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"SOLVATION OF COBALT SALTS BY OLIGOMERIC POLYETHERS"

by

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Abstract

Polyether-salt systems involving CoBr_2 dissolved in oligomeric polyethylene glycol (PEG) and polytetramethylene glycol (PTMG) have been investigated. Both systems demonstrated conductivity maxima as a function of salt concentration. PTMG electrolytes had dramatically lower conductivities (max. $s = 3.6 \times 10^{-7}$ S/cm for PTMG, max. $s = 1.45 \times 10^{-5}$ S/cm for PEG at room temperature) which can be explained on the basis of spectral data which indicate the existence of predominantly neutral species in PTMG. The reason for the difference in the types of species present in PEG and PTMG can be rationalized on the basis of the chelate effect.

Key Words: polymer electrolytes; ionic conductivity; complex ions

Introduction

An intriguing example of the ubiquitous process of solvation can be found in the solid polymeric electrolyte systems, in which high molecular weight polymers, typically polyethers, act as hosts for inorganic salts. These systems are capable of significant ionic conductivities in the amorphous regions and, due to their potential application in secondary batteries, have been studied extensively for about a decade[1,2]. In spite of considerable developments in the field, the specific ways that the polymer chains interact with and solvate salts in these systems are not completely understood. One fundamental approach towards gaining further insight into these unique electrolyte systems involves the use of low molecular weight polyethers as model systems[3]. These short-chain molecules, or oligomers, possess several crucial advantages over their higher molecular weight brothers for the purposes of fundamental research: the oligomers are fully amorphous and thus single-phase systems; also, they are liquids, which allows easy preparation and handling, as well as convenient analysis by conventional electrochemical, spectroscopic, and viscosity methods. Previous studies have focused on polyethylene glycol-based systems[4-6], polypropylene glycol systems[7-9], and ethylene oxide-propylene oxide (EO/PO) copolymers[10-12]. This study explores the polyethers, polyethylene glycol (PEG) and polytetramethylene glycol (PTMG).

Spectroscopic techniques are generally the most convenient routes to learning about local structure in amorphous systems. Unfortunately, the alkali metal cations, the ions studied most commonly in this field, are not very easily probed by most spectroscopic methods. On the other hand, ultraviolet-visible (uv-vis) spectroscopy has been used for many decades to derive quantitative, specific information about the local environment of transition metal ions. In fact, in the late 1950's, when Katzin [13,14] began his groundbreaking work in the area of nonaqueous solvents, he chose to confine his preliminary studies largely to divalent cobalt salts particularly because of the information so readily accessible for the Co^{2+} ion by uv-visible spectroscopy. In this work, following the logic of Katzin, we have used uv-visible spectroscopy to probe the nature of the complex species present in solutions of CoBr_2 in polyethers. Essential to our work have been the spectra of the complex ions present in the CoBr_2 -acetone system, which have been elegantly identified by Fine[15].

Experimental Procedures

Anhydrous CoBr_2 (Alfa) was dried in a vacuum oven at 120°C overnight and stored in a drybox prior to use. Polyethylene glycol (PEG), mol. weight. 400, and polytetramethylene glycol (PTMG), mol. weight. 650, were supplied by Scientific Polymer Products and used as received. The electrolyte solutions were prepared by the mutual solvent method: the salt was first dissolved in ethanol; then the oligomer was added; finally, after sufficient mixing, the ethanol was allowed to evaporate overnight in air. Traces of ethanol and moisture were then removed by heating the samples to 90°C for 48 hours in a vacuum oven. The samples were stored in evacuated dessicators prior to use. Karl-Fischer titration indicated that the resulting samples contained approximately 200 ppm of water. Thermogravimetric analysis combined with a mass spectrometer showed that ethanol was eliminated to within 0.02%.

