Clays and Clay Minerals, Vol. 44, No. 6, 727–733, 1996.

PARTITIONING OF BINARY SOLVENTS ON CHARGED EXPANDABLE CLAYS

JOSEPH R. FELDKAMP[1] AND THOMAS B. STAUFFER[2]

[1] 331 E. Barbarita Avenue, Gilbert, Arizona 85234

[2] Armstrong Laboratory, Environmental Research Division, 139 Barnes Drive, Suite 2, Tyndall AFB, Florida 32403

Abstract—The present paper represents an extension of recent work that considered the partitioning response of binary solvents placed into contact with charged, expandable clays. Previous theoretical work yielded a model of partitioning by performing a thermodynamic analysis, involving the work of polarization, on a binary solvent, treated as a continuum and residing within the interlayer space of a layered aluminosilicate clay. Partitioning, or the tendency for sorbed and bulk phases to have different compositions, was shown to be sensitive to the dielectric properties of the 2 solvents of the binary mixture and to the surface charge density on the clay, among other factors. Although previous experimental work has helped to validate the theory, additional work is reported here that looks at hysteresis effects, the role of the exchangeable cation (usually organic), the prediction of adsorption isotherms and the contribution that partitioning, or sorption, makes to the disjoining pressure that develops in binary solvent systems. In this current study, 3 different organo-clays were considered: Cetyltrimethylammonium (CTMA), Isopropanolammonium (IPA), and Benzylammonium (BA) montmorillonite. Solvent systems under study included: acetone/chloroform (a-c), acetone/quadricyclane (a-q) and acetonitrile/chloroform (an-c). While partitioning of the a-c system on CTMA-clay follows theory quite well, theory tends to over-predict partitioning for the a-q system on the same clay and under-predict partitioning for the an-c system on all clays. Predicted adsorption isotherms range from highly nonlinear to nearly linear. Finally, the delamination and subsequent swelling processes of BA-clay in a water/acetonitrile binary solvent system are very sensitive to composition, a result that is directly linked to the partitioning process.

Key Words—Clays, Isotherms, Partitioning, Solvents, Swelling.

INTRODUCTION

Whenever a binary solvent, defined herein as a 2-component solution of fully miscible solvents, is placed into contact with clay, the solvent having a greater affinity for the surface will experience some measure of enrichment at the interface while that with lesser affinity will be depleted. That is, sorbed phase and bulk phase compositions are caused to differ. Such processes are usually treated empirically through determination of the adsorption isotherm and then fitting the results to some model equation. Finally, an attempt is then made to understand the molecular basis for the observed solvent-surface interaction by comparing the ability of various model equations to fit the data.

For a clay having little or no surface charge, preferential adsorption of one solvent over the other usually proceeds via differences in the polarizability of the 2 substances. If the 2 components of the solution tend to form a highly non-ideal solution and perhaps are not fully miscible, such as with benzene and water, then the interactions between solution constituents may dominate the adsorption process.

When clays bear a significant surface charge, as with the smectites, the preferential adsorption of one solvent from the mixture can be heavily governed by the magnitudes of the solvent dielectric constants. In particular, it was shown (Feldkamp and Stauffer 1994a, 1994b) that whenever dielectric constants for the 2 solvents are widely separated or whenever both dielectric constants are small, but different, partitioning or preferential adsorption of the more polar component results. Considering only energetics, the component of greater polarity would tend to reside exclusively in the sorbed phase, with the nonpolar substance rejected completely. Allowing for the mutual miscibility of the 2 solvents, that is, entropic effects, some amount of the nonpolar constituent will dissolve into the polar sorbed component. The actual sorbed phase (interlayer) composition may be determined by including the work of polarization of the sorbed phase into the First Law of Thermodynamics and then proceeding as described by Feldkamp and Stauffer (1994a). Let x_p^f and x_p^i represent the final and initial mole fractions of the more polar component in the sorbed phase, with the former corresponding to the fully charged state of the clay and the latter to the fully discharged condition. The partitioning response, $x_p^f - x_p^i$, is obtained from:

$$\int_{x_p^i}^{x_p^f} \left(\frac{RT}{x_p x_n} - 2A \right) \frac{K^2}{\bar{v}(dK/dx_p)} dx_p = \frac{\sigma_o^2}{2\epsilon_o} \qquad [1]$$

Symbols have the following familiar meanings: R = universal gas constant; T = absolute temperature; x_p = mole fraction of polar component; x_n = mole fraction of nonpolar component; K = dielectric constant of interlayer liquid; σ_o = surface charge density; ϵ_o = permittivity of vaccum; and $\bar{v}$ = total molar volume.

