Journal of Applied Sciences

ISSN 1812-5654

Journal of Applied Sciences 9 (12): 2301-2306, 2009
ISSN 1812-5654

Effect of Organic Additives on the Cloud Point of Triton X-100 Micelles

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Abstract: The mechanism of clouding of nonionic surfactant and the effect of additives on the cloud point has been investigated. The cloud point temperature of Triton X-100 solutions in the concentration range 1-10% and the cloud point behavior of 4 and 10% Triton X-100 solutions in the presence of some aliphatic alcohols and alkanes of different concentrations have been studied. A sharp rise in cloud point of aqueous solutions of Triton X-100 occurs with increasing surfactant concentration beyond 4%. A small but significant decrease in cloud point is observed upon the addition of hexane, heptane, octane and decane to 4 and 10% Triton X-100 solutions. The alkanes of higher chain length are more effective in depressing the cloud point and the extent of depression follows the order: decane>octane>heptane>hexane. Lower alcohols enhance the cloud point while the higher alcohols including butoxyethanol depress the cloud point. The depression of cloud point of Triton X-100 solutions containing same amount of alcohols follows the order: decanol>octanol>heptanol>hexanol>butanol.

Key words: Nonionic surfactant, cloud point, turbidity, solubilization and dehydration

INTRODUCTION

The nonionic surfactant, p-tert-alkylphenoxy poly (oxyethylene) ether (Triton X-100, abbreviated as TX-100), widely used in many biological, pharmaceutical and industrial systems are rapidly increasing mainly due to their wide range of physicochemical properties. The solubilization of water insoluble drugs in nonionic surfactant systems is used in drug formulation because of little or no physiological side effects by the surfactant material. Nonionic surfactant exhibit clouding behavior when their aqueous solutions are heated to a certain temperature known as Cloud Point (CP), which is characteristic of the molecular architecture of the surfactant (Schott, 2001; Iwanaga and Kunieda, 2000; Inoue *et al*., 2003). The cloud point is an important property of nonionic surfactants; below this temperature a single phase of molecular or micellar solution exists, above it the surfactant loses sufficient water solubility and a cloudy dispersion appears (Myers, 2005). This phase separation occurs within a narrow temperature range. This phenomenon is attributed to sudden dehydration of the polyoxyethylene chain at the cloud point temperature. This dehydration has been suggested to be induced by the conformational change of the POE chain associated with temperature rise (Hey *et al*., 1995; Tasaki, 1996). It is believed that the micellar weight of a nonionic surfactant increases when the temperature (Winson, 1968) of the solution approaches cloud point. It seems, therefore that the micelles becomes much larger with a rise in temperature and finally separates from water phase. In other words, the clouding phenomenon and the succeeding phase separation occur as the result of the formation of giant aggregates. The phase separation is reversible and on cooling the mixture to a temperature below the cloud point, the two phases merge to form once again a clear solution. The separation is believed to be due to the sharp increase in the aggregation number of the micelles and the decrease in the intermicellar repulsions (Staples and Tiddy, 1978) resulting from the decreased hydration of the oxyethylene hydrophilic group with increase in temperature.

The clouding behavior of nonionic surfactant is strongly affected by the presence of various additives (Qian *et al*., 2005) in the solution either by changing the structural properties of the micelle by solubilization in the micellar aggregates or by dissolving in water phase and thus changing the environment of the micelle (Schott, 1995; Sadaghiania and Khan, 1991). The appearance of turbidity in the aqueous solution and its separation into two phases introduce certain disadvantages in its utilization and has resulted investigation to determine the effect of solubilizates on the temperature where clouding appears. The effect of additive on the cloud point of nonionic surfactant is, therefore, of fundamental importance to have an

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understanding on the nature of cloud point of nonionic surfactants and the effect of additives. The practical importance of the cloud point lies in the fact that suspensions (Schott and Royce, 1986), emulsions (Schott and Royce, 1983) and ointments and foams (Schott, 1988) stabilized with nonionic surfactants become unstable when heated in the vicinity of the cloud point, e.g., during manufacturing, steam sterilization, or some end uses. On the other hand, the rate of solubilization by nonionic surfactant solutions increases near their cloud point.

