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SOLVATION METHODS FOR EXPANDABLE LAYERS

Key Words—Ethylene glycol, Expansion, Glycerol, Smectite, Solvation.

The variability in expansion of layer silicates that occurs with water can be reduced with organic solvation. MacEwan and Wilson (1980) succinctly stated the case—"To be of use in identification, organic complexes should be readily formed from hydrated clay, should be stable, and should provide an unequivocal spacing." Unfortunately, neither MacEwan and Wilson nor any other contributor to Monograph #5 (Brindley and Brown, 1980) provide any detail for what constitutes optimum solvation. The unequivocal spacing is interpreted to mean that an integral series of basal X-ray diffraction reflections yields a characteristic mean spacing. Results obtained in this study completely confirm the finding of Środoń (1980) that different smectites give slightly different mean spacings. While each smectite has its own spacing, there is an optimum solvation level that yields the greatest regularity for the integral series. It is the objective here to examine briefly the three requirements for a satisfactory organic-clay complex: (1) clay hydration state, (2) complex stability, and (3) unequivocal complex spacing.

EXPERIMENTAL

Coefficient of variation

A very simple statistical parameter for evaluating the regularity of the integral series is the coefficient of variation, CV,

$$CV = 100/\bar{d}[\Sigma\ (ld - \bar{d})/(n - 1)]^{\frac{1}{2}},$$

where l is the integer order of the basal spacing d, $n = \Sigma\, l$ (number of basal spacings of observed), and $\bar{d}$ is the mean value of the basal spacing.

The statistical parameter CV was used as a measure of optimum solvation for the organic complexes. To facilitate an understanding of CV, experimental values of CV for non-expanding materials are given in Table 1. X-ray powder diffraction (XRD) peaks were recorded to yield one to four inches of chart per degree 2θ and the peak position was taken as the centroid at 0.8 to 0.9 of the peak height without any corrections. For the experimental conditions employed, CV values less than 0.2 indicated a very good integral series of reflections.

Homoionic smectites complexed with either ethylene glycol or glycerol were prepared as oriented aggregates on glass slides for XRD examination. The organic liquid was added to the clay by four different procedures that will be explained below.

Full hydration method of complex formation

Slurry method. The organic solvating agent was added directly to the clay suspension, thoroughly mixed, and an aliquot of the resultant slurry allowed to dry on a glass slide. This organic complex, produced from the maximum possible hydration state, is the easiest to prepare and is the most reproducible of the complexes prepared by the four methods studied.

Different amounts of glycerol added to two different smectite slurries shown in Figure 1 indicated that for each clay there was a minimum CV of about 0.2. For montmorillonite, SWy-1, a fairly broad range of glycerol to clay ratios was used, but the CV changed little, whereas for the California saponite the glycerol to clay ratio for optimum solvation (minimum CV) was narrow. Away from the optimum amount of glycerol, the first order peak had a large effect upon the CV; however, the value of the CV increased away from optimum even when the 1st order peak was omitted from the CV computation. Solvation with ethylene glycol gave the same general effect as shown in Figure 1 for glycerol. The data for both organic complexes consistently showed that if the CV was decreased significantly by exclusion of the 001 peak, the clay-organic complex was not at optimum solvation. For very broad peaks commonly found in the XRD patterns of natural sediments, the measurement error for the 001 peak position may preclude its use in the calculation of the CV; however, as shown in Table 3, the fairly broad peaks from the Washington smectite, SWa-1, were not affected.

Partial hydration methods of complex formation

All other methods for adding the organic solvating agent involved some partial hydration stage for the clay because the clay suspension was either air dried or oven dried prior to addition of the solvating material. Efforts to solvate oven-dry specimens (110°C for 24 hr) yielded erratic results irrespective of the saturating cation. Air-dry procedures gave rise to ill defined variable hydration states. For example, Mg-montmorillonite air dried in Cambridge, Massachusetts, gave 001 values ranging from 12.1 to 14.7 Å. Organic complexes were formed by adding the organic either as vapor or as liquid to air dried clay films. Three methods were used to add the organic liquid to air-dried clay films. Drops of liquid placed at the edge of the clay film produced organic complexes that gave erratic results; therefore, the liquid drop method was abandoned. All ethylene glycol solvated specimens were stored and X-rayed in an eth-

Table 1. Experimental coefficient of variation for basal spacings of non-expandable materials oriented on a glass slide.

Phase	Range of l	Mean basal spacing (ld)	Coefficient of variation (CV)	Width of 001 @ A/2 ($°2\theta$)
Kaolinite	1–7	7.15	0.10	0.34
Illite	1–5	9.97	0.14	0.60
Muscovite	1–5	9.97	0.17	0.24
Sheridanite	1–7	14.20	0.15	0.26
n-tetradecanol	1–8	39.66	0.12	0.09
n-tetradecanol	4–12[1]	39.68	0.11	0.11[2]

[1] l = 9 absent.
[2] Width of 004 @ A/2.

