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Letter

TEM study on extractive organic phase containing lanthanide ions*

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1. Introduction

Solvent extraction is used widely in lanthanide separation. Previously, more attention was paid to the study of extraction equilibrium distributions. Structural studies of the organic phases have seldom been attempted. However, knowledge on the structure of organic phases will help us to understand the extraction process.

Extractants are generally amphiphilic. The extractant molecules are composed of two parts, i.e., the hydrophilic groups which will coordinate with the extracted metal ions and the hydrophobic chains which ensure the oil solubility [1,2]. Therefore, they tend to aggregate in the organic phase to form reversed micellae or microemulsions [1–6]. This is also true of the metal-extractant complexes [7].

The microstructures of reversed micellae and microemulsions are often difficult to measure due to small size and complicated composition. Light scattering (LS) is useful to a certain extent, but it can only obtain indirect evidence, and needs a model to interpret the results. Transmission electron microscopy (TEM) is an attractive method to solve this problem. However, the reversed micellae and microemulsions cannot be observed directly with TEM, mainly because of the high vapour pressure of the solution and insufficient contrast [8]. Hence, in recent years, the freeze-fracture replication method was used in colloid science [8–10]. The freeze-fracture replication method was used in this paper to view the structure of the extractive organic phase containing lanthanide ions and the widely used extractants, naphthenic acid [11] (Fig. 1). The results were compared with those of the light-scattering method.

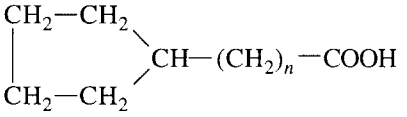

Fig. 1. The structure of naphthenic acid.

2. Experimental

Instruments used were: JEOL JEM-100CXII electron microscope; HITACHI HUS-5GB high vacuum evaporator; light scattering apparatus, installed by the Department of Chemistry, Peking University; light source was argon laser; Wave length was 514.5 nm and power was 200 mW.

2.1. Materials

Naphthenic acid, an industrial product, was purified by distillation. The average molecular weight is 269.2 and the equivalent number is 0.0342 mol g^{-1}. Other reagents used are all of A.R. grade.

Naphthenic acid (HA) was saponified with metallic sodium. The lanthanum naphthenate was obtained by reacting sodium naphthenate with lanthanum chloride. Lanthanum naphthenate and naphthenic acid were dissolved in toluene to produce two equivalents per liter (2N) of HA (sample C), 1N LaA_3 (sample D) and 1N HA + 1N LaA_3 (sample E) solutions.

A 1M sodium naphthenate–2M 2-octanol–n-heptane solution was stirred together with aqueous europium chloride solution to get the extractive organic phases

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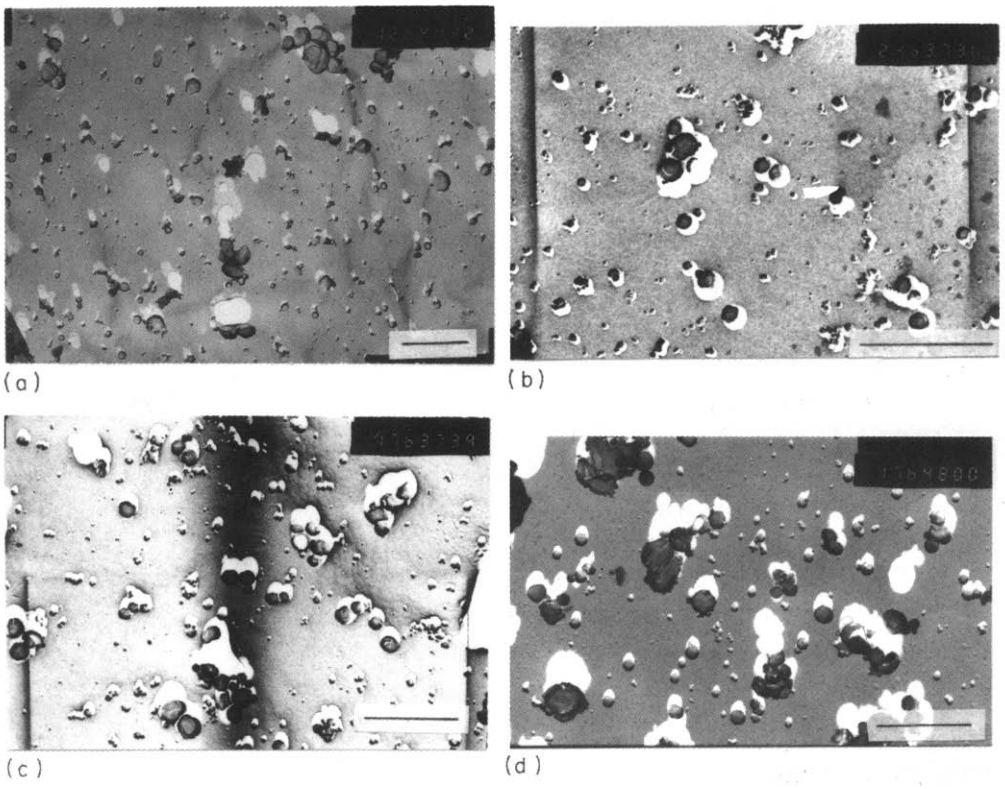

