RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Extractant mediated nano-aggregate formation in Triton X-114 aided cloud formation: TEM and SANS studies[†]

N. Kumari, P. K. Verma, P.N. Pathak, A. Gupta, A. Ballal, V.K. Aswal, P.K. Mohapatra[*]

Graphical Abstract

Journal Name
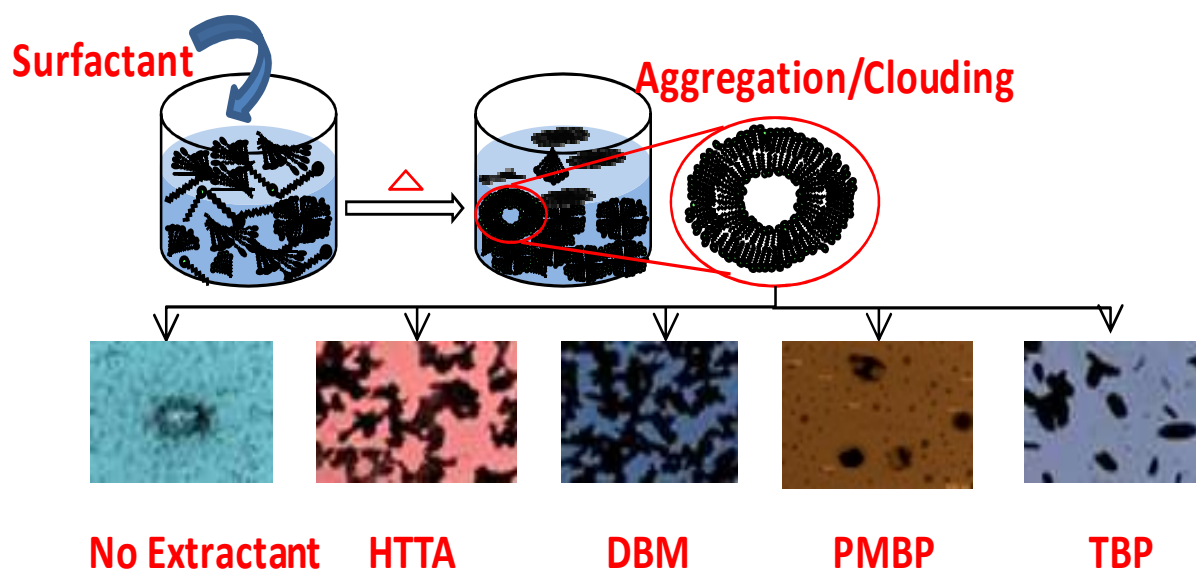
COMMUNICATION

Extractant mediated nano-aggregate formation in Triton X-114 aided cloud formation: Structural insights from TEM and SANS studies[†]

N. Kumari[a], P. K. Verma[a], P.N. Pathak[a], A. Gupta[b], A. Ballal[b], V.K. Aswal[c], P.K. Mohapatra[a,*]

Nanoaggregate formation by self assembly was noticed during the cloud formation of Triton X-114 (1,1,3,3-tetramethylbutyl) phenyl-polyethylene glycol) in the presence of dibenzoylmethane (DBM), thenoyltrifluoroacetone (HTTA) and 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) and tributyl phosphate (TBP). Transmission Electron Microscopy (TEM) measurements showed that the nature of the extractant influences the clouding behaviour of Triton X-114 and the formation of vesicles of different orientations. SANS studies suggested that majority of Triton X 114 participated in the cloud formation process. The viscosity measurements at different temperatures were used to calculate the activation energy for viscous flow.