Copyright © 1996, The Clay Minerals Society

https://doi.org/10.1346/CCMN.1996.0440602 Published online by Cambridge University Press

The empirical parameter A comes from regular solution theory and links the activity coefficient γ_i to its associated mole fraction x_i by the relation:

$$\ln(\gamma_i) = \frac{A}{RT}(1 - x_i)^2 \quad [2]$$

Note from Equation [1] the sensitivity to both the dielectric constant and the surface charge density (each is squared). In the absence of surface charge or in the event that the dielectric constant is essentially independent of composition, no partitioning results so that $x_p^f = x_p^i$. The dielectric constant plays somewhat of a competing role with itself in the integrand of Equation [1]. Considering K in the numerator, a small K is desirable for promoting partitioning inasmuch as the limits of integration are then forced to be farther apart. In the denominator, however, a small K could possibly imply that K is not very sensitive to composition, a condition not conducive to partitioning. Equation [1] treats the binary solvent solution as a nonideal classical liquid continuum, with activity coefficients modeled by regular solution theory. Alternative activity coefficient models may be incorporated into the present theory, should regular solution theory prove inadequate. Though the integration in Equation [1] is readily carried out under certain circumstances, an explicit solution for x_p^f in terms of x_p^i is still not possible and a numerical solution is required. Details concerning integration are available from the authors upon request.

A very substantial side-effect of a partitioning response can be the generation of a significant contribution to the disjoining pressure, which would tend to de-laminate and thus swell the smectite clay. This mechanical effect may occur even in cases where partitioning has resulted from dispersion forces alone. An "adsorption contribution" to the disjoining pressure seems to have been first recognized by Derjaguin (1978) who had concluded that "disperse systems may be stabilized in the presence of binary, nonionic solutions". Furthermore, his analysis of the problem had included only adsorption due to classical dispersion forces, that is, those forces that derive from induced dipoles. The presently described partitioning ultimately originates from ion-dipole forces and perhaps represents a more important component of Derjaguin's "adsorption disjoining pressure" when an electrical double layer is associated with the surface.

The theory leading to Equation [1] was tested by directly measuring the sorbed phase composition on an organo-clay using Fourier transform infrared spectroscopy (FTIR) (Feldkamp and Stauffer 1994b). The exchange of quaternary ammonium ions for the naturally occurring sodium ions was employed so as to facilitate the exclusion of water from the surface. Thus, true nonaqueous systems were studied. Here we report on partitioning behavior on clays bearing different types of exchanged cations. Furthermore, we will consider hysteresis effects in the partitioning response, the nature of adsorption isotherms calculated from Equation [1] and, finally, a brief look at the mechanical effects of binary solutions on the dispersion processes alluded to in the previous paragraph.

EXPERIMENTAL

Organo-Clay Complexes

Organo-clay complexes were prepared using 3 different organic cations: 1) Cetyltrimethylammonium (CTMA) or Hexadecyltrimethylammonium; 2) Isopropanolammonium (IPA); and 3) Benzylammonium (BA). The raw sodium exchanged clay was not used in experiments due to its tenacity for binding water which would necessarily require that water be 1 of the 2 solvents of the binary solvent solution. All organo-clay materials were prepared from a sodium montmorillonite clay, which originated from Crook County, Wyoming (Swy-1, obtained from the Clay Minerals Society). Organo-clay complexes were prepared by dispersing 15 g of the sodium clay in 0.5 L of distilled water and subsequently washing 6 times with 16 mL (96 mL total) of an aqueous organo-ammonium chloride salt solution (0.75 equiv/L, CTMA-chloride was supplied as a 25 wt% aqueous solution). Resuspension volume was 125 mL, with additional volume made up with distilled water. Resulting suspensions were washed 3 times with distilled water and then 3 times with denatured ethanol. In the case of the CTMA-clay, the suspension was subsequently washed twice in toluene. This last step facilitated the formation of very even, air-dried films on infrared (IR) transparent windows.

Mounting of Clay Films

Thin films of organo-clay were deposited on ZnSe windows as described in Feldkamp and Stauffer (1994b). This reference should be consulted for details of film preparation and processing prior to FTIR examination.

