Complexation and Crystallization of Rare Earth Salts in DEG and TEG

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(Received October 29, 1996)

Solubility of a series of rare earth salts ($LnCl_3\cdot6H_2O$; Ln=La, Ce, Pr, Nd, Sm, Gd, Dy, Er and Yb) was studied in diethylene glycol (DEG) and triethylene glycol (TEG). Almost all rare earth salts were dissolved in TEG at room temperature, and they were separated out as crystals by heating. Against this, their solubility in DEG depended on the atomic number (number of electrons in f-orbital). Crystals grew after heating in DEG. The crystal obtained from DEG solution of $NdCl_3\cdot6H_2O$ was analyzed with X-ray crystallography. It was anhydrous crystal and one Nd^{3+} cation was revealed to be solvated with nine oxygen atoms of three DEG molecules.

The stability of rare earth ions in poly(ethylene oxide) (PEO) can be explained by the polarity of PEO. Polar environment provided by PEOs is easily comprehended by the structural similarity with water molecule. In general, the solubility of salts increased with increasing temperature. However, it was already reported that the solubility of some alkali metal salts in PEO oligomers had negative temperature dependence.[1] Such unique solubility curve was found for salts with relatively large lattice energy and larger cation radius.[2] The solubility of hydrated lanthanide chlorides ($LnCl_3\cdot6H_2O$; Ln=La, Ce, Pr, Nd, Sm, Gd, Dy, Er and Yb) was analyzed in different molecular weight PEO oligomers (Mw=106, 150, 200, 400). Crystallization of a series of rare earth salts from TEG solution by heating was already found.[3] The crystallization had not been observed in DEG solution. There are no crystal formation within a day or two after heating DEG solution of hexa hydrated rare earth salts. The reason for this no crystallization by heating in DEG was considered to be due to the effective ligation of relatively short DEG molecules. Solubilizing temperature of a series of $LnCl_3\cdot6H_2O$ salts in DEG was high and almost the same with each other when salt concentration was more than 0.5 mol·l^{-1}. On the other hand at lower concentration than 0.1 mol·l^{-1}, there were no phase change observed up to an oxidative degradation temperature of DEG or TEG (around 200 ℃). The present study was therefore carried out at the concentration of 0.2 mol·l^{-1}.

The solubilizing temperature of 0.20 mol·l^{-1} $LnCl_3\cdot6H_2O$ in DEG is shown in Figure 1 (○). In the DEG solution, La salt was dissolved completely at room temperature. The solubilizing temperature of Ce, Pr, and Nd salts was 55, 95, and 104 ℃, respectively. All the other salts were solubilized at temperature in between 120 and 140 ℃. On the other hand, all samples (0.20 mol·l^{-1} $LnCl_3\cdot6H_2O$ in TEG) were dissolved at room temperature, and formed crystals were phase-separated by heating (Figure 1, ●). This suggested that the difference of solubility in Figure 1 was originated by the atomic number, in other words, the number of electrons in f-orbital. This can be comprehended to be the recognition of lanthanide ions with polyethers. Lanthanides are generally classified into two groups as light and heavy rare earth groups. The solubility of light rare earth salts increased with increasing atomic number (decreased cation radius generally known as lanthanide contraction). By contrast, heavy rare earth salts showed the inverse tendency. These results indicate that the difference of solvation should be attributed to the cation radius of lanthanides, and this effect is different between light and heavy rare earth salts. With this difference in solubility manner, new separation method of lanthanide salts will be presented with PEO derivatives as solvents. Experiments are now in progress in our laboratory.

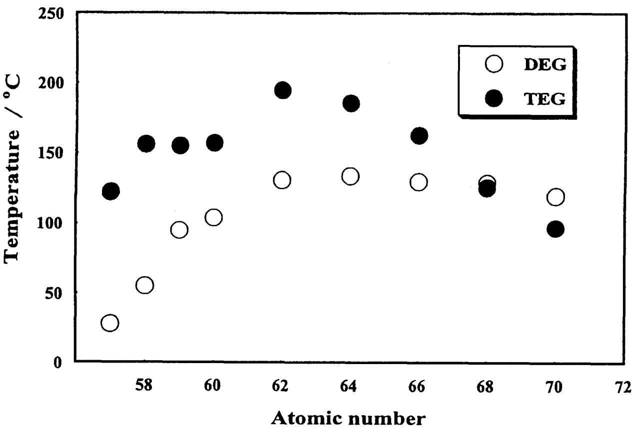

Figure 1. Solubilization or crystallization temperature for $LnCl_3\cdot6H_2O$ in DEG and TEG. Temperature to solubilize 0.20 mol·l^{-1} salts (open plots) in DEG or to crystallize them (closed plots) in TEG were plotted against atomic number of Ln.

There were no sample solutions producing crystals during heating up to 160 ℃ in DEG solutions. Although there were no salt crystals in every sample solution after leaving it for 24 h at room temperature after heating, deposits appeared a few days after that. In spite of difference in deposit time, crystals were obtained in most samples (except La salt, which was highly soluble at room temperature).

