MONTMORILLONITE–POLYALCOHOL COMPLEXES: PART II*

by

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ABSTRACT

Oscillating-heating X-ray diffraction was used to determine *d*-spacings and intensity changes of the (001) diffraction maximum for various combinations of 3 clays, 6 cations and 7 polyalcohols from 20°C to 1000°C under non-equilibrium conditions.

The temperature of collapse of the one layer complex was measured. Analysis of variance of this parameter for a model containing 3 clays, 6 cations and 7 polyalcohols showed that there is a significant difference among cations and polyalcohols but not among clays.

Additional work on one clay, 6 cations and 18 polyalcohols shows that ΔT—the difference in temperature between the collapse of the clay-organic complex and the boiling point of the polyalcohol—is proportional to the length of the carbon chain; ΔT is also a function of the number and position of the OH groups.

The mean temperatures of final collapse for all polyalcohols are related to the valence of the interlayer cations and inversely related to their ionic radii.

There are two groups of *d*-spacings for the one-layer complexes. Complexes with polyalcohols having OH groups at the ends of the chain have mean *d*-spacings between 13.6–13.7 Å, while complexes with polyalcohols with interior OH groups have mean *d*-spacings of 13.9–14.0 Å.

INTRODUCTION

This investigation is a continuation of a portion of the work described by Tettenhorst, Beck, and Brunton (1960).

In brief, the object of this study was to investigate thermal stability of polyalcohols on montmorillonite clays under non-equilibrium conditions. The effect of the exchangeable cation also was investigated. Additional data have been obtained on the behavior of various polyalcohol–monoionic clay combinations at elevated temperatures under non-equilibrium conditions. Three montmorillonites with different exchange capacities were made homoionic with six metal cations and, subsequently, were treated with excess of polyalcohol liquids. Five triols and thirteen diols were studied; chain length varied from two to six carbon atoms.

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PROCEDURE

Oscillating-heating X-ray diffraction was used to determine *d*-spacing and intensity changes of the (001) diffraction maximum for various combinations of clays, cations, and polyalcohols from 20°C to 1000°C under non-equilibrium conditions. Three clays, six cations, and seven polyalcohols were used in the preliminary factorial design experimental model. Two temperature measurements were taken from each oscillating-heating X-ray diffraction pattern; (1) temperature of maximum intensity of one-layer complex (Table 1), and (2) temperature of final collapse of one-layer complex (Table 2). The final collapse probably represents complete removal of polyalcohol molecules from interlayer positions. Five of the X-ray patterns were replicated and these results are in Table 3.

The variability in temperature measurement increases with temperature and in order to make valid statistical tests, the temperatures must be transe formed to make the variances linear and additive. The temperatures were converted to log T for the determination of analysis of variance and confidence limits.

Table 1.—Temperature in °C of Maximum Intensity of One-layer Complex

	Li Hector	Mg Hector	Na Hector	Ca Hector	K Hector	Ba Hector
e. glycol	105	125	120	110	80	105
1,2 propanediol	105	150	95	110	85	95
1,3 butanediol	105	155	110	100	100	110
1,4 butanediol	135	130	130	135	110	120
1,5 pentanediol	140	170	135	150	120	145
glycerol	175	175	160	175	140	160
1,2,4 butanetriol	170	190	170	160	160	175
	Li Argentina	Mg Argentina	Na Argentina	Ca Argentina	K Argentina	Ba Argentina
e. glycol	100	125	80	115	95	110
1,2 propanediol	95	145	70	100	100	120
1,3 butanediol	115	145	60	120	95	95
1,4 butanediol	140	150	100	105	125	130
1,5 pentanediol	135	145	80	115	125	165
glycerol	160	170	120	145	145	145
1,2,4 butanetriol	195	185	165	175	155	175
	Li Cheto	Mg Cheto	Na Cheto	Ca Cheto	K Cheto	Ba Cheto
e. glycol	95	140	90	100	90	100
1,2 propanediol	90	140	90	130	70	90
1,3 butanediol	115	140	80	105	90	105
1,4 butanediol	115	155	100	145	110	115
1,5 pentanediol	135	165	110	145	110	150
glycerol	155	180	190	180	135	170
1,2,4 butanetriol	160	210	175	220	145	175

