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M. Mendolia, H. Cai and G.C. Farrington

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Department of Chemistry
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The work described in this review demonstrates that UV/Visible spectroscopy is a very useful texhnique for learnig about the coordination of certain transition metal ions in polymer electrolytes. The results demonstrate unequivocally that complex ions exist in polymer electrolytes of this sort, particularly at moderate to high salt concentrations and at elevated temperatures. Furthermore, it appears that free anions and anionic complex species are the predominant charge carriers in the electrolytes studied here. In fact, out studies indicate that the principal mechanism of cation mobility in Co(II) and Ni(II)-PEG electrolytes is by the motion of complex anions, not the diffusion of uncomplexed cations.

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"THE STUDY OF POLYETHER SOLVATION MECHANISMS USING UV-VISIBLE SPECTROSCOPY"

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M. Mendolia, H. Cai and G.C. Farrington

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University of Pennsylvania
Department of Chemistry
Philadelphia, PA 19104-6323

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The Study of Polyether Solvation Mechanisms Using UV-Visible Spectroscopy

Michael Mendolia, H. Cai, and Gregory C. Farrington
Department of Materials Science and Engineering
University of Pennsylvania
3231 Walnut Street
Philadelphia, PA 19104 U.S.A.

I. Introduction

Since the proposal by Armand [1] that high molecular weight polyethers containing dissolved ions could be used as solid polymeric electrolytes (SPE's), there has been considerable research dedicated to the pragmatic issues of improving the ionic conductivities of these systems and of developing polymer-based high energy density rechargeable batteries. Macromolecular solvents, while solid in the bulk state, have almost liquidlike mobility on the microscopic scale. This unique quality makes these systems an extremely interesting branch of electrochemical materials which cannot be fully understood in terms of more classical models either of conventional low molecular weight liquid electrolytes or of the well-known crystalline ionic conductors (e.g. the β-alumina family). Exploring the more fundamental aspects of these systems is important in its own right, but should also serve to clarify the mechanism of ionic conductivity and lead to the selection of more suitable battery materials.

Current theories regarding the mechanism of ionic conductivity in polymer electrolytes [2, 3] are necessarily vague. The general idea is that the motion of free ions or charged ionic clusters or the exchange of single ions among these clusters is brought about by the high segmental mobility of the polar polymer host. In one conception, the ionic species are thought to hop along coordination sites on the polymer chains. Many fundamental questions remain to be answered. First of all, how do macromolecular polyethers solvate ionic salts? What are the local environments of the ions? Since the dielectric constant (ε) of polyethers is very low (around 4-8; compare 79 for water), the existence of ion-pairs or clusters in these solvents is virtually inevitable. So what charged species should we expect? Which of these species is the most mobile? Do cations in fact hop along the polymer chains or is charge carried more rapidly through the motion of complex anions? In fact, a great deal of evidence indicates that anions are far more mobile than cations in these systems, despite continuing controversy over the measurement of transport numbers

[4]. In fact, assuming largely anionic conductivity, some researchers [5] have come to expect high conductivities in systems where the presence of the salt dramatically increases the glass transition temperature of the polymer. The reasoning is this: strong cation bonding to the polymer chain (hence high T_g) liberates anions from cation association and thus results in higher anion mobility and conductivity. Is this concept valid?

Learning about the local structure of the ions in these systems is certainly the first step towards answering these questions. Unfortunately, structural information is difficult to acquire for amorphous systems. The standard structural techniques such as X-ray diffraction lose their usefulness in systems lacking translational symmetry, and spectroscopic techniques become generally the most convenient probes of local structure. In particular, ultraviolet-visible spectroscopy could provide critical information about the nature of the ion/ion and ion/polymer interactions in polymer electrolytes, though its use has been neglected because most research on polymeric electrolytes has focused on lithium as a cation. As discussed by Gauthier et al. [6], lithium is the foremost choice for battery applications mainly because lithium ion transport allows the use of lithium metal as the anode material. Because lithium has a low equivalent weight and is highly reactive, lithium electrodes help to achieve batteries with very high energy densities.

Regrettably, the very characteristics that make lithium interesting technologically impede fundamental studies. The local environment of lithium is not easily investigated by most spectroscopic methods. In contrast, transition metal ions such as divalent cobalt or nickel have rich spectroscopies which have been employed successfully to determine the coordination of these cations for many decades. Although the incorporation of transition metals has not been investigated by most researchers of polymer electrolytes, there has been some interest in these "exotic" cations [7-12] . In earlier studies, the polymer host of interest was usually high molecular weight, linear polyethylene oxide (PEO) whose inherent semicrystalline nature greatly complicated experimental studies. The advantages of visible spectroscopy in these systems have not been exploited with the exception of one study in which Huq et al. [10] used visible spectroscopy to investigate PEO-Ni(II) and PEO-Co(II) systems. However, their focus was on issues of hydration/dehydration, and they made no attempt to identify specific polymer-salt complex species.

The availability of worthwhile spectroscopic information strongly argues for the use of transition metal salts in fundamental studies of polyether-salt systems. However, high molecular weight PEO, the most commonly studied polymer host, exhibits complicated multi-phase behavior when complexed with most inorganic salts which make it impractical for such basic studies.

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Some preliminary work has been done on low molecular weight polyethers whose chains are so short that they are actually liquids. These liquids certainly retain the chemistry of their longer-chained analogs (except for a higher concentration of endgroups), but in addition to being single-phase amorphous systems, they are easily handled and lend themselves readily to elecrochemical, spectroscopic, and viscometric analysis. Thus, they are suitable model systems, at least for the chemical interactions which occur with the longer chain materials if not the full spectrum of dynamics.

The short-chain version of polyethylene oxide (PEO) is polyethylene glycol (PEG) or polyethylene glycol dimethyl ether (PEGM) (See Fig. 1). PEGM is thought to approximate the chemistry of PEO more closely because it lacks the active hydroxyl endgroups of PEG. These materials are liquids at room temperature below a molecular weight of roughly 600 daltons. Thus the molecular chains are truly very short (the PEO ordinarily studied for use as a polymer electrolyte usually has a molecular weight near 1,000,000 daltons) and these materials are called oligomers, not polymers (the definition "polymer" normally becomes applicable at molecular weights near 15,000 daltons when chain entanglements begin to develop).

It is interesting to note that polyethylene glycol can be used to extract metal ions into noncomplexing organic solutions. Studies [13, 14] indicate that this ability occurs with PEG's of roughly 7 repeat units or more (i.e. the molecular weight must be at least 300 daltons). Because of this limit, we have worked principally with PEG of average molecular weight 400, commercially available (Polysciences, Inc.). Our goal has been to understand the solvation of transition metal salts in low molecular weight polyethylene glycol and other oligomers by using uv-visible spectroscopy to determine local ionic environments and the nature of complex ion species. The results provide considerable insight into the structure and mechanism of conductivity in electrolytes formed with high molecular weight polymers and other types of salts.

II. A Brief Review of Solvation and Complexation

In solid polymeric electrolytes, polyethers solvate inorganic salts. These polymers can be considered to be "immobile" nonaqueous solvents; they have the chemical characteristics of typical nonaqueous solvents but are macroscopically immobile, unlike normal nonaqueous solvents which are small molecules, free to move long distances. When considered from this viewpoint, one immediately sees that these systems are an exotic extension of nonaqueous solution chemistry, and that the classical chemical studies on the nature of solvation carried out on liquid electrolytes are extremely pertinent.

Thermodynamically, an inorganic salt will spontaneously dissolve in a solvent if the process reduces the total energy (Gibb's free energy) of the system. For the lattice energy of the salt to be overcome, an energetically favorable association must occur between the dissolved salt and the solvent. The change in Gibb's free energy (ΔG) is written:

$$\Delta G = \Delta H - T\,\Delta S$$

where ΔH is the enthalpic change, ΔS is the entropic change, and T is the absolute temperature. The destruction of the crystal lattice upon dissolution leads to a large gain in entropy, but the alteration of the solvent structure must also be considered in calculating the overall entropy change. For example, specific short-range interactions may cause a net ordering of the solvent by the ions. In polymeric media, the loss of translational entropy of the solvent caused by ion solvation is much smaller than that for low molecular weight solvents. As Vincent [3] points out, the entropy of solvation is likely to be always positive in polymeric systems and would not be expected to vary greatly from salt to salt. On the other hand, the enthalpy of the process will be very dependent on the nature of the salt in question.

Enthalpic ion-solvent interactions may be grouped into three general categories: 1) long range electrostatic forces; 2) short range specific chemical interactions between the ions and the solvating groups, such as coordinate bond formation; and 3) nonelectrostatic interactions.

The strongest electrostatic interactions occur between ions, but they also arise between ions and neutral dipolar molecules. The latter interactions are quite important for the case of ions dissolved in a polar solvent. Van der Waals forces and hydrogen-bonding also play a role in stabilizing ionic solutions. Hydrogen bonding is particularly important as a mechanism of solvating anions. Solvents not containing acidic hydrogen (aprotic solvents) cannot form hydrogen bonds with anions. Despite their poor ability to solvate anions, aprotic solvents may be capable of dissolving salts up to high concentrations, primarily through strong cation solvation. High molecular weight PEO, with only a negligible concentration of hydroxy endgroups, is considered aprotic. This is clearly not the case for low molecular weight PEG.

Other enthalpic interactions depend on the chemical nature of the species being solvated. For example, solvents that can act as electron-pair donors (Lewis bases) can undergo specific interactions with metal cations that are electron-pair acceptors (Lewis acids). Notably, the transition metals may act as Lewis acids due to their unfilled d-orbitals; the specific nature of the interaction depends on the particular coordination characteristics of the metal ion. Lewis acid-base interactions are categorized as specific chemical.

The third type of enthalpic interactions are simply called nonelectrostatic. One example is solvent cavity formation. If strong solvent-solvent bonds exist in a system (e.g. in water, where hydrogen bonding is prevalent among the water molecules), the solvent may be considered structured. For solvation to occur, a cavity must be formed in the liquid to accommodate the ion and some solvent-solvent bonds must be broken. This effect is expected to be minimal for polyether solvents, which are unstructured and have low energy densities. For polymer solvents, a more important nonelectrostatic interaction may be the energy associated with the formation of strained conformations required for optimal ion coordination.

An early attempt to model the solvation process was presented by Born in 1920 [15]. Among his simplifying assumptions, Born neglected all interactions other than electrostatic. He also assumed that the ions could be described by rigid charged spheres and that the solvent was a structureless continuum of uniform dielectric constant ε, corresponding to the bulk value. Born's solvation energy, ΔG_{solv}, is then computed as the net electrostatic work of discharging one ionic sphere in vacuum and then recharging it in a medium of dielectric constant ε:

$$\Delta G_{solv} = \frac{-NZ^2e^2}{2r} \left[1 - \frac{1}{\varepsilon} \right]$$

where N is Avogadro's number, Z the charge on the ion, and r the crystallographic radius. Although an oversimplification, this model does explain some general empirical trends: smaller ions are more easily solvated (larger negative free energy change), and solvents with higher dielectric constants are usually more effective at solvation.

However, there are several problems with the Born model. First of all, the energy ΔG_{solv} is always negative, signifying that all ions would rather exist in a solvent than in vacuum. As such, the model does not consider the lattice energy of the crystalline salt, which in reality must be overcome for solvation to occur. Also, the representation of is ions as independent rigid spheres or the solvent as a uniform continuum is often dangerously unrealistic.

There have been numerous efforts to correlate various solvent characteristics with solvating ability. One parameter widely used is the dielectric constant of the solvent. The higher its dielectric constant, the more effective a solvent should be in shielding oppositely charged ions from each other and in decreasing ion pair formation. In solvents of low dielectric constant, such as benzene ($\varepsilon = 2.27$), solvation energies are very low and contact ion pairs are to be expected. Even in solutions as dilute as 10^{-6} M in benzene, extensive ion pair formation is found [16]. Pettit and Bruckenstein developed expressions to describe ion pairing in low dielectric constant solvents [17]. Their fundamental thermodynamic consideration treats ionic aggregates as polarizable spheres in contact, held together by electrostatic forces, in a solvent of uniform dielectric constant. They reached several interesting conclusions: for solvents with dielectric constants less than 7, ion pairs AB predominate over free ions, A^+ and B^-, even at low concentration (e.g. 10^{-5} M); as the concentration increases, association of ions in solution occurs by a stepwise mechanism (e.g. first AB, then ABA^+, then neutral $(AB)_2$, and so forth). Interestingly, charged species play only a small part in the total equilibrium; neutral species such as AB predominate while charged aggregates like ABA^+ or BAB^- are virtually absent. These results are pertinent to the study of polymeric electrolytes because for polyethers, whose dielectric constant is ≈5, the fraction of dissolved salt present as charged species could be quite small, in complete contrast to the picture many researchers envision, that of free ions floating in a polymeric sea. Of course, this study was done for small molecule solvents. The unusual complexing abilities of polyethers might be able to lead to a higher concentration of charged species than would otherwise be expected.

Unfortunately, the dielectric constant is not, on its own, a good measure of the solvating ability of a solvent. Generally, liquids with higher dielectric constants are better solvents, but the salt KCl dissolves equally well in propylene carbonate (ε =64.4) and in 1-butanol (ε =17.1) [18], a discrepancy that demonstrates other factors are also important in solvation.

Coordination chemists are more likely to classify solvents on the basis of their ability to donate electron pairs to solutes. Solvating power is not simply a function of dipole moment; the best solvents generally have molecular structures conducive to solvation. For example, water solvates anions effectively through hydrogen bonding because not only does hydrogen have a high charge density (due to its small size), but it juts out from the molecule and is well-exposed. Several water molecules can cluster about the anion without crowding. The dipolar aprotic solvents dimethylsulfoxide (*dmso*) and dimethylformamide (*dmf*) are highly polar. For these solvents, the electron lone pairs are situated on the oxygen atom which protrudes from the rest of the molecule. Due to the electron pairs on these well-exposed atoms, cations are solvated very strongly. On the other hand, the positive charge is diffused over so many atoms that only weak solvation of anions is accomplished.

The best-known scheme for classifying solvents as electron-pair donors is Gutmann's scale of "donor numbers" (DN) [19]. The donor number is defined as the negative enthalpy of the reaction between the solvent in question and antimony pentachloride ($SbCl_5$). The general experimental trend in solvation ability, pyridine > acetonitrile > nitromethane, is confirmed by the DN parameter (i.e. 33.1 > 14.1 > 2.7), but Gutmann's scale also predicts that the very poor solvent diethyl ether should be better than water (DN = 19.2 and 18.0, respectively). This anomaly arises because the Gutmann scale does not consider the hydrogen bonding ability of the molecules.

The work of Katzin [20-23] in the years spanning 1950-1970 greatly illuminated the processes of solvation in nonaqueous solvents. Katzin challenged the view that all solvation mechanisms result in solvated, dissociated ions and proposed the idea that the behavior of inorganic salts in water is just a special case of a more general solvation phenomenon. Confronted with the problem of making exploratory studies of nonaqueous solvents, about which so little was known at the time, Katzin chose to largely confine his initial studies to the cobalt(II) cation, just as we have used transition metal ions to explore the nature of polymer solvation, and for the very same reason -- the particular affinity of these ions to spectroscopic investigation.