In the present study we have investigated the effect of some selected alkanes and alcohols of different chain length on the cloud point of Triton X-100 in order to understand the nature of cloud pint of Triton X-100 and the effect of those additives on the cloud point. All the results have been interpreted in terms of the hydration effects of the micelles, location of the solubilizates in the micellar aggregates, possible changes in the size and shape of the micelles and the interactions between the solubilizate and surfactant species within the micellar aggregates.

MATERIALS AND METHODS

Triton X-100 was obtained from Aldrich Chemical Co., England. Its purity was 98% and used without additional purification. The additives hexane, heptane and octane were obtained from Merck-Schuchardt (Germany). Decane was obtained from Gillingham Dorset-England. Their purity was >99%. Methanol ethanol, propanal-1, hexanol used in this work were obtained from Merck (Germany). Butanol and 2-Butoxyethanol (BE) were obtained from Aldrich Chemical Co. Heptanol, octanol and decanol were obtained from Merck-Schuchardt. Their purity was >99%. They were of reagent grade and used without further treatment. Water used in this experiment was double distilled. Solutions of TX-100 of different concentrations were prepared in weight percentage and used as mixed solvent in cloud point determination in the presence of alkanes and alcohols.

Solubilizates in mixed solvent was stirred for at least 1 h to ensure the equilibrium conditions are established. Cloud point temperatures of surfactant solutions were determined by visual observation of the abrupt change in the appearance of the surfactant solutions, which occurs during the heating of the sample solutions. Solutions were filled in thin test tubes and gradually heated in a temperature-controlled water bath with internal circulation and digital temperature display. The sample was heated at the rate of about 0.2°C min^{-1} after the temperature reached a few degrees below the preestimated cloud point temperature. After the temperature exceeds the cloud point, the sample was cooled below the cloud point temperature and then it was heated again to check the reproducibility of the measurements. This procedure was repeated at least three times and the cloud point temperatures were determined with a reproducibility of ±0.2°C.

RESULTS AND DISCUSSION

Cloud point of triton X-100-water system: This study report an investigstion on the effect of organic additives on the cloud point of Triton X-100. The cloud point of nonionic surfactant is a useful property among others because of its application as emulsifier, as detergents and in pharmaceutical formulations. For such reason the solution behavior of nonionic surfactant has been the subject of many studies (Chu, 1995; Alexandridis and Hatton, 1995; Da Silva *et al*., 1998). The concentration dependence of cloud point of TX-100 solutions in the concentration range 1-10% have been measured. The estimated cloud point of TX-100 solutions over this concentrations range is reported in Table 1. Figure 1 shows the variation of cloud point of TX-100 as a function of its concentration. It is observed that the cloud point remains constant up to 4% solution and then

Table 1: Cloud point of aqueous micelle solutions of Triton X-100 of different concentrations

TX- 100 conc. (wt. %)	Cloud point (0°C)
1	63.7
2	63.7
3	63.7
4	64.0
5	64.5
6	65.2
7	66.0
8	66.7
10	68.0

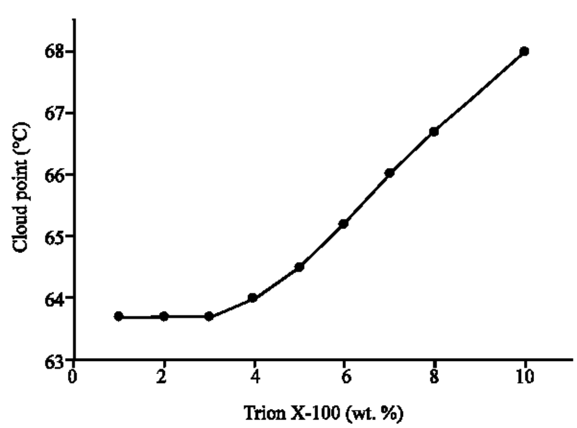

Fig. 1: Cloud point of aqueous solutions of Triton X-100 as a function of its concentration

