Small angle neutron scattering from micellar solutions of triton X-100

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Abstract. Micellar solutions of non-ionic surfactant triton X-100 (8% by weight) show phase separation at cloud point $T_{cp} \sim 335$ K. This paper reports results of small angle neutron scattering (SANS) experiments from this solution as a function of temperature between 298 and 332 K. The range of wave-vector transfer Q, covered in these experiments is from 0·02 to 0·15 Å^{-1}. It is seen that as one approaches T_{cp}, the neutron scattering cross section diverges in the region of low Q ($< 0·06$ Å^{-1}) while it is independent of temperature in region of large $Q(> 0·06$ Å^{-1}). We believe that the divergence of scattering at low Q with an increase in temperature is because of changes in the structure factor $S(Q)$ of the solution. The measured distributions have been analyzed using four different models for inter-micellar potential. The models used to calculate the structure factor $S(Q)$ are (1) mean spherical approximation (MSA) with Yukawa tail for attractive potential, (2) MSA with an attractive square well potential, (3) random phase approximation (RPA) with an attractive square-well potential and (4) Sticky hard sphere model (attractive square-well potential with Percus-Yevick approximation). The strengths of the attractive potential required to fit the SANS data are $(-6·6$ to $-14·4)/kt$ for model (1), $(-6·6$ to $-15·0)/kt$ for model (2), $(-3·8$ to $-7·3)/k_B T$ for model (3) and $(-2$ to $-2·7)/kt$ for model (4). On the basis of reasonableness of the derived strength of the potential near the phase separation temperature and its relative temperature dependence, it is concluded that present data favour the Sticky hard sphere model.

Keywords. Neutron scattering; triton X-100; cloud point; nonionic surfactant.

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1. Introduction

Surfactant molecules dissolved in water remain as monomers up to a certain concentration, called critical micellar concentration (CMC), above which they aggregate to form micelles. Micelles are ionic or nonionic depending upon whether the surfactant molecule ionizes or not. Micellar solution of nonionic surfactant becomes cloudy on heating, at a well defined temperature, called cloud point (Shinoda *et al* 1963). The cloud point is a function of the surfactant concentration. Above the cloud point (T_{cp}) the solution separates into two phases, one rich and the other dilute, in micellar concentration. The coexistence curve shows a minimum consolute point at (C_c, T_c). The cloud point of nonionic systems has been investigated very well and it appears that the interactions between the micelles play a dominant role in deciding the cloud point (Corti and Degiorgio 1980; Nilsson and Lindman 1984; Nilsson *et al* 1985; Hayter and Zulauf 1982; Evans *et al* 1987; Reatto and Tau 1984).

The characteristics of the individual micelles like the aggregation number, charge, radius, shape etc., have been well investigated in the literature (Lindman and

Wennerstrom 1980). With the availability of small angle neutron scattering (SANS), a powerful technique has become available to investigate, not only the above mentioned parameters but also, the intermicellar interactions (Hayter 1985). The pioneering work by Hayter and Penfold (1981) and by Chen (1986) have laid the foundation for a quantitative analysis of important SANS data which are available on micellar solutions (Sheu *et al* 1987; Hayter and Penfold 1983).

Brown *et al* (1989) have investigated static and dynamic properties of triton X-100 in aqueous solutions. They have used pulsed field gradient (PFG) NMR, time resolved fluorescence quenching and static and quasi elastic light scattering (QELS) techniques. The temperature range spanned was from 283–315 K and concentration range was from 0·5 to 30 weight per cent. The main conclusion from their studies is that the radius of the micelles is 30 Å with the corresponding aggregation number of around 100.

To obtain the strength of inter-micellar interactions, especially near the cloud point, we have studied SANS from 8% (by weight) solution of triton X-100 (isooctylphenoxy polyethoxy ethanol) in D_2O, this concentration being close to the consolute point. The cloud point for this solution is ~ 335 K; SANS measurements have been made in the temperature range of 298 to 332 K.