There is a growing interest in the development of environmentally benign analytical techniques for the pre-concentration of toxic metal ions from different effluent streams. In this context, Cloud Point Extraction (CPE) has drawn significant attention of researchers and has low cost, minimizes the use of hazardous organic solvents, and offers very high preconcentration factors.[1] This extraction technique exploits the clouding phenomenon of surfactants which depends on the phase behavior of non-ionic and ionic surfactants in aqueous solutions, that exhibit phase separation after an increase in temperature or the addition of a salting-out agent.[2] The cloud point (CP) is referred to as the temperature beyond which aqueous solutions of surfactants (non-ionic and zwitter ionic) turn turbid and the solution separates into two phases, viz. (a) surfactant rich phase contained in a very small volume, and (b) the surfactant depleted phase having a concentration close to the critical micelle concentration (CMC) of the surfactant.[1(a)] The phase separation takes place as a result of attractive interaction between the micelles which increases further with surfactant concentration and consequently the cloud point temperatures are reduced. Non-ionic surfactant, Triton X-114 (1,1,3,3-tetramethylbutyl)phenyl-polyethylene glycol) has been extensively evaluated for CPE studies from different media.[1(a),(c)-(e)] The reported CMC value for Triton X-114 in aqueous medium is ~2×10^{-4} M.[3] The extraction of metal ions can take place either by direct interaction with the surfactant micelles or after complexation with a hydrophobic extractant. The development of CPE protocol requires the optimization of several experimental
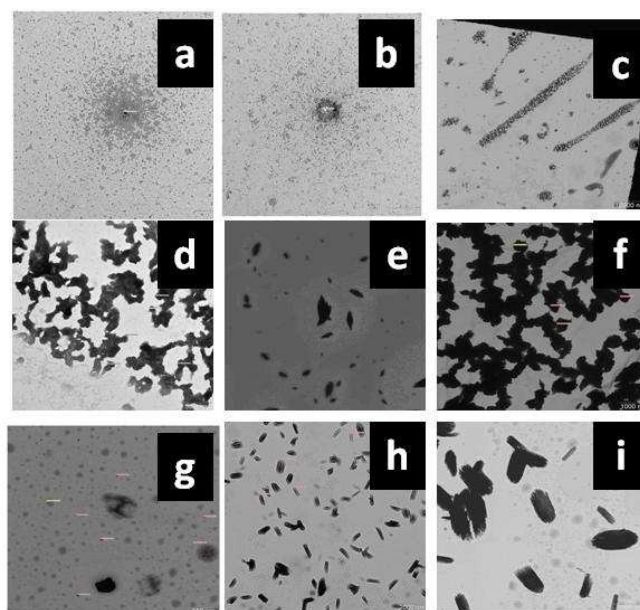
Fig. 1 TEM snapshots of different samples obtained at 25°C (a) 0.12 % (w/v) Triton X114 in 0.1 M Na-acetate; (b) 1.2 % (w/v) Triton X114 in 0.1 M Na-acetate; (c) 1×10^{-4} M HTTA (dissolved in methanol) + 0.12 % (w/v) Triton X114 in 0.1 M Na-acetate; (d) magnified version of (c); (e) 1×10^{-4} M DBM (dissolved in methanol) + 0.12 % (w/v) Triton X114 in 0.1 M Na-acetate; (f) magnified version of (f); (g) 1×10^{-4} M PMBP (dissolved in methanol) + 0.12 % (w/v) Triton X114 in 0.1 M Na-acetate; (h) 7.3×10^{-3} M TBP + 0.12 % (w/v) Triton X114 in 0.1 M Na-acetate; (i) magnified version of (h)

parameters, such as pH, concentrations of the chelating agent and surfactant, presence/absence of salts, temperature etc. There is, however, a need to understand the role of different physical parameters which are responsible for the clouding behavior of the surfactants. In addition, the nature and size of the aggregates may provide explanation for variation in the clouding behavior of a surfactant in the presence of complexing extractants. The size variation of different aggregates during the clouding process can be influenced by the surfactant concentration which was attributed to the changes in the solvent environment and the packing patterns of the surfactant molecules.[3] The nature of the aggregates formed due to the above mentioned factors is expected to have influence on the metal ion extraction by CPE.
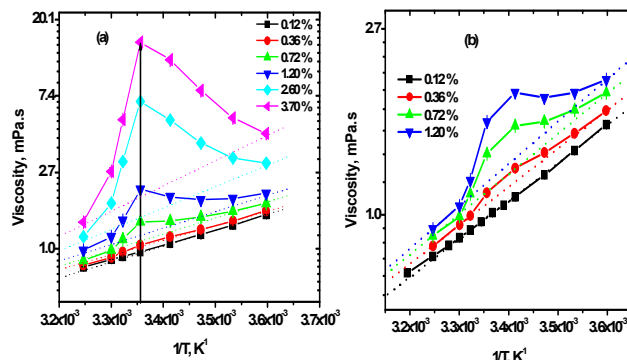
COMMUNICATION