Clay Film-Vapor Experiments

Deposited clay films were exposed to the vapor phase above a binary solvent solution as described in Feldkamp and Stauffer (1994b). Since all 3 phases (clay film, vapor and liquid) are in equilibrium with each other, the chemical potential of each component is the same in each phase. As made clear in the theory, which has been developed in the context of liquid phase compositions, this condition completely obviates the need for worry about differences in composition between vapor and liquid phases. The vapor phase is merely an intermediary system that brings liquid and clay into chemical contact. Subsequent to an exposure time of approximately 1 h, the clay film

https://doi.org/10.1346/CCMN.1996.0440602 Published online by Cambridge University Press

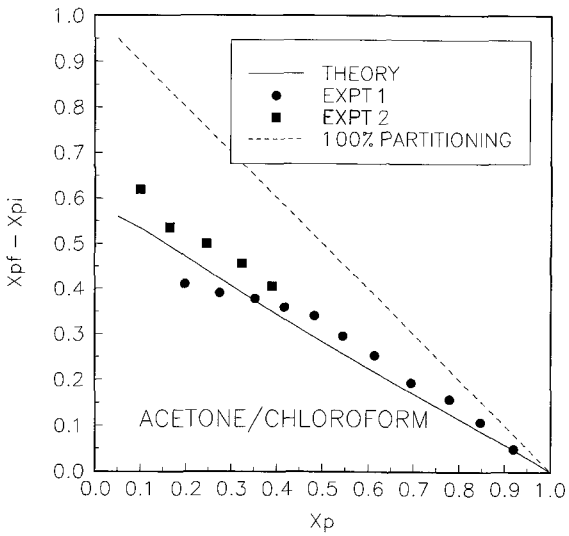


Figure 1. Partitioning of acetone/chloroform on CTMA-clay.

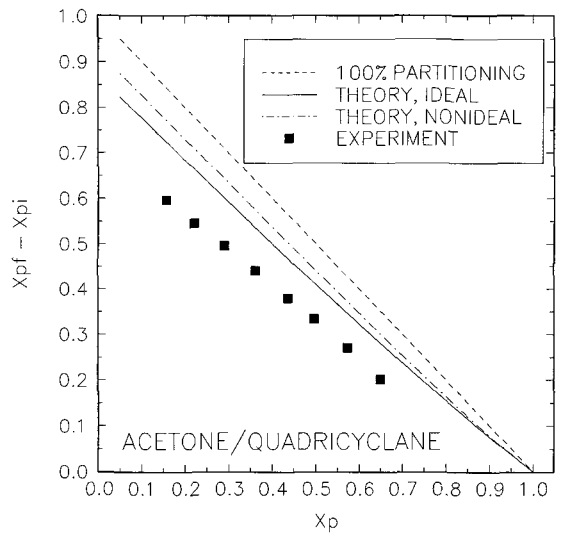


Figure 2. Partitioning of acetone/quadricyclane on CTMA-clay.

was subjected to IR examination at selected wavenumbers to determine sorbed phase composition. The determination of the sorbed phase composition required a knowledge of the ratio of molar extinction coefficients for the 2 solvents in the sorbed phase. This ratio was assumed to be identical to that measured in either pentane or toluene. For acetone at 1722 cm^{-1} and chloroform at 762 cm^{-1}, the ratio of molar extinction coefficients was determined to be 0.274 (acetone:chloroform). For acetone, again at 1722 cm^{-1}, and quadricyclane at 766 cm^{-1}, the molar extinction coefficient ratio was 1.12 (acetone:quadricyclane). Finally, the ratio of the molar extinction coefficient for chloroform at 762 cm^{-1} to that for acetonitrile at 2253 cm^{-1} was found to be 53.0.

FTIR Spectra

Infrared spectra of clay films and solvent mixtures were obtained using a Nicolet Model 740 FTIR spectrometer equipped with a liquid N_2 cooled mercury cadium telluride detector. Each spectrum was obtained as the average of 128 scans at a resolution of 2 cm^{-1}. Spectral subtraction was implemented by using the untreated, evacuated clay film as reference. If necessary, base line correction was employed to help isolate the desired peaks from the absorbance spectrum. Measured absorbances, together with the molar extinction coefficient ratios, were then used to compute the mole fraction of the sorbed phase on the clay film.

RESULTS AND DISCUSSION

Effects of Exchange Ions on Partitioning

Figure 1 illustrates the partitioning response observed for an acetone/chloroform binary solvent system over a CTMA-clay. The degree of partitioning is represented on the ordinate as the excess mole fraction of the polar component in the sorbed phase while the horizontal axis gives the corresponding mole fraction of the polar component in the liquid phase. If partitioning did not occur, then the experimental data would fall on the horizontal axis. At the other extreme, that is, 100% partitioning, acetone alone would reside in the interlayer space and the data would be expected to fall on the dashed line which runs diagonally from upper left to lower right. The theoretically expected behavior is given by the solid curve ($A = -2.0$ kJ mol^{-1} and $\sigma_o = 0.12$ C/m^2). Experimental data and theory agree reasonably well in this case. Two sets of experimental data appear in Figure 1. Set 1, indicated by solid circles, was obtained by progressively increasing the mole fraction of acetone in the external solution from approximately 0.20 to 0.92. Subsequent to exposing the clay film to the vapor phase of such a series of solutions, the clay film was re-exposed to a second series of solutions with progressive increase in the acetone mole fraction starting from approximately 0.10 (solid squares). The new curve does not retrace its original path until the mole fraction is approximately 0.50. Though hysteresis is clearly indicated, the origin of the behavior is not at all apparent without the benefit of additional data, such as interlayer spacing as a function of composition.

