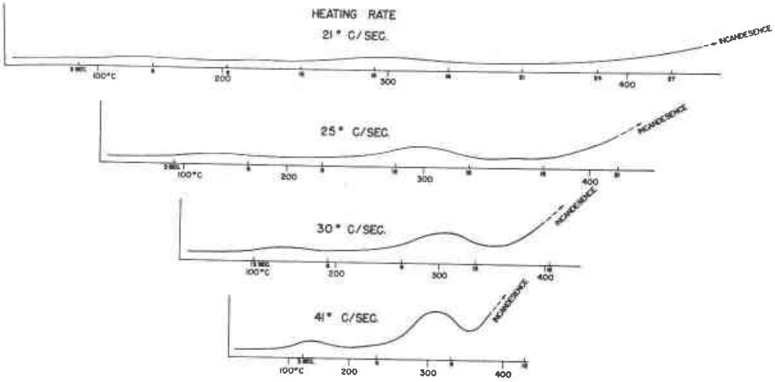

FIG. 3. Resolution of low level thermoluminescence in NaCl by fast heating.

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THE AMERICAN MINERALOGIST, VOL. 46, MARCH-APRIL, 1961

ADSORPTION OF ETHYLENE GLYCOL AND GLYCEROL BY MONTMORILLONITE*

(Clay-Organic Studies, Part V†)

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The swelling of montmorillonite immersed in ethylene glycol or in glycerol has been used for many years to identify montmorillonite in

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† Part IV. See Hoffmann and Brindley (1961).

mixtures of clay minerals. It is sometimes believed that montmorillonite has an 'affinity' for these compounds such that they are strongly absorbed from aqueous solutions. The present note describes measurements which show that they are not preferentially absorbed from aqueous solutions to any appreciable extent.

In previous work (Brindley and Rustom, 1958, and more particularly, Hoffmann and Brindley, 1960) isotherms for the adsorption of a variety of non-ionic organic compounds of Ca-montmorillonite from aqueous solutions have been determined to study the features of the organic molecule which affect the adsorption. Two factors were found to affect the adsorption equilibria in solution: chain-length and CH-activity. For molecules with small CH-activity, a minimum chain-length of about 6 carbon atoms is required for preferential adsorption and on this basis neither ethyleneglycol nor glycerol would be expected to show preferential adsorption.

Experiments have been made to determine the adsorption isotherms of ethylene glycol and glycerol on Mg-montmorillonite from aqueous solutions. The Mg-saturated clay was used because it was immediately available and other studies (Brindley, Hoffmann and Bender, 1960) had shown that for several substances the exchangeable inorganic cation has no significant influence on the organic adsorption, at least for the ions Na^+, Ca^{2+}, and Mg^{2+}.

Suspensions containing 15 mg. clay per ml. and ethylene glycol or glycerol in concentrations varying from 2.5×10^{-2} to 50×10^{-2} molar were equilibrated for 20 hr. After centrifuging for 2 hr., the organic content of the supernatant liquid was determined by dichromate oxidation. For neither compound could any depletion in concentration be detected except for small variations within the accuracy of the analytical determinations ($\pm1\%$). Therefore these compounds do not show any preferential adsorption from aqueous solutions on montmorillonite.

Part of the clay paste remaining in the centrifuge tubes was taken with a minimum of adherent liquid and allowed to dry on glass slides. The clay-organic films were then examined in a stream of dry air by *x*-ray diffraction using a Phillips Norelco diffractometer with filtered CuKα radiation. The results showed that complexes were formed containing one layer of water, one layer of organic material, two layers of organic material, or mixtures thereof according to the organic concentration of the adherent solution in the initial clay paste.

The spacings for the one- and two-layer organic complexes are $13.9_0 \pm 0.1$ Å and $16.8_5 \pm 0.1$ Å for ethylene glycol, $13.9_5 \pm 0.1$ Å and $17.7_5 \pm 0.1$ Å for glycerol respectively, and $11.9_5 \pm 0.0_5$ Å for a single water layer.

It has been pointed out already (Hoffmann and Brindley, 1960) that the type of complex formed after drying a clay-water-organic mixture does not depend so much on the adsorption equilibria existing in aqueous solution as on the relation of the volatility of the organic compound to that of water. Among the substances investigated, two extremes have been found:

(i) Substances with high volatility may be adsorbed strongly from aqueous solutions under equilibrium conditions, but may not form complexes on drying as both the water and the organic substance evaporate.

(ii) Substances with low volatility which show little or no adsorption from aqueous solution, may still form complexes on drying because the water evaporates leaving the clay and organic material behind.

The second mechanism has already been proposed by Bradley (1945) who suggested that ethylene glycol may form complexes with montmorillonite by replacement of the adsorbed water due to their difference in volatility. This is now confirmed experimentally. Ethylene glycol and glycerol belong to the second group since they show no preferential adsorption from aqueous solution under equilibrium conditions but form complexes after drying due to their low volatility compared with that of water.

Grateful acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this reasearch.

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