Journal Name

This communication presents the Transmission Electron Microscopy (TEM) and Small Angle Neutron Scattering (SANS) measurements on aqueous solutions of Triton X-114 in the presence of different commonly used analytical extractants viz. dibenzoylmethane (DBM), thenoyltrifluoroacetone (HTTA) and 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP), and tributyl phosphate (TBP). The choice of these extractants was driven by their extensive use in the separation of actinide elements (like U, Pu) in the nuclear fuel cycle (TBP)[4] and in analytical separations (DBM, HTTA and PMBP). This communication reports the formation of nano-aggregate formation during the clouding process of Triton X-114 in the presence of organic extractants. TEM has been used to find out the exact orientation/shape of aggregates such as the micelles (smaller units) and vesicles (larger aggregates)[5] and to get morphological and topological information of nanomaterials.[5,6] This is particularly of interest to understand the clouding behavior of surfactants like Triton X-114 which finds extensive use in CPE of several valuables like inorganic nanoparticles (NPs) under varying experimental conditions.[7] TEM measurements on such systems have shown that the size of the aggregates depends on the experimental conditions. The viscosity data at different temperatures have been used to calculate the activation energy for viscous flow. The sample preparations for TEM, SANS and viscometric measurements were done following standard procedures (Supporting Information).[†]

Generally, an increase in the size of the aggregate was noticed from TEM snapshots when the solution approached the CP which may be due to the self assembly of small aggregates caused by the change in solvent environment leading to a size selective separation. A recent report shows that the presence of different additives nonionic surfactants in aqueous medium affects the self-assembly of the aggregates which can be due to the change in packing pattern of the surfactant in the aggregates.[8] Typically, two types of aggregates

Fig. 2 (a) Variation of viscosity with temperature for different concentrations (w/v) of Triton X 114 in distilled water (a) and in 0.1 M Na-acetate (b); Dotted lines: Theoretically expected Arrhenius type variation

amphiphilic surfactant revealed that nanoparticles aggregated into
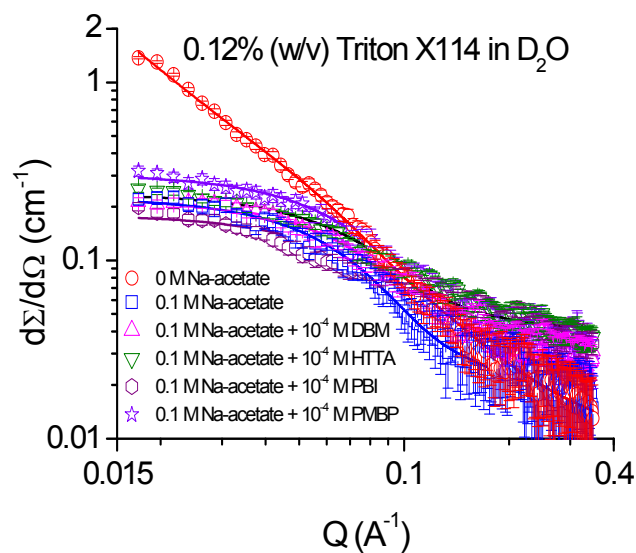
Fig. 3 Plots of SANS data (differential scattering cross section per unit volume versus scattering vector) for 0.12 % (w/v) Triton X114 solutions in D_2O in the absence and presence of salt and extractants at 25 °C. The lines shown are theoretical fits.

Table 1 Aggregate sizes and their shapes of different Triton X 114 samples observed in TEM snapshots in 0.1 M Na-acetate medium. Data obtained at 25°C.