The partitioning behavior of acetone/quadricyclane solutions over a CTMA clay film is shown in Figure 2. In this example, theory over-predicts the extent of partitioning regardless of whether or not the solution is treated as ideal or real ($A = 2.0$ kJ mol^{-1}). This contrasts with the behavior observed in Figure 1, where theory slightly under-predicts the partitioning response. Agreement between theory and experiment

https://doi.org/10.1346/CCMN.1996.0440602 Published online by Cambridge University Press

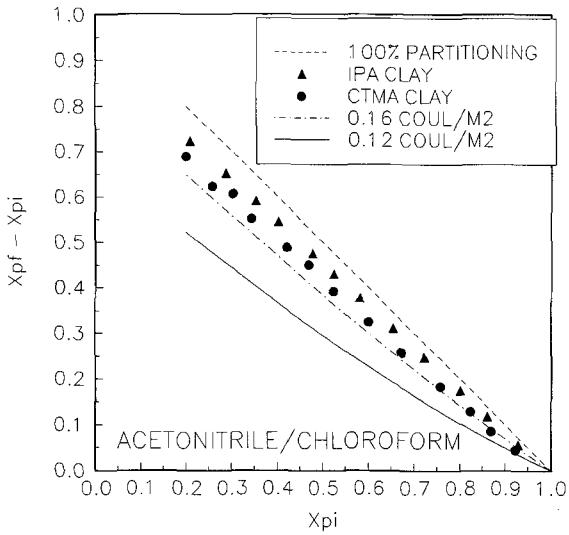


Figure 3. Partitioning of acetonitrile/chloroform on IPA-clay and CTMA-clay.

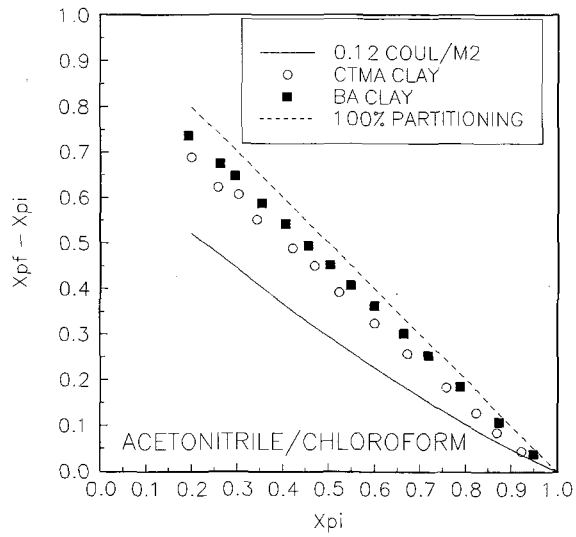


Figure 4. Partitioning of acetonitrile/chloroform on BA-clay and CTMA-clay.

in Figure 2 could be improved by making A negative, but such values for A are not reasonable, implying that intermolecular interactions between solvents could not explain our observations. Since acetone, the polar constituent, is common to both systems, the different behaviors implied by Figures 1 and 2 must result from specific differences in the way that the 2 nonpolar components, chloroform and quadricyclane, interact with the surface or its exchange ions. There appears to be some feature of the quadricyclane molecule, perhaps its size or shape, that permits it to be more compatible with the sorbed phase than chloroform.

Agreement between theory and experiment for acetonitrile/chloroform systems ($A = 0.0$) over various clays, as indicated in Figures 3 and 4, is rather poor when compared to the previous results of Figures 1 and 2. Theory substantially underestimates the degree of partitioning, regardless of the nature of the exchangeable cation on the clay surface. Noting that the acetone/chloroform system behaved essentially in agreement with theory, the under-prediction by theory must be due to specific differences in the way that acetonitrile and acetone interact with the clay surface rather than any peculiar behavior exhibited by chloroform which is common to both systems. The smaller size and linear geometry of acetonitrile, relative to acetone, probably permit a more intimate interaction with exchange ions, allowing it to reside in regions of higher electric field strength. To test that suggestion and to more fully appreciate the differences between theory and experiment in Figures 3 and 4, the theoretical curve obtained by increasing the surface charge density by ⅓ is shown in Figure 3. The improved agreement between experimental data and the recalculated theory curve lends credence to the idea that the smaller size of acetonitrile permits it to reside in higher-field locations.