Table 2: Cloud point of 4 and 10% Triton X-100 solution in the presence of hexane, heptane, octane and decane

Conc. of alkanes (mol kg^{-1})×10^2	Cloud point (0°C) Hexane	Heptane	Octane	Decane
4% Triton X-100 solution				
0.00	64.0	64.0	64.0	64.0
1.00	64.0	63.7	63.6	63.3
1.50	63.8	63.6	63.3	62.7
2.00	63.8	63.5	62.7	61.8
2.50	63.6	63.2	61.8	
3.00	63.2	62.5	60.7	
3.50	62.5	62.0		
4.00	61.5	60.8		
5.00	60.3	59.3		
10% Triton X-100 solution				
0.00	68.0	68.0	68.0	68.0
1.00	67.8	67.6	67.4	66.8
1.50	67.8	67.5	67.0	65.9
2.00	67.4	66.8	66.8	64.8
3.00	66.8	66.5	65.8	
3.50	66.4	65.8	65.2	
4.00	66.0	65.5	64.8	
5.00	65.0	64.5	63.5	

increases with increasing surfactant concentration. A sharp increase in its value is observed upon increasing the surfactant concentration beyond 4%. The clouding of each solution of TX-100 in water is likely to be due to a large increase in the aggregation number of the TX-100 micelles and a decrease in intermicellar repulsions, resulting from decreased dehydration of the oxyethylene oxygens in the polyoxyethylene hydrophilic group with increase of temperature. The increase in aggregation number and the intermicellar interaction produce large micellar aggregates at that temperature in the solution, which becomes visibly turbid and the two liquid phases separates out. The constancy of cloud point of TX-100 solution up to 4% followed by a sharp increase in it indicates that TX-100 micelles, with nearly same aggregation number, maintains its spherical structure up to 4% with definite amount water molecules bound to them. Upon increasing the concentration of TX-100 solution to 5% and above the spherical micelle grow in size and a shape transition (Mandal *et al*., 1980) occurs from sphere to disk-like. This shape transition will increase the surface area of the micelle resulting an increased hydration thereby increasing the cloud point of solution.

Cloud point of Triton X-100-water-alkane systems: The cloud point of 4 and 10% TX-100 solutions containing various amounts of hexane, heptane, octane and decane are shown in Table 2. Figure 2 and 3 show the variation of cloud point of 4 and 10% TX-100 solutions as a function of hexane, heptane, octane and decane concentration. The results of our studies show that the addition of alkanes to surfactant solution (4 and 10%) lowers the cloud point of

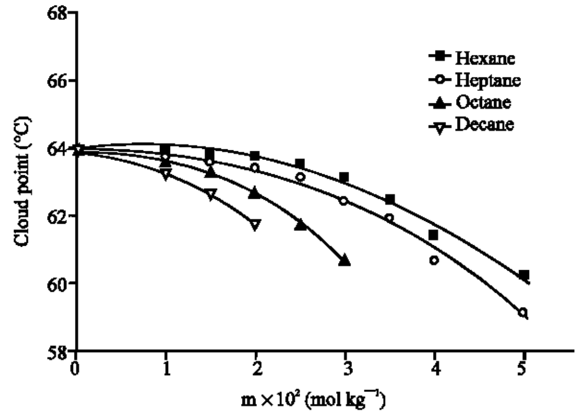

Fig. 2: Cloud point of 4% Triton X-100 solution in the presence of n-alkanes of different concentrations