While ions in water are usually completely dissociated and interact only electrostatically, in organic solution Katzin proposed that cations and anions may be associated to give neutral molecular species. In such a case, cations and anions do not have separate identities, and it would be completely inaccurate to model the ions as independent, charged spheres as Born's model does. On the other hand, the interaction Katzin proposed does not simply imply ion-pairing, the close approach of oppositely charged ions. In Katzin's model, the anion is in contact with the cation, and some degree of covalent electron-sharing occurs between the two. This phenomenon in which anions are unusually strongly bound to certain cations in nonaqueous solvents was dubbed the *Katzin effect* by Jorgensen [24] in 1963.

The fact that the transition metal salts are on the whole more soluble in nonaqueous solvents than alkali or alkaline earth salts implies that the Katzin effect is more effective in promoting the dissolution of salts of transition metals than of other cations. For example, as ethanol is added to an aqueous solution of KCl, the solubility of the salt steadily decreases; in the system, $CoCl_2$-water-acetone, although the salt solubility drops initially with increased concentration of the organic component, there is a high solubility region at high organic content. Katzin explains this behavior in the following way: in aqueous solution, the cations are completely surrounded by water molecules, but as the organic component is added, a competition between water and the organic solvent occurs, and eventually the organic solvent successfully displaces some water from the primary solvation shell; as this occurs, the system's overall dielectric constant is lowered, causing increased cation-anion attraction, and so the anions also begin to compete for inner coordination positions; eventually the cobalt has two chlorides in its primary shell, the other positions (2 or 4) taken up by a combination of water or organic molecules. The final result is a neutral, undissociated salt molecule dissolved in a neutral solvent. Generally, the attachment between cation and anion is not permanent and the anions are *labile*, able to rapidly replace one another.

Katzin reasons that the alkali and alkaline earth metal ions such as Na^+ (note that Li^+ is an exception) exhibit lower solubility in organic solvents due to their lower coordinating ability. NaCl for example does not form a hydrated crystalline phase, indicating that water is coordinated weakly. One presumes then that the interaction with organic Lewis bases would be even weaker. On the other hand, the transition metal ions are noted for their ability to bind water and form stable complexes.

To be sure, the idea that anions could enter the solvation shell of a cation did not have its origins with Katzin. In fact, the recognition of the true nature of "complexes" began with Alfred Werner [25, 26] at the beginning of this century. Werner made it clear that neutral molecules such as water or ammonia, and anions such as Cl^- could stably exist in the first coordination sphere of an ion. The donor molecules are termed *ligands* and the entire molecular aggregate is called a *complex*. We now define a ligand as any molecule or ion that has at least one electron pair that can be donated. Werner showed that neutral molecules were bound directly to metal ions so that complex salts such as $CoCl_3 \bullet 6NH_3$ were better represented as $[Co(NH_3)_6]^{3+}Cl_3^-$ where the bracketed species is the complex. The revolutionary aspect that these hypotheses must have had in the early 1900's cannot be fully appreciated today. Werner established that distinguishable entities existed in solution and proposed the existence of symmetry-based species long before such structures were indicated in crystalline solids by X-ray diffraction. Complexation phenomena of this sort are the basis of coordination chemistry and discussed in most general inorganic chemistry texts [27].

Complexation chemistry applies equally well to main group metal ions and to transition metal ions, though transition metal ions are the most commonly studied because their partly filled d shells have spectral and magnetic properties which can be related to the nature of their coordination spheres in a straightforward way. Common ligands include the halide ions and molecules involving nitrogen or oxygen. In a fundamental sense, even aqueous solutions of inorganic salts involve complex formation -- the metal ions are surrounded by water ligands.

When a complex forms, the ligands, either anions or dipoles, direct their electron pairs toward the positive central metal ion. Although electrostatic attraction to the metal is significant, some repulsion among the ligands ensues because they possess the same charge. The balance between the metal-ligand attractions and ligand-ligand repulsions is generally found in a symmetrical arrangement of the ligands around the metal such as to maximize metal-ligand interaction while minimizing ligand-ligand interaction. The most common arrangements are octahedral and tetrahedral coordination, but all values of coordination number from 2 to 9 are known. It has been noted that high cation charge and low ligand charge favors high coordination numbers (e.g. compare $Co(H_2O)_6^{2+}$ and $CoCl_4^{2-}$; the lower charge on H_2O compared to Cl^- permits a higher coordination number). Of course, there is an upper limit to the number of donor atoms which can be accommodated physically about the cation, determined by steric arguments.

Some ligands form particularly strong complexes due to various structural factors. Ligands such as diethyl ether or Br^- possess only one donor atom capable of attaching to a metal ion and are termed unidentate ligands. But some molecules have several donor sites and are able to make several connections to the central ion: ethylenediamine (*en*) $NH_2CH_2CH_2NH_2$ is able to establish two bonds (with its two nitrogen atoms) and is bidentate; diethylenetriamine (*dien*) $NH_2CH_2CH_2NHCH_2CH_2NH_2$ can establish three bonds and is tridentate, etc. Some multidentate ligands are able to force the metal ion into a normally disfavored coordination geometry. For example, terpyridine (Fig. 2) can only coordinate when the three donor nitrogen atoms and the metal ion are in the same plane. However, other ligands such as the linear polyethers, lacking the structural rigidity of conjugated double bonds, are flexible and stereochemically undemanding. Unidentate ligands can also bridge metal ions; for example, a Br^- can simultaneously be shared by two cobalt ions, but this is a different type of interaction. Multidentate ligands are found to produce much more stable complexes than their unidentate analogs. For example $[Ni\ en_3]^{2+}_{(aq)}$ is nearly 10^{10} times as stable as $[Ni(NH_3)_6]^{2+}_{(aq)}$ [27], although in both cases the complex consists of six nitrogen atoms bound to the central nickel ion. Such enhanced stability is known as the "chelate effect". Although not always so pronounced, the effect is indeed general. Considering the thermodynamic law $\Delta G = \Delta H - T\Delta S$ again, it is clear that the essence of this effect is steric. The enthalpic effect should be nearly the same for unidentate and multidentate ligands of similar chemical nature. Hence, the only major difference can be entropic. Pictorially, we can envision a bidentate ligand such as *en* with one donor attached to the metal ion. The other donor cannot get very far away and the probability of it becoming attached to the same metal atom is greater than if it were instead another independent ligand. Chelating ligands can be seen in terms of "rings". Compare the ways in which the ligands *en* and trimethylene diamine (*tn*).$NH_3(CH_2)_3NH_2$ complex to a metal ion M (Fig. 3). Counting the atoms involved, we see that *en* gives rise to 5-membered chelate rings, *tn* to 6. It has been established experimentally [27] that 5-membered chelate rings are by far the most stable, probably due to the minimization of conformational strain. This would appear to be why the most efficient linear polyether ligands involve the repeat unit (CH_2CH_2O).

Another important effect in complexation chemistry is the macrocyclic effect, which describes the greater thermodynamic stability of a complex with a cyclic multidentate ligand when compared to the complex formed by a comparable acyclic ligand. This effect explains the observation that crown ethers form much more stable complexes than their linear analogs. The basis of this effect is also steric. We may consider the cyclic molecules as pre-organized for complexation, and thus lose little entropy when coordinating an ion. On the other hand, when a linear molecule wraps about an ion, it gains considerable structure and the loss of entropy is much more significant. In this way, the cost in energy for complex formation is largely prepaid during the synthesis of such pre-organized ligands. Discussion of these concepts and others related to pre-organized hosts can be found in an insightful recent review by Busch and Stephenson [28].

This brief overview demonstrates that solvation involves a subtle interplay of numerous factors including the dielectric constant and molecular structure of the solvent, the coordination ability of the cation, and the interaction between cation and anion. The behavior of the solvent water is clearly not universal, but simply the specific case of a solvent with moderate dielectric constant and excellent hydrogen-bonding capability.

III The Coordination Chemistry of the Cobalt(II) Ion

Previous investigations of cobalt complexes are far too numerous to list here. What follows is a brief overview of studies pertinent to the present work. General discussions of cobalt complexes can be found in several standard texts [29-32].

Octahedral and tetrahedral coordination are most typical of Co(II). In fact, there are more tetrahedral complexes of Co(II) than for any other transition metal ion, presumably because, from crystal field arguments, the energy destabilization on going from octahedral to tetrahedral environments is minimized for the d^7 ion. The color of the complexes is often indicative of the geometry - usually octahedral Co(II) complexes are pink, and tetrahedral ones greenish-blue. This method of classification is not infallible though; for example, the anhydrous crystalline $CoCl_2$ is blue although the coordination is octahedral. (In this case, the six Cl^- ligands generate such a weak crystal field that the energy gap Δ is unusually small.)

Octahedral complexation occurs with many neutral ligands, including water and ammonia (i.e. $Co(H_2O)_6^{2+}$ and $Co(NH_3)_6^{2+}$). Bidentate nitrogen-donor ligands, such as *en*, also form octahedral complexes with Co(II) and are much more stable towards oxidation than $Co(NH_3)_6^{2+}$. Tetrahedral coordination is common with unidentate anionic ligands (such as Cl^-, Br^-, I^- and SCN^-) or with a combination of these ligands and neutral ligands, giving complexes such as CoX_3L^- and CoX_2L_2 where X= anionic ligand and L= neutral ligand. More outlandish geometries, such as square planar or 5-coordination, can be found but are usually restricted to multidentate ligands with specific stereochemical requirements, such as the tripod ligands. In some cases a donor atom may bridge between two cobalt ions, thus forming an association structure.

The electronic structure of cobalt(II) in octahedral and tetrahedral systems has been well studied. For octahedral configuration, three transitions are predicted from ligand field theory: 1) ν_1, $^4T_{2g}(F) \leftarrow ^4T_{1g}(F)$, experimentally seen in the near-ir, generally ≈ 8,000-10,000 cm^{-1}; 2) ν_2, $^4A_{2g} \leftarrow ^4T_{1g}(F)$, a 2-electron process with very low probability, rarely observed; and 3) ν_3, $^4T_{1g}(P) \leftarrow ^4T_{1g}(F)$, seen in the visible region ≈ 20,000 cm^{-1} giving rise to the characteristic pink color. For tetrahedral coordination, the cobalt(II) ground state is $^4A_2\ (e^4)(t_2^3)$, and three transitions are predicted: 1) ν_1, $^4T_2(F) \leftarrow ^4A_2(F)$, rarely observed; 2) ν_2, $^4T_1(F) \leftarrow ^4A_2(F)$, found in the near infrared, and 3) ν_3, $^4T_1(P) \leftarrow ^4A_2(F)$, a band occurring in the visible region ≈ 15,000 cm^{-1}. Ligand field theory [31] predicts that the tetrahedral crystal field splitting is only four-ninths that in an octahedral field. As a result, the tetrahedral bands are shifted towards the infrared compared to the octahedral bands, and the tetrahedral bands are more intense (by a factor of about ten times) as a result of the absence of a center of symmetry in these complexes. Table 1 lists some experimentally determined frequency absorptions, as well as the calculated 10 Dq and B parameters, for some common octahedral and tetrahedral complexes. Identification of the complexes using spectroscopy in this way is more accurate than assignment based on color alone.

Interest in the structures cobalt halides form in acetone and in the reason for the color changes observed upon the addition of excess halide can be traced back to 1925 [33]. The phenomenon was not completely understood until 1962, when Fine [34] presented his definitive work "Halide Complexes of Cobalt(II) in Acetone Solution." Fine added cobalt(II) perchlorate and lithium halides to acetone and studied the stepwise complex formation as a function of the halide/cobalt (H/C) ratio. His results indicated three tetrahedral complex species: CoX_2L_2, CoX_3L^-, and CoX_4^{2-} (where X=halide and L=acetone). The first two complexes were found predominantly when H/C=2 and 3 respectively, but the CoX_4^{2-} species did not become the predominant species until H/C reached values from 8 to 40. Using the mole ratio method, Fine isolated the spectra of the individual complexes. He ascribed the visible transition to $^4A_2(F) \rightarrow ^4T_1(P)$ in each case, but noted the failure of crystal field theory to explain the fine structure (e.g. the C_{2v} dihalo and C_{3v} trihalo species, lower in symmetry than the T_d tetrahalo species, should demonstrate more fine structure, but in fact the tetrahalo species exhibits the most spectral peaks).

Trutia and Musa [35] found that CoX_2L_2 predominates in cobalt halide-acetone systems, but noted that at very high concentrations other species began to form. Ishihara and coworkers [36, 37] studied the effects of pressure on the cobalt halides in acetone and derived spectra for the isolated halogen complexes very similar to Fine's.

In contrast to the behavior of the cobalt halides, $Co(ClO_4)_2$ dissolved in acetone [38] produces mainly CoL_6^{2+} while $Co(NCS)_2$ in acetone [39] produces a mixture of octahedral $Co(NCS)L_5^+$ and tetrahedral $Co(NCS)_3L^-$. These facts demonstrate the importance of ligand properties in determining complex formation.

The solvent properties are also crucial. Studies [35, 40] have shown that the tetrahalo CoX_4^{2-} species will not form in ethanol even when the halide/cobalt ratio is greater than 150. It is hypothesized that ethanol, with a higher donor number DN than acetone (compare DN=30 for ethanol and DN=17 for acetone), is more difficult to displace from the cobalt primary coordination sphere. On the other hand, in nitromethane, a solvent with a very low donor number (~3), the higher halogen complexes form quite readily [41].

In dimethyl formamide (*dmf*) and dimethyl sulphoxide (*dmso*), the following cobalt(II) halide complexes are hypothesized [42]: ${}^{oct}CoL_6^{2+}$, ${}^{oct}CoXL_5^+$, ${}^{tet}CoX_2L_2$, ${}^{tet}CoX_3L^-$, and ${}^{tet}CoX_4^{2-}$ (notice the coordination change from octahedral to tetrahedral at the third complex). In the chloride system, $CoCl(dmso)_5^+$ and $CoCl_2(dmso)_2$ are always very minor species in dmso, and in dilute concentrations $Co(dmso)_6^{2+}$ is the predominant species. The halogen complexes are much more stable in *dmf*, with the species $CoX(dmf)_5^+$ and $CoX_3(dmf)^-$ present at most concentrations. Suzuki et al. [42] reason that the higher halogen complexes are discouraged in *dmso* due to that solvent's higher donor number and its associated liquid structure.

These varied experimental results indicate that the natures of both the anion and the solvent are important factors in the solvation of cobalt(II) salts. Halogen complexes seem to be quite common in the solvents studied. As Katzin indicated, neutral complexes predominate in organic solution, especially for solvents of very low dielectric constant. Furthermore, the tendency to form higher complexes such as CoX_3L^- or CoX_4^{2-} seems to be stronger in solvents of low Gutmann number.

IV Cobalt Bromide-Polyether Systems

$CoBr_2$ can be dissolved in the oligomeric polyethers, poly(ethylene glycol) (PEG) (av. mol. wght. 400) and poly(tetramethylene glycol) (PTMG) (av. mol. wght. 600), using ethanol as an intermediate solvent which is later evaporated. Solutions of varying salt content have been prepared and studied by uv-visible spectroscopy, as described previously [43]. The solutions were one-phase viscous liquids of varying hues of blue.