Both IPA-montmorillonite and BA-montmorillonite partition the acetonitrile/chloroform solvent system slightly more than CTMA-montmorillonite clay. Differences between the CTMA clay and the other two may be due to the presence of trace amounts of water on the IPA and BA clay surfaces, measured by IR.

Relation of Partitioning to Adsorption Isotherms

To state that sorbed phase and bulk liquid phase have different compositions is entirely equivalent to saying that one or the other of the 2 components has been preferentially adsorbed. This subsection illustrates that equivalence, or relation between the 2 concepts. If the volume of the sorbed phase per g of sorbent, V_s, is known, it is possible in principle to calculate the adsorption isotherm from Equation [1]. The molar excess of the more polar component is given by:

$$n_p^{exc} = V_s\left(\frac{x_p^f}{\bar{v}^f} - \frac{x_p^i}{\bar{v}^i}\right) \qquad [3]$$

Initial and final total molar volumes, $\bar{v}^i$ and $\bar{v}^f$, are indicated by superscripts. Dividing Equation [3] by the surface area per g of the sorbent gives the moles of polar component adsorbed per unit area. The quantity in parentheses in Equation [3] is readily obtained from Equation [1], while V_s must be approximated. For a sodium montmorillonite, the N_2 surface area is approximately 32.0 $m^2\ g^{-1}$, while the water-vapor surface area ranges from about 140 to 200 $m^2\ g^{-1}$, depending upon whether adsorption or desorption is used (Grim 1968). Using 80.0 $m^2\ g^{-1}$ as the surface area for the organo-clays of the current study and 0.5 nm as the sorbed layer thickness (1.0 nm interlayer gap dis-

https://doi.org/10.1346/CCMN.1996.0440602 Published online by Cambridge University Press

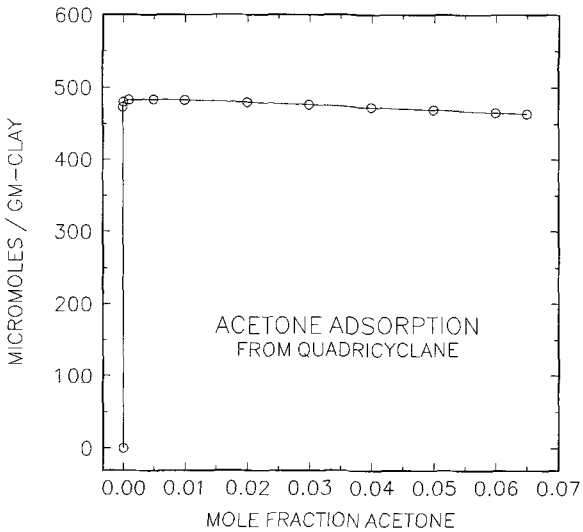


Figure 5. Computed adsorption isotherm for acetone in quadricyclane.

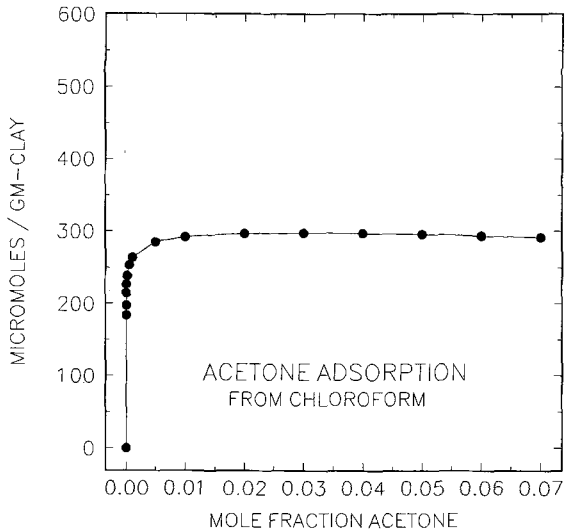


Figure 6. Computed adsorption isotherm for acetone in chloroform.

tance), V_s was calculated as the product of the two. With such an approximation in hand, the adsorption isotherms for the acetone/quadricyclane and acetone/chloroform systems were calculated. These isotherms, applicable to any of the clays, are shown in Figures 5 and 6, with the same V_s being used in either case. Notice that the isotherms are extremely nonlinear, a result of substantial partitioning in either system. Therefore, regardless of the mole fraction of acetone in the bulk phase, the mole fraction of acetone in the sorbed phase climbs to very high values.

