

DEL-SG-08-90

**New Intercalation Complexes of Chitin and
Selected Organic Compounds**

\$2.00

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November 1990

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This publication is the result of research sponsored by NOAA Office of Sea Grant, Department of Commerce, under Grant No. NA83AA-D-00017 (Project No. R/N-8) and funds from the University of Delaware. The U.S. Government is authorized to produce and distribute reprints for governmental purposes, notwithstanding any copyright notation that may appear hereon.

The University of Delaware Sea Grant College Program is supported cooperatively by the National Oceanic and Atmospheric Administration, U.S. Department of Commerce, and by the State of Delaware.

NEW INTERCALATION COMPLEXES OF CHITIN AND
SELECTED ORGANIC COMPOUNDS

ABSTRACT

Chitin, with its lamellar and helical molecular structure, affords interstices that permit it to act as host for certain guest molecules of relatively small size and/or planar shape to yield intercalating complexes. Examples include the chitin complexes with dimethylformamide, dimethylsulfoxide, N-acetylethanolamine, 2,2'-oxydiethanol, and pyruvic acid. The complexes are apparently electron-bonded coordination compounds of variable composition, with 5-25% guest molecules, rather than stoichiometric proportions.

These chitin intercalated complexes are dry, free-flowing powders, soluble in orthodox 5% LiCl-dimethylacetamide solvent. They may offer opportunities in dissolution studies, filament preparation, slow release drugs and other biomedical applications.

INTRODUCTION

Discovery of the compatibility of dimethylsulfoxide (DMSO) with beta-chitin from squid (1), together with indication of intercalation complexes of chitosan with carboxylic acids (2), alpha-chitin with alcohols and carbonyl compounds (3), and the softening action of N-acetylethanolamine (NAEA) on dispersed chitin (4), prompted a renewed investigation of the incorporation of DMSO, NAEA and other organic solvent-plasticizers into chitin isolates. Broadening the utility of chitin has been the primary goal.

Evidence of the intercalations includes (a) weight and volume increase of the dry, free-flowing products, (b) variability in the amount of guest molecule incorporated, (c) changes in specific gravity and (d) differential in evaporation rates of surficial and intercalated organics from these chitin complexes.

Intercalation occurs by insertion of a small, usually planar guest molecule into the interstices of a lamellar host, such as chitin, which has open core spacings from its helical structure as well. An intercalation complex may display physical removal of guest molecules, e.g., by heat, solvent extraction or evaporation. In our initial program it was found that under ambient laboratory conditions, DMSO and DMF are slowly lost from their chitin complexes, but at a much slower rate than as surficial solvents. These findings encouraged the further studies described here.

MATERIALS AND METHODS

Chitin Isolates

Chitins from brown shrimp (*Penaeus Aztecus*) (alpha chitin), squid (*Loligo pealei*) (beta chitin) and prawn (*P. Chinensis*) were obtained from commercial sources or prepared in the laboratory.

Since some samples of the chitin isolates may be partially denatured and insoluble, all chitins were checked before their use to assure their solubility in 5% LiCl-dimethylacetamide (DMAc).

Preparation of Intercalated Chitins

Intercalation of chitin with an appropriate organic compound may be carried out with the neat compound, if liquid, or preferably with an axillary volatile solvent, such as ethyl acetate, acetone or acetonitrile. These agents reduce viscosity, aid penetration and most importantly, remove surficial organics in the final washing step. Preferably, the volatile solvent is one in which the guest organic has limited solubility; otherwise the solvent may dissolve away the organic being introduced.

Most reactions were carried out at laboratory temperature, and overnight or longer, as a matter of convenience. Usually a gram or so of chitin was employed with a portion of the organic compound and sufficient volatile solvent to permit ready agitation of the heterogeneous mixture.

To isolate the intercalation product, it is filtered rapidly with suction, the reaction flask is cleared quickly with small amounts of the volatile solvent that is then poured onto the filtered complex, which is thus

further cleansed of surficial organic. The product is dried at laboratory temperature with good air circulation or under vacuum and occasional stirring to expose new surfaces. The operation is complete when the product is a free-flowing powder. Its weight and calculation of its composition is taken at this point. The systems studied are summarized in Table I. Several examples are described in further detail below.

If desired, one may follow solvent weight loss with time and so differentiate loss of surficial volatile solvent from the intercalated organic (Fig. 1), which may be compared with the more regular DMSO loss on paper, A9-62, both at ambient temperature.