We have analyzed the SANS data using four different models. All the models involve a hard core repulsion (within micellar diameter) and a short range attractive potential (outside micellar diameter). The first model (Hayter and Zulauf 1982) is the one used earlier in literature to analyze neutron scattering results (Zulauf and Rosenbusch 1983; Chen *et al* 1984). It uses Yukawa-type attractive potential. It tends to give rather large value ($> 10 k_B T$) of the intermicellar potential near T_c and this seems unreasonable. In view of this the following three models were tried. The Yukawa potential was changed to a square well and MSA was retained in model 2. In model 3, the square well was retained and RPA was used to calculate the structure factor $S(Q)$ (Sharma and Sharma 1977). In the last model a square well, as defined by Baxter, was used with Percus-Yevick approximation (Baxter 1968). By comparing the results of models 1 and 2 (using the same liquid state theory), we will be able to comment upon sensitivity of the SANS data on the detailed shape of potential. Also by comparing the results of the models 2, 3 and 4 (all of them use exactly identical potential namely square well) will enable us to comment upon the suitability of a liquid state theory for short-ranged potential.

2. Experimental

The surfactant triton X-100 (isooctylphenoxy polyethoxy ethanol) marketed by Rohm and Haas was used. Cloud point of 8% (by weight) solution was found to be 339 K in water (H_2O) and 335 K in heavy water (D_2O). SANS experiments were performed using triton X-100 in D_2O on the SANS spectrometer (Desa *et al* 1985) at Cirus reactor, Trombay. The incident neutron wave length was $\lambda = 5\cdot2$ Å and the scattering angle, 2θ, covered was in the range of 0·75 to 7·375° which correspond to wave vector transfer ($Q = \pi \sin\theta/\lambda$) range of 0·016 to 0·155 Å^{-1}. The gradient and stability of temperature along and across the sample were within 0·5 K. The experiment was performed at five temperatures, viz 298·4 K, 308·6 K, 317·6 K, 326·3 K and 332·3 K.
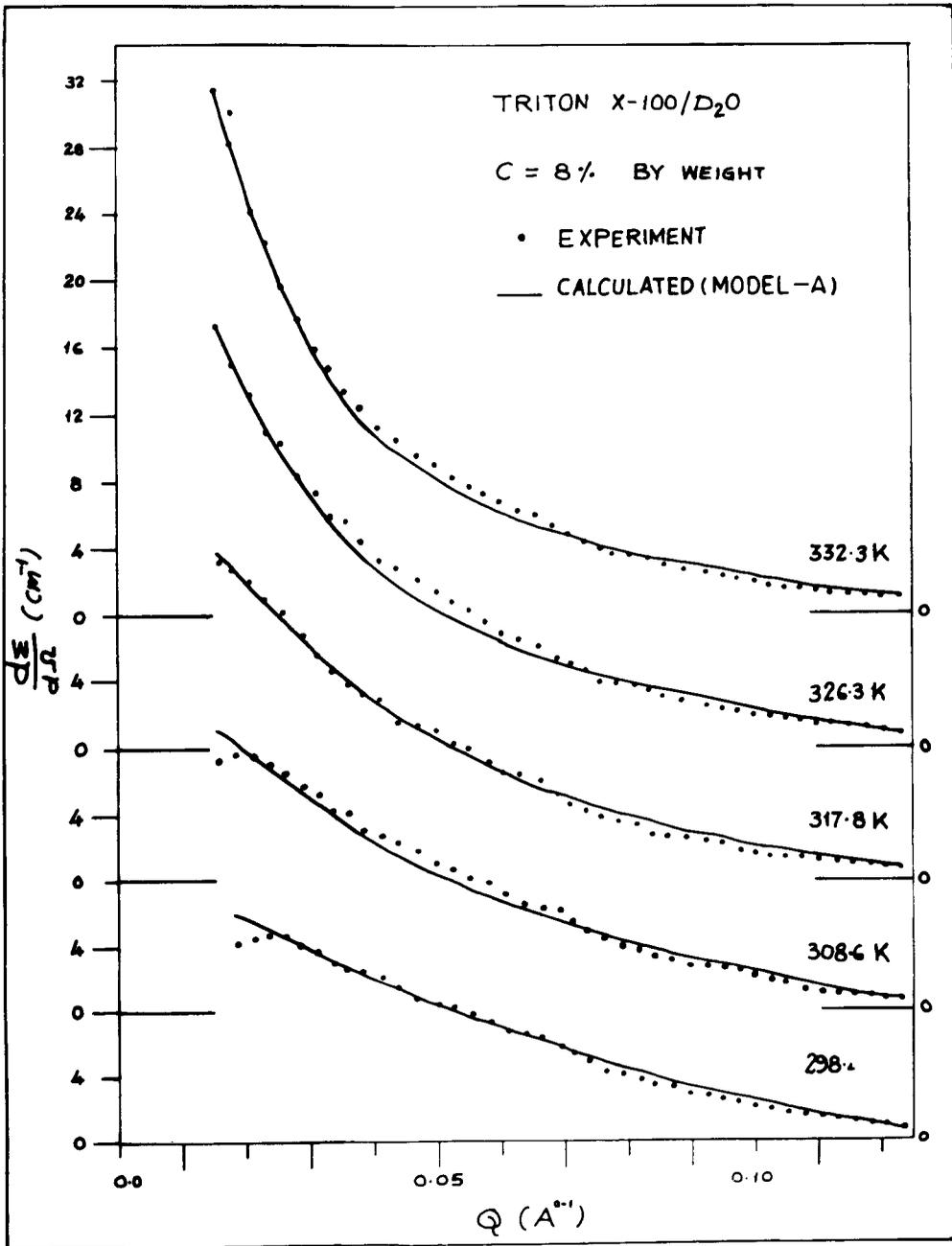
Figure 1. Comparison of experimental (dots) and theoretical (continuous curve) scattering cross sections. The calculated values are by using model 1 (Yukawa tail & MSA).

