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OCCURRENCE OF COLLAPSED AND EXPANDED CRYSTALS IN MONTMORILLONITE–DEXTRAN COMPLEXES*

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Abstract– X-ray diffraction patterns obtained from montmorillonite–dextran complexes prepared with either B-512F or Polytran dextran showed maximum oven-dry crystal expansions of about 5·3 Å. X-ray diffraction patterns of individual complex preparations containing < 20 per cent dextran showed evidence of both expanded and collapsed crystals. The observation of expanded and collapsed crystals in individual preparations has not been previously reported and was apparently related to clay preparation. An estimate of the quantity of dextran which could be interacting with the silicate surface was obtained using polymer adsorption weights and volumes. At maximum adsorption almost all adsorbed B-512F could be in contact with the mineral surface, but only two thirds of the adsorbed Polytran could be in contact with the mineral surface.

INTRODUCTION

PREVIOUS reports of interlamellar adsorption of polysaccharides by montmorillonite show a single first order diffractogram peak in individual clay-complex preparations (Clapp *et al.*, 1968; Parfitt, 1969; Parfitt and Greenland, 1970) which indicates a single basal spacing exists. The (001) spacings of montmorillonite B-512F dextran complexes have been reported by Clapp *et al.* (1968) and Parfitt and Greenland (1970) for several complexes. Parfitt and Greenland (1970) have also reported (001) spacings for montmorillonite–amylose complexes. There has been no suggestion of more than one first order peak observed, although the added dextran was often insufficient to saturate the mineral surface area. A comparison of previously published spacings is shown in Table 1.

This paper reports the formation of montmorillonite–dextran complexes exhibiting both collapsed and expanded crystals in individual complex preparations. Adsorbed volumes of dextran and volume available for dextran adsorption are also compared.

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‡Company or trade names are mentioned for the reader's benefit and do not imply preference by the USDA over products or companies not mentioned.

EXPERIMENTAL

Materials

The montmorillonite used was a bentonite from Clay Spur, Wyoming (obtained from J. W. Jordan, Baroid Division, NL Industries, Inc., Houston, Texas). The clay consisted of $< 2\,\mu$m esd particles which had been centrifuged and spray dried. The partially refined clay was hydrated and treated with 30 per cent H_2O_2 to remove any traces of organic matter. After destruction of excess peroxide, the clay was flocculated with NaCl and washed five times with 1M NaCl. The clay was subsequently washed with water until the resistance of the supernatant solutions showed no further increase with continued washing (4–5x). A large portion of very fine clay remaining in suspension after centrifugation (35,000 rcf, 15 min) during excess chloride removal was discarded and complexes were prepared with the coarse fraction of refined clay. Final wash solution resistance was about $1{\cdot}6 \times 10^5\,\Omega$ and final clay suspension pH was about 6·9. After excess salt removal, the clay was resuspended in water and freeze-dried. Further details are given elsewhere (Olness, 1973).

Two glucose polymers, identified as Polytran and B-512F, which had linkage variations as a primary distinguishing feature, were used in this study. Both polysaccharides had molecular weights $\geqslant 2 \times 10^6$ as determined by Sephadex gel filtration. Polytran‡ (obtained from the Pillsbury Company, Minneapolis, Minnesota) is a fermentation product which has about 75 per cent $\beta - 1 \rightarrow 3$ linked

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Table 1. Basal spacings of montmorillonite–polysaccharide complexes

Saturating cation	Dextran		(001) Spacing		Ref.*
	Type	Content	Air-dry	Oven-or P_2O_5-dry	
		(%)	(Å)		
Na	None	0·0	11·4 ± 0·2	9·7 ± 0·1	COH
Na	B-512F	4·8	12·8 ± 0·2	10·0 ± 0·2	COH
Na	B-512F	9·2	14·0 ± 0·1	13·8 ± 0·1	COH
Na	B-512F	16·3	15·4 ± 0·4	14·6 ± 0·4	COH
Na	B-512F	20·0	16·0	14·7	PG
Na	B-512F	25·6	16·6 ± 0·6	15·8 ± 0·2	COH
Na	B-512F	31·4	17·6 ± 0·1	16·9 ± 0·1	COH
Ca	B-512F	10·7	14·3	13·7	PG
Al	B-512F	9·0	14·8	13·5	PG
Na	Amylose	9·0	13·0	12·7	PG
Ca	Amylose	9·0	15·8	14·1–15·5	PG