It has been shown earlier by us [43] that the spectra of the $CoBr_2$-PEG and $CoBr_2$-PTMG systems are extremely similar to the spectra of the bromo complexes of cobalt in acetone, as identified by Fine [34]. In fact, analysis has shown that, in relatively dilute $CoBr_2$-PTMG solutions, all of the cobalt exists in the neutral tetrahedral $CoBr_2L_2$ form, where L=ligand atom (in this case L=polyether oxygen donor). Adding successively greater amounts of LiBr to $CoBr_2$-PTMG solutions forces the formation of higher bromo complexes, causing the uv-visible spectra to change accordingly, in a manner completely analogous to Fine's earlier work [34] in which LiBr was added to $Co(ClO_4)_2$-acetone systems. In this way, the spectra of the isolated tetrahedral species $CoBr_2L_2$, $CoBr_3L^-$, and $CoBr_4^{2-}$ in PTMG were identified (Fig. 4). These spectra are very similar to Fine's calculated spectra of these species in acetone.

Using the spectra of the isolated tetrahedral species, it is possible to calculate the concentrations of tetrahedral species in PEG systems and more concentrated PTMG systems with a partial least-squares algorithm [43]. The presence of negatively charged $CoBr_3L^-$ and $CoBr_4^{2-}$ species in the absence of added LiBr indicates either some bromide ions are shared between cobalts (halogen-bridging) or the presence of positively charged species containing fewer than two bromide ions per cobalt. A far-ir study [44] has shown no evidence of halogen-bridging. Indeed, from the known coordination chemistry of cobalt, one would expect the presence of the octahedral species, $CoBrL_5^+$ or CoL_6^{2+}, anyway. Unfortunately, though these octahedral species do absorb in the visible region (~570 nm), their intensities are 20-100 times lower than those of the tetrahedral species, and the bands are difficult to resolve, especially when masked by the highly absorbing tetrahedral bands. However, it is possible to calculate the concentration of octahedral species by subtraction: octahedral species concentration = total cobalt concentration (known) - tetrahedral species concentration (calculated from spectra). The concentrations of complex species as a function of overall salt content for the PEG-$CoBr_2$ systems is presented in Fig. 5.

These results answer two of our earlier questions: How does solvation occur in polyethers, especially considering their low dielectric constant? And, what charged species should we expect? For $CoBr_2$ systems, clearly the solvation mechanism involves the formation of the halogeno complex species, just as in acetone and other conventional low viscosity solvents. The charged species present are CoL_6^{2+} (and/or $CoBrL_5^+$), $CoBr_3L^-$ and $CoBr_4^{2-}$ (to a lesser extent). But not all of the dissolved cobalt exists in charged forms; in PTMG, for example, the cobalt exists predominantly in the neutral $CoBr_2L_2$ form.

As mentioned earlier, these low molecular weight oligomers are composed of molecular chains so short that the concentration of endgroups is significant. One concern has been that many of the results were influenced by the hydroxy endgroups of PEG and PTMG. To clarify the importance of endgroup chemistry, PEGM-$CoBr_2$ systems were studied [45], where PEGM (polyethylene glycol dimethyl ether, av. mol. wght. 400) is the methyl-terminated analog of PEG. The spectroscopic results are indicated in Fig. 6. The cobalt species in PEGM cannot be differentiated from the species in PEG, within the limits of error. Although this result does not imply that the endgroups can be ignored, it does allow us to infer that the nature of the endgroup does not drastically alter the favored solvated species.

Another curious issue is that neutral species are favored in PTMG, but not in PEG. Earlier, we discussed the chelate effect and the particular stability of 5-membered chelate rings. Note that when PEG complexes a cobalt ion with two adjacent ether oxygens, a 5-membered ring involving -Co-O-C-C-O- is formed; on the other hand, PTMG is capable of only the weaker 7-membered chelate rings (-Co-O-C-C-C-C-O-). Thus, PEG is able to complex metal ions quite efficiently whereas PTMG is an inferior ligand due to its weaker chelating ability. In PTMG systems, the oligomer is generally unable to displace the anions from the metal ion's first coordination sphere, and neutral species predominate. But due to the stable 5-membered chelate rings possible with its molecular structure, 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.

V The Coordination Chemistry of Ni(II) [29-32, 46]

At its maximum coordination number of 6, Ni(II) generally forms complexes that are either regular or distorted octahedral. Three spin allowed transitions associated with octahedral geometry are [27]: 1) ν_1, $^3A_{2g} \rightarrow {}^3T_{2g}$, located generally at 7,000→13,000 cm^{-1}; 2) ν_2, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, at 11,000→20,000 cm^{-1}; and 3) ν_3, $^3A_{2g} \rightarrow {}^3T_{1g}(P)$, at 20,000→28,000 cm^{-1}. Ni(II) also forms many complexes which are 5-coordinate (square pyramidal and trigonal bipyramidal) and 4-coordinate (tetrahedral and square planar). Ni(II) in tetrahedral coordination has the following general spectral characteristics [27]: 1) ν_1, the lowest energy band corresponding to the $^3T_1 \rightarrow {}^3T_2$ transition, not frequently observed; 2) ν_2, $^3T_1 \rightarrow {}^3A_2$, a near infrared band around 7,000

cm^{-1}; and 3) v_3, $^3T_1 \rightarrow ^3T_1(P)$, in the 15,000 cm^{-1} region. Table 2 lists some transition bands from common octahedral and tetrahedral complexes of Ni(II).

As with Co(II), complexes of Ni(II) can be classified according to whether they contain cationic, neutral or anionic Ni(II). A typical cationic nickel(II) complex is $[Ni(H_2O)_6]^{2+}$, which gives the green color to many Ni(II) salt hydrates and their solutions. The water molecules are readily replaced by other neutral or anionic ligands. The ease of ligand exchange is determined by the electron donor ability of the ligand which, for common ligands, has the following sequence [47]:

$$I^- < Br^- < SCN^- < Cl^- < F^- < H_2O < NH_3 < en < NO_2^- < CN^-$$

Neutral Ni(II) complexes are most commonly of the types NiX_2L_2 (which may be tetrahedral or square planar) and NiX_2L_4 (usually octahedral) where X=anionic ligand and L=neutral monodendate ligand. The six coordinate complexes of the type NiX_2L_4 have spectra typical of octahedral Ni(II) complexes; the v_2 and v_3 bands are not greatly affected by the low symmetry, but the v_1 band is frequently split into two components [46].

Anionic Ni(II) complexes are typically of the type $[NiLX_3]^{1-}$ and $[NiX_4]^{2-}$. In general only those of the type $[NiX_4]^{2-}$ are truly tetrahedral. The more regular the geometry of such a complex, the more closely its spectral and magnetic properties match those characteristic of the truly tetrahedral complexes [27].

An interesting aspect of the Ni(II) complexes is that stereochemical transformations occur rather easily among them, since the free energy differences between the various stereochemistries are small. Therefore, equilibria among different structural types, which are temperature and concentration dependent, often exist in solution.

VI $NiBr_2$-Polyether Electrolytes

Polyether solutions of $NiBr_2$ of the general formula, $NiBr_2(PEG)_n$ where n is the number of ether oxygens per cation, can be easily prepared over a wide composition range, typically n=8 to 1000 [Cai,1991]. With PEG of average molecular weight 400, the electrolytes are viscous liquids at room temperature, and their viscosity increases with salt concentration such that the most concentrated samples are solids at room temperature and must be heated to 100-150°C before the salt dissolves.

Spectra of $NiBr_2(PEG)_n$ electrolytes

Absorption spectra for $NiBr_2(PEG)_n$ electrolytes with different $NiBr_2$ concentrations are shown in Fig. 7. At low salt concentrations (n=100 to 64), the spectra have absorption peaks at 436 nm, 794 nm and 1306 nm, which correspond to the ligand transitions, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, respectively. These absorptions arise typically from Ni(II) in an octahedral environment [27]. At higher $NiBr_2$ concentrations, greater than n=32, a doublet at 708 nm and 758 nm begins to grow along with a shoulder around 658 nm. The transition bands v_1 and v_3 shift from 1306 nm and 436 nm, peak positions of a low salt concentration solution with n=100, to 1407 nm and 447 nm, respectively, for n=8. Furthermore, the absorbances at 708 nm and 758 nm for concentration n=8 are about 10 times larger than those of low salt concentration at the same positions. These characteristics of the spectra of high salt concentration solutions indicate the growing formation of Ni(II) complex species with tetrahedral symmetry [27, 46]. The doublet at 708 nm and 758 nm, as well as the peak at 1407 nm can be assigned to the ligand transitions, $^3T_1(F) \rightarrow {}^3T_1(P)$ and $^3T_1(F) \rightarrow {}^3A_2(P)$, respectively [30, 46]. The peak at 447 nm for n=8 solution is still at too high a transition energy to be assigned to a transition from tetrahedral coordination [48], which implies a coexistence of octahedrally coordinated Ni(II) species and tetrahedrally coordinated Ni(II) species in solutions with high salt concentrations.

Determining whether a Ni(II) complex is tetrahedral or octahedral is far easier than determining its specific chemical composition. Several different species of the same geometry will generally exist in equilibrium in solution, and their transition bands either overlap or have too large an intensity difference at positions which are too close to each other to be resolved [27, 43, 46]. Fortunately, a number of studies identifying the different species of Ni(II) in organic solvents such as acetone [49-51] and acetonitrile [52] have been reported and are helpful in attempting to resolve the species present in PEG.

For a solution of $NiBr_2$ in PEG, possible octahedral species include: $[NiO_6]^{2+}$, $[NiBrO_5]^{1+}$, $[NiBr_2O_4]^0$, $[NiBr_3O_3]^{1-}$, $[NiBr_4O_2]^{2-}$, $[NiBr_5O]^{3-}$, and $[NiBr_6]^{4-}$. Among these, $[NiBr_3O_3]^{1-}$ and $[NiBr_4O_2]^{2-}$ are unlikely to exist because they have never been identified for monodentate solvent molecules [46, 48, 53]. $[NiBr_5O]^{3-}$ and $[NiBr_6]^{4-}$ are also unlikely because the low dielectric constant of PEG should favor the formation of complexes with low charge, particularly at low salt concentrations. It should be noted, however, that the $[NiBr_6]^{4-}$ complex has indeed been identified in molten $NiBr_2$ [32, 54, 55].

Three species remain: $[NiO_6]^{2+}$, $[NiBrO_5]^{1+}$, $[NiBr_2O_4]^0$. The general behavior of Ni(II) spectra in solution, such as in alcohols [56], acetone [49-51], acetonitrile [52] and dimethylformamide [22, 57], is that the absorption bands of Ni(II) shift to longer wavelengths when an oxygen ligand, L, is replaced by a halide ion. The shift is accompanied by an increase in the intensity of the absorption. For example, Fine [58] studied dilute solutions of $NiBr_2$ in 2-methoxyethanol (L) and was able to identify the spectrum of $[NiBrL_5]^{1+}$ in which the v_3 band is at 422nm (23,697 cm^{-1}). He also observed that the reaction, $[NiL_6]^{2+} \rightarrow [NiL_5Br]^{1+}$, is accompanied by a 1500 cm^{-1} shift in the position of the v_3 band and approximately a 60% increase in molar absorptivity. A 1000 cm^{-1} shift due to the change from $[Ni(H_2O)]^{2+}$ to $[Ni(H_2O)Cl]^{1+}$ with about a 20% increase in molar absorptivity was reported by Angell [54]. Griffiths and Scarrow [59] have found the v_3 band of $[NiL_6]^{2+}$ to be at 410 nm in a solution of $NiClO_4$ in acetone (L) to which LiCl had been added. They also expected the v_3 band of $[NiCl_2L_4]^0$ to be at 460 nm, but the concurrent presence of other species which have some absorption in this region made a precise determination of the position impossible.

In the case of PEG, the v_3 band of octahedral Ni(II) shifts from 436 nm (22,936 cm^{-1}) to 447 nm (22,472 cm^{-1}), an 500 cm^{-1} shift in energy, as the $NiBr_2$ concentration is increased from n=1000 to 8. For Br(I), which has weaker donor ability than Cl(I), the v_3 band of $[NiBr_2L_4]^0$ should be at a longer wavelength than 460 nm. Therefore, while the existence of $[NiBr_2L_4]^0$ cannot be definitively ruled out, it is more reasonable that an absorption maximum in the region of 410 nm to 460 nm is associated with either $[NiO_6]^{2+}$ or $[NiBrO_5]^{1+}$ or a superposition of both species.

Table 3 is a list of the absorbance, A, at 447 nm versus Ni(II) concentration. The value of A follows Beer's law quite well at low salt concentrations, with a constant absorbtivity a= , but it deviates from Beer's law at high salt concentrations, a change consistent with an absorbtivity increase of about 30%. The implication is that at low salt concentration $[NiO_6]^{2+}$ is the most likely species, but as the salt concentration increases, $[NiBrO_5]^{1+}$ emerges and coexists with $[NiO_6]^{2+}$.

Similarly, the possible tetrahedral species in the PEG-$NiBr_2$ electrolytes are $[NiBr_4]^{2-}$, $[NiBr_3O]^{1-}$, $[NiBr_2O_2]^0$, $[NiBrO_3]^{1+}$ and $[NiO_4]^{2+}$. Cationic tetrahedral species, $[NiBrO_3]^{1+}$ and $[NiO_4]^{2+}$, are rare and occur only in complexes of bulky ligands [46]. The species $[NiBr_4]^{2-}$ can be identified from the shape of its spectrum in the 500-800 nm region and the positions of the absorption maxima of the two bands [49, 52] Since the atoms at the first nearest shell of Ni(II) are all bromines, the transition bands of this species hardly change with solvent and generally occur at v_1: 670(Sh), 706, 754 nm and v_2: 1450 nm. In the spectrum of $NiBr_2(PEG)_8$ (Fig.7), a doublet at 708 and 758nm and a shoulder at 658nm are close to the absorption maxima of the doublet associated with the $^3T_1(F) \rightarrow {}^3T_1(P)$, a transition of $[NiBr_4]^{2-}$ in regular tetrahedral symmetry. There is no evidence on the high energy side of the doublet for an absorption band in the 620-650 nm region, which would be indicative of a tribromo complex of $[NiBr_3O]^{1-}$ [52, 58]. Therefore, the amount of such species in the electrolytes is minimal.

The species $[NiBr_2O_2]^0$ has never been found in acetone, acetonitrile and methyl ethyl ketone solvents [53] (although the neutral $CoBr_2O_2$ species is quite common for Co(II)). Many solid tetrahedral dibromo complexes of the type NiL_2Br_2 have, however, been reported [52] and their solid and solution spectra measured. The principal effect of the substitution of a solvent molecule for a halide is to shift the transition band toward higher energies (smaller wavelength). Therefore, the spectra of $[NiL_2X_2]^0$ species should be expected to be in the 550-600nm region [52, 59], the high energy side of $[NiBr_3O]^{1-}$ spectra. No spectra corresponding to $[NiBr_2O_2]^0$ were observed for Ni(II)-PEG solutions. This does not completely rule out the presence of a tetrahedral dibromo complex but does indicate that if such a complex exists it incorporates such a small fraction of the total Ni(II) that its absorption bands are completely obscured by those of tetrabromo complex.