Some unusual features of intercalation are illustrated in the following experiments.

Chitin Intercalation with Neat DMF, Followed by Extraction (A9-74,95).

A simple mixture of 2.03 g shrimp chitin and 10 mL dimethylformamide (DMF) (Table I) stood over night at 25°C, was filtered with suction and was dried further in air and, as the DMF boiling point (153°C) is not very high, the intercalate became free-flowing in about 2 hours; the product weight was 2.7 g, of which the DMF was 0.64 g or 24%, sp. gr. 1.44-1.45. Evaporation for another 2.5 hours reduced the product weight to 2.18 g; 0.15 g DMF or 6.8% intercalation (Fig. 2). After standing over night, the weight was 2.08 g, 0.05 g DMF, or 2.4%.

A similar product, A9-74, containing 7.3% DMF, 1.0 g, was extracted with 10 mL acetonitrile for an hour, filtered and dried. The sample then weighed 0.92 g, a loss of 0.08 g, 8%, i.e., all of the intercalated DMF. Hence the caution to wash the complexes rapidly and with limited amounts of the volatile solvent.

Strong Intercalation of Chitin: NAEA (A9-89)

An illustration of the different degrees of intercalation follows: 2.03 g shrimp chitin, 2 mL N-acetylaminoethanolamine (NAEA) and 20 mL of a 1:1 (v:v) mixture of ethyl acetate and acetone (3:2 ratio now preferred) were allowed to stand over night; temp. 26°C. The mixture was filtered, and the flask and product washed quickly with 10 mL of the mixed solvent. In open air the material dried in half an hour to a free-flowing product; wt. 2.22 g containing 0.19 g or 8.6% NAEA.

This same sample was then heated in an oven at 80°C. In half an hour it reached constant weight at 2.14 g, a NAEA content of 0.11 g, or 5.1% (Fig. 3).

Chitin Intercalation with Diethylene Glycol (DEG) (2,2'-oxydiethanol) (A9-15B)

A mixture of 0.5 g shrimp chitin, 1 mL g DEG, 5 mL of 1,1,1-trichloroethane and 3 mL of ethyl acetate was allowed to stand at room temperature for several days, with occasional shaking. It was filtered with suction, flask and product were washed with a small amount of 1,1,1-trichloroethane and the product dried to a free-flowing powder. Yield, 0.54 g, an intercalation of 0.04 g or 7.4%.

Chitin-Pyruvic Acid Complex (A7-101,106,107,108,117)

A one-gram sample of 40 mesh, shrimp alpha-chitin with a mol. wt. of several hundred thousand was added to 10 mL 1,1,1-trichloroethane and 1 mL pyruvic acid and the mixture allowed to stand at room temperature for a week. There was a 36% sorption of the pyruvic acid. The sp.gr. (sink and float) of the product was 1.45 compared with 1.41 for the unmodified chitin.

The chitin-pyruvic acid complex dissolved rapidly in either 7% LiCl/dimethylacetamide or 7% LiCl/N-methyl-2-pyrrolidinone to yield beautifully clear solutions.

The strength of the bond in the complex between chitin and pyruvic acid is indicated by efforts to extract the pyruvic acid with alcoholic organic solvents. Samples of the above chitin-pyruvic acid complex were extracted for 1 hour at room temperature with 1 butanol or with a 40:60 (v:v) mixture of ethanol/methyl ethyl ketone; 50% of the pyruvic acid was retained in each case.

Further, when 1 g of the original moderately high mol. wt., 40 mesh, shrimp alpha-chitin was dispersed in 10 mL of 1-butanol and 1 mL of pyruvic acid, and allowed to stand for an hour under ambient conditions, the wt. gain was 7%.

RESULTS AND DISCUSSION

Chitin intercalation (guest molecules into chitin interstices) has been shown to be operative with a new series of organic compounds. The preferred process involves use of a volatile carrier solvent along with the organic additive, which reduces the viscosity, aids penetration and facilitates washing and drying. Ambient temperature is adequate and although reaction proceeds readily in a few hours, overnight exposure provides opportunity for the system to reach equilibrium.

The properties of this new group of intercalated chitin complexes are attractive. Most important, they are dry, free-flowing powders, which facilitates their further handling of storage and use. They do not appear

moisture sensitive. In general, most densities are somewhat greater than the parent chitin. The complexes are still soluble in orthodox LiCl-dimethylacetamide systems, though not in simpler solvents explored to date.