*COH = Clapp, Olness and Hoffman (1968); PG = Parfitt and Greenland (1970).

units and 25 per cent $\beta-1\rightarrow6$ linked monoglucoside branch units. This dextran was purified by repeated precipitation in ethanol–acetone mixtures after resuspension in water and freeze dried. The final preparation contained about 5 per cent low molecular weight dextran (10^4–10^5 MW).

The B-512F dextran (obtained from A. Jeanes, Northern Regional Research Laboratory, USDA, Peoria, Illinois) is a fermentation product containing about 95 per cent $\alpha-1\rightarrow6$ and 5 per cent $\alpha-1\rightarrow3$ linkages produced by *Leuconostoc mesenteroides* (Jeanes *et al.*, 1954). The freeze-dried B-512F dextran contained no trace of $< 10^5$ MW polymer and was used as received.

Methods

Complexes were prepared by pipetting solutions of dextran into 1 per cent clay suspensions in 50-ml polycarbonate centrifuge tubes. The clay was suspended for about 1 hr with a magnetic stirrer prior to dextran addition. Polysaccharide solutions were centrifuged (1 hr, 35,000 rcf) to remove any traces of particulate or incompletely dissolved material immediately prior to addition to the clay suspensions. The clay–dextran mixtures were equilibrated with stirring for about 4 hr on a magnetic stirrer. Complexes were centrifuged, washed twice with water, and freeze-dried.

Adsorbed dextran was determined by subtracting the quantity of polysaccharide recovered in the supernatant and wash solutions from the total amount applied. Carbohydrate was determined by a modification of the anthrone procedure (Olness, 1973) of Scott and Melvin (1953).

Clay and clay–polymer complex X-ray analyses were obtained with a General Electric XRD-5 diffractomer using nickel filtered copper Kα radiation in an atmosphere of about 10 per cent r.h. Oriented samples were prepared by pipetting clay or clay complex suspensions on glass slides and allowing the suspension to air dry to a paste consistency. Slides were then equilibrated in a desiccator for 2 1-week periods, the first week over saturated $K_2Cr_2O_7$ (52 per cent r.h.) and the second week over saturated $CaCl_2$ (32 per cent r.h.). After the slides had been examined at these moist states, they were oven-dried at 105°C for 24 hr and stored in a desiccator over P_2O_5. Examination of the oven-dry complexes under vacuum (10^{-4} mm Hg), by R. Gast, University of Minnesota, St. Paul, substantiated observations reported here and indicated no change due to water vapor adsorption in the oven-dry complexes during X-ray analysis.

RESULTS AND DISCUSSION

Adsorption curves for the dextrans are shown in Fig. 1. All added dextran was adsorbed for application levels ≤ 10/100 mg clay. The Polytran adsorption maximum was approximately 62/100 mg clay and was significantly greater than the B-512F adsorption maximum of 44/100 mg clay.

A compilation of the (001) X-ray diffraction peaks for complexes equilibrated at 52, 32 per cent r.h., and oven-dried is presented in Table 2. Only slight differences exist between the (001) spacings of montmorillonite–dextran complexes equilibrated at 52 and 32 per cent r.h. Diffractograms of clay–Polytran complexes that had been oven-dried for 24 hr at 105°C show two first order (001) peaks and shoulders in the patterns of the 3·6, 7·3, and 16·6 per cent dextran complexes (Fig. 2 and Table 2) indicating more than one basal spacing. This result is in contrast with previously published work, which reported single basal spac-

