

Relation between unusual solubility of salts in poly(ethylene oxide) oligomers and complex formation

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The solubility of many alkali metal salts shows negative temperature dependence in poly(ethylene oxide) (PEO) oligomer. When a PEO oligomer solution containing salt is heated, salt crystals are phase separated. This unusual phenomenon was analysed systematically for a variety of inorganic salts. These salts were shown to have relatively high lattice energy and are known to form no complex with PEO.

(Keywords: poly(ethylene oxide); alkali metal salts; solubility)

A large dipole moment of poly(ethylene oxide) (PEO), especially on the ether oxygen, could solubilize many inorganic salts without solvent. Since such salts are partly dissociated into ions in PEO, this PEO/salt mixture is known to be a starting system for the development of ion-conductive polymers. However, although there are many studies on ion conduction in PEO, little physicochemical analysis of salts in PEO has been carried out¹⁻³. We have already reported the solubility of a series of inorganic salts in PEO oligomers^{4,5}. It was confirmed that the terminal hydroxyl groups of PEO made a great contribution to solubilizing salts. We found that the solubility of potassium chloride had a negative temperature dependence in PEO oligomers⁶. Salt crystals were separated out from PEO solution by heating. Similar phenomena have been observed in poly(propylene oxide) oligomers but have been briefly reported without practical data⁷⁻¹⁰, and have not been analysed systematically. Here, we summarize the relation between the complex formation with PEO and salt species that show a negative temperature dependence of solubility.

A series of alkali metal salts [combination of cation (Li^+ , Na^+ , K^+ , Rb^+ and Cs^+) and anion (Cl^- , Br^- , I^- , NO_3^- and SCN^-)] was dried *in vacuo* at 60°C for 2 days. These were individually dissolved in PEO with average molecular weight of 200 (PEO_{200}) under nitrogen gas to form a final concentration of 0.05–2.5 mol l⁻¹ salt solution, depending on the salt species. These were pipetted and sealed in test tubes, then heated in an oil bath at a rate of 1°C min⁻¹. The solution temperature was monitored with a thermocouple inserted directly into the PEO standard solution containing no salt. Most chloride and bromide salts were phase separated as crystals by heating. A salt-saturated PEO solution was regarded to have been formed when the solution turned turbid. The temperature at which the crystals started to phase separate was plotted against the salt concentration of the corresponding sample.

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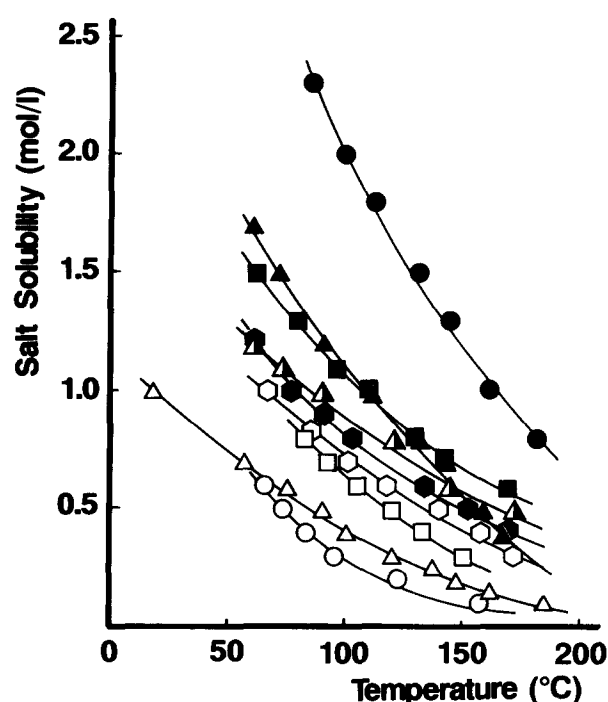


Figure 1 Effect of temperature on the solubility of a series of inorganic salts in PEO with average molecular weight of 200: ●, NaBr; ▲, KBr; ■, RbBr; ◆, CsBr; △, KNO_3 ; ○, NaCl; □, KCl; ◇, RbCl; ○, CsCl

Figure 1 shows the temperature dependence of nine alkali metal salts in PEO_{200} . The solubility of all of these salts showed negative temperature dependence. The crystals were solubilized again by cooling the PEO solution. The phase-separated crystals were confirmed to be of the same type as the corresponding salt, as obtained through recrystallization from an aqueous medium.