The plateau region for acetone adsorption from quadricyclane is predicted to be about 50% higher than that for acetone adsorption from chloroform. Attempts were made to experimentally determine the location of the 2 adsorption isotherm plateaus by analyzing a series of batch adsorption isotherm experiments for acetone mole fractions ranging from approximately 0.01 to 0.06 on CTMA-clay. The experimental value of the plateau adsorption for the acetone/quadricyclane system is 428 ± 62 $\mu M\ g^{-1}$ clay while that for the acetone/chloroform system was 473 ± 187 $\mu M\ g^{-1}$ clay. The former exhibits good agreement with theory while agreement is somewhat poorer for the case of acetone adsorption from chloroform.

The highly nonlinear behavior shown in Figure 6 is not always predicted from the model. Within other systems, it is quite common that linear or near-linear adsorption isotherms are predicted. As an example, the adsorption isotherm for the acetonitrile/acetone system was calculated at 2 different surface charge densities, 0.117 C/m^2 and 0.160 C/m^2. The V_s value previously used in Figures 5 and 6 was used once again. As is readily observed in Figure 7, the adsorption of acetonitrile increases nearly linearly with mole fraction. In this case, doubling the surface charge density (squared) essentially doubles the adsorption. Hence, a comparison with the behavior depicted by Figures 5 and 6 shows that a wide range of adsorption behavior may be predicted, depending of course, upon material properties.

Effects of Partitioning on Dispersion

Finally, an experiment was performed to examine the impact of partitioning on the colloidal dispersion process. A 0.5-g sample of benzylammonium clay (BA-clay) was placed into each of 6 glass tubes. The composition of the binary solvent medium, water/acetonitrile, was varied in each of the tubes, ranging from

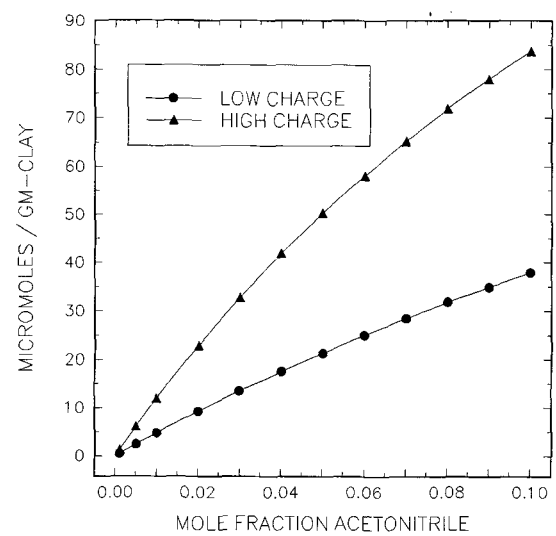


Figure 7. Computed adsorption isotherm for acetonitrile in acetone.

https://doi.org/10.1346/CCMN.1996.0440602 Published online by Cambridge University Press