Based upon these arguments, it is logical to conclude that although species such as octahedral $[NiBr_2O_4]^0$ and tetrahedral $[NiBr_2O_2]^0$ and $[NiBr_3O]^{1-}$ cannot be ruled out completely, the concentrations of these species in the PEG-$NiBr_2$ solutions are at most quite small. The predominant species appear to be $[NiO_6]^{2+}$ at low salt concentrations and $[NiO_6]^{2+}$, $[NiBrO_5]^{1+}$ and $[NiBr_4]^{2-}$ at high salt concentrations. This conclusion provides a basis for further discussion of issues such as the solvation process of $NiBr_2$ in PEG and the relationship between Ni(II) complexes and ionic conductivity.

Solvation of $NiBr_2$ in PEG

If it is assumed that $NiBr_2$ at low concentrations is solvated by the formation of $[NiO_6]^{2+}$, and $[NiBr_4]^{2-}$ forms at higher concentrations, the following equilibrium expression can be written (Eqn. 1).

$$[NiO_6]^{2+} + 4Br(-I) \Leftrightarrow [NiBr_4]^{2-} + 6O \qquad (1)$$

The oxygen ligands, naturally, are those from PEG molecules.

The addition of excess Br(-I) or of extra or more strongly coordinating oxygen ligands to an electrolyte with a fixed concentration of Ni(II) should shift the concentration of Ni(II) toward either the tetrahedral or octahedral complexes. This prediction was tested with $NiBr_2$ electrolytes by increasing the concentration of Br(-I) through the addition of LiBr, and by increasing the concentration of O_L by adding H_2O. The results are shown in Fig. 8 and 9. Initially, the spectrum of $NiBr_2(PEG)_{32}$ is of Ni(II) principally in an octahedral environment. In fact, a linear least-squares fit of the low concentration portion of Fig. 10 shows that below n=60 Ni(II) ions are exclusively in an octahedral environment. The addition of LiBr changes the color of the electrolytes from pale yellow-green to emerald green, then through blue-green to blue, which indicates that the equilibrium shifts from octahedral Ni(II) to tetrahedral Ni(II) [60] with increasing LiBr addition.

In contrast, the addition of deionized water to $NiBr_2(PEG)_{16}$ shifts the Ni(II) coordination from that characteristic of the tetrahedral-octahedral equilibrium just described to a spectrum typical of $[Ni(H_2O)_6]^{2+}$ [46] (Fig. 9), which shows that the position of the $[Ni(H_2O)]^{2+}$ transition band is shifted to shorter wavelengths than that arising from $[NiO_6]^{2+}$, a result consistent with the logical assumption that the ether oxygens of the polymer chains are weaker electron donors than H_2O.

To be more quantitative, a plot of the absorbance at 758 nm, a typical absorption peak of a tetrahedral Ni(II) complex of the type $[NiBr_4]^{2-}$ but not a peak position of octahedral Ni(II), with respect to the Ni(II) concentration is shown in Fig. 10. Two regions of Beer's law dependence with different absorptivities are evident. The first, at low salt concentrations (insert at upper left), corresponds to Ni(II) ions in an octahedral environment. The second, at concentrations greater than n=30, has an absorptivity about ten times higher than that of the first and is characteristic of Ni(II) in a tetrahedral environment. We attribute this to a growing concentration of $[NiBr_4]^{2-}$. In between, there is a region which deviates from Beer's law because the electrolyte consists of a mixture of a small amount of $[NiBr_4]^{2-}$ and $[NiBrO_5]^{1-}$ in a dominant population containing $[NiO_6]^{2+}$.

The data in Fig. 10 are particularly interesting in light of several other observations. The most concentrated $NiBr_2$ solution that has been easily prepared in PEG (average MW=400) corresponds to a 1:8 molar ratio of Ni(II) to ether oxygens. One PEG chain of molecular weight 400 is composed of 8 ether oxygens and 2 OH end groups (i.e. $HO\text{-}[CH_2CH_2O]_8CH_2CH_2\text{-}OH$), which means, at least hypothetically, that one average PEG chain might complex with one $NiBr_2$ molecule: the Ni(II) ion coordinating with the ether oxygens and each anion associated with a terminal OH group. Sterically, if it is assumed that the C-O and C-C bonds of the liquid PEG can rotate freely and the C-O and C-C bond lengths are 1.43Å and 1.53Å, respectively, as determined from X-ray diffraction measurements [61], it is possible to construct a structure in which the six oxygens from each PEG chain wrap around a Ni(II) to form an octahedral configuration [Fig.11] with a Ni-O distance about 2.1Å. In fact, a Ni-O distance of 2.1Å has been observed in EXAFS measurements on electrolytes of this composition [62]. However, according to the data in Fig. 10, $[NiBr_4]^{2-}$ species form as soon as there are four OH groups for each Br(-I), less than the maximum hypothetical concentration of two OH groups for each Br(-I). Realistically, it is more likely that the octahedrally-coordinated Ni(II) ions are associated with more than one PEG chain and include bromides as well as oxygens in their coordination shells. Evidence for Ni(II) association with more than one chain includes the observation that the viscosity of the electrolytes increases with increasing salt concentration and the most concentrated compositions (n=8 and 16) are virtually solid at room temperature.

Relationship between Ni(II) Complexation and Ionic Conductivity

A plot of ionic conductivity vs. molar concentration of $NiBr_2$ in PEG is shown in Fig. 12. A marked discontinuity is apparent around n=60. To correlate conductivity and local structure more precisely, Beer's law (Eqn. 2)

$$A = \log \left(\frac{I_0}{I} \right) = a\, b\, c \qquad (2)$$

was applied to the data shown in Fig. 10 to yield the molar concentration of Ni(II) in octahedral and tetrahedral environments vs. the total $NiBr_2$ salt concentration (Fig. 13a, 13b). In equation 2, A is the absorbance; I and I_0 are the intensity of the transmitted beam and incident beam respectively; a is the molar extinction coefficient (also called the absorptivity); b the sample thickness; and c the molar salt concentration.

Four assumptions were made to permit such a semi-quantitative analysis of spectra data obtained from the $NiBr_2$-PEG samples: (1) only two types of coordination, $[NiO_6]^{2+}$ and $[NiBr_4]^{2-}$, exist in the samples so that the sum of the concentrations of these two coordinations equals the total concentration of $NiBr_2$; (2) the octahedral and tetrahedral Ni(II) complexes are $[NiO_6]^{2+}$ and $[NiBr_4]^{2-}$, respectively; (3) at very low $NiBr_2$ concentrations (n=1000 to 60), Ni(II) is exclusively in an octahedral environment, thus making it possible to obtain the absorptivity of Ni(II) in octahedral coordination from Beer's law; (4) at the highest concentration, n=8, all the Br(-I) species form $[NiBr_4]^{2-}$. With these assumptions, the absorptivities of Ni(II) in tetrahedral and octahedral coordinations as well as the concentrations of $[NiO_6]^{2+}$ and $[NiBr_4]^{2-}$ can be obtained.

In this way, a value for N_{Br}, the number of Br(-I) ions not in the first nearest neighbor shell of Ni(II), was calculated as a function of total salt concentration (Fig. 14) as in the following:

$$N_{Br} = 2C_{NiBr2} - 4\, C_{[NiBr4]2-} \qquad (4)$$

The electrolyte conductivity is controlled by the charge carrier concentration and the mobility of the charge carriers (Eqn. 5):

$$\sigma = \Sigma\, q_i\, n_i\, \mu_i \qquad (5)$$

where σ is the conductivity, q_i the charge of i-type species, n the number of i-type charge carriers, and μ_i the mobility of the i-type charge carriers. If the conductivity of these electrolytes were solely the result of the motion of Br(-I) ions with mobility independent of concentration, then Fig. 14 should resemble Fig. 12, which it does not; the maxima in two plots are not at the same concentration. No data on the mobility of Br(-I) ions in PEG electrolytes are available, but it is reasonable to believe that it should decrease rapidly with increasing $NiBr_2$ concentration, because, as mentioned earlier, the viscosity of electrolytes quickly increases as $NiBr_2$ is added (Fig. 15).

Another approach toward examining the variation of conductivity with $NiBr_2$ concentration is that of calculating the equivalent molar conductivity, Λ, which is the ratio of the actual conductivity and the total $NiBr_2$ concentration added to the electrolyte. The variation of Λ with $NiBr_2$ concentration is shown in Fig.16. The steep decrease in Λ at low $NiBr_2$ concentration, a region in which the concentration of Br(-I) charge carriers should be increasing, suggests that the factor which dominates the conductivity variation is a decrease in mobility resulting from an increase in viscosity, rather than the change in charge carrier concentration.

Temperature dependence of absorption spectra of Ni(II)

It is interesting to note that PEG-based $NiBr_2$ electrolytes are faintly yellow at ambient temperature at low salt concentrations, such as n=100. However, upon heating they become bright blue. Similarly, a solution with a high salt concentration (e.g. n=32) changes color from green at ambient temperature to bright blue upon heating. These reactions are reversible. The observed color change with temperature, however, reflects a change in the type of Ni(II) complexes that exist as the the temperature is increased. To understand what happens in these electrolytes during increasing temperature and the possible relationship between the change of Ni(II) complexation with temperature, the thermal stability of the electrolytes, and the ion conduction mechanism, two absorption spectra for $NiBr_2$ concentrations of n=100 and 32 were recorded as a function of temperature (Figs. 17 and 18).

For n=100 (Fig. 17), as the temperature is increased, a transition band with an absorption maximum at 628 nm starts to grow around 80°C; it is characteristic of $[NiBr_3O]^{1-}$ formation [48, 58, 60]. The transition band associated with Ni(II) in an octahedral environment shifts from 436 nm at ambient temperature to 481 nm at 180°C, a 2317 cm^{-1} shift in energy. Based upon the discussion in previous section, the appearance of a band at around 481 nm is not likely to be the result of a deformation of $[NiBrL_5]^{1+}$ species and is still at too high an energy to arise from a regular or distorted tetrahedral species. As also mentioned previously, the principal effect of substituting a solvent molecule by a halide in the ligands of an Ni(II) complex is to shift the transition band to a lower energy [49, 53] Therefore, because no octahedral complexes of the type $[NiBr_3O_3]^{1-}$ or $[NiBr_4O_2]^{2-}$ have been established for monodentate solvent molecules [46, 48, 53], we have concluded that the 481 nm band probably arises from $[NiBr_2O_4]^0$ species. However, it must be pointed out that there are reports [54, 55] which identify a band in this region with the presence of octahedral $[NiBr_6]^{4-}$. It has been assumed previously that $[NiBr_6]^{4-}$ has too high a charge to exist in a low dielectric constant medium such as PEG, at least at room temperature. But, $[NiBr_6]^{4-}$ and $[NiBr_4]^{2-}$ are, in fact, two major species observed in molten $NiBr_2$ [55]. Based on the fact that $NiBr_2$ is observed to precipitate from electrolytes containing high salt concentrations (around 210°C for sample with n=32) [62] the existence of this species, $[NiBr_6]^{4-}$, cannot be ruled out. Nevertheless, salt precipitation has not been observed for either the n=100 and n=32 samples in the temperature region in which the spectra in Fig. 17 and 18 were recorded. It is important to note that upon cooling from 180°C to 25°C, the spectra are the same as before heating, which indicates that the changes in coordination that occur upon heating are reversible, at least up to 180°C.

For a sample with a high $NiBr_2$ concentration, n=32, the changes in complex ion formation with increasing temperature for the most part follow the behavior described for dilute salt concentrations. The differences are that some $[NiBr_4]^{2-}$ occurs in an n=32 but not in an n=100 electrolyte at 25°C. In both electrolytes, $[NiBr_2O_4]^0$ and $[NiBr_3O]^{1-}$ form with increasing temperature; the higher the salt concentration, the more $[NiBr_4]^{2-}$ persists at elevated temperature.

Temperature Dependence of Conductivity and Viscosity

The temperature dependence of the conductivity and viscosity is shown in figure 19 and 20, respectively. In Figure 20, all the viscosity data of the electrolytes, $\eta(T)$, have been normalized to the viscosity of pure PEG, $\eta_0(T)$, at corresponding temperatures, since $\eta_0(T)$ represents the lowest viscosity that the electrolytes can reach at any temperature. At temperatures so high that salt starts to precipitate, $\eta(T)/\eta_0(T)$ should approach one.

A possible correlation between the date in Figs. 19 and 20 is evident. At low salt concentration, n=100, changes of conductivity with temperature are small. From 40°C to 90°C, the conductivity increases, $\Delta\sigma/\sigma$ $(=[\sigma(90°C)-\sigma(40°C)]/\sigma(40°C))$, by a factor of about 1.2 and the viscosity decreases, $\Delta\eta/\eta$ $(=[\eta(40°C)-\eta(90°C)]/\eta(90°C))$ by a factor of about 5.3. At high salt concentration, n=16, the conductivity changes dramatically with temperature. From 40°C to 90°C, the conductivity increases about 20 times, but the viscosity decreases about 28 times.

Quite early in the study of electrolytic conductance in aqueous solutions, a correlation was noted between the mobilities of ions and the fluidity Φ (which is defined as $1/\eta$) of the medium in which they move. This is especially evident in the increase of conductance with temperature in a given solvent which parallels the decrease of its viscosity. It was summarized as Walden's rule and is frequently expressed as [63, 64]:

$$\Lambda * \eta = \text{constant}$$

where Λ is equivalent molar conductivity and is η the shear viscosity.. The applicability of this classical correlation to systems involving oligmer electrolytes requires two assumptions: 1). in the oligmer electrolytes, the macroscopic viscosity represents correctly the frictional force impeding ion motion; 2). the charge carrier number for a given electrolytes remains unchanged at different temperature. It has been reported that in the oligmer electrolytes, the macroviscosity measured in a conventional viscometer is a proportional to the microscopic viscosity which controls the ion conduction process [65]. Therefore, the macroscopic viscosity in particular its temperature dependence can at least serve as a useful guide to the force impeding the motion of ions in these electrolytes.

According to the discussions in the previous section, the major charge carriers in PEG-based $NiBr^2$ electrolytes are possibly Br^{1-} at low salt concentration and $[NiBr_4]^{2-}$ at high salt concentration. It is interesting to note that at low salt concentration, for example n=100, with increasing temperature, charge carriers change from Br^{1-} to ion complexes such as $[NiBr_3]^{1-}$ and $[NiBrO_5]^{1-}$ and neutral species, $[NiBr_2O_4]^0$, as well. Such changes possibly decrease the number of charge carriers. For the high salt concentration electrolytes, the number of charge carriers does not change very much with temperature, because at high salt concentrations, $[NiBr_4]^{2-}$ rather than Br^{1-} is the dominant charge carrier at room temperature [Cai,1991]. The charge carrier number change as a result of ion complexes change from $[NiBr_4]^{2-}$ to $[NiBr_3]^{1-}$ and Br^{1-} is logically minimal. Therefore, it is apparent that as the temperature is increased, the number of charge carriers either decreases or remains essentially the same, depending on salt concentration in the electrolytes. 'The overall increase in conductivity with increasing temperature is the result of a large decrease of the viscosity, i.e. an increase in the mobility of the charge carriers.