The corrected intensity was calculated using the formula

$$I(Q) = [I_{obs}(Q) - I_{bkg}(Q)]/T_s - [I_m(Q) - I_{bkg}(Q)]/T_m$$

where $I_{obs}(Q)$ is the measured intensity from sample, $I_{bkg}(Q)$ is the background contribution due to fast neutrons and is found by inserting cadmium in the neutron beam, $I_m(Q)$ is the intensity due to pure D_2O and cell, T_s is the transmission of the cell with the sample and T_m is that of cell with pure D_2O. The differential cross section, $d\Sigma/d\Omega$, for the samples was obtained by multiplying the corrected intensity by a constant, which is the calibration constant for the instrument. The measured scattering cross section, $d\Sigma/d\Omega$, at different temperatures is shown in figure 1. It can be seen that scattering cross section is diverging at small Q as the cloud point is approached.

3. Analysis of the data

The coherent scattering cross section from a micellar solution, in static approximation, is given by (Chen 1986)

$$d\Sigma/d\Omega = n \cdot N^2 [b_m - b_w]^2 \cdot P(Q) \cdot S(Q) \tag{1}$$

where n is the micellar number density, N is the aggregation number of a micelle, b_m is the scattering length of a triton X-100 molecule and b_w is the scattering length for an equivalent volume of D_2O. $P(Q)$ is the square of the form factor of the micelle and it depends on the shape of the micelle. $S(Q)$ is the structure factor representing the interference term arising from the interaction between the micelles.

We assume, following Hayter and Zulauf (1982) that triton X-100 micelles are spherical in the temperature range of the measurements. For spherical particles with radius R, $P(Q)$ is given by

$$P(Q) = 9 \cdot (\sin QR - QR \cdot \cos QR)^2/(QR)^6. \tag{2}$$

The structure factor $S(Q)$ depends on the model used for the inter-micellar potentials. Now we will describe the different models used to analyse the data.

