

Small angle neutron scattering study of U(VI) third phase formation in HNO₃/DHDECMP–*n*-dodecane system

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Abstract. Small angle neutron scattering studies (SANS) were carried out to understand the formation of third phase in DHDECMP–dodecane–UO₂(NO₃)₂/HNO₃ system. It was observed that third phase formation takes place due to the formation of UO₂(NO₃)₂.DHDECMP reverse micelles in the dodecane phase. SANS data obtained were interpreted with particle interaction model using Baxter sticky spheres model.

Keywords. Small angle neutron scattering; U(VI); third phase; DHDECMP.

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1. Introduction

Bi-functional neutral donors (DHDECMP, CMPO) are being proposed for the extraction of trivalent actinides (Am³⁺) from waste generated at the back end of the nuclear fuel cycle because they can extract actinides over a wide range of acidities (0.5 M–6 M). But these extractants form third phase when used along with commonly used diluents like dodecane [1,2]. The third phase formation, i.e. two organic phases and one aqueous phase, in solvent extraction experiments can be encountered in certain extraction systems, which is undesirable because it leads to the accumulation of these actinides in the process vessel thereby creating criticality problem. One of the two organic phases is rich in diluent (lighter organic phase) and the other is rich in extractant (heavier organic phase). The latter phase contains the metal solvate and is commonly referred to as third phase accumulating in the interface between lighter organic phase and aqueous phase.

Since nitrates of actinide elements are extracted by neutral donors like DHDECMP as M(NO₃)_{*n*}·*x*DHDECMP and these solvates exhibit limited solubility in long chain aliphatic diluents and, therefore, separate out as third phase (heavy organic phase) at higher loading of actinide element. Earlier we have studied the third phase formation in DHDECMP–HNO₃–dodecane system and the phenomenon was explained with the help of equilibrium densities of phases [3]. However

very little information is available on the structural aspects of third phase formation. It has been reported [4] that in some subsystems, third phase formation is due to the formation of large aggregates in the organic phase. In order to understand the formation of third phase in DHDECMP–dodecane– $\text{UO}_2(\text{NO}_3)_2$ – HNO_3 system, small angle neutron scattering studies were carried out. Information on the size and shape of the objects in solution and the interparticle interactions can be obtained by SANS (small angle neutron scattering) and the neutron interacts with the nuclei in the sample and the interaction depends on the sample.

2. Experimental

DHDECMP obtained from Columbia Chemicals was used as such (88%). Deuterated dodecane (98%) was obtained from Aldrich Chemical Co. Equal volumes of known concentrations of extractant, DHDECMP in deuterated dodecane and an aqueous acid solution were shaken in a thermostatted water bath for 30 min. The phases formed were allowed to settle. Measurements were performed on six samples (S1 to S6) at SANS instrument at BARC, Mumbai [2]. Sample S1 was 30% (v/v) solution of DHDECMP in deuterated *n*-dodecane (d_{26} , 98 atom% D) contacted with 0.5 M nitric acid + mg of U(VI). Sample S2 was prepared by continuous addition of $\text{UO}_2(\text{NO}_3)_2$ to the extractant phase till LOC was reached. When the addition of $\text{UO}_2(\text{NO}_3)_2$ was beyond LOC, the organic phase splitted into light organic phase (dodecane-rich) sample S3 and heavy organic phase (DHDECMP-rich) sample S4. Sample S5 was 30% DHDECMP/D-dodecane without any treatment and sample S6 was 30% DHDECMP phase which was equilibrated with 0.5 M HNO_3 . The SANS measurements were carried out with a SANS diffractometer at Dhruva reactor, BARC, Trombay [5]. The mean wavelength of the incident neutron beam is 5.2 Å with a wavelength resolution of approximately 15%. The Q range of the instrument is 0.017–0.35 Å⁻¹. The measured SANS data were corrected and normalized to a cross-sectional unit using standard procedures.

3. SANS Analysis

In SANS, one measures the differential scattering cross-section per unit volume [$d\Sigma/d\Omega(Q)$] as a function of Q . For a system of interacting particles dispersed in a medium, $d\Sigma/d\Omega(Q)$ can be expressed as

$$\frac{d\Sigma}{d\Omega}(Q) = n(\rho_p - \rho_s)^2 V^2 P(Q) S(Q), \quad (1)$$

where n is the number density of the particles, ρ_p and ρ_s are respectively, the scattering length densities of the particle and the solvent, and V is the volume of the particle. $P(Q)$ is the intraparticle structure factor and is decided by the shape and size of the particle. $S(Q)$ is the interparticle structure factor, which depends on the spatial arrangement of particles and is thereby sensitive to interparticle interactions. We have fitted the data using $P(Q)$ of spherical particles (diameter σ) and $S(Q)$ has been calculated assuming attractive interaction between the particles

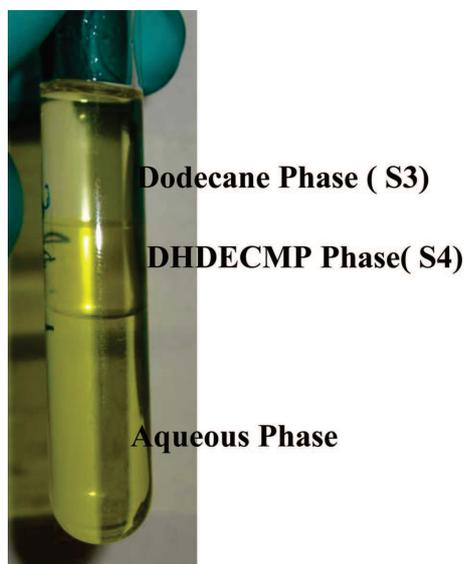


Figure 1. Pictorial representation of third phase formation.