Sample	Shape	Dimensions, nm
0.12 % Triton X114	Spherical	12(±1) (small units); 69(±5) (aggregates)
1.2 % Triton X114	Spherical	11(±1) (small units); 177(±10) (aggregates)
1×10^{-4} M HTTA + 0.12 % Triton X114	Spherical	106(±11) (small units); rod type aggregates (at low magnification)
1×10^{-4} M DBM + 0.12 % Triton X114	Needle	389(±80) (small units); No proper orientation
1×10^{-4} M PMBP + 0.12 % Triton X114	Spherical	28(±6) (small units); 148 and 355 (aggregates)
7.3×10^{-3} M TBP + 0.12 % Triton X114	Rod	1032(±222) (length, small units); staking of rods like bundles

were identified for Triton X-114 system as per their sizes as micelles and vesicles, respectively. The change in the clouding behaviour with temperature led to self assembly of the small size micelles resulting in the formation of large size vesicles. Similarly, TEM measurements on the thermo-responsive aggregation behavior and morphology of the nanoparticles formed after the dispersion of the

spherical particles with a size of more than 200 nm, which after fusion with each other yielded large size microparticles (~ 1000 nm).[9] TEM measurements on different samples also showed the presence of species of two types i.e. the micelles (smaller units) and vesicles (larger aggregates) (Figs. 1(a)-(i)). There were also nano tapes (Fig. 1(c) and needles (Figs. 1(e) and (h)) which could be considered directional self-assembly of the micelles. Similar transition of micelles to vesicles by self-assembly has been reported recently.[10]

The diameter/length of the smaller units for pure Triton X-114 was in the range 11(±1) nm while those of spherical aggregates sizes were 68.79 nm (0.12 % (w/v) Triton X-114) and 177 nm (1.2 % (w/v) Triton X-114). The presence of large size aggregates was noted in the presence of beta diketones (viz. 105(±11) nm (HTTA, spherical), 389(±80) nm (DBM, needle), 355(±20) (PMBP, spherical) (Table 1). Interestingly, significantly larger aggregates were formed in the presence of TBP (1032(±222) nm). The structural changes of the aggregates

and their mutual interactions are associated with the changes in solution viscosities. The viscosity values for dilute solutions, having minimum interactions between the aggregates, are sensitive to the shapes of particles. The transition from smaller to larger aggregates (micelles) shows a significant increase in the viscosity values. However, the analysis of solutions (surfactant + additives) having equal viscosity is difficult during transition from one shape to the other as they could have micelles which may differ in sizes.[11] The clouding phenomenon can be visualized as an assembly of nonionic micelles in a solution containing a minor proportion of an ionic surfactant (or additives). These micelles may include both charged and uncharged aggregates, with the former incorporating one or more ionic species. The size range of the particles in such a system is governed by their relative proportions of nonionic and ionic surfactant (or the additives, in the present case).[7(a)]

The measured viscosity data showed an increase with increased surfactant concentration at a specific temperature (Figs. 2(a)&(b)). This was attributed to the presence of more surfactant molecules for

Table 2 Viscosity and activation energy values for Triton X-114 solutions containing varying concentrations of extractants; [Triton X114]: 0.12 w/v%); 0.1 M Na-acetate

[Extractant], M	CP, K	η, mPa.s at CP	E (kJ·mol^{-1})
1×10^{-4} DBM	288	1.2603 ±(0.0004)	17.417±(0.011)
2×10^{-4} DBM	278	1.6448±(0.0008)	17.909±(0.036)
3×10^{-4} DBM	278	1.6732±(0.0015)	18.117±(0.006)
4×10^{-4} DBM	278	1.6682±(0.0013)	19.075±(0.021)
5×10^{-4} DBM	278	1.7084±(0.0020)	19.130±(0.029)
1×10^{-4} HTTA	296	1.0368 ±(0.0005)	16.784±(0.010)
2×10^{-4} HTTA	296	1.0533±(0.0005)	17.095±(0.025)
3×10^{-4} HTTA	296	1.0643±(0.0003)	17.312±(0.007)
4×10^{-4} HTTA	296	1.0625±(0.0005)	17.932±(0.015)
5×10^{-4} HTTA	296	1.0720±(0.0114)	18.063±(0.027)
1×10^{-4} PMBP	295	1.0671 ±(0.0040)	16.138±(0.026)
2×10^{-4} PMBP	296	1.0409±(0.0007)	16.253±(0.027)
3×10^{-4} PMBP	296	1.0529±(0.0013)	16.595±(0.016)
4×10^{-4} PMBP	296	1.0513±(0.0012)	16.855±(0.006)
5×10^{-4} PMBP	296	1.0607±(0.0114)	17.223±(0.010)
7.3×10^{-3} TBP	278	1.6631 ±(0.0006)	17.602±(0.007)
1.46×10^{-2} TBP	278	1.6344±(0.0012)	17.830±(0.023)
2.19×10^{-2} TBP	278	1.6099±(0.0015)	18.184±(0.040)
2.92×10^{-2} TBP	278	1.6544±(0.0010)	18.285±(0.024)
3.65×10^{-2} TBP	278	1.6621±(0.0006)	18.437±(0.024)