TABLE 2.—TEMPERATURE IN °C OF FINAL COLLAPSE OF ONE-LAYER COMPLEX

	Li Hector	Mg Hector	Na Hector	Ca Hector	K Hector	Ba Hector
e. glycol	180	285	155	210	95	180
1,2 propanediol	200	260	165	230	120	190
1,3 butanediol	215	250	175	245	125	215
1,4 butanediol	230	280	185	245	175	255
1,5 pentanediol	290	420	220	240	190	275
glycerol	270	295	210	260	170	220
1,2,4 butanetriol	295	585	280	300	230	375
	Li Argentina	Mg Argentina	Na Argentina	Ca Argentina	K Argentina	Ba Argentina
e. glycol	175	255	105	210	140	270
1,2 propanediol	165	250	105	220	145	320
1,3 butanediol	195	250	115	230	130	225
1,4 butanediol	220	300	200	230	150	315
1,5 pentanediol	220	360	160	240	180	350
glycerol	240	280	160	250	170	230
1,2,4 butanetriol	350	485	300	450	200	450
	La Cheto	Mg Cheto	Na Cheto	Ca Cheto	K Cheto	Ba Cheto
e. glycol	225	340	120	200	100	175
1,2 propanediol	215	340	135	255	140	175
1,3 butanediol	220	270	110	210	105	235
1,4 butanediol	170	315	140	215	130	245
1,5 pentanediol	260	370	150	245	170	310
glycerol	225	350	210	300	150	290
1,2,4 butanetriol	350	345	220	400	250	300

TABLE 3

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
	135°C	210°C	235°C	350°C	335°C
	135	180	260	350	210
	135	170	260	320	235
	125	180	285	290	230
Total	530	750	1040	1310	1010
X	132.5	185	260	327.5	252.5
95% confidence limits					
Upper	139.4	194.6	273.5	344.5	265.6
Lower	126.0	175.9	247.2	311.3	240.0

The 2θ values for the (001) diffraction maxima were recorded at regular closely-spaced temperature intervals for the one-layer complexes. The 2θ values for sharp diffraction maxima were used in the calculation of mean d-spacings for one-layer complexes. The number of 2θ values used to calculate mean d values varied from 2 to 20. The means for the 2θ values of all maxima were calculated and converted to d-spacings (Table 4).