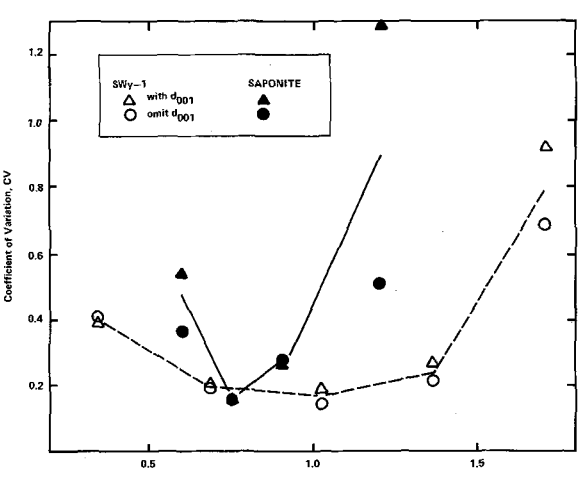


Figure 1. Glycerol solvation for two Mg-smectites.

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Table 2. Reproducibility for glycerol solvation of montmorillonite by different methods.

a. *Mg saturated smectite (SWy-1)*

	Slurry		Vapor		Towel	
	$\overline{ld}$[1]	CV[2]	$\overline{ld}$[1]	CV[2]	$\overline{ld}$[1]	CV[2]
Average of 6	17.79	0.15	17.78	0.28	17.83	0.34
Maximum	17.81	0.19	17.80	0.42	17.87	0.50
Minimum	17.78	0.12	17.76	0.15	17.76	0.18

b. *1 μm "Volclay"*

Slurry				001 before solvation	Vapor		Spray	
Ion	$\overline{ld}$[3]	CV[2]	Ion		$\overline{ld}$[3]	CV[2]	$\overline{ld}$[3]	CV[2]
Mg	17.84	0.13	Mg	14.7	17.81	0.28	17.82	0.24
Mg	17.84	0.10	Mg	14.7	17.81	0.32	17.83	0.19
K	17.84	0.40	K	12.1	17.75	2.21	17.84	1.35
			K	12.1	13.80	1.66	—	—
			K	11.8	—	—	13.8[4]	
			Mg	11.8	—	—	17.91	0.26

[1] $\overline{ld}$ = mean basal spacing for l = 1 to 9.
[2] CV = coefficient of variation.
[3] $\overline{ld}$ = mean basal spacing for l = 1 to 6.
[4] Maximum.

ylene glycol atmosphere. The importance of such experimental control with ethylene glycol solvation was demonstrated by Kunze (1955). Optimum glycerol solvated specimens do not change measurably after standing 3 years on a laboratory shelf.

Vapor method. Previously dried clay films on glass slides were placed over the organic liquid in a sealed container and heated for 16 to 24 hr. For ethylene glycol the temperature was 60°C which gave a vapor pressure of 1.5 torr. The temperature for glycerol was 100°C yielding a glycerol vapor pressure of 0.2 torr.

Towel method. The air-dried clay on a glass slide was placed clay-side down on a filter paper saturated with ethylene glycol or glycerol. Contact time on the moist filter paper was 2–3 min followed by at least 2 hr of equilibration prior to XRD examination.

Spray method. The air-dried clay on a glass slide was sprayed with a fine mist using an atomizer which contained a 15% organic liquid in water. After standing 15 min, any clay film that looked dry was sprayed a second time. The XRD data were not changed on a given sample for equilibration time after spraying from 0.5 to 25 hr.

RESULTS AND DISCUSSION

To compare both solvation methods and reproducibility, 18 specimens were prepared from the same clay suspension. Six specimens were glycerol-slurry solvated. After air drying, six specimens were glycerol-vapor solvated and six were glycerol-towel solvated. The data in Table 2a indicate that slurry solvation gave the lowest CV and that vapor- and towel-solvation methods gave about the same CV. Reproducibility was the best for slurry solvation.

In another set of experiments, Mg- and K-montmorillonite were prepared from the <1 μm fraction of commercial "Volclay." The results in Table 2b for the Mg-form, glycerol solvated by slurry or by vapor, were essentially the same as in Table 2a. The spray-solvation method on Mg-montmorillonite gave an average CV between that obtained from slurry and

Table 3. Slurry glycerol solvation for different homoionic smectites.

Smectite	Ion	Mean basal spacing ($\overline{ld}$)	Coefficient of variation l = 1–6 (CV)	Coefficient of variation l = 2–7 (CV)	Width of 001 @ A/2 (°2θ)
Dioctahedral:					
Wyoming (SWy-1)	Mg	17.80	0.10	0.10	0.52
	K	17.73	0.39	0.40	0.80
	Li	17.83	0.10	0.11	0.54
Montana	Mg	17.94	0.14	0.16	0.38
	K	17.83	0.65	0.65	0.70
	Li	17.78	0.23	0.23	0.40
Washington (Swa-1)	Mg	17.86	0.55	0.55	0.8
	K	17.61	0.59	0.55	1.3
Trioctahedral:					
Ballarat, California (saponite)	Mg	18.03	0.16	0.18	0.29
	K	18.03	0.22	0.25	0.37
	Li	17.92	0.35	0.35	0.30

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Table 4. Ethylene glycol solvation of smectites by different methods.