Model 1   (Yukawa-type potential and MSA)
This was first used by Hayter and Zulauf (1982) to explain the SANS data on C_8E_5, another non-ionic micelle forming surfactant. They assume that micelles are hydrated. The effect of heating is to "melt" the hydration layer which is about 3 Å in thickness (consistent with hydrogen bond length). The inter-micellar potential is approximated as

$$U(r) = \infty \text{ for } r < \sigma$$

$$= U(T)\sigma \exp[-\chi(r - \sigma)]/r \text{ for } r > \sigma \tag{3}$$

where $\sigma(= 2R)$ is the diameter of the micelle, $U(T)$ is temperature dependent parameter which is a measure of the strength of the interaction and χ is the inverse screening length which is taken to be $0.33 \text{ Å}^{-1}(=$ reciprocal of the hydration layer thickness). The above form of the potential has been chosen because of the fact that the Ornstein-Zernicke (O–Z) equation has been solved analytically for this type of potential in the MSA and the structure factor $S(Q)$ is obtained in closed analytical

form (Hayter and Penfold 1981; Hansen and Hayter 1982). The two parameters required to fit the data are σ and $U(T)$. As remarked earlier this is the conventional way of analysing SANS data from non-ionic micellar solution.

Model 2   (Square well potential and MSA)

Since we are going to use an attractive square well potential in models 3 and 4 (because of the availability of analytical results), a comparison of the results based on MSA with that of the other models will be meaningful only if we use same functional form of the potential in all the models. Since no analytical solution exists for a square well fluid using MSA, one has to resort to solving O–Z equation, along with MSA closure, numerically. We have analysed our data using the above procedure also and refer to it as model 2.

The interaction potential in this model is given as

$$U(r) = \infty \text{ for } r < \sigma$$
$$= \varepsilon \text{ for } \sigma < r < \sigma + \Delta$$
$$= 0 \text{ for } r > \sigma + \Delta \tag{4}$$

where Δ is the range of the potential.

The structure factor $S(q)$ has to be computed numerically by solving O–Z equation

$$h(r) = c(r) + n \int h(r') c(r - r') \mathrm{d}r' \tag{5}$$

along with MSA closure $c(r) = -U(r)$ for $r > \sigma$ and the standard hard sphere condition $h(r) = -1$ for $r < \sigma$. To do this we have followed a method due to Stanislav *et al* (1985). This method consists of solving fourier transformed and discretized O–Z equation for $h(r)$ in the region $r > \sigma$ and for $c(r)$ in the region $r < \sigma$. The discretization is done such that for a given R_{max} the resolution in the fourier space (q-space) is given as $\Delta q = \pi / R_{max}$ (where R_{max} is the maximum r value for which O–Z equation has been solved). The value of R_{max} chosen should be much larger compared to the largest correlation length involved. For the kind of Δq step used in our experiment, we have to solve O–Z equation for $R_{max} = 20 \cdot 9\,\sigma$. Calculations have also been done with $R_{max} = 41 \cdot 8\,\sigma$ and no change was found in the value of potential depth. Also the grid size in the r-space is made successively smaller till the results are independent of grid size.

Model 3   (Square well potential and RPA)

In this the attractive potential is taken as square well potential which is treated as a perturbation to hard sphere potential and is given by (4). The expression for the structure factor was derived in the RPA by Sharma and Sharma (1977). The parameters required to fit the data are σ, ε the depth of the potential and Δ the width of the potential.

Model 4   (Sticky hard sphere model and PY approximation)

In this model also the potential is a square well and its form is taken as (Baxter 1968)

$$U(r) = \infty \text{ for } r < \sigma$$
$$= \log[12\tau\Delta/(\sigma + \Delta)](= \varepsilon) \text{ for } \sigma < r < \sigma + \Delta$$
$$= 0 \text{ for } r > \sigma + \Delta \tag{6}$$

