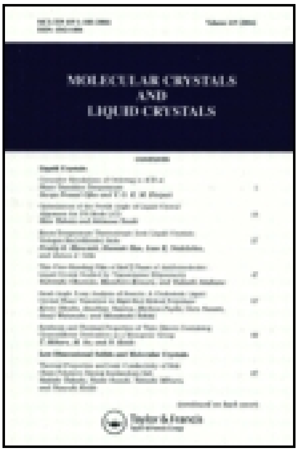

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Ion-Ion and Ion-Solvent Interaction Effects in the Acoustic Responce of Aqueous Polymeric Solutions

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ION–ION AND ION–SOLVENT INTERACTION EFFECTS IN THE ACOUSTIC RESPONCE OF AQUEOUS POLYMERIC SOLUTIONS.

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Abstract Ultrasonic and hypersonic measurements on PEG and PEGME aqueous solutions allow us to study the fundamental hydration phenomena occurring in such a system. The data are also discussed in the framework of current theories.

Keywords: polymer, PEGME, acoustic velocity, PEG

GENERAL CONSIDERATIONS.

In the present work we present the results of ultrasonic and hypersonic measurements on solutions of polyethylene oxyde (PEO) at low molecular weight (MW=600). Usually, in literature, low molecular weight PEO is named poly(ethilene glycol) (PEG) when the end groups are hydroxil groups. Its simple molecular structure $HO-(CH_2-CH_2O-)_n-H$ makes PEG a good model system for the study of water structure effects in aqueous solutions of macromolecules. In water PEG evidenciates a high degree of association with formation of well defined hydration shells[1,2]. Its strong hydrophilic effects are due to the oxygens of the oxirane C_2H_4O and to the OH end groups of the chain. The existence of associated polymer–water complexes is interpreted[2] as induced by a delicate balance between hydrophilic and hydrofobic effects. As a consequence the system shows a solubility gap, in water, at high temperature. Increasing the temperature, the strong structuring effect on H_2O molecules around the PEG chain becomes unfavorable, due to entropic reasons, and hence the system separates into two phases. It was shown that the activity of PEG increases under addition of neutral salts and, as a consequence, the cloud temperature, i. e. the lower temperature critical point, lowers considerebly[3]. The main effect of the ion–water interaction is to induce a higher polymer–polymer association that results in an asymmetric hydration shell near the PEG. In particular, in the case of alkali halides salts, such an effect increases passing from Lithium to Cesium ions, due to the different degree of salt penetration into the region around chains. Recent NMR and neutron scattering experiments[4] on the system PEO/H_2O/NaCl showed that the first hydration shell around chlorines is not significatively influenced by the presence of the polymer. In particular, the noticeable change below the cloud temperature (T=320 K) in the ^{35}Cl longitudinal relaxation rate, obtained by NMR, is induced by the presence of a longer range effect (>4Å) generated by the presence of the polymer. Ultrasonic measurements at 25.1 MHz[5] on PEO (MW=$5\cdot10^6$) aqueous solutions revealed an increasing of velocity with temperature and concentration while the normalized absorption α/f^2 decreases with temperature and increases with concentration. The fact that α/f^2 increases with concentration lower than the zero frequency shear viscosity, was rationalized in terms of a low frequency relaxation phenomenon, usual in many polymeric aqueous solutions[6].

In this paper we report on ultrasonic (25 MHz) and hypersonic measurements, as a function of temperature (0°C$\leq$T$\leq$80°C), on the systems PEG (MW=600)/H_2O , PEG/H_2O/LiCl, poly–ethylene glycol metyl ether (HO–(CH_2–CH_2O–)$_n$–CH_3, PEGME, MW=550) plus H_2O and PEGME/H_2O/LiCl. The main goal of such an experiment is to compare the results from the two different polymers, that differ only for one of the two end groups, in order to determine the hydration effects played by the oxirane monomeric units.

EXPERIMENTAL SECTION

PEG (MW=600) and PEGME (MW=550) samples were purchased from Aldrich–Chemie. The solutions were prepared using PEG and PEGME without further purification and double distilled deionized water. LiCl salt, high chemical purity grade from Aldrich–Chemie was used for the ternary systems. All the samples were prepared with a constant polymer to water ratio (10:90 by weight). The concentrations of LiCl were 1 and 2 m (molality) and in the ternary compound the same polymer/water ratio was mantained. Care was taken, following the description of ref. 2 and 3 in order to obtain stable, clear and dust free samples.

The ultrasonic measurements were performed by means of a standard pulse–echo Matec apparatus using a home made acoustic interferometer[7].

The velocity (v_s) and absorption (α/f^2), at the fixed frequency value f=25MHz, were taken in the temperature range 0÷80°C with an accuracy of ~0.5% and ~3% respectively.