More interestingly, the plots $\log\{\eta(T)/\eta_0(T)\}$ vs 1000/T follow Arrhenius behavior for all three electrolytes, namely n=100, 32 and 16. A linear least square fitting to these plots reveals that the temperatures at which the viscosity of the electrolytes reaches a minimum, i.e. $\eta(T)/\eta_0(T)=1$, are 200 and 250°C for n=100 and 16 electrolytes, respectively. This indicates that for n=100 and n=16 electrolytes, at 200°C and 250°C respectively, ion-polymer interactions should completely diminish and phase separation occur. However, an implication of such salt precipitation for n=16 is observed from DSC at about 180°C, and not observed for n=100 up to 250°C, which interestingly may be due to the dynamics involved in such process.

VII Summary and Conclusions

Continuing uncertainty regarding the ionic conduction mechanism in solid polymeric electrolytes reflects, to a large degree, the absence of a complete understanding of solvation mechanisms in polyether systems. The work summarized in this review demonstrates that uv-visible spectroscopy can provide considerable insight into the species formed as the result of solvation, at least for transition metal systems.

The work summarized here focused on the oligomeric liquid polyethylene glycol (PEG, av. mol. wght. 400) as the primary polyether host, with the thought that solvation behavior in PEG should be closely analogous to that in the amorphous regions of high molecular weight PEO. Concern over the importance of the hydroxy endgroups of PEG was somewhat allayed by preliminary investigations of $CoBr_2$ systems, which indicated that changing the endgroups from hydroxy to methoxy resulted in no significant differences in solvated species observed. Drawing from the results of several earlier investigations of Co(II) and Ni(II) in conventional low-molecular weight solvents, we found it possible to interpret our spectroscopic results for the PEG-$CoBr_2$ and PEG-$NiBr_2$ systems, for the most part unambiguously. We were able to determine the nature of the local solvated species present in solution, usually quantitatively, and to trace the evolution of the populations of these species as salt concentration and temperature were increased.

First of all we noted the importance of the formation of complex ions in these systems (the Katzin effect) and found that the species formed are typically those that would be expected for low dielectric constant, low molecular-weight solvents. For PEG-$CoBr_2$ electrolytes, our spectroscopic investigations were consistent with the presence of the following species: CoL_6^{2+}, CoL_5Br^+, $CoLBr_3^-$, $CoBr_4^{2-}$, and Br^-. For PEG-$NiBr_2$ systems, only the following species were found to be present to an significant degree: NiL_6^{2+}, NiL_5Br^+, $NiBr_4^{2-}$, and Br^-. At low salt concentrations for both systems, our results indicate that octahedral ML_6^{2+} species predominate.

The chelate effect, well-known in coordination chemistry, can be used to rationalize the high degree of dissociation in PEG despite its low dielectric constant. At low concentrations of $NiBr_2$ and $CoBr_2$, the conductivity seems to be mainly due to motion of the Br^- anions. As the salt concentration increases, the solution viscosity increases and the molar conductivity plummets, indicating that the ionic mobility may be the controlling factor for conductivity in these systems. As the salt concentration is increased further, the development of cation-anion complexes becomes unmistakable.

The large increase in conductivity observed for these electrolytes as the temperature is increased can be attributed to a concomitant decrease in electrolyte viscosity, which again stresses the importance of the ionic mobility in controlling conductivity. However, we must emphasize that increasing the temperature does more than just increase ion mobility, it also shifts the nature of the ion population towards the formation of significant populations of complex species.

Above all, the work described in this review demonstrates that uv-visible spectroscopy is a very useful technique for learning about the coordination of certain transition metal ions in polymer electrolytes. The results demonstrate unequivocally that complex ions exist in polymer electrolytes of this sort, particularly at moderate to high salt concentrations and at elevated temperatures. Furthermore, it appears that free anions and anionic complex species are the predominant charge carriers in the electrolytes studied here. In fact, our studies indicate that the principal mechanism of cation mobility in Co(II) and Ni(II)-PEG electrolytes is by the motion of complex anions, not the diffusion of uncomplexed cations.

All of our observations underscore the role of polymer electrolytes as a curious, arguably unique, class of electrochemical materials which share aspects both of conventional low molecular weight electrolytes and of molten salts and are both scientifically intriguing and of considerable technological interest.

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FIGURE CAPTIONS

Fig. 1 Chemical Structures of Relevant Polyethers

Fig. 2 Structure of terpyridine ligand

Fig. 3 Examples of Chelate Rings

Fig. 4 Uv-visible Spectra of Isolated Species in the PTMG-$CoBr_2$ system. Bold line, $CoBr_4^{2-}$; dotted line, $CoBr_3L^-$; dashed line, $CoBr_2L_2$.

Fig. 5 Concentrations of Solvated Species versus Overall Salt Concentration in PEG-$CoBr_2$ system.

Fig. 6 Concentrations of Solvated Species versus Overall Salt Concentration in PEGDM-$CoBr_2$ system.

Fig. 7 Electronic spectra of $NiBr_2(PEG)_n$ at $NiBr_2$ concentrations of n=8, 16, 32, 64, 100 (top to bottom).

Fig. 8 Electronic spectra of $NiBr_2(PEG)_{32}$ at Li/Ni ratios (m) of 2, 1, 0.5, 0.1, 0 0 from top to bottom.

Fig. 9 Electronic spectra of $NiBr_2(PEG)_{16}$ at H_2O/ether oxygen ratios (p) of 0, 0.25, and 0.5 (top to bottom).

Fig. 10 Plot of absorbance, A, at 758 nm vs. $NiBr_2$ salt concentration (mole per cm^3).

Fig. 11 Schematic diagrams of tetrahedral (a) and octahedral (b) coordinations of Ni(II) in PEG electrolytes.

Fig. 12 Ionic conductivity of $NiBr_2(PEG)_n$ vs. $NiBr_2$ concentration.

Fig. 13 (a) Concentration of Ni(II) in octahedral environment vs. total $NiBr_2$ concentration, (b) Concentration of Ni(II) in tetrahedral environment vs. total $NiBr_2$ concentration.

Fig. 14 Free Br(-I) concentration, N_{Br}, vs. total $NiBr_2$ concentration.

Fig. 15 Viscosity, h, of $NiBr_2(PEG)_n$ with n=1000 to 30; h_0 is the viscosity of pure PEG.

Fig. 16 The equivalent conductivity, L, of $NiBr_2(PEG)_n$ electrolytes vs. total $NiBr_2$ concentration.

Fig. 17 Temperature dependence of UV/visible spectra of $NiBr_2(PEG)_{100}$ electrolyte. T=30, 40, 60, 80, 100, 120, 140, 160, 180 °C along the direction of array.

Fig. 18 Temperature dependence of UV/visible spectra of $NiBr_2(PEG)_{32}$ electrolyte. T=30, 40, 60, 80, 100, 120, 140, 160, 180 °C along the direction of array.

Fig. 19 Temperature dependence of the conductivity of $NiBr_2(PEG)_n$ electrolytes, where n=100, 32, 16, respectively, along the direction of the array.

Fig.20 Temperature dependence of the viscosity of $NiBr_2(PEG)_n$ electrolytes, where $n=\infty$, 100, 32, 16, respectively, along the direction of the array.

Table 1: Electronic Spectra of Cobalt(II) Complexes

Octahedral

Complex	$v_1(cm^{-1})$	v_3 (cm^{-1})	10 $Dq(cm^{-1})$	$B(cm^{-1})$
$[Co(NH_3)_6]^{2+}$	9000	21100	10200	885
$[Co(H_2O)_6]^{2+}$	8100	19400	9200	825
$CoCl_2$	6600	17250	6900	780

Tetrahedral

Complex	$v_2(cm^{-1})$	v_3 (cm^{-1})	10 $Dq(cm^{-1})$	$B(cm^{-1})$
$[Co(NCS)_4]^{2-}$	7780	16250	4550	691
$[CoCl_4]^{2-}$	5460	14700	3120	710
$[CoI_4]^{2-}$	4600	13250	2650	665

Data from Greenwood, N.; Earnshaw, A. Chemistry of the Elements, (Pergamon, New York, 1984), p.1314.

Table 2: Electronic Spectra (nm) of Some Octahedral Ni(II) Complexes

	$^3A_{2g}(F)\rightarrow{}^3T_{1g}(P)$	$^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$	$^3A_{2g}(F)\rightarrow{}^3T_{2g}(F)$
General	800-1480	500-900	350-500
$NiBr_2$	1470	847	485
$[Ni(H_2O)_6]^{2+}$	1177	725	395
$[Ni(NH_3)_6]^{2+}$	930	571	355

Electronic Spectra (nm) of Some Tetrahedral Ni(II) Complexes

	$^3T_1(F)\rightarrow{}^3T_1(P)$	$^3T_1(F)\rightarrow{}^3A_2(P)$
General	around 670	around 1450
$[NiBr_4]^{2-}$	756 707 658(Sh) 599(Sh)	1430

Table 3 Absorbance, A, at 436 nm vs. $NiBr_2$ salt concentration C (mmole per cm^3)

n(O/Ni)	a	C (mol/cm^3)	A(arbitrary unit)
1000	2.23	2.5652×10^{-5}	0.5796
500	2.23	5.1249×10^{-5}	1.1532
400	2.23	6.4026×10^{-5}	1.4534
300	2.27	8.5290×10^{-5}	1.9360
200	2.32	1.2770×10^{-4}	2.9586
100	2.29	2.5401×10^{-4}	5.8244
64	2.33	3.9448×10^{-4}	9.1914
32	2.41	7.7585×10^{-4}	18.713
16	2.72	1.5018×10^{-3}	40.834
8	2.70	2.8219×10^{-3}	76.191

Electronic Spectra (nm) of Some Tetrahedral Ni(II) Complexes

	$^3T_1(F)\rightarrow{}^3T_1(P)$	
$^3T_1(F)\rightarrow{}^3A_2(P)$		
General	around 670	around 1450
$[NiBr_4]^{2-}$	756 707 658(Sh) 599(Sh)	1430

Table 3 Absorbance, A, at 436 nm vs. $NiBr_2$ salt concentration C (mmole per cm^3)

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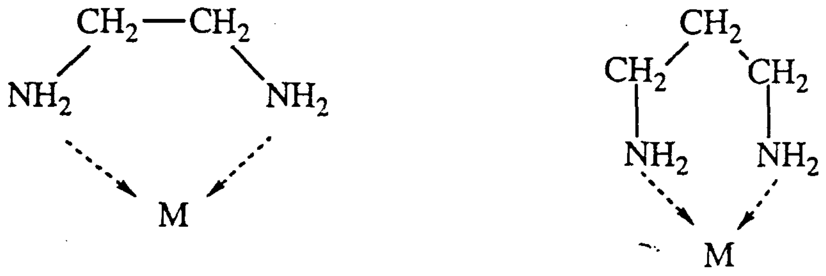
32	2.41	7.7585×10^{-4}	18.713
16	2.72	1.5018×10^{-3}	40.834
8	2.70	2.8219×10^{-3}	76.191


CH2—CH2
NH2
NH2
M
CH2
CH2
CH2
NH2
NH2
M

ligand en complexing metal M
5-membered ring

ligand tn complexing Metal M
6-membered ring

Figure 3

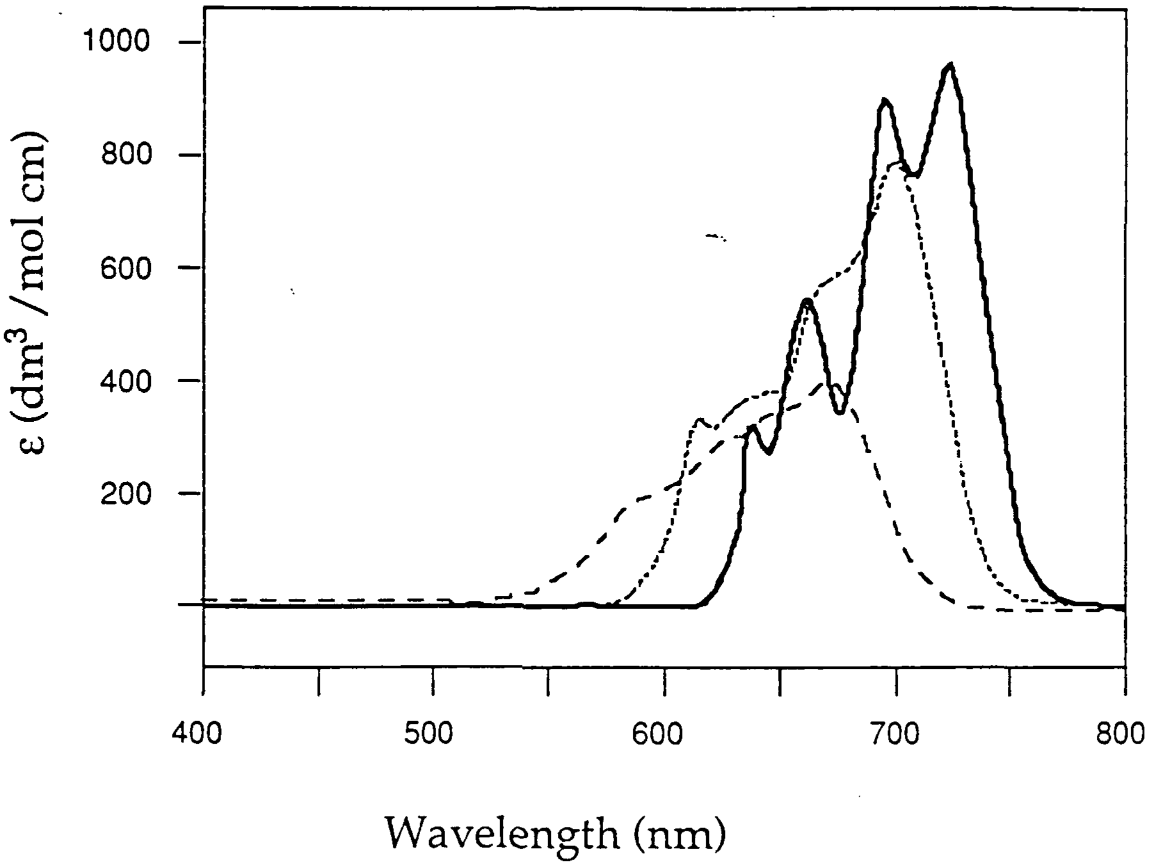

1000
800
600
400
200
ε (dm^3 /mol cm)
400
500
600
700
800
Wavelength (nm)