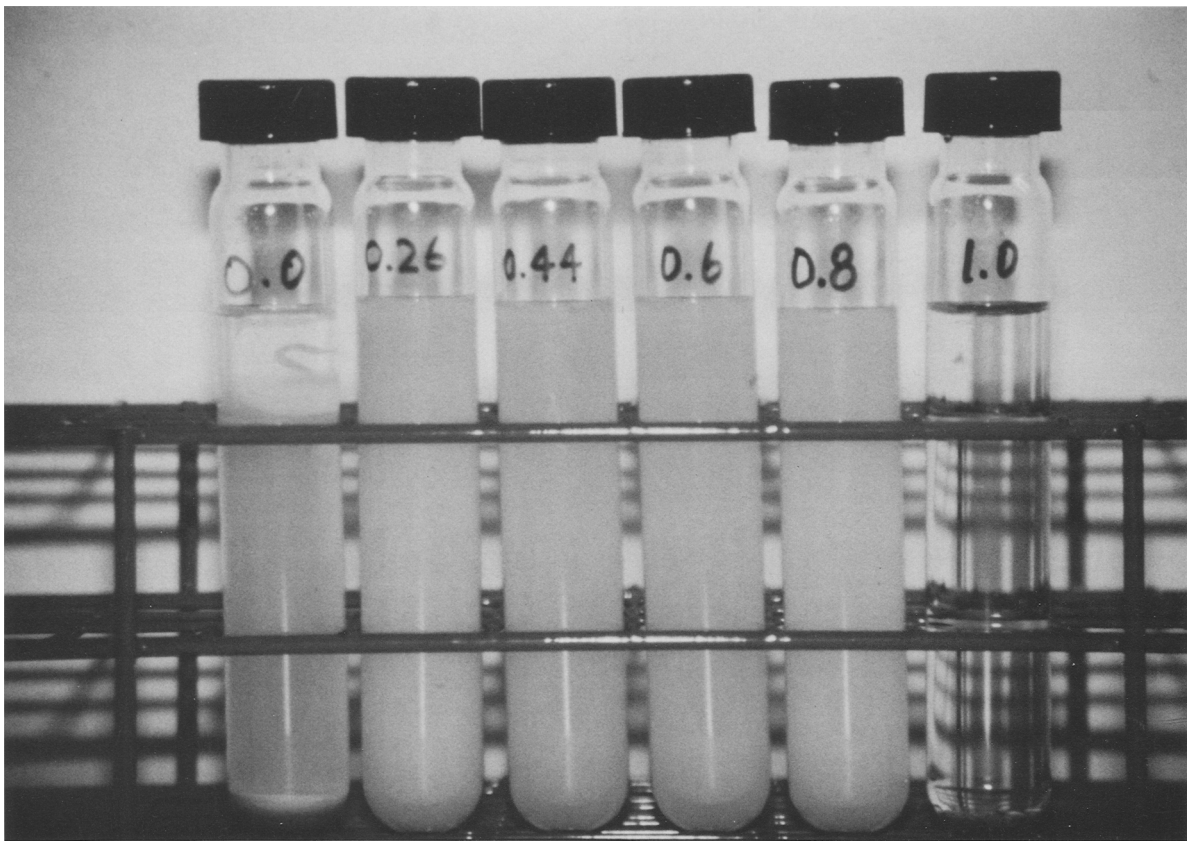


Figure 8. Benzylammonium-montmorillonite dispersed in binary mixtures prepared from water and acetonitrile. The numbers on the tubes indicate the mole fraction of water. The tubes were photographed 48 h after initial mixing.

pure acetonitrile to pure water. IR examination indicated that water was not completely removed from the BA-clay so that, in reality, the "pure-acetonitrile" tube contained trace water. Figure 8 shows the condition of the clay dispersions after 48 h and clearly indicates that an adsorption contribution to the disjoining pressure exists as described by Derjaguin (1978) and Derjaguin and Churaev (1977). The physical mechanism is quite simple. A partitioning response occurs as described by Equation [1], followed by the development of an added contribution to the osmotic swelling pressure. The latter results by virtue of the difference in composition between sorbed and bulk phases. The dispersions undergo self-weight consolidation until equilibrium gel volumes are attained in about 3 months, as illustrated in Figure 9. No additional change was observed over a 1-y period.

Other experiments, similar to the one just described, were performed by Jordan (1949) many years ago using organic solvents only. As a consequence, the more polar solvent, usually an alcohol, was viewed or considered as a dispersant, in the same fashion as traditional surfactants. This unfortunate choice of terminology perhaps thwarted a proper understanding of the mechanism responsible for the observed swelling in nonaqueous solvent media. For the systems shown in Figures 8 and 9, the terminology of older literature would have us regard water as a dispersant in much the same way as surfactants have been considered as dispersants. There is, of course, nothing about the molecular geometry of water to suggest that it bears any resemblance to traditional surfactants or dispersants.

The adsorption contribution to the swelling pressure, dramatically depicted in Figures 8 and 9, may lead to potentially important mechanical side-effects in compacted clayey materials such as clay liners. Sometimes clay liners are legally required to retard the passage of solvent mixtures from hazardous waste sites to groundwater. In spite of their low hydraulic conductivity, liquids will eventually pass through the clay liner so that, after long-term leaching has occurred, the composition of the solvent that contacts the clay may change substantially. In view of the behavioral changes in dispersion that are demonstrated in Figures 8 and 9, significant changes in the shear strength of the clay liner can also be reasonably expected. Obviously, the propensity for such events to occur should be thoroughly investigated before implementing a clay liner system to retain multicomponent solvents.

https://doi.org/10.1346/CCMN.1996.0440602 Published online by Cambridge University Press