Many salts are reported to form a complex with PEO^{11} . To clarify the effect of lattice energy and cation species on the negative temperature dependence, the lattice energy of salts was plotted against cation radius, as shown

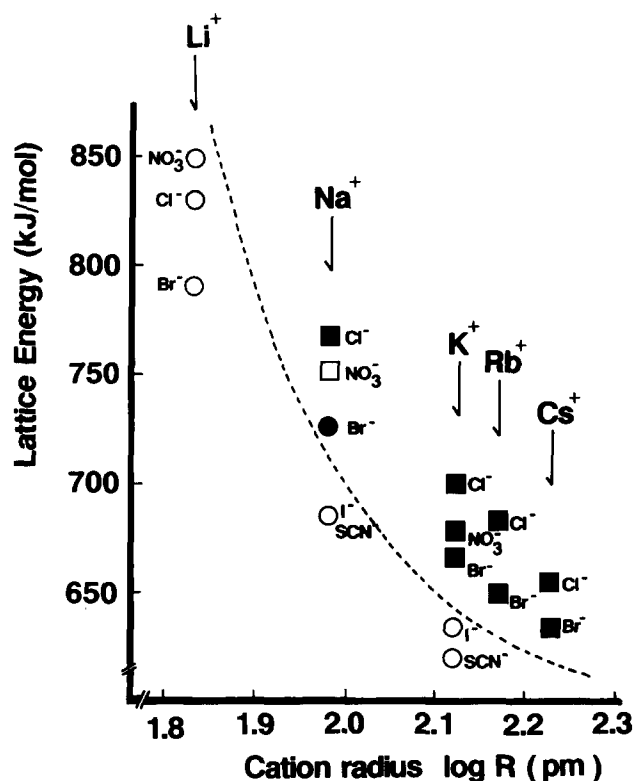


Figure 2 Relation between lattice energy and cation radius of a series of inorganic salts. ○, ●, forms complex with PEO; □, ■, forms no complex with PEO. Solid symbols, salt crystallized in PEO by heating; open symbols, no crystal was phase separated by heating. Lattice energy (calculated, in kJ mol^{-1}) from ref. 13

in *Figure 2*. Salts were then classified into two main groups by both the ability to form a complex with PEO¹¹ and whether the solubility showed a negative temperature dependence. It was clear that almost all the salts that do not form a complex with PEO showed this negative temperature dependence. The crystals obtained by heating in PEO should not therefore be the PEO/salt complex. The PEO/salt complex, also prepared by us, was totally different from the ordinary inorganic salt crystals. The boundary line of these two different groups is drawn as a dotted line in *Figure 2*. The threshold of lattice energy decreased with increasing cation radius. There are, however, two exceptions: for example, NaNO_3 was reported to form no complex with PEO¹¹, but no crystal was phase separated by heating PEO solution containing NaNO_3 . Anion structure is considered to affect this sequence not only through the lattice energy but also the steric effect, in spite of no direct experimental data.

By considering the complex formation with PEO, a mechanism can be presented for these phenomena. The salt was incompletely solubilized in PEO oligomer. Generally, the cation is solvated by oxygen atoms in PEO chains¹². Since smaller cations, such as Li^+ , have a higher surface charge density, a stronger ion-dipole interactive force was found with PEO. This means that PEO can form a complex with these smaller cations in spite of the larger lattice energy. The threshold line in *Figure 2* increases with decreasing cation

radius. When the interactive force was not strong, the entropic neighbouring (cooperative) effect of PEO solvation decreased with increasing temperature. This may correspond to the decrease of solubility in PEO. Details of this will be reported later.

A preferential pseudo-solvation of salts by PEO should be observed in the PEO containing two different salts. The phase separation of one salt (without the ability to form a complex) must be induced by the addition of another salt (with complex formation ability) to the PEO solution. KSCN powder was added slowly to a clear solution of PEO_{200} containing 1.70 mol l^{-1} KBr under stirring. KSCN was easy to solubilize in this PEO solution. Crystals of the cubic system gradually appeared when KSCN salt was solubilized in PEO_{200} solution with concentration greater than 0.10 mol l^{-1} . Since KSCN crystals are classified as orthorhombic, the crystals that appeared are strongly suggested to be KBr crystals. This suggests that PEO interacted more strongly with complex-forming salts than with non-complex-forming salts. The latter were phase separated by the addition of the former in PEO. Since the cation species of both salts is potassium, in this case, the effect of the anion species was considered to control the solubility in PEO. Detailed analysis on the exchange reaction of the salt species in PEO is now in progress.

PEO oligomers showed unusual solubility to inorganic alkali metal salts. In particular, we clarified that the solubility of salts that do not form a complex with PEO showed negative temperature dependence. A preferential pseudo-solvation of salts by PEO was also observed in the system containing two salts with different complex-forming ability.

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