TABLE 4

Sample	Å average	Sample	Å average
Li-Hectorite & Ethylene Glycol	13.49	Li-Argentina & Ethylene Glycol	13.55
Mg-Hectorite & Ethylene Glycol	14.04	Mg-Argentina & Ethylene Glycol	13.87
Na-Hectorite & Ethylene Glycol	13.90	Na-Argentina & Ethylene Glycol	13.50
Ca-Hectorite & Ethylene Glycol	13.92	Ca-Argentina & Ethylene Glycol	13.54
K-Hectorite & Ethylene Glycol	14.01	K-Argentina & Ethylene Glycol	13.65
Ba-Hectorite & Ethylene Glycol	13.58	Ba-Argentina & Ethylene Glycol	13.37
Li-Hectorite & Glycerol	14.23	Li-Argentina & Glycerol	14.05
Mg-Hectorite & Glycerol	14.29	Mg-Argentina & Glycerol	13.77
Na-Hectorite & Glycerol	14.07	Na-Argentina & Glycerol	13.85
Ca-Hectorite & Glycerol	14.49	Ca-Argentina & Glycerol	14.03
K-Hectorite & Glycerol	14.68	K-Argentina & Glycerol	13.88
Ba-Hectorite & Glycerol	14.28	Ba-Argentina & Glycerol	13.85
Li-Hectorite & 1,2 Propanediol	14.15	Li-Argentina & 1,2 Propanediol	13.97
Mg-Hectorite & 1,2 Propanediol	14.10	Mg-Argentina & 1,2 Propanediol	14.09
Na-Hectorite & 1,2 Propanediol	14.03	Na-Argentina & 1,2 Propanediol	13.89
Ca-Hectorite & 1,2 Propanediol	14.30	Ca-Argentina & 1,2 Propanediol	13.88
K-Hectorite & 1,2 Propanediol	13.96	K-Argentina & 1,2 Propanediol	13.54
Ba-Hectorite & 1,2 Propanediol	13.83	Ba-Argentina & 1,2 Propanediol	13.56
Li-Hectorite & 1,3 Butanediol	14.16	Li-Argentina & 1,3 Butanediol	14.16
Mg-Hectorite & 1,3 Butanediol	14.49	Mg-Argentina & 1,3 Butanediol	14.36
Na-Hectorite & 1,3 Butanediol	14.20	Na-Argentina & 1, 3 Butanediol	14.01
Ca-Hectorite & 1,3 Butanediol	14.63	Ca-Argentina & 1,3 Butanediol	14.20
K-Hectorite & 1,3 Butanediol	13.97	K-Argentina & 1, 3 Butanediol	13.77
Ba-Hectorite & 1,3 Butanediol	13.93	Ba-Argentina & 1,3 Butanediol	14.56
Li-Hectorite & 1,4 Butanediol	13.99	Li-Argentina & 1,4 Butanediol	13.61
Mg-Hectorite & 1,4 Butanediol	14.55	Mg-Argentina & 1,4 Butanediol	14.49
Na-Hectorite & 1,4 Butanediol	13.79	Na-Argentina & 1,4 Butanediol	13.88
Ca-Hectorite & Butanediol	14.77	Ca-Argentina & 1,4 Butanediol	13.82
K-Hectorite & 1,4 Butanediol	13.67	K-Argentina & 1,4 Butanediol	13.49
Ba- Hectorite & 1,4 Butanediol	14.28	Ba-Argentina & 1,4 Butanediol	13.49
Li-Hectorite & 1,5 Pentanediol	13.77	Li-Argentina & 1,5 Pentanediol	13.82
Mg-Hectorite & 1,5 Pentanediol	13.93	Mg-Argentina & 1,5 Pentanediol	13.59
Na-Hectorite & 1,5 Pentanediol	13.75	Na-Argentina & 1,5 Pentanediol	13.79
Ca-Hectorite & 1,5 Pentanediol	14.01	Ca-Argentina & 1,5 Pentanediol	13.81
K-Hectorite & 1,5 Pentanediol	13.78	K-Argentina & 1,5 Pentanediol	13.32
Ba-Hectorite & 1,5 Pentanediol	13.86	Ba-Argentina & 1,5 Pentanediol	13.54
Li- Hectorite & 1,2,4 Butanetriol	14.07	Li-Argentina & 1, 2, 4 Butanetriol	13.89
Mg-Hectorite & 1,2,4 Butanetriol	14.40	Mg-Argentina & 1,2,4 Butanetriol	13.84
Na- Hectorite & 1,2,4 Butanetriol	14.05	Na-Argentina & 1,2,4 Butanetriol	13.79
Ca-Hectorite & 1,2,4 Butanetriol	14.61	Ca-Argentina & 1,2,4 Butanetriol	13.99
K-Hectorite & 1,2,4 Butanetriol	14.15	K-Argentina & 1,2,4 Butanetriol	13.90
Ba-Hectorite & 1,2,4 Butanetriol	14.24	Ba-Argentina & 1,2,4 Butanetriol	13.91

TABLE 4 (Continued)