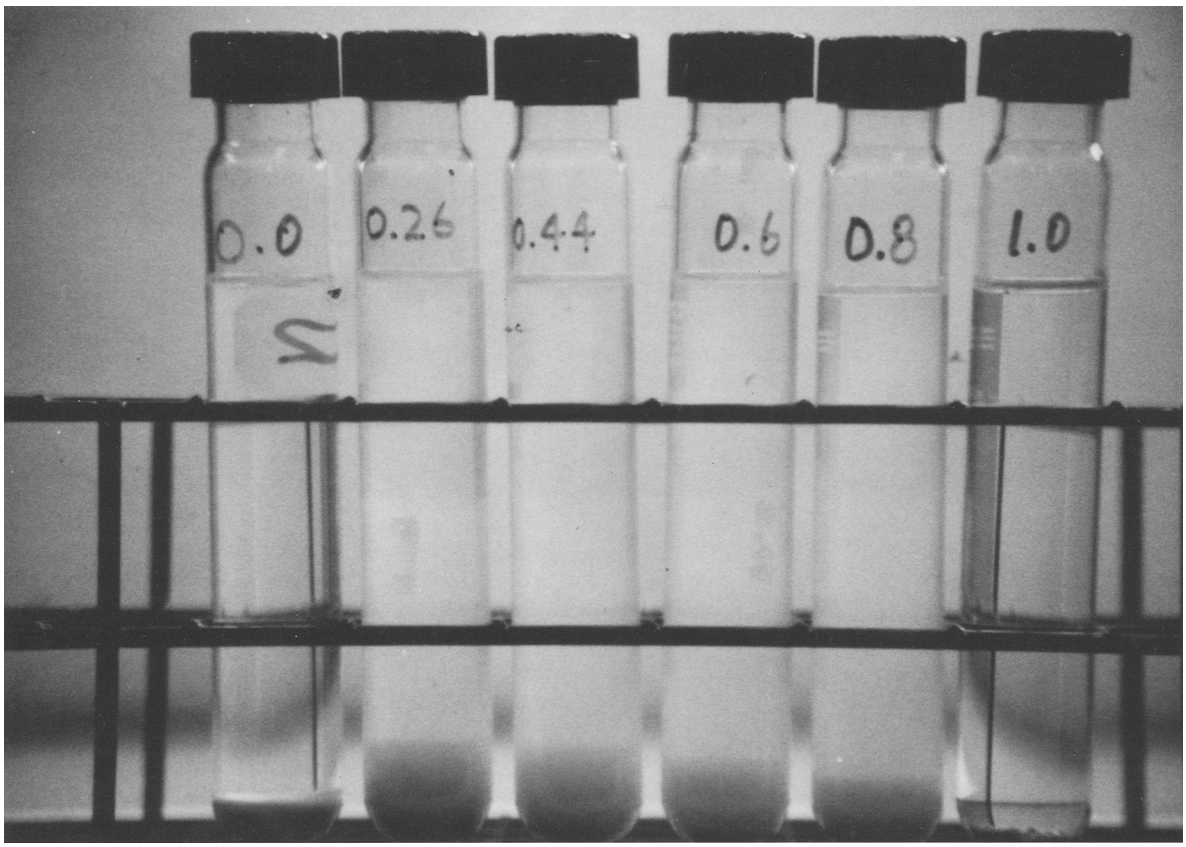


Figure 9. Benzylammonium-montmorillonite dispersed in binary mixtures prepared from water and acetonitrile. The numbers on the tubes indicate the mole fraction of water. The tubes were photographed 3 mo after initial mixing.

SUMMARY

Previous theoretical work intended to describe the degree of partitioning of a mutually miscible 2-component solution, or more simply, binary solvent, placed into contact with a charged, expandable clay was more rigorously evaluated than before. The theory certainly gives qualitatively correct predictions of the excess mole fraction of the polar component in the interlayer space and, in some cases, predictions are quantitative. Where there is substantial disagreement between theory and experiment, specific interactions between either polar or nonpolar components and the surface or exchange ions must be occurring above and beyond that which is accounted for by a continuum thermodynamic analysis that includes the work of polarization in the First Law.

The theory is shown to be useful in calculating adsorption isotherms, inasmuch as the partitioning process defined herein is equivalent. Predicted isotherms range from nearly linear to highly nonlinear. Furthermore, the partitioning response predicted by the theory over the full composition range is very useful in explaining, if not qualifying, the "adsorption contribution" made to the disjoining pressure, which has an enormous consequence for the dispersion of charged clays in binary solvent media.

ACKNOWLEDGMENT

Funding for this research was provided by the US Air Force Office of Scientific Research.

REFERENCES

Derjaguin BV. 1978. Some new aspects and of conclusions on theory of stability of colloids and their experimental verification. J Faraday Discuss Chem Soc N65:306–312.

Derjaguin BV, Churaev NV. 1977. Disjoining pressure of thin layers of binary solutions. J Colloid Interface Sci 62(3):369–380.

Feldkamp JR, Stauffer TB. 1994a. Interactions of binary solvents with charged expandable clays. 1. Theory. J Phys Chem 98(51):13594–13600.

Feldkamp JR, Stauffer TB. 1994b. Interactions of binary solvents with charged expandable clays. 2. Experiment. J Phys Chem 98(51):13601–13606.

Jordan JW. 1949. Organophilic bentonites, I: Swelling in organic liquids. J Phys Colloid Chem 53:294–306.

Grim RE. 1968. Clay Mineralogy. 2nd ed. New York: McGraw-Hill. 265 p.

(Received 27 July 1995; accepted 12 January 1996; Ms. 2673)

https://doi.org/10.1346/CCMN.1996.0440602 Published online by Cambridge University Press