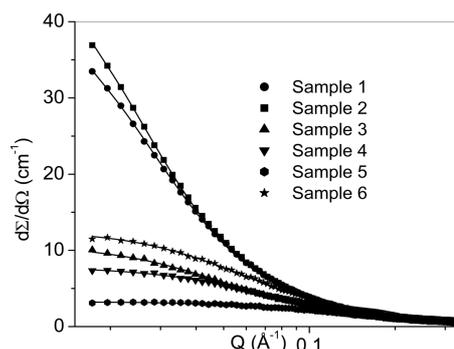


Figure 2. Baxter model plot.

by Baxter's sticky hard-sphere model. In this model, particles interact via a thin attractive square-well potential of depth u_0 (< 0) and width Δ . The basic results of the model can be derived as the lowest order solution, to the Ornstein–Zernike equation and Percus–Yevick closure relation. The stickiness parameter (τ) is related to the potential parameters (u_0, Δ, σ) and temperature T as $\tau = [(\sigma + \Delta)/12\Delta] \exp(u_0/k_B T)$, where k_B is the Boltzmann's constant.

4. Results and discussion

During the initial stages of the present study, it was observed that when a solution of DHDECMP in dodecane was equilibrated with nitric acid solution above 1 M or a solution of $UO_2(NO_3)_2$ with suitable concentrations, the organic phase splitted into two phases, lighter organic phase rich in dodecane and heavier organic phase rich in DHDECMP. The third phase formation was observed over a wide range of compositions, mainly governed by the equilibrium densities of phases regardless of the initial DHDECMP concentration. In order to understand more about third phase formation in DHDECMP system, it was considered interesting to study the morphology of the species present in the organic phase before and after third phase formation using SANS. All the evidence from the SANS data including the large aggregates in the organic phase seems to point towards the formation of reverse micelle-like particles in dodecane phase.

When DHDECMP/dodecane was equilibrated with $UO_2(NO_3)_2$ solution, solute particle size increases steadily due to the formation of 1:2 complex of $UO_2(NO_3)_2 \cdot 2DHDECMP$ which self-assembles into aggregates. A dramatic change

Table 1. Fitted parameters from Baxter model.

Sample	Micelle diameter (σ)	Aggregation number (N)	Stickiness parameter ($1/\tau$)	Potential energy ($U_0/k_B T$)
1	15.5	7.9	19.2	-2.64
2	16.7	10.5	19.5	-2.72
3	10.7	2.5	14.2	-2.02
4	8.8	1.6	15.9	-1.97
5	7.9	3.1	8.8	-1.28
6	10.7	6.6	14.4	-2.03

in the solution leading to phase splitting takes place by increasing $\text{UO}_2(\text{NO}_3)_2$ concentration in the aqueous phase which is in equilibrium with the organic phase. SANS data suggest that largest aggregates are seen at LOC condition (just before third phase formation).

The increase in intensity values I_0 obtained with increase in U concentrations indicates either a particle growth phenomenon or particle interaction in the organic phase. This can in principle be due to progressive increase in the size of the particle ($P(Q)$) or progressive increase in the attractive interaction between the particles ($S(Q)$). The increasing scattering intensity $I(Q)$ at lowest Q value is the qualitative indication that the size of the solute particles increases progressively as more and more $\text{UO}_2(\text{NO}_3)_2$ forms solvated complex with DHDECMP up to complete saturation of the extractant. It was also observed that after phase splitting, the size of the aggregate in the third phase has become significantly smaller than in the LOC samples (table 1).

When the effect is solely attributed to particle growth, the results showed substantial increase of aggregation number. It neglects the interactions between the reverse micelles, in spite of their high concentration (>30%) and, therefore the data were fitted using Baxter model (interacting) (figure 2). We found that in this model, micelle sizes are much smaller than those obtained from the non-interacting model of micelles. The formation of third phase was explained on the basis of the increase in the attractive interaction on approaching LOC.

5. Conclusions

A particle interaction model using Baxter sticky spheres model explains the formation of third phase as due to increase in the attractive interaction on approaching LOC. The DHDECMP micelles are subjected to two contrasting physical forces. On the one hand, the thermal energy $k_B T$ keeps the micelles dispersed in the solvent and on the other hand, the energy of intermicellar attraction makes the micelles stick together. When the energy of attraction becomes substantially larger than thermal energy, third phase formation takes place. Therefore, the data were interpreted using particle interaction model (Baxter sticky spheres model) [6] which provided more consistent results (figure 2). The calculated Baxter fit parameters

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for hard spheres with surface adhesion are given in table 1. We found that in this model, micelle sizes are much smaller than those obtained from the non-interacting model of micelles. Baxter model for hard spheres with surface adhesion provides a simple explanation of the phenomenon of third phase formation.

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