Sample	Å average	Sample	Å average
Li-Cheto & Ethylene Glycol	13.55	Ba-Cheto & 1,3 Butanediol	14.15
Mg-Cheto & Ethylene Glycol	13.95	Li-Cheto & 1,4 Butanediol	13.84
Na-Cheto & Ethylene Glycol	13.78	Mg-Cheto & 1,4 Butanediol	14.37
Ca-Cheto & Ethylene Glycol	13.81	Na-Cheto & 1,4 Butanediol	13.83
Ba-Cheto & Ethylene Glycol	13.53	Ca-Cheto & 1,4 Butanediol	14.73
Li-Cheto & Glycerol	14.16	K-Cheto & 1,4 Butanediol	13.33
Mg-Cheto & Glycerol	13.93	Ba-Cheto & 1,4 Butanediol	13.31
Na-Cheto & Glycerol	13.90	Li-Cheto & 1,5 Pentanediol	13.57
Ca-Cheto & Glycerol	14.11	Mg-Cheto & 1,5 Pentanediol	13.60
K-Cheto & Glycerol	13.77	Na-Cheto & 1,5 Pentanediol	13.63
Ba-Cheto & Glycerol	14.00	Ca-Cheto & 1,5 Pentanediol	13.65
Li-Cheto & 1,2 Propanediol	14.00	K-Cheto & 1,5 Pentanediol	13.37
Mg-Cheto & 1,2 Propanediol	13.95	Ba-Cheto & 1,5 Pentanediol	13.45
Na-Cheto & 1,2 Propanediol	14.44	Li-Cheto & 1,2,4 Butanetriol	14.25
Ca-Cheto & 1,2 Propanediol	14.30	Mg-Cheto & 1,2,4 Butanetriol	13.77
K-Cheto & 1,2 Propanediol	13.85	Na-Cheto & 1,2,4 Butanetriol	13.62
Ba-Cheto & 1,2 Propanediol	14.03	Ca-Cheto & 1,2,4 Butanetriol	14.15
Li-Cheto & 1,3 Butanediol	14.17	K-Cheto & 1,2,4 Butanetriol	13.33
Mg-Cheto & 1,3 Butanediol	14.12	Ba-Cheto & 1,2,4 Butanetriol	13.89
Na-Cheto & 1,3 Butanediol	14.37		
Ca-Cheto & 1,3 Butanediol	15.05		
K-Cheto & 1,3 Butanediol	13.65		

Additional oscillating-heating X-ray patterns under non-equilibrium conditions were run on the Argentina clay with six metal cations and eleven more polyalcohols. Temperatures for final collapse of one-layer complexes are shown in Table 5 and *d*-spacings of one-layer complexes are shown in Table 6.

RESULTS

Results of analyses of variance for the data in Tables 1 and 2 for temperatures of (1) maximum intensity of the one-layer complex and (2) the final collapse of the one-layer complex are shown in Table 7 and 8, respectively. The "F" values for the among-cations, among-alcohols and second order interaction clays-and-cations are significant at the 0.005 level. Inasmuch as results for the temperature at maximum intensity of the one-layer complex and the final collapse of the one-layer complex are similar, the latter temperatures were used for the remainder of this study.

The analysis of variance model is Model I (Brownlee, 1960), therefore the sums of squares for interactions such as that between clays and cations cannot be pooled with the error term. A separate analysis of variance for each clay is

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TABLE 5.—ARGENTINA CLAY TEMPERATURE IN °C OF FINAL COLLAPSE OF ONE-LAYER COMPLEX