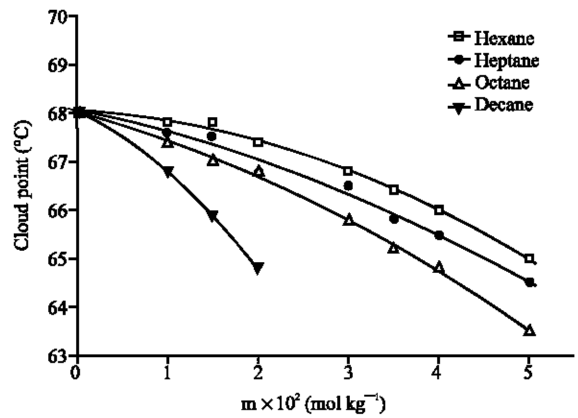

Fig. 3: Cloud point of 10% Triton X-100 solution in the presence of n-alkanes of different concentrations

TX-100 solutions and the alkanes of higher chain length are more effective in depressing the cloud point of TX-100 solution. The extent of decrease follows the order: decane >octane> heptane> hexane. The cloud point of aqueous TX-100 solution is not expected to change significantly if the additive molecules do not create a considerable change in the properties of micelle either by micellar growth or by changing the hydration of TX-100 micelle. This suggests that, the nonpolar alkanes, which generally occupy the hydrocarbon part of the micelle, are comfortably solubilized in the inner core of the micelle between the ends of the hydrophilic polyoxyethylene group of this surfactant molecule. It is expected that, this solubilization occur without any significant change in the properties of micelles and the extent of hydration of micelle as well as the intermicellar interaction. It is, however, likely that the dielectric constant of the micellar solution decreases upon the solubilization of alkanes in the micellar aggregates thereby decreasing the solubility of surfactant in solution.

A proton NMR study (Podo *et al*., 1973) of some nonionic polyoxyethylene compounds suggest that the alkyl portion of the chain are not in contact with water but that the polyoxyethylene groups, which constitute the outer part of micelle interior are highly hydrated. Accordingly, a significant decrease in the cloud point of TX-100 at relatively higher concentration of alkanes can be attributed to the solubilization of a fair portion of alkanes in the outer portion of the micelle interior close to the inner part of polyoxyethylene chain. This reduces the EO-water interactions thereby decreasing the cloud point. It appears that, the higher alkanes are more effective in depressing the cloud point of TX-100. This is not unexpected, because the long chain alkanes are likely to be more, in contact with the polyoxyethylene chains of the micelles.

Cloud point of Triton X-100-water-alcohol systems: The results show that lower alcohols methanol, ethanol, propanol, enhance the cloud point while the higher alcohols hexanol, heptanol, octanol, decanol including butanol and butoxyethanol depress the cloud point of TX-100 solutions remarkably (Table 3). It appears that the cloud point of TX 100 increases with increasing amount of methanol, ethanol, propanol added to the system while the presence of butanol and butoxyethanol lowers the cloud point and the lowering depends on the amount of the alcohols present. It appears that the increase in cloud point of both 4 and 10% TX-100 solution containing same amount of propanol, ethanol and methanol follows the order: propanol>ethanol>methanol. In the case of butanol and butoxyethanol cloud point becomes lower than the values obtained for methanol, ethanol, propanol and decreases upon increasing their concentrations (Fig. 4, 5).

It appears that the depression of cloud point of both 4% and 10% of TX-100 solutions containing same amount of each alcohol follows the order: decanol>octanol> heptanol>hexanol (Fig. 6, 7). This depression of cloud point indicates that the solubilization of long chain alcohols occur by a large decrease in hydration of TX-100 micelles. This suggests that, these alcohols are preferentially solubilized by adsorption at micelle-water interfacial region with hydrocarbon part in the outer shell of hydrated polyoxyethylene chain. The solubilization of these alcohols close to the surface in the palisade layer of the micelle decrease the hydration of TX-100 micelle and increase the micelle-micelle interaction resulting a decrease in cloud point. It probably decreases the dielectric constant at the micellar surface due to

Table 3: Cloud point of 4 and 10% Triton X-100 solution in the presence of methanol, ethanol, propanol, butanol, butoxyethanol (BE), hexanol, heptanol, octanol and decanol.