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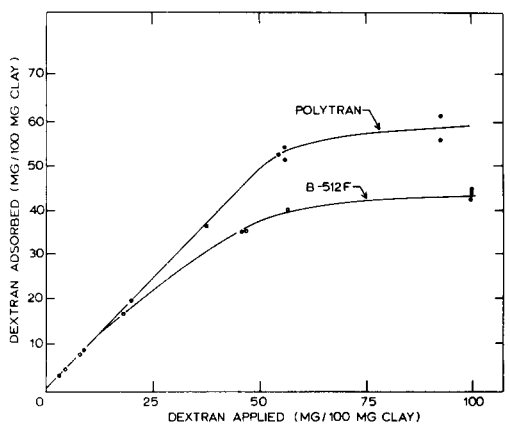


Fig. 1. Adsorption of Polytran and B-512F dextran on Na–montmorillonite.

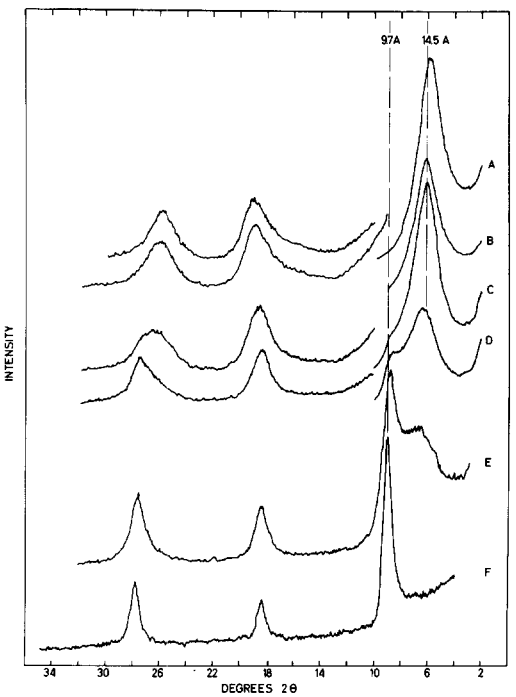


Fig. 2. X-ray diffractograms of oven-dry montmorillonite–Polytran complexes. Patterns: A, 37·2%; B, 34·8%; C, 16·6%; D, 7·3%; E, 3·6%; F, Na–montmorillonite.

Table 2. Basal spacings of montmorillonite–polysaccharide complexes equilibrated at different r.h.*

Dextran		(001) Spacing		
Type	Content	52%	32%	O.D.
	(%)		(Å)	
None (clay only)	0·0	12·6	11·7	9·7
Polytran	3·6	12·8	12·6	9·9 & (13·5)†
Polytran	7·3	13·6	13·4	13·8 & (10·5)
Polytran	16·6	13·0	14·2	14·5 & (10·5)
Polytran	34·8	14·5	14·7	14·5
Polytran	37·2	16·4	17·0	15·5
Polytran	14·5‡	15·2	14·7	15·5
B-512F	4·5	13·0	13·0	9·8 & (13·6)
B-512F	8·2	13·4	13·6	14·0 & (10·4)
B-512F	14·6	15·2	14·5	14·2 & (10·4)
B-512F	26·3	15·6	15·9	14·8
B-512F	30·5	16·8	16·2	14·6
B-512F	12·7‡	16·8	15·9	15·1

*Equilibration conditions: 52%, saturated $K_2Cr_2O_7$; 32%, saturated $CaCl_2$; O.D., oven-dried at 105°C.

†Values in parentheses represent secondary first-order reflections which produced shoulders or peaks on the same patterns.

‡Complexes flocculated with sodium sulfate.

ings (Clapp *et al.*, 1968; Parfitt, 1969; Parfitt and Greenland, 1970). The 3·6 per cent Polytran complex pattern (Fig. 2, e) shows a well-defined peak at about 9·9 Å indicating a collapsed crystal structure. Also present is a well-defined shoulder located at about 13·5 Å, suggesting the presence of expanded crystals.