	Li	Mg	Na	Ca	K	Ba	BP of alcohol 760mm	X
e. glycol	175	255	105	210	140	270	197	193
1,2 propanediol	165	250	105	220	145	320	189	201
1,3 butanediol	195	250	115	230	130	225	204	191
1,4 butanediol	220	300	200	230	150	315	230	236
1,5 pentanediol	220	360	160	240	180	350	239	252
glycerol	240	280	160	250	170	230	290	222
1,2,4 butanetriol	350	485	300	450	200	450	297	372
1,3 propanediol	265	290	150	240	135	260	214	224
2,3 butanediol	265	275	150	260	150	220	184	220
2,5 hexanediol	230	600	200	175	185	460	221	308
1,2,6 hexanetriol	350	575	400	525	235	490	325	429
1,2,5 pentanetriol	260	530	215	525	220	335	310	348
1,6 hexanetiol	250	530	205	300	210	300	250	299
2,4 pentanediol	210	330	120	175	200	250	196	214
2,3 pentanediol	240	510	190	350	220	355	187	311
2,3 hexanediol	285	480	170	325	195	410	208	311
3,4 hexanediol	375	380	410	300	365	310	230	357
1,2,5 hexanetriol	640	625	410	600	360	630	298	545
X	274	405	209	311	199	343		

TABLE 6

Sample	Å average	Sample	Å average
Li-Argentina & Ethylene Glycol	13.55	K-Argentina & 1,2 Propanediol	13.54
Mg-Argentina & Ethylene Glycol	13.87	Ba-Argentina & 1,2 Propanediol	13.55
Na-Argentina & Ethylene Glycol	13.50	Li-Argentina & 1,4 Butanediol	13.61
Ca-Argentina & Ethylene Glycol	13.54	Mg-Argentina & 1,4 Butanediol	14.49
K-Argentina & Ethylene Glycol	13.65	Na-Argentina & 1,4 Butanediol	13.88
Ba-Argentina & Ethylene Glycol	13.37	Ca-Argentina & 1,4 Butanediol	13.82
Li-Argentina & 1,3 Propanediol	13.77	K-Argentina & 1,4 Butanediol	13.49
Mg-Argentina & 1,3 Propanediol	14.25	Ba-Argentina & 1,4 Butanediol	13.49
Na-Argentina & 1,3 Propanediol	14.20	Li-Argentina & 1,3 Butanediol	14.16
Ca-Argentina & 1,3 Propanediol	14.20	Mg-Argentina & 1,3 Butanediol	14.36
K-Argentina & 1,3 Propanediol	13.56	Na-Argentina & 1,3 Butanediol	14.01
Ba-Argentina & 1,3 Propanediol	13.82	Ca-Argentina & 1,3 Butanediol	14.20
La-Argentina & 1, 2 Propanediol	13.97	K-Argentina & 1,3 Butanediol	13.77
Mg-Argentina & 1,2 Propanediol	14.09	Ba-Argentina & 1,3 Butanediol	14.56
Na-Argentina & 1,2 Propanediol	13.89	Li-Argentina & 2,3 Butanediol	13.95
Ca-Argentina & 1,2 Propanediol	13.88	Mg-Argentina & 2,3 Butanediol	14.02

TABLE 6 (Continued)