Figure 4

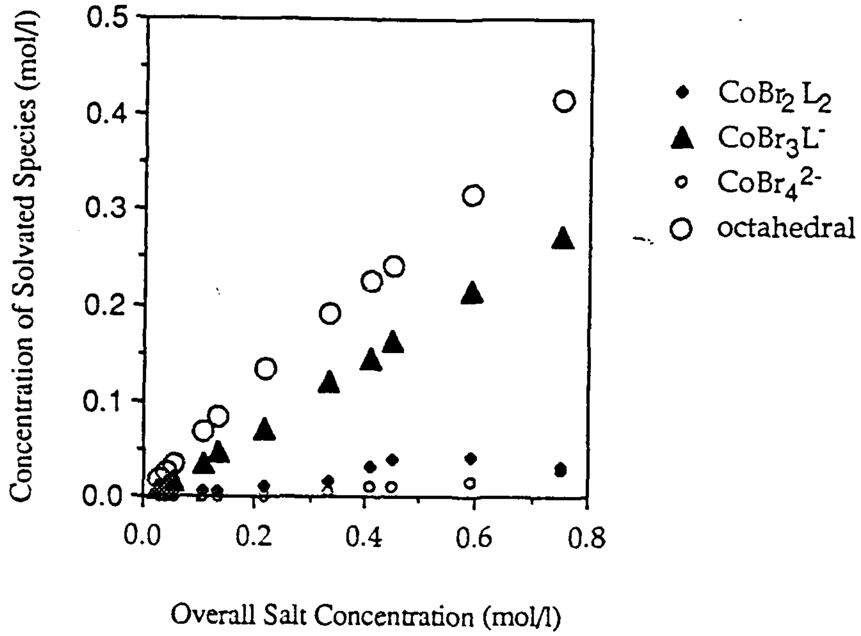


Figure 5

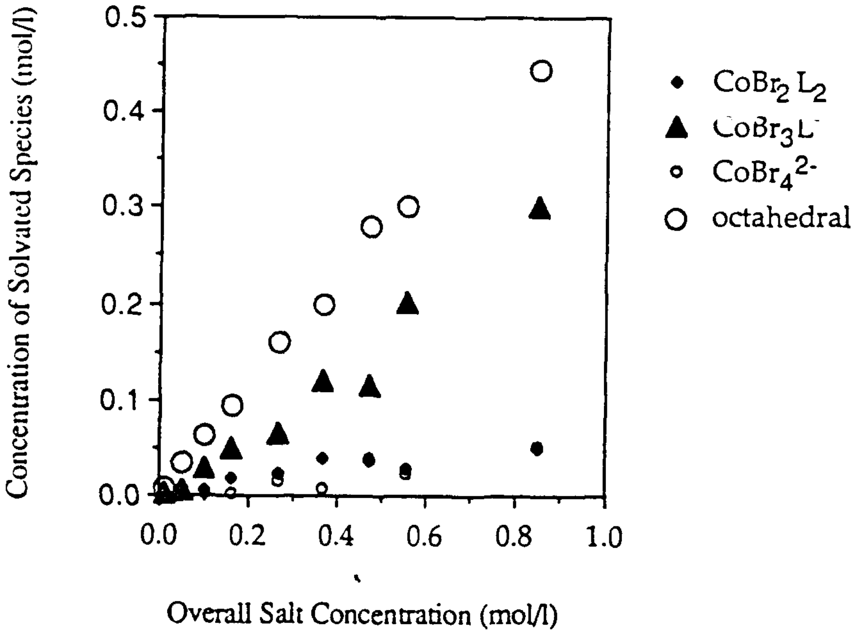


Figure 6

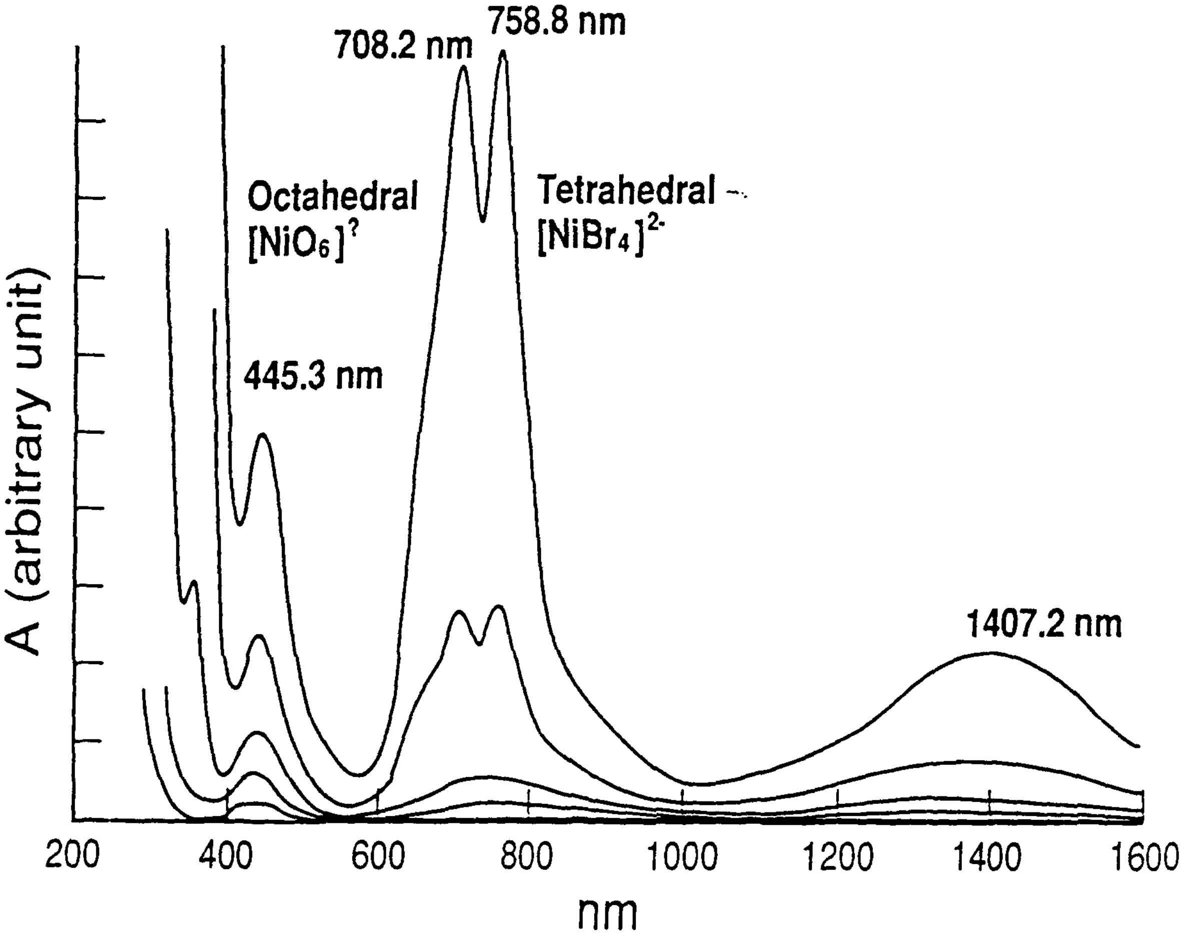

708.2 nm
758.8 nm
Octahedral
[NiO6]?
Tetrahedral
[NiBr4]2-
445.3 nm
1407.2 nm
A (arbitrary unit)
200
400
600
800
1000
1200
1400
1600
nm

Fig. 7

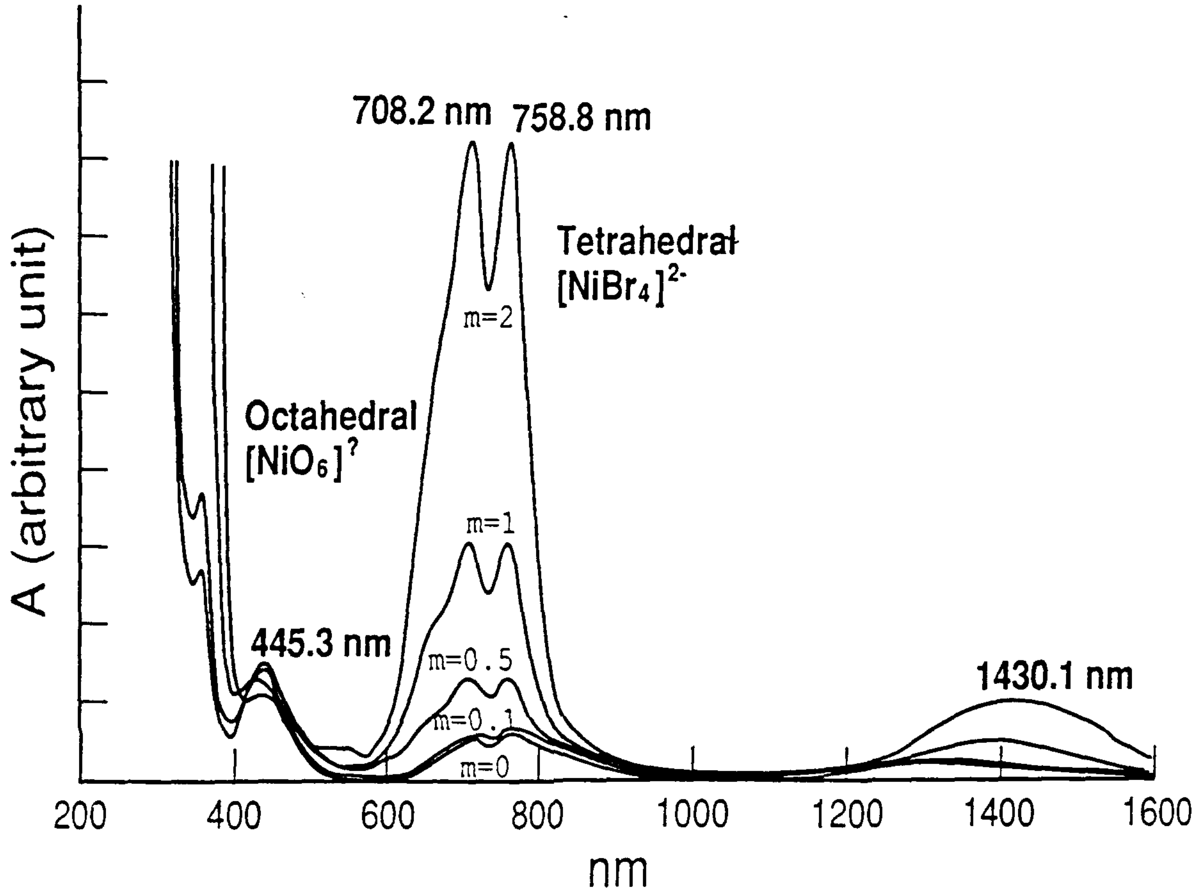

708.2 nm
758.8 nm
Tetrahedral
[NiBr4]2-
m=2
Octahedral
[NiO6]?
m=1
445.3 nm
m=0.5
m=0.1
m=0
1430.1 nm
A (arbitrary unit)
200
400
600
800
1000
1200
1400
1600
nm

Fig. 8

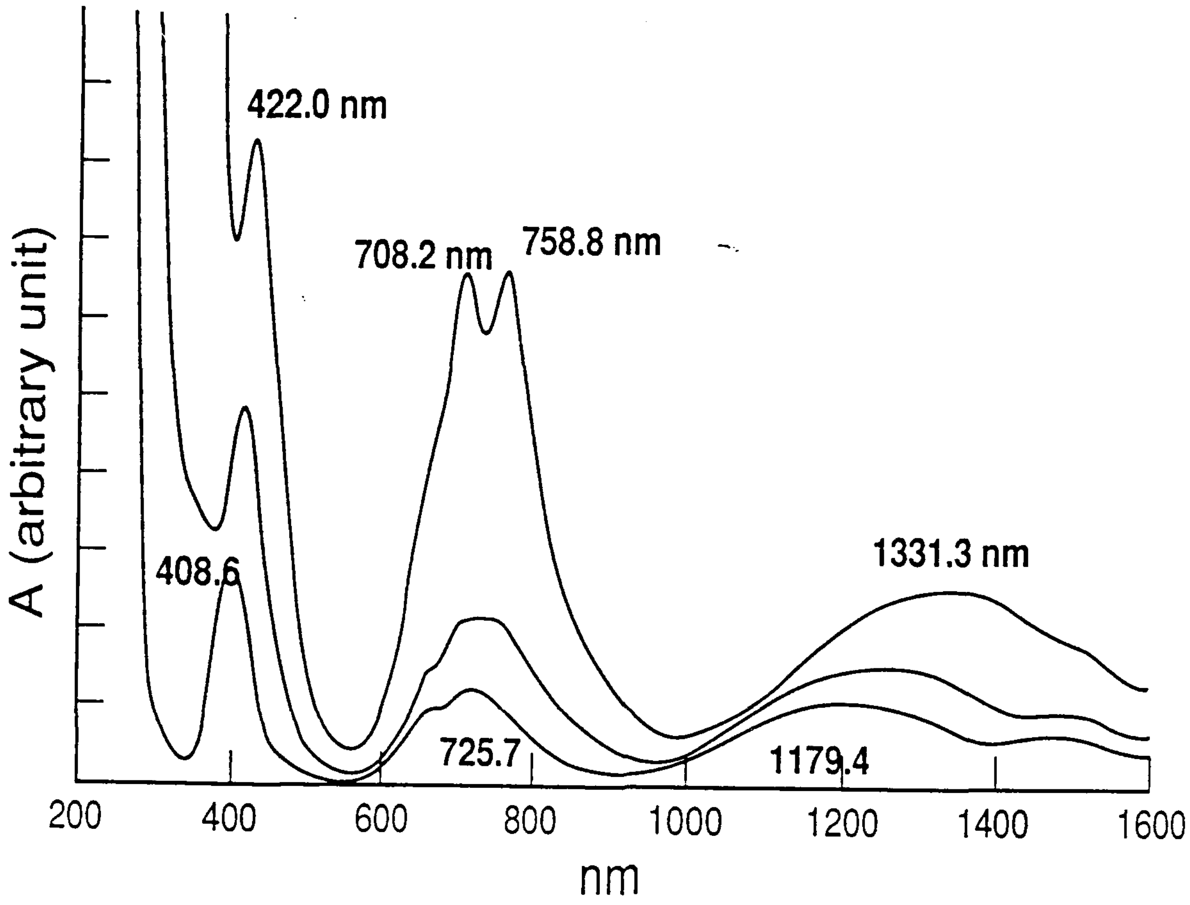

422.0 nm
708.2 nm
758.8 nm
408.6
1331.3 nm
725.7
1179.4
A (arbitrary unit)
200
400
600
800
1000
1200
1400
1600
nm