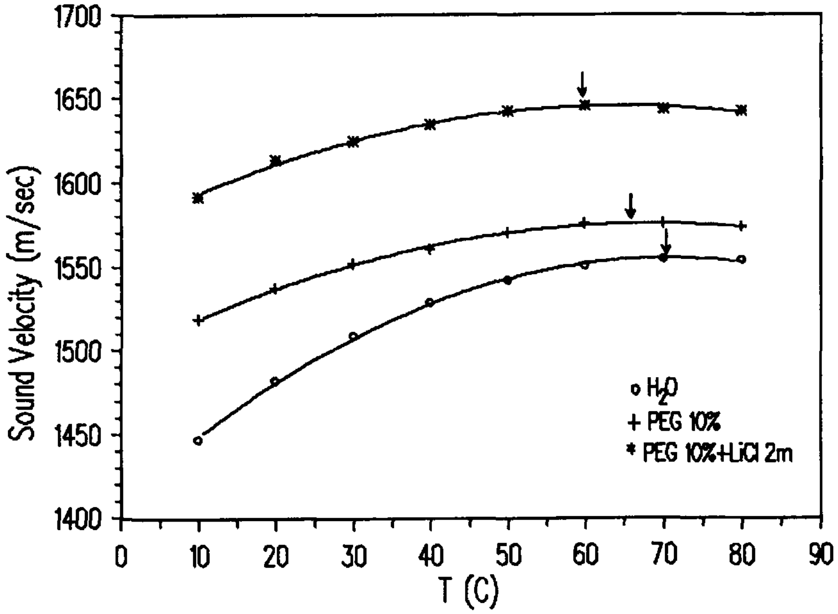

FIGURE 1 Temperature dependence of ultrasonic velocity v_s, at 25 MHz, in PEG 10% aueous solutions.

The Brillouin scattering measurements, in a 90° geometry, were performed by means of a Tropel mod. 350, piezoelectrically scanned, Fabry–Perot interferometer working at free spectral range of 16 GHz and an overall finesse of 45, while the 4880 Å line of an Ar^+ laser, at a mean power of ~800 mW, was used as probe. All the experiment was authomatized and controlled by means of an IBM PC–XT. In order to increase the photon statistics, several runs were performed at each temperature and concentration and then computer added. The good data reproducibility allowed us the determination of the hypersound velocity with an error of ~2%. The refractive index data n(c,T) necessary to the evaluation of the velocity values were measured by an Abbe′ refractometer. The density was determined by standard picnometers. The shear viscosity $\eta_s = \nu_s \cdot \rho$ (ν_s being the kinematic viscosity) determination was performed with calibrated Ubbelhode viscosimeter.

DATA REDUCTION AND RESULTS

In order to compare the results from ultrasonic and hypersonic response, the data were appropriately reduced, following an elsewhere described procedure, to obtain the two probe independent acoustic parameters v_s and α/f^2. It is well known that the light scattering response, obtained from a Brillouin scattering experiment, is composed of a central non–shifted component plus two symmetric lines (Brillouin doublet) and two asymmetric contributions originated by the conservation of the first moment sum rule[8].

$$
\begin{aligned}
I_{vv}(\omega)= & \frac{A_R\Gamma_R}{\omega^2+\Gamma_R^2}+\frac{A_B\Gamma_B}{\left[I_\omega-(\omega_0^2-\Gamma_B^2)^{1/2}\right]^2+\Gamma_B^2}+\frac{A_B\Gamma_B}{\left[I_\omega-(\omega_0^2-\Gamma_B^2)^{1/2}\right]^2+\Gamma_B^2}+ \\
& +\frac{\Gamma_B}{(\omega_0^2-\Gamma_B^2)^{1/2}}\cdot\left[\frac{\omega-(\omega_0^2-\Gamma_B^2)^{1/2}}{\Gamma_B^2+\left[\omega-(\omega_0^2-\Gamma_B^2)^{1/2}\right]^2}+\frac{\omega-(\omega_0^2-\Gamma_B^2)^{1/2}}{\Gamma_B^2+\left[\omega+(\omega_0^2-\Gamma_B^2)^{1/2}\right]^2}\right]
\end{aligned}
\tag{1}
$$

where ω_0 and Γ_B are the "true" Brillouin shift and the linewidth respectively related to the hypersonic velocity and absorption by $v_s=\omega_0/k$ and $\alpha/f^2=2\pi\Gamma/v_0\omega_0^2$. The hypersonic and ultrasonic results can be compared as it follows:

i) v_s is frequency independent while it marked changes with T and concentration;

ii) the normalized absorption turns out to be almost concentration and frequency independent and definitely lower than the corresponding classical Stokes value. Such evenience could suggest a relaxation of shear viscosity at higher frequency and/or temperature.