where τ is a dimensionless measure of the temperature of the system. The O–Z equation was solved analytically in Percus–Yevick approximation for this type of potential (Baxter 1968) in the limit $\Delta \to 0$. This model, predicts an asymmetric liquid-gas type of phase transition with critical volume fraction of 0·12 and τ_c of 0·098. Though the potential function used in the above model appears at first sight to be complicated, it is nothing but a square well potential of depth ε, written in a particular fashion so that PY theory can be applied for the above potential. Though this model has been solved in the limit $\Delta \to 0$, we have shown the applicability of this model to cases where the range (Δ) is very small compared to the particle diameter σ (Srinivasa Rao *et al* 1991). In the case of non-ionic micelles as $\Delta/(\sigma + \Delta) < 0·06$, one can apply Baxter's analytical result for $S(Q)$ as such. Menon *et al* (1991) have demonstrated the applicability of this model to cloud point transition of nonionic surfactant solution C_8E_5. They also found that this model to be successful in accounting both light scattering as well as SANS data in addition to the experimentally observed phase diagram. The two parameters of the model are σ and τ. The value of Δ was taken to be 3 Å (consistent with the hydration layer thickness used in model 1) for calculating ε for given τ and σ. In short, model 1 uses Yukawa-type potential and is the most commonly used model in the literature. Models 2, 3 and 4 are based on square well potential but use MSA, RPA and PY approximation respectively for structure factor $S(Q)$.

In the following section we will discuss the results obtained by using the above four models.

4. Results and discussion

Figure 1 shows the results of the SANS experiments at five different temperatures together with the best fits obtained using model 1. The measured distributions (figure 1) show that $d\Sigma/d\Omega$ is independent of temperature at large $Q(> 0·06 \text{ Å}^{-1})$. However, in region of low $Q(< 0·06 \text{ Å}^{-1})$, it is seen that $d\Sigma/d\Omega$ increases as solution temperature approaches T_{cp}. At large Q, as $S(Q) \sim 1$, $d\Sigma/d\Omega$ is mainly decided by $P(Q)$. In principle, there are two possibilities which could give temperature independent $P(Q)$ at large Q. This can, for example, happen if individual micelles do not change their shape and size with temperature. It can also happen if the original spherical micelles join together to form cylindrical micelles such that while the lengths of the cylinders increase with temperature but their radius remain independent of temperature. For non-ionic micelles of C_8E_5, Zulauf and Rosenbusch (1983) have demonstrated, on the basis of neutron spin-echo experiments, that the former assumption is more reasonable. We accept this view, that is, we assume that micelles are spherical and that their diameter is independent of the temperature. The value of σ, the diameter of the micelle, obtained from present experiments is found to be 56 Å. We attribute the large increase in scattering cross section at low Q to structure factor $S(Q)$. The results of data analyses based on above mentioned four models are given below.

The micellar radius obtained from the fits (28 Å) is consistent with the dimension of triton X-100 molecule (10 Å for hydrophobic core + 17 Å for hydrophilic chains). Similar value was obtained by Brown *et al* (1989) from PFG NMR and light scattering studies. The aggregation number calculated from packing consideration comes to about 95 for the above radius. The $U(T)$ values obtained from the above fits are shown in table 1. The derived potential depth for model 2 is also tabulated in table 1.

Table 1. Comparison of the model parameters.

	Model 1 Y-MSA	Model 2 SW-MSA	Model 3 SW-RPA	Model 4 SW-PY	
$\sigma(\text{Å})$	56	56	57	55	
Temp.	$U(T)$	ε	ε	τ	$U(T)^*$
298·4	−6·56	−6·56	−3·80(−7·72)	0·216	−1·96
308·6	−8·38	−8·05	−4·92(−10·10)	0·164	−2·23
317·8	−9·94	−9·86	−5·62(−11·50)	0·140	−2·39
326·3	−12·28	−12·56	−6·60(−13·74)	0·116	−2·58
332·3	−14·36	−15·01	−7·30(−15·25)	0·104	−2·69

The strengths U and ε values are in units of $k_B T$.
The ε values in brackets correspond to $\Delta = 3\,\text{Å}$.
* Values calculated using eq. (6) with $\Delta = 3\,\text{Å}$.

From the depth of the potential derived using models 1 and 2, it is clear that the SANS data is not very sensitive to distinguish the detailed form of the potential. This is to be expected because the potentials used in models 1 and 2 are not much different in their characteristics such as range.