Fig. 9

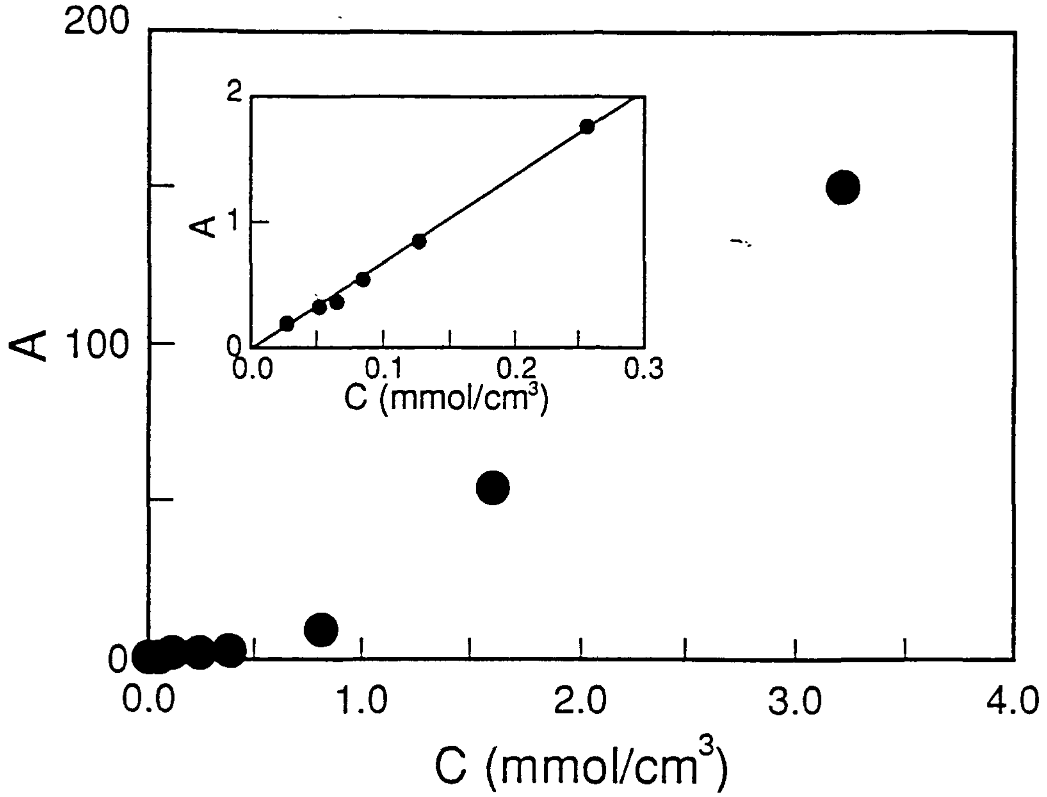


Fig. 10

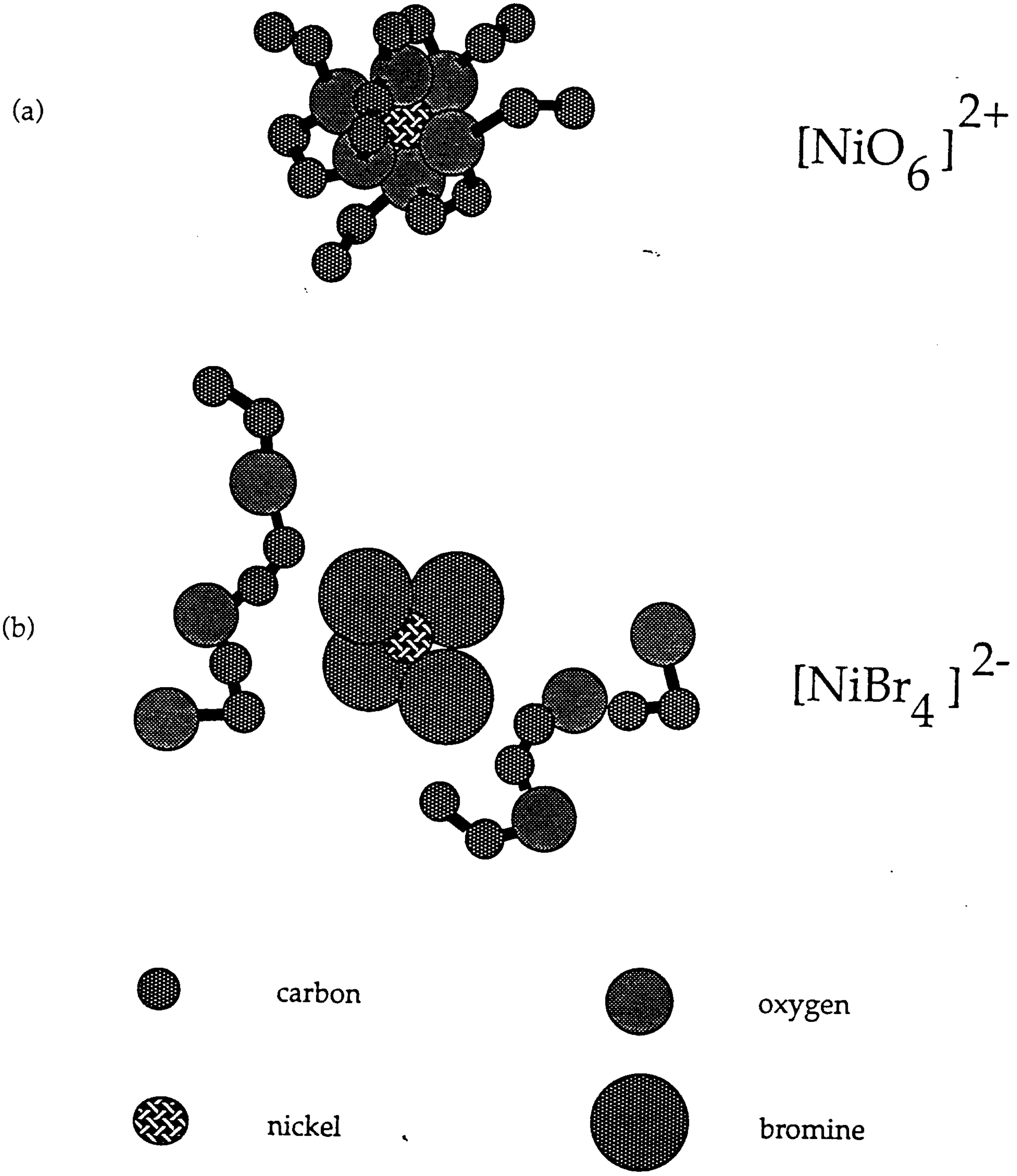

(a)
$[NiO_6]^{2+}$
(b)
$[NiBr_4]^{2-}$
carbon
oxygen
nickel
bromine

Fig. 11

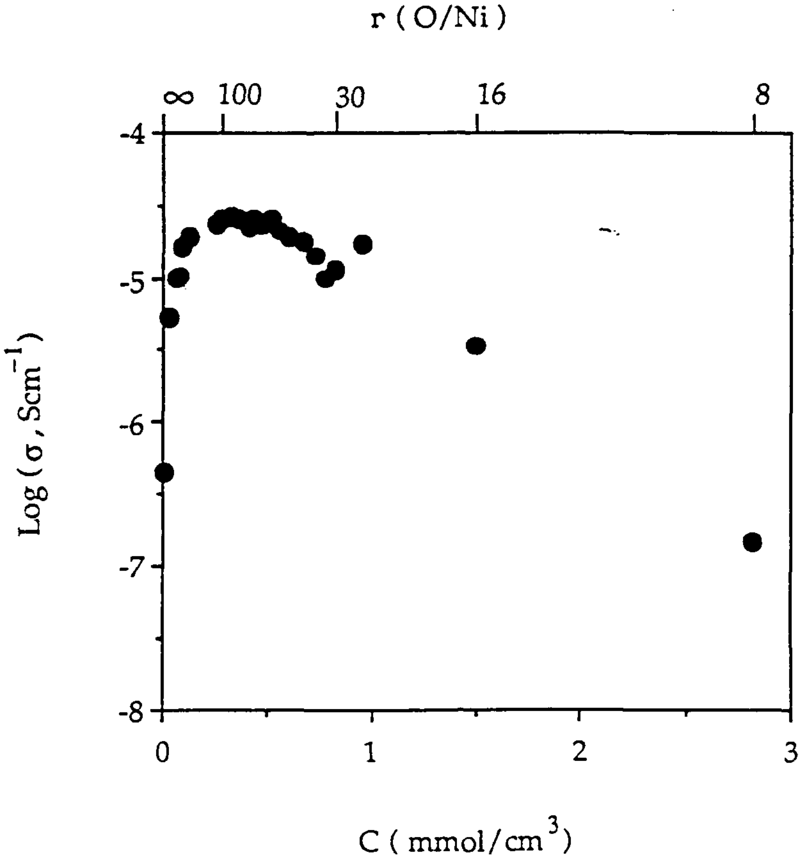


Fig. 12

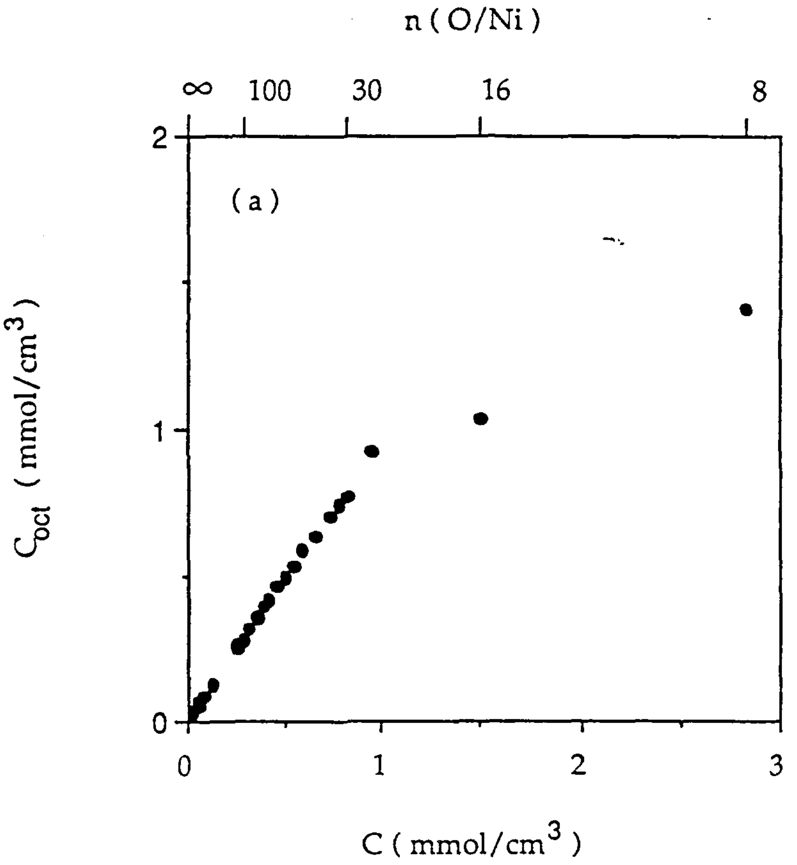


Fig. 13a

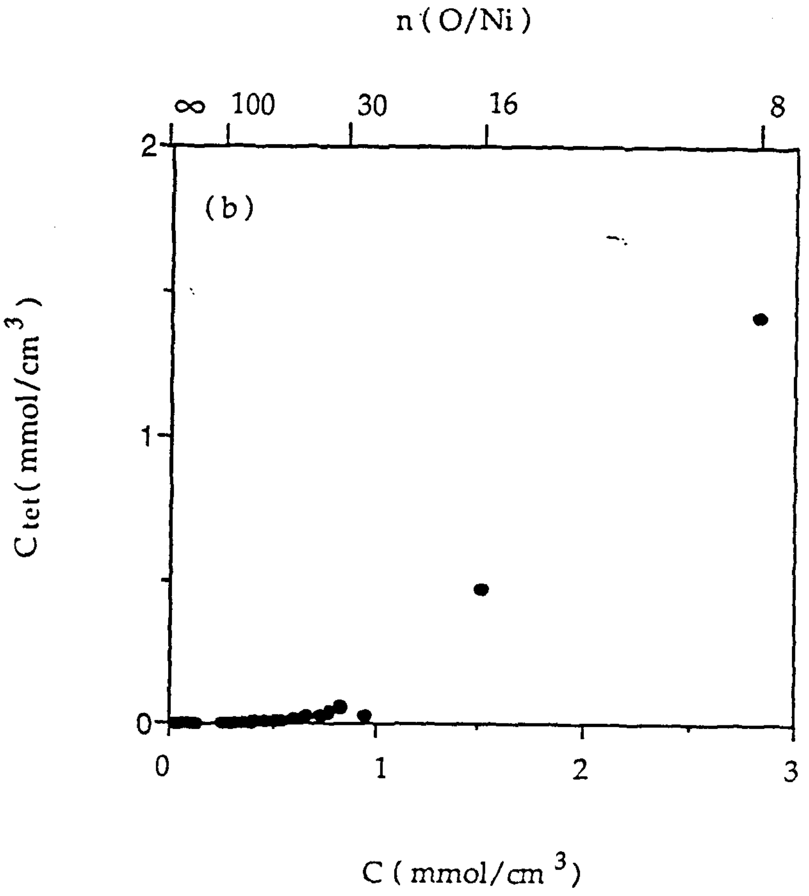


Fig. 13b