	Mean basal spacing (Å)	Coefficient of variation	
		with 001 (CV)	without 001 (CV)
Towel method			
Ca-smectite, Cheto, Arizona[2]	16.72	0.58	0.34
Ca-smectite, Garfield, Washington[2]	16.74	0.80	0.39
Wyoming smectite[2]	16.06	—	0.44
Mg-smectite, Crook County, Wyoming (SWy-1)[4]	17.07	0.34	0.34
Mg-smectite, Crook County, Wyoming (SWy-1)[4]	17.11	0.38	0.39
Vapor method			
Ca-smectite, Askangel, U.S.S.R.[3]	16.89	0.66	0.38
Ca-smectite, Chambers, Arizona[3]	16.98	2.26	2.12
Ca-smectite, Belle Fourche, South Dakota[3]	16.85	0.36	0.37
Ca-smectite, Manito, Washington[3]	16.78	1.74	1.91
Ca-smectite, Polkville, Mississippi[3]	16.87	1.62	1.67
Ca-smectite, Michajlov, Bulgaria[3]	17.00	1.52	0.58
Ca-smectite, Zajsanskij, U.S.S.R.[3]	16.87	0.39	0.36
Mg-smectite (SWy-1),[4] average of 4	17.03	0.27	0.26
Liquid + vapor method[1]			
Na-smectite, Fayette County, Texas (F_1)[5]	16.95	0.91	—
Ca-smectite, Fayette County, Texas (CaF_1)[5]	16.88	0.41	—
Na-smectite, Upton, Wyoming, U_3	—	0.43	—
Na-smectite, Upton, Wyoming, U_1	—	0.43	—
Smectite, Chambers, Arizona, C	—	0.59	—
Ca-smectite, Polkville, Mississippi, P	—	0.58	—
Na-smectite, Mowry Formation, Crook County, Wyoming, M[5]	17.03	0.20	—

[1] Calculated from Tettenhorst and Roberson (1973).
[2] Calculated from Środoń (1980).
[3] Calculated from Čičel and Machajdík (1981).
[4] Present study.
[5] Roberson *et al.* (1968).

vapor methods. For K-montmorillonite the CV increased even for the slurry-solvation method. The increase in CV for the K-form vs. the Mg-form prepared by the slurry-solvation method was observed consistently with glycerol and with ethylene glycol. Vapor solvation of the K-form gave erratic results as shown in Table 2 for two supposedly identical specimens, treated in exactly the same way, at the same time. Increasing the vapor solvation time to 96 hr did not change the XRD traces for these two specimens of the K-smectite which had been glycerol-vapor solvated.

Table 3 shows data for four different smectites glycerol slurry solvated. These data substantiate the observation of Środoń (1980) that different smectites have a different basal spacing. The effect of ion saturation also appears to be slightly different for the different smectites. Omitting the 1st order peak did not change the CV significantly which suggests that the specimens were near optimum solvation.

Slurry solvation of Mg-smectite (SWy-1) with ethylene glycol gave CVs between 0.1 and 0.2, very similar to glycerol solvation. Ethylene glycol solvation by other methods are given in Table 4. Calculated CV values from literature XRD data are listed for comparison purposes. With the 16-hr soaking recommended by Środoń (1980) for the towel method, about ⅓ of the specimens were found to be unusable. A change to a 2- to 3-min soak followed by an equilibration time always gave usable specimens and CV values comparable to those obtained from Środoń's data.

The ethylene glycol vapor-solvation data in Table 4 for Mg-smectite (SWy-1) gave about the same CV as glycerol vapor. The data of Čičel and Machajdík (1981) for ethylene glycol vapor solvation of smectites show a fairly wide range of coefficients of variation for presumably high-quality smectites. Only three of the specimens have CVs less than 0.75.

Tettenhorst and Roberson (1973) stated that the vapor complexing method gave non-reproducible results on montmorillonites; therefore, they added to the dried clay an excess of liquid followed by vapor saturation for several days and still found that "None of the montmorillonites studied, organic treated or heated, gave a rational sequence of basal orders." Interpolating from Tettenhorst and Roberson's (1973) graphical data, CV values given were obtained (Table 4) which cover the range of deviations from ideal order shown by the graphical data. Most of the CV values are fairly low with only one CV exceeding 0.75. It is interesting to compare the CV values for the Chambers and Polkville montmorillonites obtained by different methods. Whether or not slurry solvation on the same clay type by the different investigators would have given comparable CV values is unknown. However, it is clear that there still is a divergence of results from different investigators that may be due to small variation in solvation procedure especially when applied to partially hydrated clay films.

It is extremely unfortunate that the combination method of slurry-vapor used by Kunze (1955) was never widely adopted. Such a procedure would ensure that the organic complex was formed from a fully hydrated clay and followed by the vapor phase stage would ensure optimum solvation treatment. The greater the refinement applied toward the interpretation of XRD data from expandable layer materials the more critical be-

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comes the need to satisfy completely the three requirements for organic complexes so succinctly stated by MacEwan and Wilson (1980).

Constructed Facilities Division BRUCE E. NOVICH
Department of Civil Engineering R. TORRENCE MARTIN
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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