The model 3 has three parameters namely σ, Δ and ε. The best fits yielded $\sigma = 57\,\text{Å}$ and $\Delta = 5\cdot7\,\text{Å}$. The corresponding values of $\varepsilon/k_B T$ are given in table 1. Though the model 3 gives smaller value of potential depth, the value of the range obtained is very large and physically not acceptable (Israelachvili and Wennerstrom 1990). In view of this, we froze the range parameter in model 3 to be $3\,\text{Å}$ as was measured by Israelachvili and Wennerstrom (1990) and fitted the SANS distribution. The values of $U/k_B T$ obtained with the above range parameter are comparable to those of models 1 and 2, and are put in brackets in table 1.

The model 4 has two parameters, namely σ and τ. In this model σ was found to be $55\,\text{Å}$. The τ values are given in table 1. Though the sticky hard sphere model is strictly valid only in the limit $\Delta \rightarrow 0$, we justify its use in our case since the range of the potential is very small compared to diameter of the particle ($\Delta/\sigma \sim 0\cdot05$). The $U/k_B T$ values for this model calculated from eq. (5) using $\Delta = 3\,\text{Å}$ are also given in table 1. The fits obtained by the three models are of some quality and hence are not shown separately.

If we compare the four models, the size of the micelle is predicted to be the same by them but the values of the strength of the interaction are very different. The value of $U/k_B T$ for models 1 and 2 (~ 15) and model 3 (~ 7) are too large to be acceptable. Usually one would expect $U/k_B T \sim 1$ at the cloud point. Thus we find that out of the three models under discussion only model 4 gives $U/k_B T \sim 1$ and it is the least sensitive to temperature as compared to that for the other models.

The reasons for the success of the Sticky hard sphere model in explaining the SANS data over the other three models is believed to be due to the approximation involved in obtaining $S(Q)$ from a given potential. Model 1 uses MSA. Tau and Reatto (1986) have also argued that MSA is not suitable for short-range attractive potentials. Recently Regnaut and Ravey (1989) have examined the use of Percus–Yevick approximation with the short range square well (SW) potential using Baxter's results. Their conclusion, based on comparison with Monte-Carlo data, is that PY approximation is more justified that RPA. But their analysis is based on the approximation

of equating the second virial co-efficient of the square-well and Baxter potential. But our procedure of using Baxter results for short range square-well potential is different and we match all the virial co-efficients (Srinivasa Rao *et al* 1991). The RPA and MSA have the same defect in the sense that both require deep potential well for phase transition to occur. Sticky hard sphere model which is based on PY approximation appears to be better in estimating the depth of the potential. It is also known that MSA is inadequate in explaining the light scattering data (Hayter and Zulauf 1982) in that the position of $S(O)$ shifts to higher volume fraction with temperature. This discrepancy is removed in Baxter model (Menon *et al* 1991) as well as in square well-PY treatment (Regnaut and Ravey 1989). Considering the strength of the potential derived from SANS data and the ability to predict light scattering data (Menon *et al* 1991), Sticky hard sphere model with PY approximation comes out to be the best of the four models considered.

5. Summary

SANS experiment has been carried on non-ionic micellar solution of triton X-100 close to critical concentration as function of temperature. The SANS data have been used to obtain the dimension of the micelle as well as depth of the interaction potential. Three different liquid state theoretical models are used to extract information about the strength of the interaction between the non-ionic micelles of triton X-100. While the size of the micelle is found to be same by all the models, the strength of the attractive interaction is found to vary significantly from one model to another. Comparison between models 1 and 2 shows that for different potential shapes having same range and with the same liquid state theory namely MSA, SANS data analyses gives same well depth. SANS data are not very sensitive to the detailed shape of the potential. Comparison between the models 2, 3 and 4 which all use square-well potential but different schemes for calculating the structure factor $S(Q)$ show that PY approximation gives the most reasonable value of well depth ($U \sim k_B T$). This is also weakly dependent on temperature. Other schemes give strong temperature dependence.

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