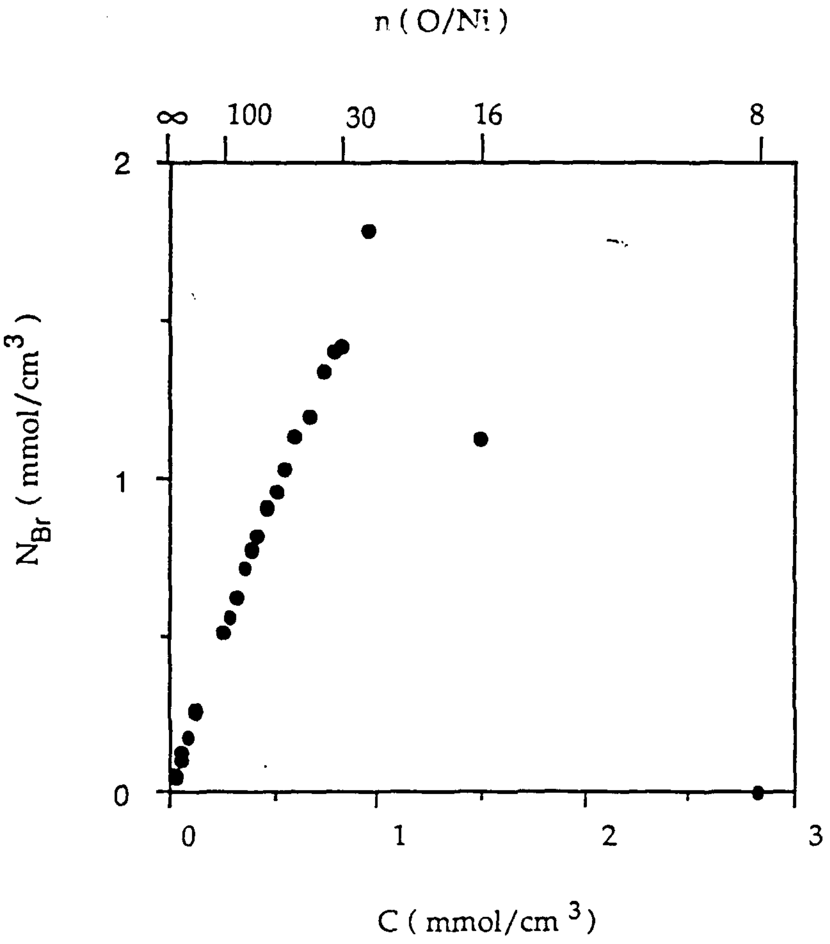


Fig. 14

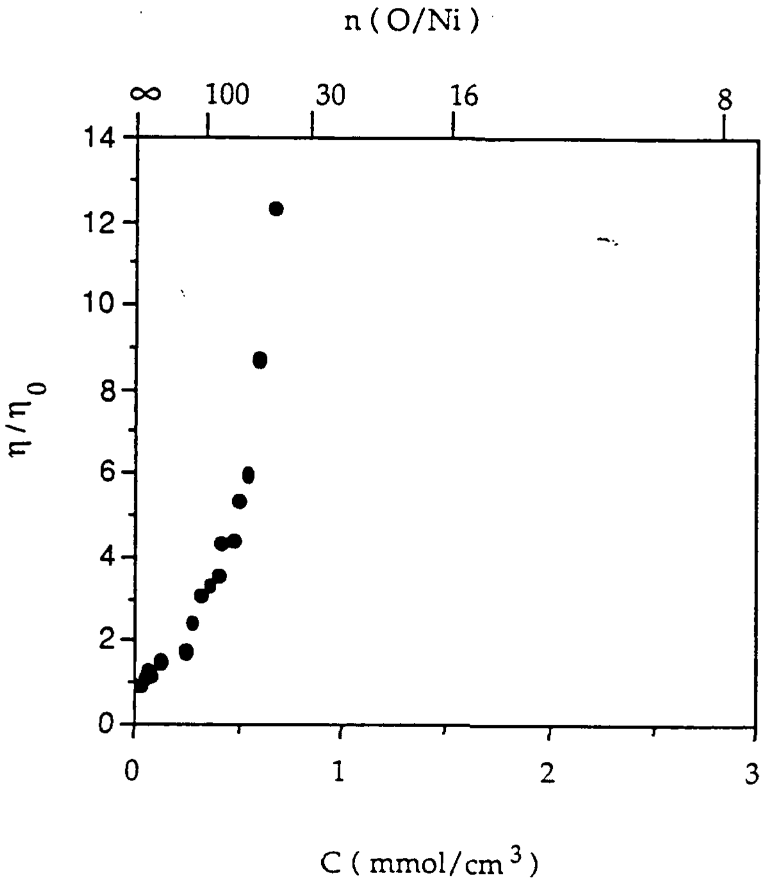


Fig. 15

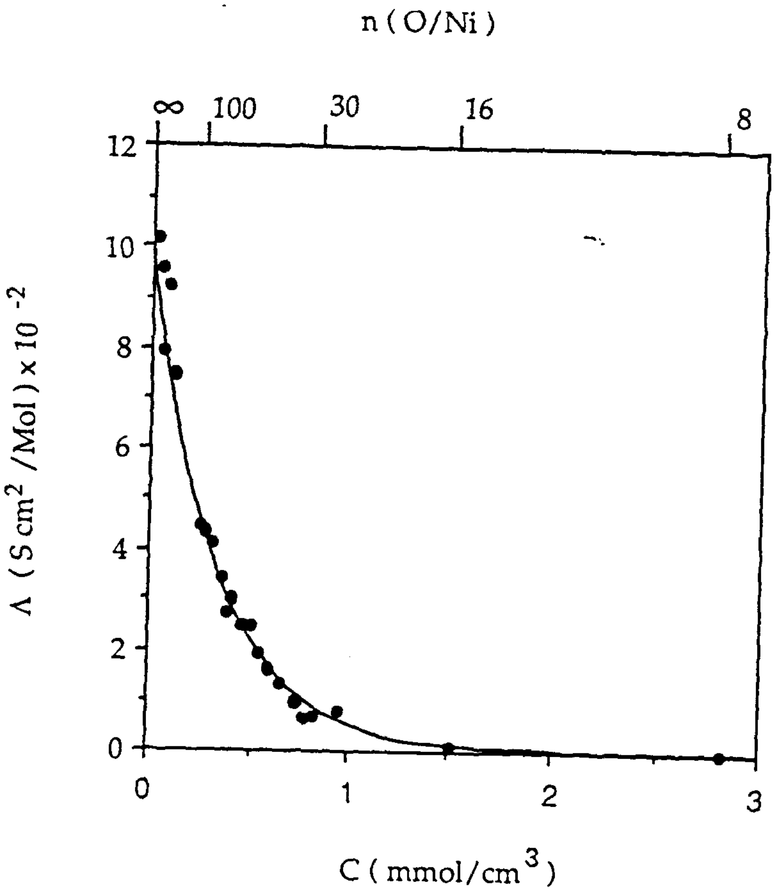


Fig. 16

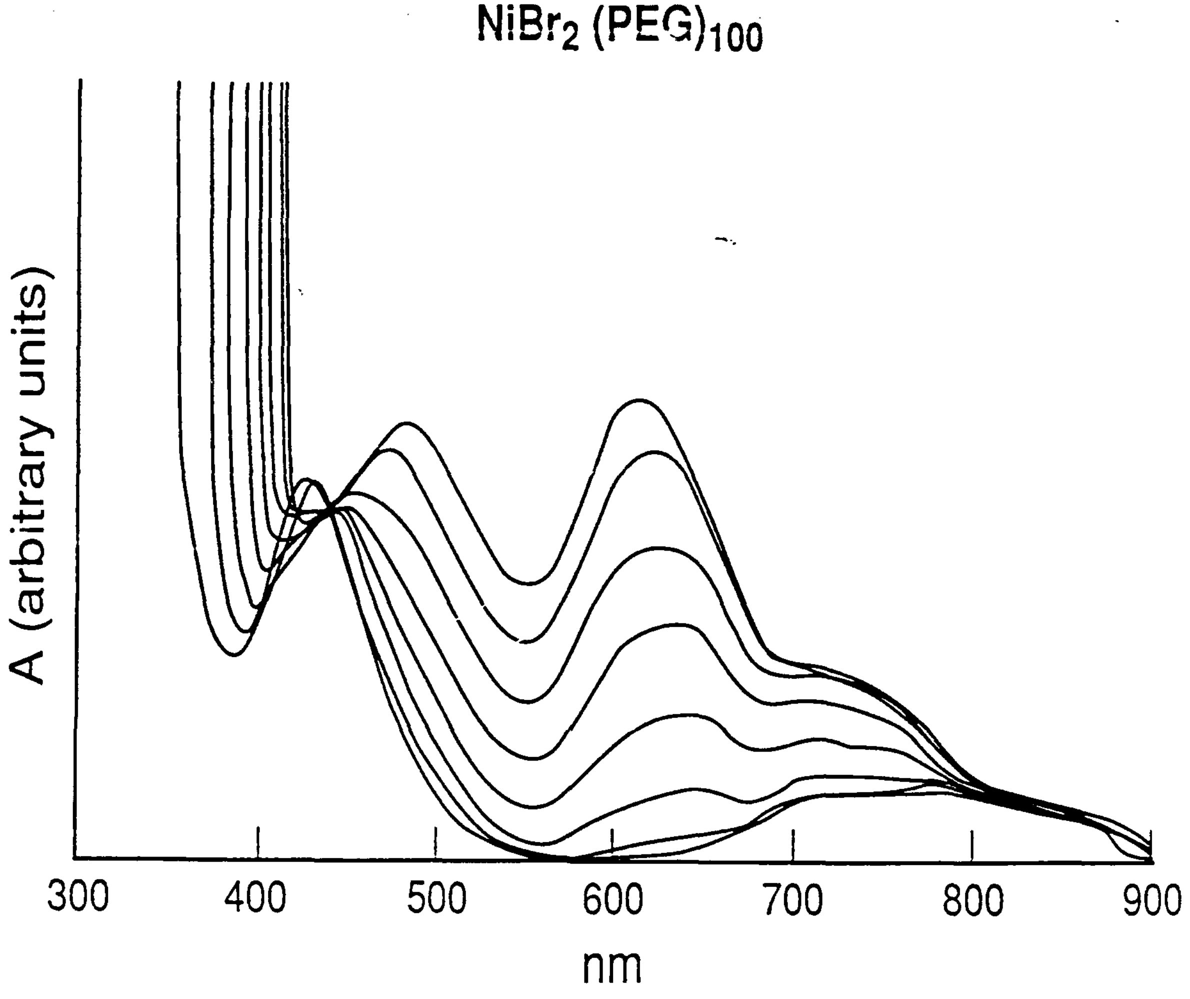


Fig. 17

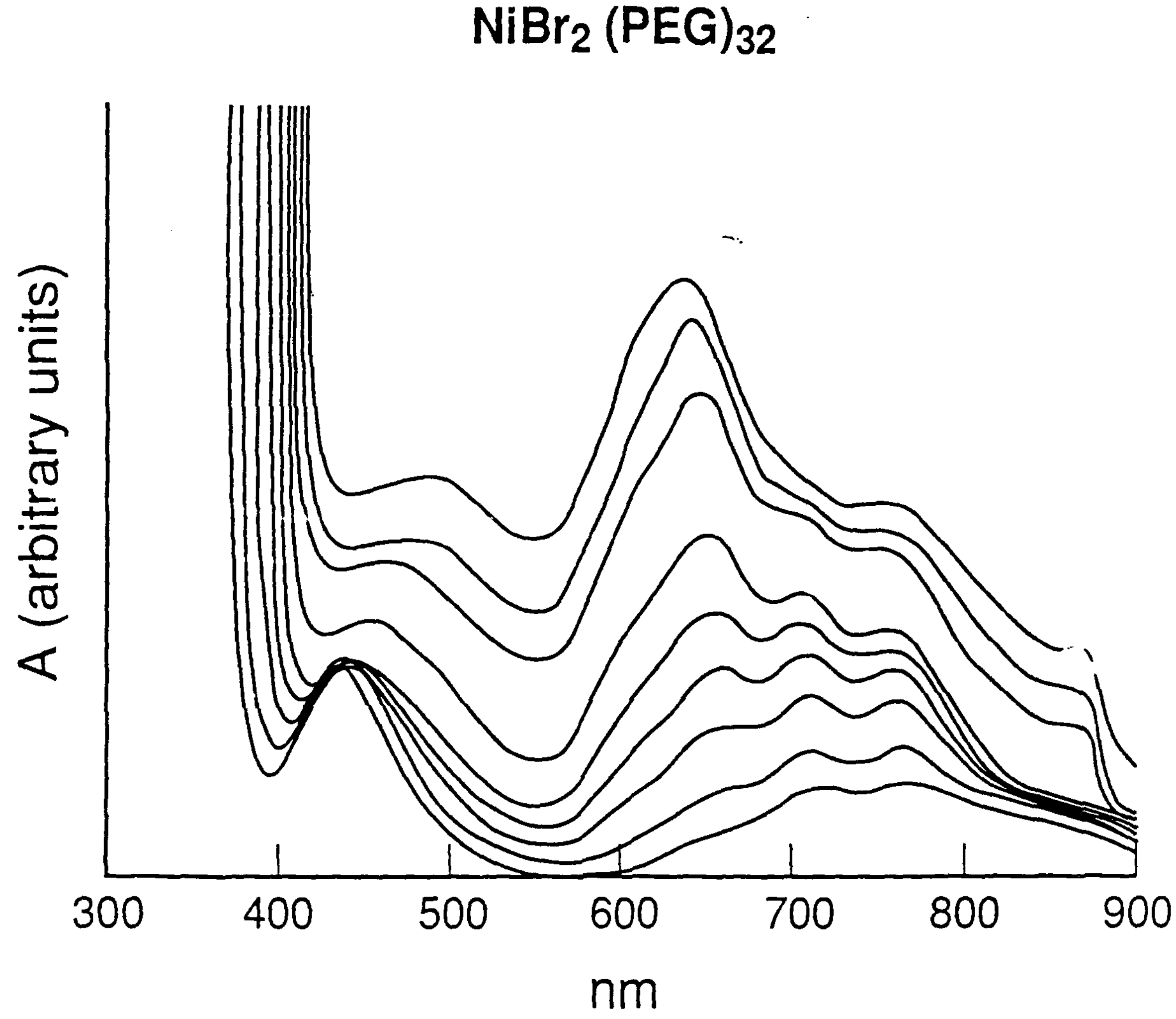


Fig. 18

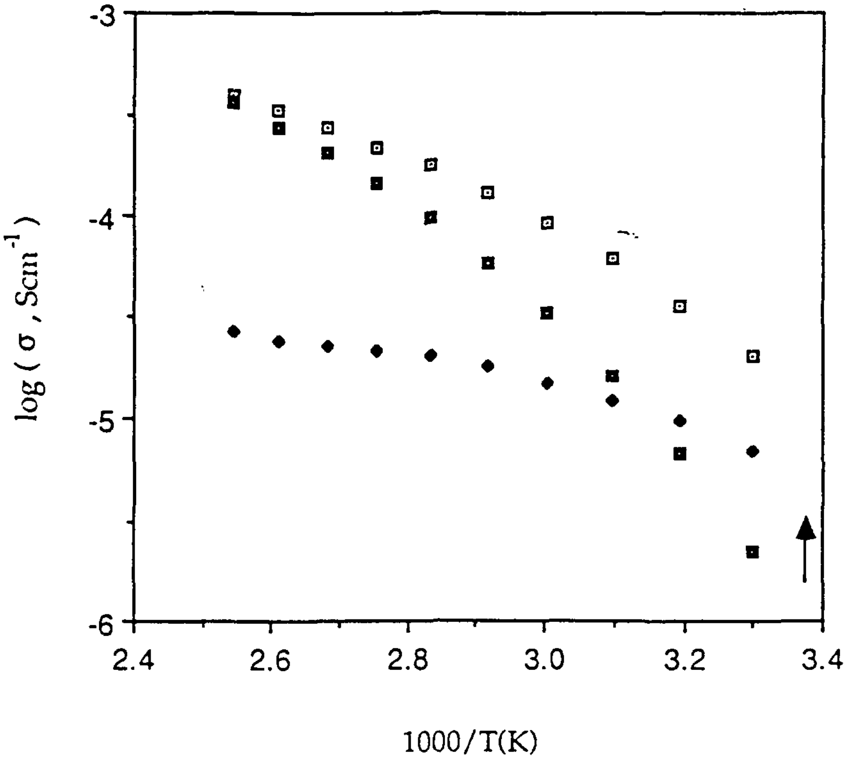


Fig. 19

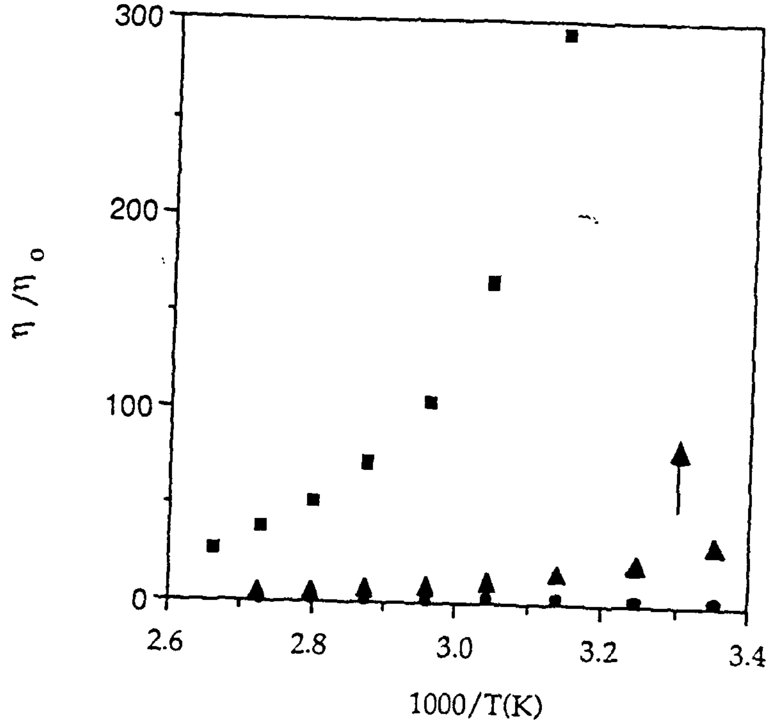


Fig. 20