

VARIABLE TEMPERATURE ATR-IR STUDY OF POLY(ETHYLENE GLYCOL) CONFORMATION IN PURE LIQUID AND IN AQUEOUS SOLUTION

INTRODUCTION

PEG is an important nonionic surfactant used widely in applications such as lubrication, drug delivery, antifouling surfaces, and cosmetics. Its properties and solubility in aqueous and organic solvents arise from it having both polar and nonpolar groups in its structure. Furthermore, the conformation of PEG responds to its environment and this conformational variability is an important aspect of its properties including solubility.¹

Infrared spectroscopy has been used to probe the influence of solvent composition and temperature on the PEG conformation with CH₂ wagging and twisting modes (1400-1180 cm⁻¹), polyether backbone modes (1180-1000 cm⁻¹), and CH₂ rocking modes (800-1000 cm⁻¹) being those principally affected.^{2,3} Three possible configurations of a PEG chain segment are illustrated in Figure 1. The TGT conformation, corresponding to a helical polymer with a trans conformation about C-O bonds and a gauche conformation about the C-C bond, gives rise to infrared marker absorptions at ~1350 and 1288 cm⁻¹.⁴ Higher

temperatures lead to less helical ordering and this influences solubility and related properties.

We have used an [Horizon](#) multiple reflection ATR accessory (Figure 2) with a ZnSe trough sample plate to record infrared spectra of PEG aqueous solutions at temperatures of 18, 26, and 40 °C. The advantage of the Horizon accessory is that spectra can be obtained over a wide concentration range with good sensitivity. The sample temperature was controlled with a flow of thermostated water through a metal block positioned beneath the prism. With this experimental arrangement changes in PEG conformation in aqueous solution were evident in infrared difference spectra.

EXPERIMENTAL

The PEG was in the dimethyl ether form with a number average molecular weight of 500 (Sigma Aldrich). A series of PEO-water mixtures were prepared by volume dilution of PEG with deionized water and compositions are given as % by volume. The IR spectrometer was a Digilab FTS 4000 using Win IR Pro 3.4 (Digilab) software and IR spectra were recorded with an Horizon ATR accessory with a

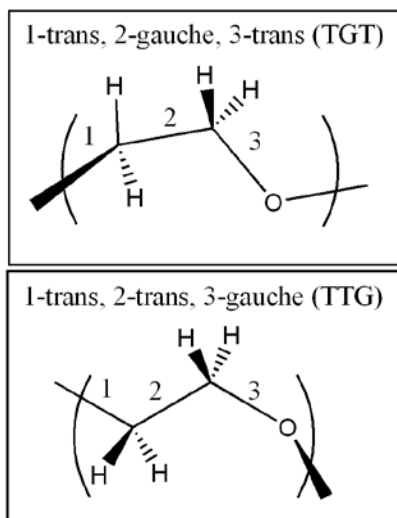


Figure 1. Three possible poly(ethylene glycol) conformations.



Figure 2. The Horizon ATR Accessory.

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ZnSe trough having approximately 13 reflections. Spectra were recorded at 4 cm^{-1} resolution and were corrected for wavelength-dependent variation in path length. The heating/cooling block gave temperature control to $\pm 0.5\text{ }^{\circ}\text{C}$

RESULTS AND DISCUSSION

The $900\text{-}1400\text{ cm}^{-1}$ region of the infrared spectrum of pure PEG at 18, 26, and $40\text{ }^{\circ}\text{C}$ is shown in Figure 3(A). This region contains the most important conformation-related bands. The spectrum is dominated by a strong mainly C-O stretch-related absorption close to 1100 cm^{-1} . The variation of the spectrum with temperature is only slightly evident in these spectra but the spectral differences are more clearly seen in difference spectra (a) between 26 and $18\text{ }^{\circ}\text{C}$, and (b) between 40 and $18\text{ }^{\circ}\text{C}$. The small amount of noise in the peak is due to the near total absorption of the IR beam from this band. The increased temperature results in a number of spectral changes of which the most general is a broadening of peaks indicating an increase in disorder.

The corresponding spectral data for a 60 % PEG aqueous solution is shown in Figure 3(B). This composition corresponds to about two water molecules for each $(-\text{CH}_2-\text{CH}_2-\text{O}-)$ chain

segment giving a minimum in the gauche/trans absorbance ratio (A_{1288}/A_{1305}) of the C-O bond (2). Only minor changes with temperature are evident again in the solution spectra but the difference spectra show more clearly the influence of temperature changes. The increase in absorbance of the 1140 cm^{-1} band and decrease in absorbance of the 1080 and 1350 cm^{-1} bands indicate that a gauche conformation about the C-C bond becomes increasingly favoured at higher temperature. A decrease in absorbance at 950 and 1288 cm^{-1} with temperature increase indicates that the trans conformation about the C-O bond becomes more stable. In general the data shows that the helical TGT configuration of PEG becomes less stable with increasing temperature.

This note illustrates the important ability of ATR-IR methods to obtain *in situ* vibrational spectra from species in aqueous environments. The addition of temperature control to the Horizon accessory extends its range of applicability to studies of thermally-influenced structural changes in bulk media and at surfaces.

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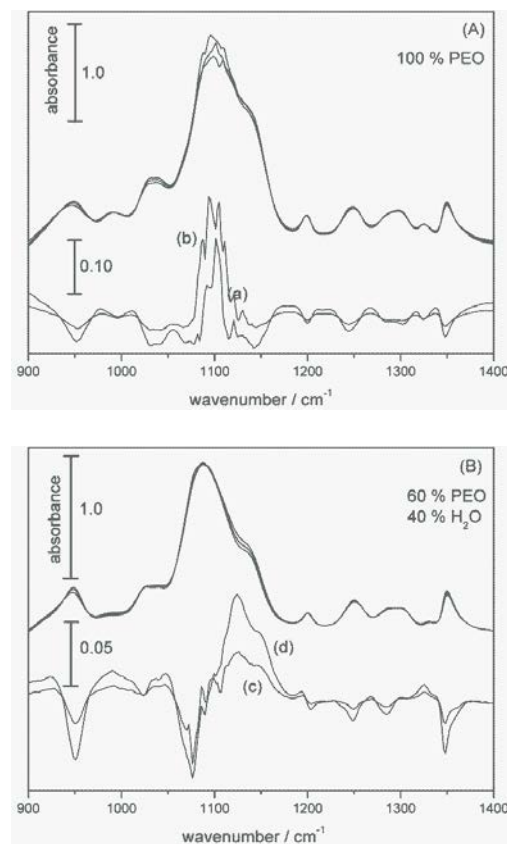


Figure 3. ATR-IR spectra of (A) poly(ethylene glycol) dimethyl ether (PEG) and (B) a 60 % aqueous PEG solution at 18, 26 and $40\text{ }^{\circ}\text{C}$. Also shown are ATR-IR difference spectra indicating the influence of temperature increase from 18 to $26\text{ }^{\circ}\text{C}$ (a and c) and from 18 to $40\text{ }^{\circ}\text{C}$ (b and d). Reprinted with permission from J.J. Shephard et al *J. Phys. Chem. B* **113**, 14229-14238 (2009). Copyright 2009 American Chemical Society.



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