Sample	Å average	Sample	Å average
Na-Argentina & 2, 3 Butanediol	14.18	K-Argentina & 2,3 Hexanediol	14.04
Ca-Argentina & 2,3 Butanediol	13.84	Ba-Argentina & 2,3 Hexanediol	14.05
K-Argentina & 2,3 Butanediol	14.06	Li-Argentina & 2,5 Hexanediol	13.70
Ba-Argentina & 2,3 Butanediol	13.91	Mg-Argentina & 2,5 Hexanediol	13.92
Li-Argentina & 1,5 Pentanediol	13.82	Na-Argentina & 2,5 Hexanediol	13.84
Mg-Argentina & 1,5 Pentanediol	13.59	Ca-Argentina & 2,5 Hexanediol	13.76
Na-Argentina & 1,5 Pentanediol	13.79	K-Argentina & 2,5 Hexanediol	13.79
Ca-Argentina & 1,5 Pentanediol	13.81	Ba-Argentina & 2,5 Hexanediol	13.85
K,Argentina & 1,5 Pentanediol	13.32	Li-Argentina & Glycerol	14.05
Ba-Argentina & 1,5 Pentanediol	13.54	Mg-Argentina & Glycerol	13.77
Li-Argentina & 2,4 Pentanediol	13.45	Na-Argentina & Glycerol	13.85
Mg-Argentina & 2,4 Pentanediol	14.23	Ca-Argentina & Glycerol	14.03
Na-Argentina & 2,4 Pentanediol	13.94	K-Argentina & Glycerol	13.88
Ca-Argentina & 2,4 Pentanediol	14.12	Ba-Argentina & Glycerol	13.85
K-Argentina & 2,4 Pentanediol	13.79	Li-Argentina & 1,2,4 Butanetriol	13.89
Ba-Argentina & 2,4 Pentanediol	14.23	Mg-Argentina & 1,2,4 Butanetriol	13.84
L-Argentina & 2,3 Pentanediol	14.10	Na-Argentina & 1,2,4 Butanetriol	13.79
Mg-Argentina & 2,3 Pentanediol	13.90	Ca-Argentina & 1,2,4 Butanetriol	13.99
Na-Argentina & 2,3 Pentanediol	14.36	K-Argentina & 1,2,4 Butanetriol	13.90
Ca-Argentina & 2,3 Pentanediol	14.12	Ba-Argentina & 1,2,4 Butanetriol	13.91
K-Argentina & 2,3 Pentanediol	15.21	Li-Argentina & 1,2,5 Pentanetriol	13.81
Ba-Argentina & 2,3 Pentanediol	14.20	Mg-Argentina & 1,2,5 Pentanetriol	13.96
Li-Argentina & 1,6 Hexanediol	13.72	Na-Argentina & 1,2,5 Pentanetriol	13.94
Mg-Argentina & 1,6 Hexanediol	13.74	Ca-Argentina & 1,2,5 Pentanetriol	13.84
Na-Argentina & 1,6 Hexanediol	13.57	K-Argentina & 1,2,5 Pentanetriol	13.88
Ca-Argentina & 1,6 Hexanediol	13.67	Ba-Argentina & 1,2,5 Pentanetriol	14.00
K-Argentina & 1,6 Hexanediol	13.68	Li-Argentina & 1,2,6 Hexanetriol	14.06
Ba-Argentina & 1,6 Hexanediol	13.65	Mg-Argentina & 1,2,6 Hexanetriol	13.95
Li-Argentina & 3,4 Hexanediol	13.93	Na-Argentina & 1,2,6 Hexanetriol	14.02
Mg-Argentina & 3,4 Hexanediol	13.87	Ca-Argentina & 1,2,6 Hexanetriol	13.95
Na-Argentina & 3,4 Hexanediol	13.80	K-Argentina & 1,2,6 Hexanetriol	13.46
Ca-Argentina & 3,4 Hexanediol	14.12	Ba-Argentina & 1,2,6 Hexanetriol	13.88
K-Argentina & 3,4 Hexanediol	13.81	Li-Argentina & 1,2,5 Hexanetriol	13.98
Ba-Argentina & 3,4 Hexanediol	14.12	Mg-Argentina & 1,2,5 Hexanetriol	13.71
Li-Argentina & 2,3 Hexanediol	13.92	Na-Argentina & 1,2,5 Hexanetriol	14.10
Mg-Argentina & 2,3 Hexanediol	14.01	Ca-Argentina & 1,2,5 Hexanetriol	14.31
Na-Argentina & 2,3 Hexanediol	14.03	K.Argentina & 1,2,5 Hexanetriol	14.13
Ca-Argentina & 2,3 Hexanediol	13.94	Ba-Argentina & 1,2,5 Hexanetriol	13.11

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Table 7.—Analysis of Variance Temperature for Maximum Intensity of One-layer Complex