The T–dependence of the ultrasonic velocities in PEG and PEGME aqueous solutions are reported in figs. 1 and 2. The results from pure H_2O are also reported for comparison. The data show a typical parabolic behaviour with a shift in the temperature of the maximum T_m (arrows in the figs.) as concentration increases. Such a result, here for the first time evidenciated in polymeric solutions, was in the past observed in aqueous electrolytic solutions[7] and pure water. In the latter case such an effect is originated by a balance between the two opposite effects of the behaviour of velocity and compressibility. The observed shift of T_m is understandable with the existence of a new more close–packed structure induced by the hydration effects originated by the presence of the polymer. A confirmation of such an effect can be obtained by the ultrasonic velocities data. In fact, if one assumes that, at low concentration, the hydrated entities behave like incompressible cavities, it is possible to extract the primary hydration number n_H through the relation:

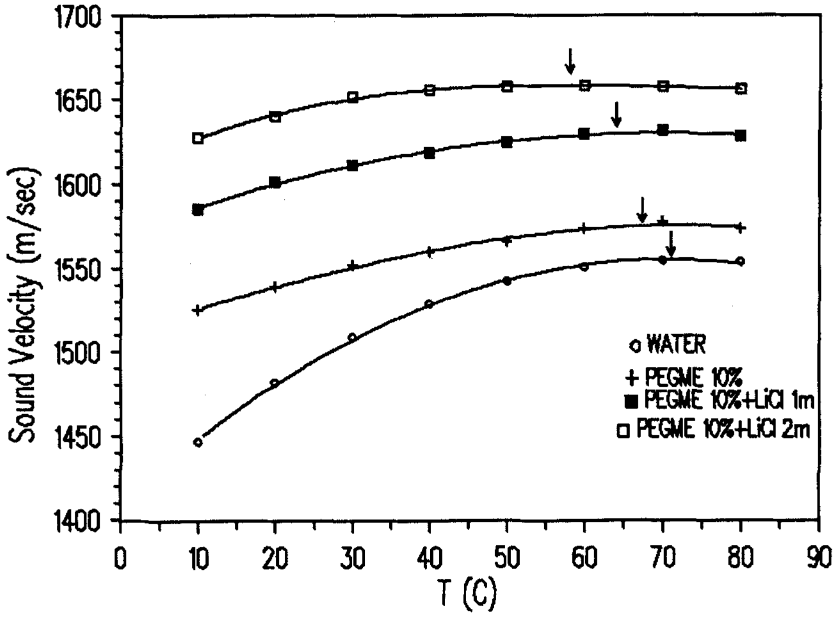

FIGURE 2 Temperature dependence of ultrasonic velocity v_s, at 25 MHz, in PEGME 10% aueous solutions.

$$n_H=\frac{\Phi_K+\Phi_S}{V_0}=\frac{1}{V_0}\left[\frac{10^3}{Md_0}(d_0\beta-\beta_0 d)+\frac{\beta_0 M_2}{d_0}+\frac{10^3}{Md_0}(d_0-d)+\frac{M_2}{d_0}\right] \qquad (2)$$

where Φ_K and Φ_B are the apparent molar compressibility and volume respectively, $\beta=1/\rho v_s^2$ and $V_0=M_0/d_0$, while the other symbols have the usual meaning.

Fig. 3 shows the T dependence of n_H for PEG and PEGME aqueous solutions. Even using such an approssimate method for the extimation of the local hydration number, the results turn out to be in good agreement with the twofold coordination of the oxygen for each oxirane monomer and of the end groups. The differences between PEG and PEGME are, in our opinion, induced by the different coordination of the different end groups in the two polymers. The addition of LiCl clearly increases the coordination number ($n_H \simeq 5$), but our LiCl concentrations are so high (1 and 2 m) that the limiting law (eq. 2) is not applicable.

Further measurements are actually in progress in our laboratory in orther to investigate the variation of n_H near the cloud point and at low concentration values of the electrolyte.

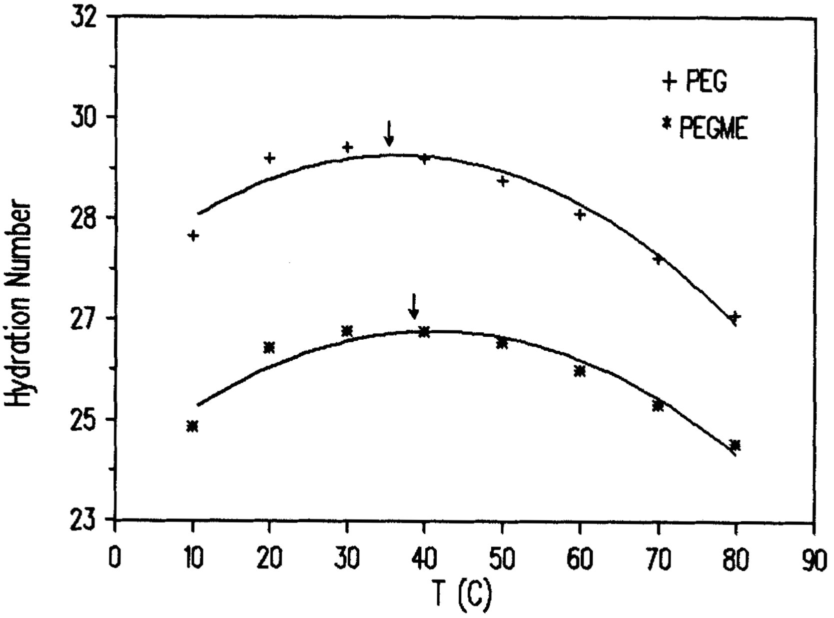

FIGURE 3 Temperature dependence of the primary hydration number n_H in PEG and PEGME aqueous solutions. Arrows indicate the temperature of the maximum value.

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