2·76 Å (3220), 2·69 Å (2900), 2·60 Å (2460), and 2·47 Å (1940 cm^{-1}).

In view of the foregoing discussion, it is proposed that previous conclusions regarding the state of hydrogen bonding in clay–water systems be accepted with reservation. Further, it is proposed that additional i.r. studies of water in clays be undertaken for the purpose of elucidating the kinds of hydrogen bonds that exist therein.

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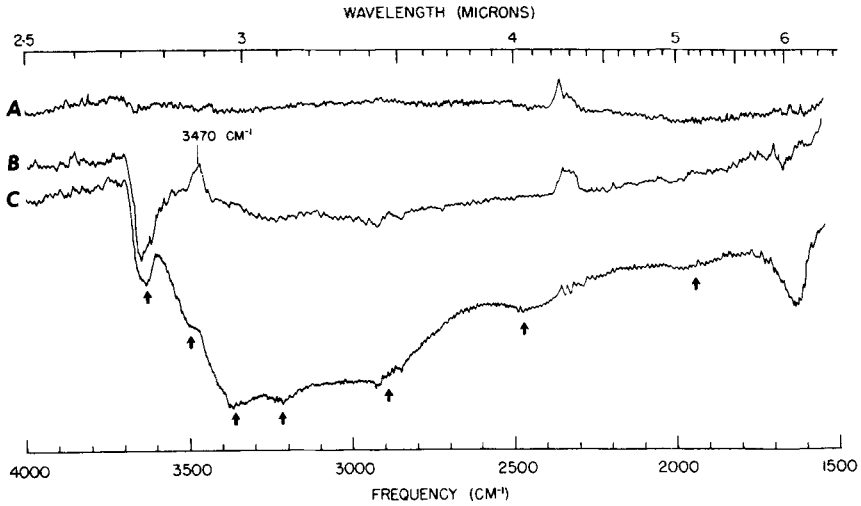


Fig. 1. Differential i.r. spectra of lithium nitrate treated muscovite after hydrogen saturation. A—Matched specimens in air-dry state; B—specimen in reference beam heated to 300°C, specimen in sample beam heated to 160°C; C—specimen in reference beam heated to 300°C, specimen in sample beam in air-dry state. Arrows indicate significant OH stretching bands for adsorbed water on air-dry mica.

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