Note: CP stands for cloud point

the growth of the micelles. However, with an increase in the temperature of the solution, there was an increase in the viscosity and after reaching a maximum, a decrease was observed. The experimental viscosity data were fitted in the following Arrhenius type of exponential function to arrive at the activation energies (E) for viscous flow:[12]

$$\ln \eta = \ln A + E / RT \qquad (1)$$

where η is the dynamic viscosity (mPa·s), A, a system specific constant, E, the activation energy (kJ·mol^{-1}) for viscous flow, R, the gas constant (J·mol^{-1}·K^{-1}), and T, absolute temperature (K).

Generally, there was a decrease in the viscosity with increasing temperature without any significant variation in the cloud point after the addition of extractant in the Triton X-114 solutions. The data fitting in Arrhenius type of exponential function was possible only at lower Triton X-114 concentration (0.12% (w/v)) under all conditions and activation energies could be calculated (Figs. S1-S4, Supporting Information).[†] On the other hand, significant deviations were noted at higher Triton X-114 concentrations in the aqueous medium. This may be attributed to the formation of larger micelles due to clouding behavior of the surfactant molecules. However, the addition of increasing concentrations of the extractant solutions showed an increase in the E values suggesting that more energy was required for the viscous flow of the surfactant molecules during cloud formation (Table 2).

Interestingly, the viscosity measurements for increasing concentrations of Triton X-114 (0.12-3.7 % (w/v)) showed a deviation from Arrhenius type exponential behavior. Initially, there was a decrease in viscosity values with increasing temperature and reached a maximum at the cloud point (299.5±1.6 K) beyond which further decrease was noted. This behavior was attributed to the movement of water molecules which could be sufficient for dehydration of the surfactant at temperatures near the cloud point (Fig.2(a)).[12] It is also observed from Fig.2(b) that the presence of salt in the sample further suppressed the CP and viscosity. This facilitated the formation of larger aggregates and induced an increase in the viscosity. However, at higher temperature, the thermal motions probably overcome the molecular interactions leading to decrease in viscosity. The CMC for Triton X-114 was obtained from the surface tension mwasurements (Supporting Information) [†] and was found to be 1×10^{-5} M which was in close agreement with that reported in the literature.[3] Addition of TBP did not affect the CMC value significantly.

SAXS (small angle x-ray scattering) studies were carried out (Supporting Information)[†] but did not yield information about the exact size of the micelles or vesicles. On the other hand, the SANS (small angle neutron scattering) studies could give rough estimates about their sizes. SANS measurements were carried out in Heavy water (D$_2$O) medium to get an insight into the aggregation behavior of Triton X-114 under the conditions of present study. Generally, one measures the differential scattering cross section as a function of wave vector transfer (Q), which can be given by

$$\frac{d\Sigma}{d\Omega}(Q) = n(\rho_m - \rho_s)^2 V_m^{\,2}[\langle F^2(Q)\rangle + \langle F(Q)\rangle^2 \{S(Q) - I\}] + B \qquad (2)$$