Next, the unit structure of crystals deposited in DEG was investigated by X-ray crystal analysis. Figure 2 shows the molecular structure of crystals [$NdCl_3\cdot3DEG$, space group P2$_1$/n, a=10.552(2) Å, b=13.239(2) Å, c=15.987(2) Å, β= 92.97(1)°, V=2230.3(6) Å^3, Z=4] obtained from DEG solution of $NdCl_3\cdot6H_2O$ after heating and incubation at room temperature for ten days. One Nd^{3+} cation was revealed to be solvated by three ether oxygen atoms and six hydroxyl terminal groups of three DEGs. It clearly showed that Nd^{3+} complex had nona-coordination structure. In the previous works, Shiokawa and Hirashima obtained complexes of hydrated Nd(NO$_3$)$_3$ with DEG oligomers from mixed solution of DEG and ethyl acetate.[4] They showed the ratio of their complex

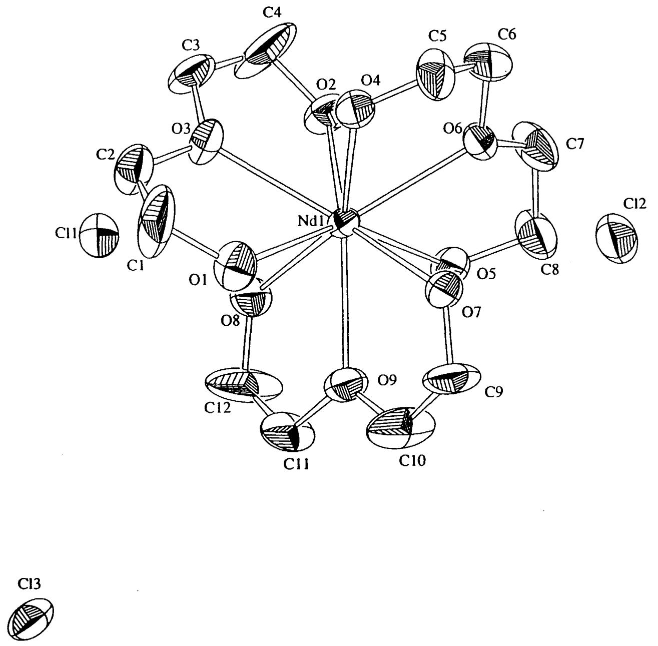

Figure 2. Molecular structure of $NdCl_3$/DEG complex crystals deposited from DEG solution. Selected bond distances (Å): Nd1-O1, 2.476(4); Nd1-O2, 2.481(5); Nd1-O3, 2.552(4); Nd1-O4, 2.491(5); Nd1-O5, 2.480(4); Nd1-O6, 2.541(4); Nd1-O7, 2.477(5); Nd1-O8, 2.488(4); Nd1-O9, 2.583(5);

to be DEG:Nd=2:1~3:1. The crystal, which was obtained in this work, was anhydrous and the ratio was DEG:Nd=3:1. The mean distance of the bond length between ether oxygen atoms and Nd^{3+} cation is 2.56 Å, however that between hydroxyl terminal groups and Nd^{3+} cation is shorter to be 2.48 Å. This tendency has also obtained in the complex of Nd-nitrate and PEO oligomers reported by Shiokawa and Hirashima.[5] For example, in the complex of tetraethylene glycol and Nd, the mean distance to the terminal hydroxyl oxygens is shorter than that for the ethereal oxygens (2.51 Å as compared with 2.65 Å)[5]. It is indicated that the terminal hydroxyl group shows stronger binding than the ether oxygen atom. It suggests that the hydroxyl terminal group is more important for the complexation in PEO oligomers.

No water molecules were found as component of crystals. This was comprehensible that all of water molecules were vaporized during heating. TG/DTA analysis strongly suggested that the formed crystal was composed of $NdCl_3 \cdot 3DEG$ and each DEG molecule was removed stepwise at 157.6, 211.4, and 245.5 ℃, respectively. No weight loss was detected attributed to the removal of water molecules. Whereas, that of $NdCl_3 \cdot 6H_2O$ showed the removal of the coordinated water molecules at 75.1 (for $3H_2O$), 115.9, 135.9, and 186.0 ℃, respectively. The details of competitive solvation of waters and DEG or TEG are however still not clear. These will be analyzed in the near future.

Since one DEG oligomer provides three coordination sites, just three oligomers are expected to solvate with one Nd cation to form nona-coordinated complex. However the coordination number of rare earth cations may be changed depending the coordination condition, nona-coordination is one of the most stable state. Whereas, TEG oligomer has four coordination sites, the crystal unit structure should be irregular since one Nd^{3+} cation was solvated by TEG oligomers in spite of inefficient coordination. They might have uncoordinated (free) ether oxygen(s) or terminal hydroxyl group(s) in the complex. It is easy for irregular complex to generate deposits of $LnCl_3$ by heating. There were no deposits of $LnCl_3$ crystals when PEOs with relatively high molecular weight (Mw=400~2000) were used. The crystallization of salts *via* the complex formation is suppressed because of the excluded volume effect. Excellent solubility of all $LnCl_3 \cdot 6H_2O$ in PEO (Mw=1000 and above) is attributed to the entropy term, in other words, advantage of complexation by oligomers.

In spite of anhydrous crystals which were obtained in this experiment, those complexes are easily dissolved again by heating. This is one of advantages for these complexes, because it is difficult to dissolve anhydrous rare earth salts in PEO oligomers.

The present study was supported by the Grant-in-Aid for Scientific Research on Priority Areas "Rare Earth Complexes" (#06241104) from the Ministry of Education, Science and Culture, Japan.

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