Factor	D.F.	Sums of squares	Mean square	F
Clays	2	0.0128	0.0064	4.114
Alcohols	6	0.9433	0.1572	101.033***
Cations	5	0.3190	0.0638	40.993***
Clays & Alcohols	12	0.0205	0.0017	1.095
Clay & Cations	10	0.0996	0.0100	6.398***
Alcohols & Cations	30	0.0895	0.0030	1.917
Error	60	0.0933	0.0016	
Total	125	1.5780	0.0126	

*** Significant at the 0.005 level.

Table 8.—Analysis of Variance Temperature for Final Collapse of One-Layer Complex

Factor	D.F.	Sums of squares	Mean square	F
Clays	2	0.0080	0.0040	1.209
Alcohols	6	0.9084	0.1514	45.811***
Cations	5	1.6218	0.3244	98.138***
Clays & Alcohols	12	0.0515	0.0043	1.299
Clays & Cations	10	0.1124	0.0112	3.399***
Cations & Alcohols	30	0.0971	0.0032	0.979
Error	60	0.1983	0.0033	
Total	125	2.9976	0.0240	

*** Significant at the 0.005 level.

shown in Table 9. The F values for cations and alcohols are significant at the 0.005 level for all clays.

One clay, the Argentina example, was complexed with eleven additional polyalcohols. The Argentina clay (No. 15 of Grim and Kulbicki, 1961) is a Wyoming-type montmorillonite. The results of analyses of variance for data of Table 5 are shown in Table 10. The results of Table 10 further indicate that a significant difference exists among cations and among polyalcohols at the 0.005 level. The *d*-spacings for one-layer complexes for the Argentina clay and all polyalcohols are listed in Tables 4 and 6.

DISCUSSION AND CONCLUSIONS

The results of replication of five samples are shown in Table 3. The confidence limits were calculated from log T and increase with increasing temperature. The variances of these samples were homogeneous.

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TABLE 9.—ANALYSES OF VARIANCE FOR EACH CLAY

HECTORITE

Factor	D.F.	Sums of squares	Mean square	F
Cations	5	1.285	0.257	16.65***
Alcohols	5	1.111	0.185	12.00***
Error	30	0.462	0.015	
Total	41	2.859	0.070	
		Cheto		
Cations	5	1.600	0.320	28.41***
Alcohols	6	1.453	0.242	21.50***
Error	30	0.338	0.011	
Total	41	3.392	0.083	
		Argentina		
Cations	5	1.681	0.336	32.33***
Alcohols	6	0.691	0.115	11.078***
Error	30	0.312	0.010	
Total	41	2.684	0.065	

*** Significant at the 0.005 level.

TABLE 10.—ANALYSIS OF VARIANCE TEMPERATURE FOR FINAL COLLAPSE OF ONE-LAYER COMPLEX—ARGENTINA CLAY

Factor	D.F.	Sums of squares	Mean square	F
Alcohols	17	1.7384	0.1023	15.047***
Cations	5	1.4104	0.2821	41.508***
Error	85	0.5776	0.0068	
Totals	107	3.7264		

*** Significant at the 0.005 level.

An arrangement of polyalcohols from low to high molecular weight with ΔT is shown in Table 11, where ΔT is the difference between the mean temperature of final collapse of one-layer complexes and the boiling point of the polyalcohol adjusted to one atmosphere. The data in Table 11 show, in general, the ΔT increases with chain length of polyalcohol molecules and molecular weight. A multiple linear regression analysis was made of ΔT versus several parameters of the type

$$\Delta T = a + bx + cy + dz + ew$$

where a, b, c, d, and e are coefficients and x, y, z and w were selected independent variables. The best results were obtained with the following independent variables:

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x = molecular weight of polyalcohol
y = position of third OH group if one is present and numbering from the right end of the molecule instead of the usual left (e.g. 1, 2, 5 pentanetriol $OH_{\#3} = 1$)
z = position of second OH group measured in the same way as y above (e.g., 1,2,5 pentanetriol $OH_{\#2} = 4$)
w = the number of carbon atoms minus the number of OH groups.

