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Chemical Interactions of Amino Acids and Peptides with Nitrocellulose and Di-n-butyl Phthalate

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ABSTRACT

The purpose of this study was to elucidate the mechanism whereby a protective animal colloid acts to prevent agglomeration of solvated nitrocellulose spheres during the manufacture of small arms propellant. To accomplish this, glycine and several glycine-containing peptides were incorporated into cast films of nitrocellulose and studied by means of infrared spectroscopy and X-ray photoelectron spectroscopy. Also, each of the amino acids and peptides were studied by means of infrared spectroscopy in water solution with suspended di-n-butyl phthalate present. The resulting interactions are described.

INTRODUCTION

A material called "colloid" or animal glue is used during the grain hardening and deterring steps in the ball propellant manufacturing process. In both steps of the process the "colloid" prevents agglomeration of the solvated nitrocellulose spheres. Manufacturing

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experience indicates that there is considerable variation in the performance of the "colloid." This is understandable since, typically, the "colloid" is produced by means of a crude digestion of animal tissue, yielding a mixture of amino acids and peptides. Further, the "colloid" manufacturing method can lead to considerable lot-to-lot variation in composition and this introduces the observed variation in performance. For this reason it was decided to investigate the mechanism of "colloid" action.

Glycine and a series of glycine peptides were incorporated into cast films of nitrocellulose (NC) in order to simulate "colloid" functioning in the grain-hardening step. Cast films were studied by means of infrared spectroscopy and X-ray photoelectron spectroscopy (XPS) in order to identify interactions between the components. Water mixtures of di-n-butyl phthalate (deterrent) and the various amino acids and peptides were examined by infrared spectroscopy. These mixtures were intended to identify the "colloid" action during the deterring process step.

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EXPERIMENTAL

Cast Films of Nitrocellulose for IR Study

The nitrocellulose used was obtained from Hercules Inc. and had a nitrogen content of 12.63% and a viscosity of 83.6P (10% NC by weight measured in a 10% ether-80% acetone solution). A standard solution of NC was prepared by dissolving 1.12 g nitrocellulose in 100 mL reagent-grade ethyl acetate. Samples for IR study were made by mixing 1 mL of the standard nitrocellulose solution with 5 mL of saturated methanol solution containing each amino acid and peptide. Each sample was subjected to roughing pump vacuum until no trace of solvents was found.

Cast Films of Nitrocellulose for X-Ray Photoelectron Spectroscopy Study

The nitrocellulose used has been described above. A standard solution was made by dissolving 0.84 g of nitrocellulose in 100 mL of reagent-grade ethyl acetate. Samples for XPS were made by mixing 2 mL of standard nitrocellulose solution with 4 mL of saturated methanol solution of glycine (Fisher reagent grade).

Peptides-DBP

Glycine, gly-glycine, gly-gly-glycine, and gly-gly-gly-glycine were each run on a Perkin-Elmer 621 IR Spectrophotometer as KBr pellets.

TABLE 1. Glycine Peptides

	NH (solid) (cm^{-1})	NH (H_2O) (cm^{-1})	NH (H_2O/ DBP) (cm^{-1})	ΔNH (H_2O/ DBP) (cm^{-1})
Glycine	3156	2882	2882	-
Glycyl-glycine	3286 3124	2870	2870	-
Glycyl-glycyl-glycine	3296 3053	2848	2837	11
Glycyl-glycyl-glycyl-glycine	3304 3042	2836	2822	14

In addition, each compound was run in IRTRAN cells as a water solution in contact with di-n-butyl phthalate. A matched cell containing water was run as a blank.

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DISCUSSION

Spectra were run of glycine, gly-glycine, gly-gly-glycine, and gly-gly-gly-glycine in KBr pellets, water solution, and in water solution containing suspended di-n-butyl phthalate. The data for the N–H stretching region are summarized in Table 1. Glycine in the solid state shows one peak in this region at 3156 cm^{-1} which has been assigned to the asymmetric stretching vibration of the NH_3^+ group [1]. When glycine is dissolved in water, this peak appears to shift to 2882 cm^{-1} and remains at that place when exposed to suspended di-n-butyl phthalate.

The spectra of gly-glycine shows a peak at 3286 cm^{-1} which has been assigned the ν-NH frequency; however, there is also a peak characteristic of an NH_3^+ asymmetric stretch at 3124 cm^{-1}. When gly-glycine was dissolved in water, a peak appeared at 2870 cm^{-1} which remained unchanged when brought in contact with di-n-butyl phthalate. Both gly-gly-glycine and gly-gly-gly-glycine show the ν-NH peak in the proper positions, indicating that there is less zwitterionic structure. In water solution, gly-gly-glycine showed a peak at 2848 cm^{-1} and gly-gly-gly-glycine a peak at 2836 cm^{-1}. When these two solutions were brought into contact with di-n-butyl phthalate, these peaks were shifted to lower frequencies, indicating an interaction between the NH group in the peptides and di-n-butyl phthalate. It appears that glycine and gly-glycine did not interact because of the stronger internal ionic interactions.

The infrared spectra of the amino acid and each peptide was taken when incorporated into nitrocellulose cast films. Previous work [2] has shown that unesterified hydroxyl groups in nitrocellulose can

TABLE 2. N(1s) Binding Energies (E_b)

	E_b neat (eV)	E_b mixture (eV)	ΔE_b (eV)
Glycine	402.6	403.5[a] 402.6	0.9
Nitrocellulose	409.4	409.6	0.2

[a]Apparently the sample was not homogeneous and mixed reactions were present.

hydrogen bond to a range of molecules. Examination of the hydroxyl stretching region indicated that no interaction occurred with the compounds used in this study. This may be due to the fact that the smaller molecules are involved in an internal ionic interaction while the longer materials were precluded by steric consideration.

In order to determine if the nitrate ester group of nitrocellulose was involved in an interaction, cast films of nitrocellulose and glycine were examined by means of X-ray photoelectron spectroscopy [3]. Spectra were recorded with a VARIAN IEE-15 photoelectron spectrometer using monochromatic MgK_α radiation. The vacuum in the spectrometer was maintained at 1×10^{-7} torr and the X-ray tube was run at 9 kV and 50 mA. The spectra were examined with the analyzer tuned to 100 eV electrons with about 1.5 eV fwhm resolution. The N(1s) electrons were observed for both the neat nitrocellulose and glycine and when present together in the cast film.

Table 2 contains the binding energies for each instance. The binding energy for glycine increased significantly when present in the cast film, indicating some form of interaction. Nitrocellulose N(1s) showed a slight increase in binding energy which could be due to an interaction or surface charging.

In summary, the data would seem to indicate that the longer peptides (3 or more glycine residues) interact with di-n-butyl phthalate in an aqueous medium while shorter members enter into intermolecular ionic interactions. With regard to the glycine nitrocellulose study, XPS measurements indicate an interaction between glycine and nitrocellulose. Therefore, it appears that a suitable material for use as a "colloid" in ball propellant manufacture must have a minimum chain length and be capable of interacting with both nitrocellulose and di-n-butyl phthalate.

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REFERENCES

[1] Avram and Mateescu, Infrared Spectroscopy, Wiley-Interscience, New York, 1972, p. 480.
[2] B. W. Brodman, M. P. Devine, and M. T. Gurbarg, J. Appl. Polym. Sci., 18, 943 (1974).
[3] J. Sharma and Z. Iqbal, Chem. Phys. Lett., 56, 373 (1978).

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