Fig. 2. TEM images by replica freeze fracture (the bars in the pictures all represent 10^5 Å). (a) Sample C at 12000× magnification; (b) Sample D at 24000×; (c) Sample E at 17000×; (d) Sample 1 at 17000×.

with 20% (sample 1), 40% (sample 2), 60% (sample 3) and 100% (sample 4) of europium loading.

2.2. Procedure

TEM: the sample was contained in a copper cell and frozen in liquid nitrogen. The frozen sample was fractured and evaporated with platinum and carbon in the high vacuum evaporator to give a solid replica with high resolution. Then the replica was washed in THF to remove the sample materials and put on a copper net for observing in TEM.

LS: the samples were centrifuged under 12,000 rpm for 30 min and then measured with the apparatus at 27 °C. The sizes of the particles were determined by doubling the hydrodynamic radii.

3. Results

It was observed with TEM that round particles are dispersed in the solvents (Fig. 2). The particle sizes of the samples C, D and E from TEM method are listed in Table 1. Those samples with different europium loading by TEM and LS are listed in Table 2.

Table 1
Particle sizes of HA-LaA_3-toluene samples

Sample	C	D	E
Composition	2N HA	1N LaA_3	1N HA + 1N LaA_3
Particle size (Å)	100–1000	100–500	100–1000

Table 2
Particle sizes of samples with different europium-loading

Sample	1	2	3	4
Percentage of loading	20%	40%	60%	100%
Concentration of Eu (N)	0.20	0.40	0.60	1.00
Particle size from TEM (Å)	200–1500	600–1200	1000–3000	80–200
Particle size from LS (Å)	700	950	2000	100

4. Discussion

1. With the help of TEM, we found the microstructure of extractive organic phases. They are complex fluids rather than true solutions. The extractant and extractive complex molecules aggregate to form certain tiny par-

ticles. The particles are round in shape and the particle sizes range from 80–3000 Å. These are within the range of micellae and microemulsions.

2. It was found from Table 1 that the concentrations of the extractants and the extractive complexes will affect the sizes of microemulsions. The higher the concentration, the larger the particle will be.

3. Table 2 shows that the percentage of metal loading has a great effect on particle size and the results from TEM are roughly in accordance with those from LS.

4. The particle sizes increase with the increase in percentage of europium loading at 60% or lower. At 100% loading, however, the particle size decreases sharply to about 100 Å. There is other evidence [12] which supports that sodium and europium coexist in the micellae particles rather than forming micellae independently. The sharp size decrease at 100% loading may be caused by a lack of sodium naphthenate to form larger particles together.

5. Conclusion

1. TEM is a useful method to investigate the microstructure of extractive organic phase when the freezing rate is high enough to maintain its original structure.

2. The extractants and extractive complexes studied aggregate in the organic phase to form reversed micellae or water-in-oil microemulsions rather than being dispersed as molecules to form a true solution.

3. The sizes of particles are within the range of 80–3000 Å depending on the extractant concentration and percentage of lanthanide loading.

Acknowledgement

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