As the dextran content of the complex increases, the peak representing a collapsed crystal spacing diminishes in intensity and disappears for complexes containing more than 20 mg dextran/100 mg clay. The shoulder at about 13·5Å increases in intensity and becomes a relatively well-defined peak having a central location at about 14·5Å. No evidence of spacings greater than 15Å are found in any of the diffractograms of the Polytran complexes dried at 105°C.

The X-ray diffractograms of oven-dried clay B-512F complexes (patterns not shown) also indicated the presence of both collapsed and expanded crystals at low levels of dextran adsorption. The 4·5 per cent dextran complex had two peaks at 9·8 and 13·6 Å which were nearly equal in intensity and distinctness. Patterns of complexes containing greater quantities of B-512F show the same trend as the Polytran complexes in that the 9·8–9·9 Å peak disappears gradually while the 13·6–14·6 Å peak increases in intensity and distinctness with increasing dextran content.

With only one exception, no oven-dried complex preparation indicated an interlamellar expansion of greater than 5·3 Å. This observation indicates that no complex formed which contained more than one equivalent interlamellar layer of adsorbed dextran. While the X-ray diffractograms are characteristic of a sodium-saturated montmorillonite (Pattern f, Fig. 2), the formation of only a monomolecular layer of adsorbed dextran in the inter-

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lamellar regions seemed inconsistent with the expected results. An adsorbed monolayer of dextran on each silicate surface might be expected.

The maximum surface area of montmorillonite is approximately 800 m^2/g (Grim, 1968). The interlamellar surface area has been estimated to be approximately 90 per cent of the total area or about 720 m^2/g (Grim, 1968). Using 5·3 Å as a maximum expansion for adsorbed dextran, the volume available for dextran adsorption can be calculated in the following manner:

V_T = Total available adsorption volume.
V_I = Total available interlamellar adsorption volume.
V_E = Total available external adsorption volume.

$$V_T = V_I + V_E$$

$$V_I = \frac{72\ m^2}{100\ mg} \times \frac{1}{2} \times \frac{10^4\ cm^2}{m^2} \times (15{\cdot}0-9{\cdot}7)\ Å \times \frac{10^{-8}\ cm}{Å}$$
$$= 19{\cdot}1 \times 10^{-3}\ cm^3/100\ mg\ clay.$$

The factor of $\frac{1}{2}$ is required in computing V_I since two interlamellar surfaces bound a single interlamellar volume. Using a similar treatment, V_E can be determined as about $4{\cdot}2 \times 10^{-3}$ $cm^3/100$ mg clay. Thus V_T is about $23{\cdot}3 \times 10^{-3}$ $cm^3/100$ mg clay.

The volume of B-512F dextran adsorbed at maximum adsorption can be calculated by assuming a volume for dextran of about 160 $Å^3$ per anhydroglucose unit (the molecular volume of glucose calculated from a density of 1·56 g/cm^3 is about 171 $Å^3$, *Handbook of Chemistry and Physics*, 1969). The use of an anhydroglucose unit volume of about 160 $Å^3$ gives a dextran density of about 1·5 g/cm^3.

$$V_D = \text{Volume of dextran adsorbed}$$
$$= \frac{160\ Å^3}{AGU} \times \frac{44\ mg}{162\ mg}\ mmole^{-1}\ AGU^{-1}$$
$$\times \frac{6{\cdot}02 \times 10^{20}\ AGU}{mmole\ AGU} \times \frac{10^{-24}\ cm^3}{Å^3}$$
$$= 26{\cdot}5 \times 10^{-3}\ cm^3/100\ mg\ clay.$$

These calculations would imply that a major portion of the adsorbed B-512F may be closely associated with the surface of the clay at maximum dextran adsorption.