Viscosities were measured using an Irvine Park Falling Needle Viscometer with constant temperature water bath. The temperature was held at $25.0 \pm 0.2^\circ\text{C}$, and all samples were allowed to equilibrate in the chamber for 20 minutes prior to measurement. Two low density needles were used for each sample to insure accurate measurements. The densities of the

solutions, needed for the calculation of viscosity, were calculated based on linear additivity of salt and oligomer densities; the error induced by this assumption was shown to be within 2%.

Conductivity measurements were performed using a Solartron frequency response analyzer. A teflon cell with platinum electrodes was used.

Visible spectra were recorded using a double-beam Perkin Elmer Lambda 6 Uv-Visible spectrometer. A 1nm slit width, 100 nm/min scan speed, and .3nm data interval were used. Quartz cuvettes of pathlength .1, .2, .5, 1, 2, and 5mm were employed. A matching cell containing pure oligomer was used as the reference.

From a close reading of coordination chemistry, one would expect the following complex ions to be most probable in a system involving CoBr_2 and a nonaqueous solvent: $^{\text{oct}}\text{CoL}_6^{2+}$, $^{\text{oct}}\text{CoBrL}^{5+}$, $^{\text{tet}}\text{CoBr}_2\text{L}_2^0$, $^{\text{tet}}\text{CoBr}_3\text{L}^-$, and $^{\text{tet}}\text{CoBr}_4^{2-}$, where the left superscript is the symmetry of the aggregate (oct=octahedral, tet=tetrahedral), L=ligand donor atom (in our case L=an ether oxygen from the oligomer), and the right superscript is the charge on the aggregate. The spectra of the isolated tetrahedral complex ions were determined (Fig. 1) in the following way: the spectrum of the PTMG- CoBr_2 system closely followed Beer's law up to 0.025M; this indicated that only one species was present in this range of concentrations. The spectrum was closely similar to the spectrum for $^{\text{tet}}\text{CoBr}_2(\text{acetone})_2$ identified by Fine[15] both in peak maxima and extinction coefficients and was thus hypothesized to be due to pure $^{\text{tet}}\text{CoBr}_2\text{L}_2$. Adding LiBr to PTMG- CoBr_2 systems forced the stepwise formation of the negatively charged higher bromo complexes, behavior again analogous to Fine's acetone systems, and allowed calculation of the isolated spectra of $^{\text{tet}}\text{CoBr}_3\text{L}^-$ and $^{\text{tet}}\text{CoBr}_4^{2-}$ (which were also undeniably similar to Fine's spectra). It was assumed that the calculated spectra are valid for both the PTMG and PEG systems due to the close chemical similarity of the oligomers. The concentrations of the tetrahedral species in PEG systems and more concentrated PTMG systems were calculated quantitatively using the PLSplus software for multicomponent analysis supplied by Galactic Industries. The Partial Least-Squares (PLS) algorithm is described by Haaland and Thomas[16]. For our study, the training set consisted of 18 standard spectra. Predicted errors are within 5% and spectral residue were often well under 5%. Unfortunately, though the octahedral species do absorb in the visible region (~ 570 nm), their intensities are 20-100 times lower than those of the

tetrahedral species. Since the octahedral bands are masked by the highly absorbing tetrahedral bands, we have resorted to calculating the concentration of octahedral species by subtraction (octahedral conc. = total conc. - tetrahedral conc.).

Results and Discussion

The room temperature conductivities (σ) and absolute viscosities (η) for PEG-CoBr₂ systems and PTMG-CoBr₂ systems as a function of salt content are depicted in Figs. 2 and 3. It can be seen that the viscosities increase dramatically with increasing salt content for both oligomers. In contrast, Cameron et al. [10,11] find very little effect on viscosity until approximately 1M salt content for alkali metal thiocyanate-EO/PO copolymer systems. Our results indicate that the complexation of the divalent cobalt salt greatly stiffens the oligomer chains, perhaps due to a strong intermolecular "crosslinking" effect.