Table 12 shows the results of the regression analysis. The equation is: $\Delta T = 273.041 - 5.284x + 132.413y + 27.559z + 92.014w$. These results are similar to those of Hoffman and Brindley (1960) where they show that the lengths of aliphatic chains, and numbers and positions of OH groups determine the amount of isothermal adsorption of non-ionic aliphatic molecules from aqueous solution on montmorillonite.

Mean temperatures of final collapse of one-layer complexes for all polyalcohols are proportional to the valence of the interlayer cation and inversely proportional to their ionic radii. Table 13 shows the results of the regression analysis.

Mean *d*-spacings of the one-layer complexes are not significantly different with respect to their interlayer cation composition, with the possible exception of the potassium complexes. Mean *d*-spacings of Li^+, Mg^{2+}, Na^+, Ca^{2+}, and Ba^{2+} complexes are approximately 13.9 Å; mean *d*-spacing of potassium complexes is 0.1–0.2 Å lower.

TABLE 11.—DIFFERENCE BETWEEN MEAN TEMPERATURE OF FINAL COLLAPSE OF ONE-LAYER COMPLEXES AND BOILING POINT OF POLYALCOHOLS

Mole weight	Alcohol	ΔT °C diols	ΔT °C triols
62.1	Ethylene Glycol	−4	
76.1	1,2, Propanediol	12	
76.1	1,3, Propanediol	10	
90.1	1,3, Butanediol	−13	
90.1	1,4, Butanediol	6	
90.1	2,3 Butanediol	36	
92.1	1,2,3 Propanetriol		−68
104.2	1,5 Pentanediol	13	
104.2	2,4 Pentanediol	18	
104.2	2,3 Pentanediol	124	
108.1	1,2,4 Butanetriol		75
118.2	1,6 Hexanediol	49	
118.2	2,3 Hexanediol	104	
118.2	2,5 Hexanediol	87	
118.2	3,4 Hexanediol	127	
120.2	1,2,5 Pentanetriol		38
134.2	1,2,6 Hexanetriol		104
134.2	1,2,5 Hexanetriol		247

TABLE 12.—LINEAR MULTIVARIATE ANALYSIS OF $\triangle T$

$\triangle T = 273.041 - 5.284x + 132.413y + 27.559z + 92.014w$ x, y, z and w are defined in text.

$\triangle T$ original	$\triangle T$ calculated
−4	−28
12	18
10	−10
−13	36
6	9
36	36
−68	−26
13	26
18	54
124	81
75	9
49	44
104	127
87	72
127	99
38	65
104	110
247	243

Multiple correlation coefficient = 0.9084.

TABLE 13.—LINEAR MULTIVARIATE ANALYSIS OF CATION TEMPERATURES

$T = -5.497 + 131.008x + 88.031y$
x = valence
y = reciprocal of ionic radius

T original	T calculated
274	272
405	392
209	218
311	345
199	191
343	321

Multiple correlation coefficient = 0.9685

Mean d-spacings of the one-layer complexes fall into two groups with respect to organic compounds, with two inconsistencies. Complexes with polyalcohols having OH groups on the ends of the chain have mean d-spacings of approximately 13.6–13.7 Å; complexes of polyalcohols with OH groups having interior locations have mean d-spacings of about 13.9–14.0 Å. The 0.3 Å difference is probably due to a steric effect provided by the OH groups. The 0.3 Å difference appears to be reasonable if the plane of the zig-zag of the carbon chains of all polyalcohols is parallel to the basal surfaces of the clay particles. Mean d-spacings of complexes with 1,3 propanediol (14.0 Å) and 1,3 butanediol (14.2 Å) are inconsistent with the general trend; both are too high.

Although some generalization concerning the nature of montmorillonite–polyalcohol complexes have been established, detailed interpretations of individual complexes may become available with controlled studies under conditions more nearly approaching equilibrium.

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