where n denotes number density of the micelles, ρ_m and ρ_s are, respectively scattering length densities of micelles and solvent and V_m is the volume of the micelle. $F(Q)$ is single particle form factor and $S(Q)$ is interparticle structure factor. $S(Q) \sim 1$ for the dilute systems. B is a constant term due to incoherent background which is mainly from hydrogen in the sample. $F(Q)$ gives the shape and size of the scatterers and is calculated for the prolate ellipsoidal shape of the micelles. The analysis of the SANS data was done according to the procedure described elsewhere.[13] Fig.3 shows the differential scattering cross section per unit volume versus scattering vector in D$_2$O solutions of Triton X-114 at 25 °C. It is important to mention that all the samples had developed cloud at 25°C and therefore measurements were done on the bulk aqueous medium. The scattering data fitted well with the prolate ellipsoidal micelles. Table 3 shows the fitted parameters for these samples. It is evident that majority of Triton X-114 has participated in the cloud formation process. The presence of salt and other organic additives (extractants) facilitates the clouding process. These micelles show

marginal variations in their major and minor axes in the lean aqueous phases.

In conclusion, TEM technique has been used to obtain the structural informations about the aggregates formed during the clouding of aqueous solutions of Triton X-114. These studies suggest that that the nature of the extractants added affects the shape of the aggregates. There was a decrease in the viscosity with increasing temperature without any significant variation in

Table 3 Fitted Parameters of 0.12 % (w/v) Triton X114 solutions in D_2O at 25 °C

System	a, nm	b = c, nm	t, nm	V, %
D_2O (No salt)	4.54	1.0	1.2	5.1
0.1 M Na-acetate	3.73	1.0	1.2	1.5
0.1 M Na-acetate + 10^{-4} M DBM	3.45	1.0	1.2	1.5
0.1 M Na-acetate + 10^{-4} M HTTA	3.31	1.0	1.2	1.4
0.1 M Na-acetate + 10^{-4} M PBI	3.42	1.0	1.2	1.1
0.1 M Na-acetate + 10^{-4} M PMBP	3.55	1.0	1.2	1.8

Note: a = semi major axis, b = c = semi minor axis

the cloud point after the addition of extractant in the Triton X-114 solutions. The addition of increasing concentrations of the extractant solutions showed an increase in the activation energy (E) values for viscous flow of the surfactant molecules during cloud formation. There was a deviation from Arrhenius type exponential behavior at enhanced concentrations of Triton X-114 (0.12-3.7 % (w/v)). The viscosity values increased initially with increasing temperature and then reached a maximum at the CP (299.5±1.6 K) beyond which a decrease was noted. The movement of water molecules from the surfactant molecules may be responsible for the dehydration of the surfactant molecules at CP. This may allow the formation of larger aggregates and induce an increase in the viscosity. By contrast, the thermal motions at higher temperature may overcome the molecular interactions leading to decrease in viscosity. SANS studies showed negligible fraction of Triton X 114 left in the solution phase.

Acknowledgement

^{a} Radiochemistry Division, ^{b} Molecular Biology Division, ^{c}Solid State Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400085, INDIA.
* Author for correspondence. Fax: +91-22-25505151; Tel: +91-22-25594576; E-mail: mpatra@barc.gov.in.

† Electronic Supplementary Information (ESI) available: Experimental procedures, viscosity, surface tension and SAXS data, etc. See DOI: 10.1039/b000000x/