Both the PEG and PTMG systems exhibit a maximum in conductivity at roughly 0.5M. In both cases this conductivity maximum is associated with the onset of a dramatic increase in solution viscosity. This phenomenon has been observed for several salt-polyether systems [3,9,10] and is attributed to the coupling of the mobility of the charged species with solution viscosity. In simple terms, although increasing the salt concentration increases the number of charged species available to carry current, the solution viscosity increases as well, making macroscopic charge transport more difficult. The conductivity maximum indicates a balance between these two opposing forces: increasing numbers of charged species and decreasing carrier mobility.

Note also that the conductivities of the PTMG system are two orders of magnitude lower than those of the PEG system (max. $\sigma \approx 3.6 \times 10^{-7}$ S/cm for PTMG, max. $\sigma \approx 1.45 \times 10^{-5}$ S/cm for PEG). This is not explained solely by the higher viscosities of the PTMG systems since the PTMG systems have viscosities only about 7 times higher than PEG systems. That electrolytes involving PTMG have low conductivities has been recognized earlier [12,17], although no satisfactory reasons for this observation have been given so far. To explore this issue we turn to the results of our spectroscopic investigation.

As expected, the complex species present in solution for the PEG and PTMG systems differ considerably. Our spectral deconvolutions indicate that for PTMG the predominant species is always ${}^{\text{tet}}\text{CoBr}_2\text{L}_2$; at concentrations above .2M, a small fraction of the cobalt becomes involved in ${}^{\text{tet}}\text{CoBr}_3\text{L}^-$ and octahedral species, but even at .89M, the neutral species accounts for over 65% of the cobalt present. On the other hand, in the PEG systems, at all concentrations studied (.02-.75M) more than 50% of the cobalt present could be attributed to charged, octahedral species. The major tetrahedral species present is always ${}^{\text{tet}}\text{CoBr}_3\text{L}^-$ although ${}^{\text{tet}}\text{CoBr}_2\text{L}_2$ is present in smaller amounts. At concentrations above .3M, the doubly charged ${}^{\text{tet}}\text{CoBr}_4^{2-}$ also becomes evident. A graphical representation of the percentage of cobalt present in the neutral form as a function of overall salt content for PEG and PTMG is presented in Fig. 4. Clearly the low conductivities in the PTMG system are due to the predominance of neutral species in this system.

Why then are neutral species favored for PTMG, but not for PEG? For an explanation, we look to the chelate effect of classical coordination chemistry [18]. When a ligand (such as a polyether in this case) possesses more than one donor atom for complexing an ion, that ligand is called "multidentate" and is found experimentally to produce much stabler complexes than those formed by monodentate ligands; this is the chelate effect. It has also been found that intramolecular "chelate rings" possessing 5 members produce by far the stablest complexes. When PEG complexes a cobalt ion with two adjacent ether oxygens, a 5-membered chelate ring is formed (involving -Co-O-C-C-O-). On the other hand, PTMG is capable of only the far weaker 7-membered chelate rings (-Co-O-C-C-C-C-O-). This means that PEG is able to complex metal ions quite effectively whereas PTMG is a weaker ligand due to the less effective chelation. For PTMG systems, for the most part, the oligomer is unable to displace the anions from the metal ion's first coordination sphere, and neutral species predominate. But because of the effective 5-membered rings possible with PEG as ligand, PEG is able to compete successfully with the bromide ions for inner coordination positions; the octahedral species which are a major species in the PEG system might involve as many as five 5-membered chelate rings.

We also note that with increasing salt concentration, higher bromo complexes are always formed to some degree. This result is consistent with the observations of several others [6,8,9]

that, in salt-polyether systems at higher salt concentrations, a higher fraction of ion aggregates develops:

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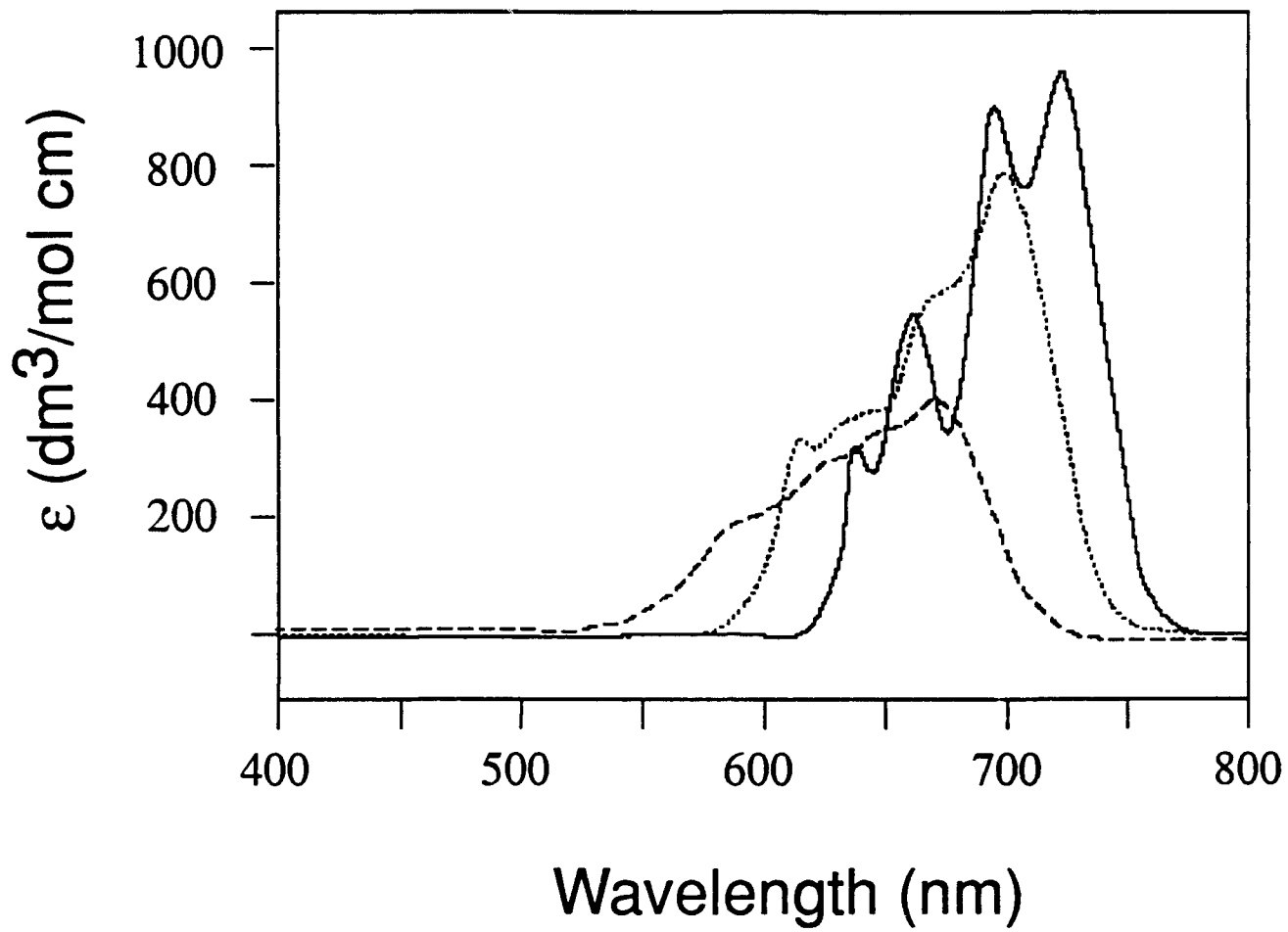
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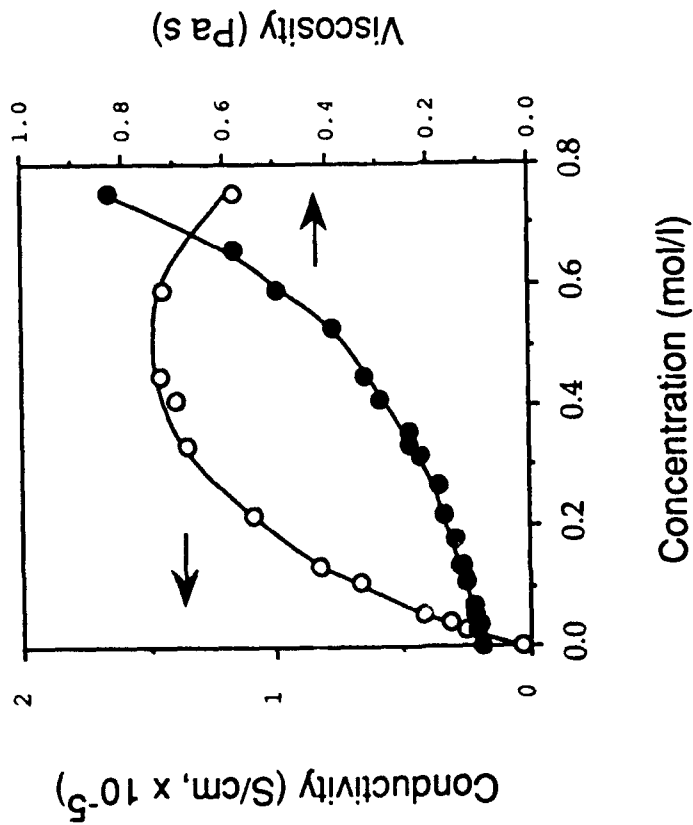
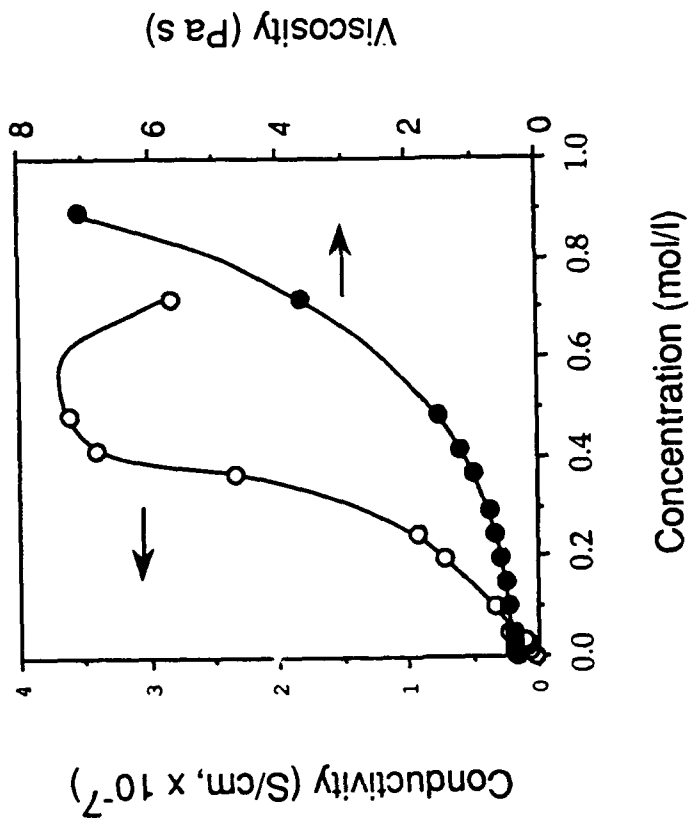
Figure 1. Visible Spectra of Isolated Tetrahedral Bromo Complexes of Cobalt. CoBr_2L_2 (- -); CoBr_3L^- (— —); CoBr_4^{2-} (—), where L=polyether oxygen ligand.

Figure 2. Room Temperature Conductivity (○) and Viscosity (●) as a function of salt concentration for PEG- CoBr_2 systems.

Figure 3. Room Temperature Conductivity (○) and Viscosity (●) as a function of salt concentration for PTMG- CoBr_2 systems.

Figure 4. Percentage of cobalt involved in neutral tetrahedral species as a function of salt concentration for PEG- CoBr_2 systems (○) and PTMG- CoBr_2 systems (●).





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