Discussion

Once one recognizes and accepts intercalation as an inherent attribute of chitin, the question arises as to why it occurs and what properties are required of the organic additive. Thus one might predict other organics that would operate in the system and so broaden the range of products and properties available.

From the limited data in hand, Table II, Properties of Chitin Intercalating (guest) Compounds, has been assembled, based on apparently pertinent items.

The occurrence of chitin-guest organic intercalated complexes apparently results from an "association" or "interaction" of these molecules as a function of such factors as the strength of hydrogen bonding in the host chitin, competition of the guest molecule with the hydrogen bonds, and its solubility parameter (cohesive energy density) (7). In addition, the molecular weight, molar volume and planar character of the guest organic relative to the chitin host must be appropriate. Distribution coefficient of the guest molecule between solvent and chitin may also be important.

Crystal Structure of Chitin

The interstices in chitin responsible for intercalation follow its crystal structure, described by Blackwell and Weih (6):

"Deproteinized lobster tendon . . . alpha-chitin, has an orthorhombic unit cell with dimensions $a = 4.74 \text{ \AA}$. and $c = 10.32 \text{ \AA}$ (fiber axis) . . . Adjacent chains along the axis form sheets linked by $\text{NH} \dots \text{O}=\text{C}$ hydrogen bonds . . . the $-\text{CH}_2\text{OH}$ groups form a 50/50 random mixture of intramolecular and intermolecular hydrogen bonds, and this intersheet bonding is probably responsible for the inability of alpha-chitin to swell in water."

CONCLUSIONS

1. Recognition of the propensity for chitin to participate as host in intercalation with a number of organic modifiers offers a new dimension in chitin chemistry and applications. It is a relatively common chitin property.
2. Chitin reactions involving certain solvents may be complicated by intercalation of some of the solvent itself.
3. Intercalation may vary depending upon the nature of the volatile solvent employed.
4. The degree of attraction or attachment of an intercalated organic varies; in some cases it may be essentially permanent under ambient conditions.
5. Novel applications for chitin in films and filaments, dispersions, slow release drugs and other biomedical uses should be promoted with this new technology (8).

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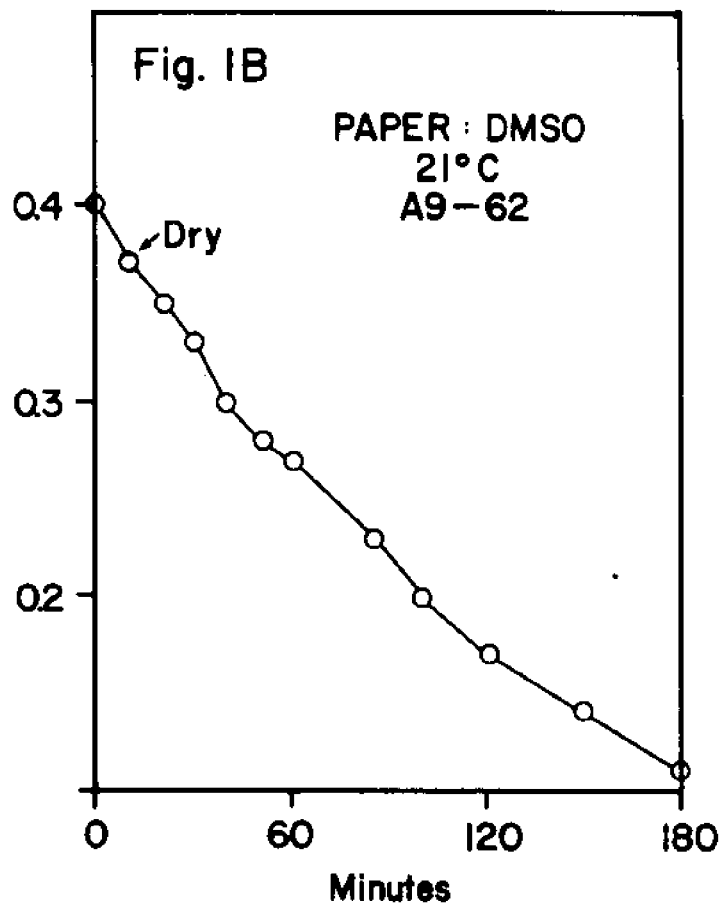
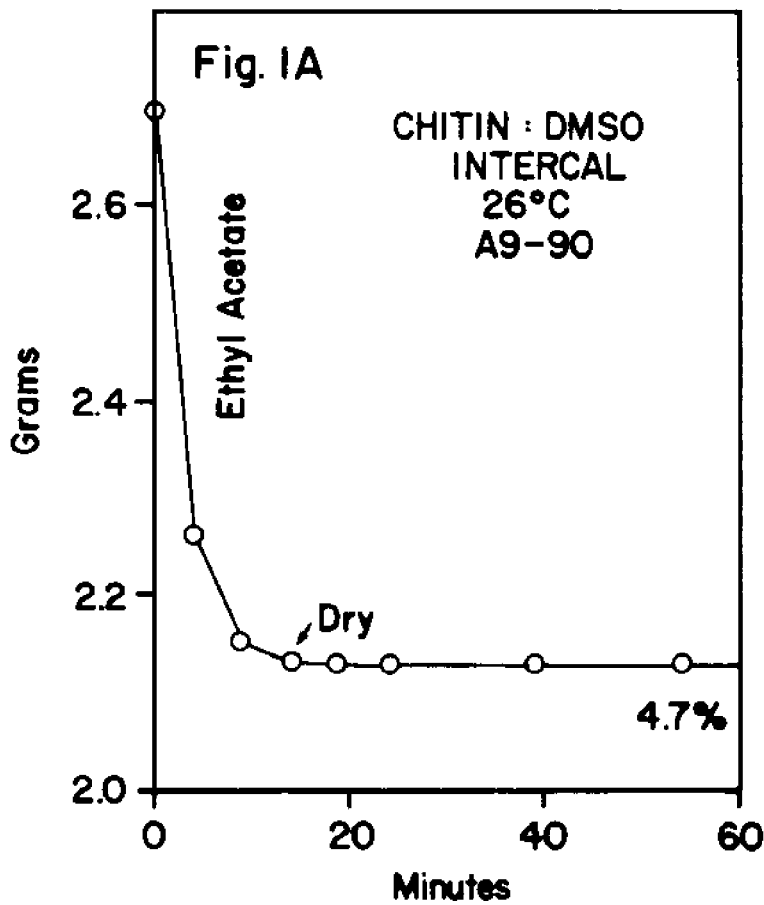
Table I. CHITINOUS INTERCALATION COMPLEXES