Notes and references

1. (a) P. Mukherjee, S.K. Padhan, S. Dash, S. Patel, B.K. Mishra, *Adv. Coll. Inter. Sci.*, 2011, **162**, 59-79; (b) J.G. Huddleston, H.D. Willauer, S.T. Griffin, R.D. Rogers, *Ind. Eng. Chem. Res.*, 1999, **38**, 2523-2539; (c) C. Larpent, S. Prévost, L. Berthon, T. Zemb, F. Testard, *New J. Chem.*, 2007, **31**, 1424-1428; (d) M. Ghaedi, A. Shokrollahi, K. Niknam, E. Niknam, A. Najibi, M. Soylak, *J. Hazard. Mat.*, 2009, **168**, 1022-1027; (e) E. Constantinou, I. Pashalidis, *J. Radioanal. Nucl. Chem.*, 2011, **287**, 261-265.
2. (a) H. Coulombeau, F. Testard, T. Zemb, C. Larpent, *Langmuir*, 2004, **20**, 4840-4850 ; (b) E. Lorin, R. Kjellander, J.C. Eriksson, *J. Chem. Soc. Faraday Trans.*, 1984, **80**, 2889-2910; (c) D.K. Rout, S. Chauhan, A. Agarwal, *Ind. Eng. Chem. Res.*, 2009, **48**, 8842-8847; (d) C. Labrecque, S. Potvin, L. Whitty-Léveillé, D. Larivière, *Talanta*, 2013, **107**, 284-291 ; (e) C. Labrecque, S. Potvin, L. Whitty-Léveillé, D. Larivière, *Anal. Chem.*, 2013, **85**, 10549-10555.
3. (a) D.E. Kile and C.T. Chiou, *Environ. Sci. Technol.* 1989, 23, 832-838; (b) D. Tragner and A. Csordas, *Biochem. J.* 1987, **244**, 605-609.
4. (a) A. Ramanujam, M.N. Nadkarni, V.V. Ramakrishna, S.K. Patil, *J. Radioanal. Chem.*, 1978, **42**, 349-357; (b) M. Shamsipur, A.R. Ghiasvand, Y. Yamini, *Anal. Chem.*, 1999, **71**, 4892-4895; (c) P.K. Mohapatra, P.B. Ruikar, V.K. Manchanda, *J. Radioanal. Nucl. Chem.*, 2006, **270**, 345-348; (d) V.K.Manchanda, P.K. Mohapatra, R. Veeraraghavan, *Anal. Chim. Acta,* 1996, **320**, 151-154; (e) Neelam Kumari, P.N. Pathak, P.K. Mohapatra, *Ind. Eng. Chem. Res.*, 2013, **52**, 15146-15153; (f) W.W. Schulz, L.L. Burger, J.D. Navratil, K.P. Bender, in *Science and Technology of Tributyl Phosphate,* volume 3, Applications of Tributyl Phosphate in Nuclear Fuel Processing. CRC Press, Inc., Boca Raton, Florida, 1990.
5. S.N. Kalmykov, M.N. Denecke, Actinide Nanoparticle Research. Springer- Verlag, Berlin Heidelberg, Chapter 1, pp.33, 2011.
6. J. Chao, J. Liu, S. Yu, Y. Feng, Z. Tan, R. Liu, Y. Yin, *Anal. Chem.*, 2011, **83**, 6875-6882.
7. (a) G. Hartmann, M. Schuster, *Anal. Chim. Acta*, 2013, **761**, 27-33; (b) M.F. Nazar, S.S. Shah, J. Eastoe, A.M. Khan, A. Shah, *J. Coll. Inter. Sci.*, 2011, **363**, 490-496.
8. (a) Hua-Neng Xu, Shu-Feng Ma, Wei Chen, *Soft Matter*, 2012, **8**, 3856-3863; (b) M.A. Silva, E. Weinzaepfel, H. Afifi, J. Eriksson, I. Grillo, M. Valero, C.A. Dreiss, *Langmuir*, 2013, **29**, 7697-7708.
9. C. Di, X. Jiang, R. Wang, J. Yin, *J. Mater. Chem.*, 2011, **21**, 4416-4423.
10. S. Mandal, J. Kuchlyan, S. Ghosh, C. Banerjee, N. Kundu, D. Banik, N. Sarkar, *J. Phys. Chem. B* 2014, 118, 5913−592
11. S. Kumar, V.K. Aswal, H.N. Singh, P.S. Goyal, Kabir-ud-Din, *Langmuir*, 1994, **10**, 4069-4072.
12. Hua-Neng Xu, Shu-Feng Ma, *J. Chem. Eng. Data.*, 2011, 56, 2677-2679.
13. (a) P.S. Goyal, V.K. Aswal, *Curr. Sci.* 2001, 80, 972-979. (b) J. Haldar, V.K. Aswal, P.S. Goyal, S.J. Bhattacharya, *J. Phys. Chem. B* 2001, 105, 12803–12808. (c) J. Dey, S. Kumar, A. Srivastava, G. Verma, P.A. Hassan, V.K. Aswal, J. Kohlbrecher, K. Ismail. *J. Colloid Interface Sci.* 2014, 414, 103-109.