A similar treatment to determine the volume of Polytran adsorbed at maximum dextran adsorption would give a value of about $36{\cdot}9 \times 10^{-3}$ $cm^3/100$ mg clay. Thus a large portion of the adsorbed Polytran may not be associated with the clay surface at maximum adsorption. This conclusion regarding Polytran has been supported by enzymatic studies (Olness, 1973) in which only the complexes with maximum adsorption were degraded. Enzymatic degradation resulted in a complex containing about 28 per cent dextran (40 mg/100 mg clay).

One possible explanation of the differences in the results reported here and those of Clapp *et al.* (1968) is the sample preparation procedures used. We prepared nominal 20 per cent complexes with each dextran using the Na_2SO_4 flocculation method of Clapp *et al.* (1968) to get a more direct comparison with their results. The diffraction patterns of the salt flocculated complexes show single peaks at about 15·5 Å for a 14·5 per cent Polytran and 12·7 per cent B-512F complex respectively. The maximum spacings of the corresponding complexes prepared without excess salt were 14·5 and 14·2 Å for the Polytran and B-512F complexes, respectively. This evidence may explain the absence of both expanded and collapsed crystals in previously reported clay–dextran complexes and the observation of relatively large (> 7 Å) crystal expansions.

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Résumé—Les diagrammes de diffraction X obtenus avec les complexes montmorillonite—dextrane préparés soit avec le dextrane B-512 F soit avec le dextrane Polytran montrent un gonflement cristallin maximum de 5,3 Å pour le matériel séché à l'étuve. Les diagrammes de diffraction X de préparations

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individuelles de complexes contenant moins de 20 per cent de dextrane prouvent l'existence simultanée de cristaux gonflés et non gonflés. L'observation de cristaux gonflés et non gonflés dans des préparations individuelles n'a jamais été faite dans des travaux antérieurs et elle est apparemment reliée à la préparation de l'argile. On a pu estimer la quantité de dextrane qui pourrait interagir avec la surface du silicate au moyen des poids et des volumes de polymère adsorbé. A l'adsorption maximum tout le B-5 12 F adsorbé pourrait être en contact avec la surface du minéral, alors que seulement les deux tiers du Polytran adsorbé se trouveraient dans la même situation.

Kurzreferat—Röntgenbeugungsdiagramme von Montmorillonit–Dextran–Komplexen, die entweder mit B-512 F oder Polytran–Dextran hergestellt waren, zeigten in ofentrockenem Zustand eine maximale Kristallaufweitung von etwa 5,3 Å. Röntgenbeugungsdiagramme einzelner Komplexpräparate, die weniger als 20% Dextran enthielten, ergaben Hinweise auf sowohl expandierte als auch kontrahierte Kristalle. Über die Beobachtung von aufgeweiteten und kontrahierten Kristallen in einzelnen Präparaten ist bisher nicht berichtet worden. Sie hängt offenbar mit der Präparation des Tons zusammen. Ein Schätzwert für die Dextranmenge, die mit der Silicatoberfläche in Wechselwirkung treten kann, wurde unter Berücksichtigung der Adsorptionsgewichte und -volumina der Polymere erhalten. Bei maximaler Adsorption kann fast das gesamte sorbierte B-512 F, jedoch nur zwei Drittel des sorbierten Polytrans in Kontakt mit der Mineraloberfläche treten.

Резюме — Рентгенограммы комплексов монтмориллонита–декстрана, синтезированных с B-512F или с Политран декстраном, показали максимальное увеличение в объеме высушенных при высокой температуре кристаллов примерно на 5,3 Å. На рентгенограммах индивидуально приготовленных образцов, содержащих $< 20\%$ декстрана, заметили как увеличенные в объеме кристаллы, так и разрушенные. Замеченное увеличение в объеме кристаллов и их разрушение ранее не было упомянуто и по-видимому это зависит от подготовки глины. Исчисление количества декстрана могущего взаимодействовать с поверхностью силиката получили при помощи весовой и объемной адсорбции. При максимальной адсорбции почти что весь адсорбированный B-512F может быть в контакте с поверхностью минерала, но адсорбированного Политрана только две трети.

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