Chitin Isolate	g	Intercal. Agent*	Volatile Wash Solvent	Complex g	% Intercal. Agent *	Ref.
Shrimp	2.03	DMF 10 mL	-----	2.67	24.0	A9-74,95
	2.03	NAEA 2 mL	EtoAc-Acetone	2.22	8.6	A9-89
	.05	DEG 1 mL	MeCLF-EtOAc	0.54	7.4	A9-15B
	2.03	DMSO 2 mL	EtOAc	2.13	4.7	A9-90
	1.0	Pyruvic Acid 1 mL	MeCLF	1.36	26.4	A7-101
	1.0	N-Me Acetamide 3 mL	TRI	1.13	11.5	A7-17A
Prawn	0.5	N-Me Paraben 0.5 g	EtOAc	0.55	9.1	A8-145
Squid	0.5	d-Camphor 0.05 g	Formic Acid/DCE (5/3)	Clear Film No Exude	9.1	A8-102

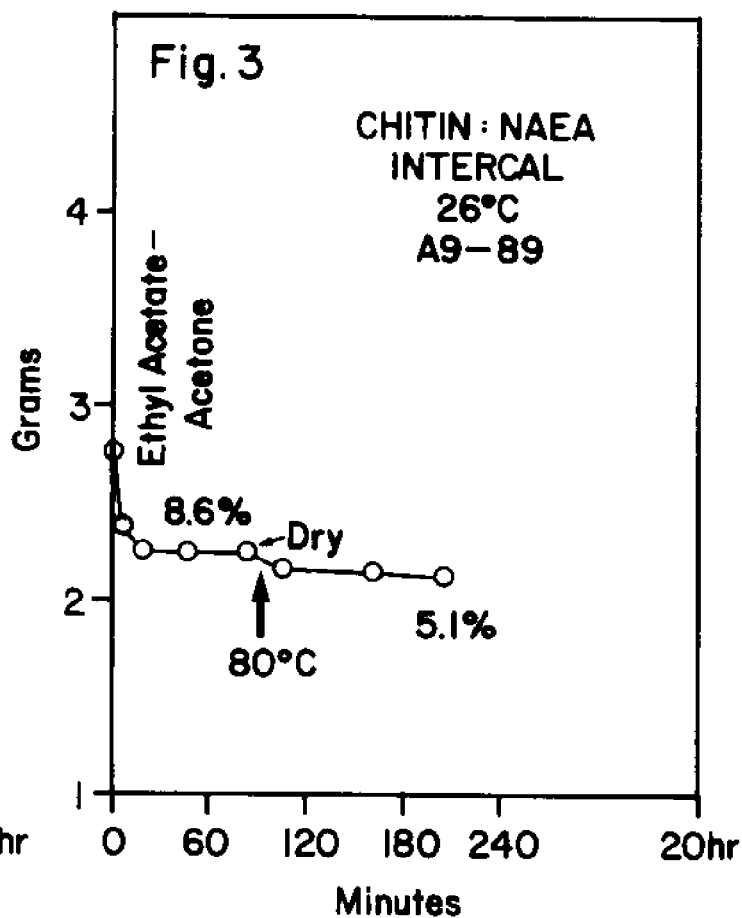
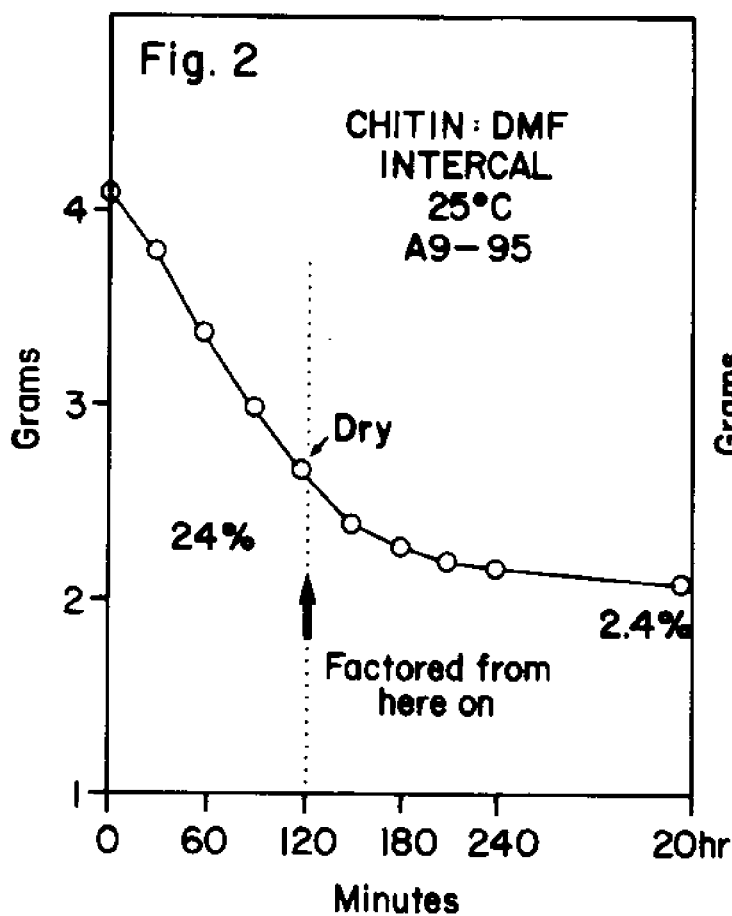
*DMF = Dimethylformamide; NAEA = N-acetylethanolamine; DEG = 2,2' - oxydiethanol; DMSO = dimethylsulfoxide; Me-Paraben = methyl p-hydroxybenzoate; DCE = 1,2-dichloroethane; EtOAc = ethyl acetate; TRI = trichloroethylene; MeCLF = methyl chloroform.

Table II. PROPERTIES OF CHITIN INTERCALATING
(GUEST) COMPOUNDS

AGENT	MW	Sp.Gr.	MV	BP°C	Sol. Param.
Dimethylformamide	73.1	0.944	77	153	24.8
Dimethylsulfoxide	78.1	1.096	71	189	24.5
N-Acetylethanolamine	103.1	1.12	92		25.6
Diethylene Glycol	106	1.118	95	245	29.1
Pyruvic Acid	88.1	1.267	69	165	25.4
N-Methyl Acetamide	73.1	0.957	76	204	29.9
d-Camphor	154.2	1.449	106	---	----



DMSO Evaporation Rates
Chitin vs. Paper



Intercalations of Shrimp Chitin
with DMF and with NAEA