Conc. of alcohols (mol kg^{-1})	Cloud point (0°C) Methanol	Ethanol	Propanol	Butanol	BE
4% Triton X-100 solution					
0	64.0	64.0	64.0	64.0	64.0
0.05	64.5	65.0	65.5	63.8	65.5
0.10	65.0	65.5	66.5	62.8	65.0
0.25	66.2	66.8	68.5	61.0	64.5
0.35	66.5	68.0	69.5	59.0	64.0
0.50	67.5	68.8	71.0	55.2	62.5

Conc. of alcohols (mol kg^{-1})×10^2	Cloud point (0°C) Hexanol	Heptanol	Octanol	Decanol
1.00	59.5	53.2	48.5	46.8
1.25	58.2	51.5	45.5	42.5
1.50	57.8	50.0	41.8	39.0
1.75	55.8	47.5	39.0	36.0
2.00	55.5	46.0	36.5	32.8
2.50	55.2	43.5		
3.00	53.8	40.5		

Conc. of alcohols (mol kg^{-1})	Cloud point (0°C) Methanol	Ethanol	Propanol	Butanol	BE
10% Triton X-100 solution					
0	68.0	68.0	68.0	68.0	68.0
0.05	68.1	68.3	68.5	67.7	69.0
0.10	68.3	68.8	69.0	66.8	68.8
0.25	68.5	69.5	70.0	65.5	68.5
0.35	68.9	70.0	71.0	63.8	68.0
0.50	71.0	72.2	72.5	60.5	67.0

Conc. of alcohols (mol kg^{-1})×10^2	Cloud point (0°C) Hexanol	Heptanol	Octanol	Decanol
1.00	63.5	62.0	58.5	56.5
1.50	60.8	58.8	55.0	52.6
2.00	59.3	57.2	51.8	49.5
2.50	57.7	54.8	48.0	46.2
3.00	55.8	53.7	46.2	44.2
3.50	55.2	52.5	45.0	43.0
4.00	54.5	51.7	44.0	42.0
5.00	63.6	50.0	42.8	40.5

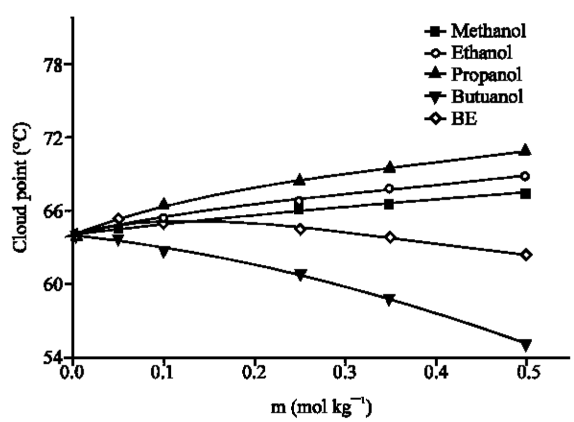

Fig. 4: Cloud point of 4% Triton X-100 solution in the presence of methanol, ethanol, propanol, butanol and butoxyethanol (BE) of different concentrations

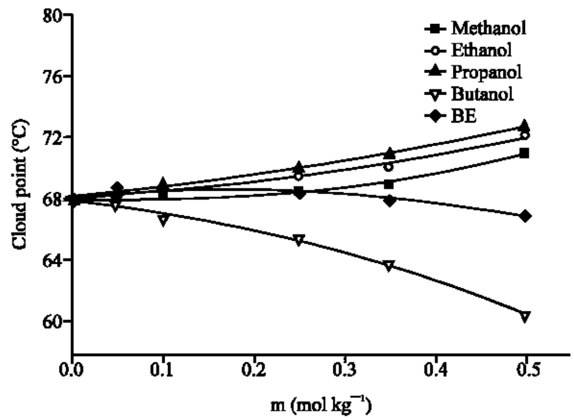

Fig. 5: Cloud point of 10% Triton X-100 solution in the presence of methanol, ethanol, propanol, butanol and butoxyethanol (BE) of different concentrations

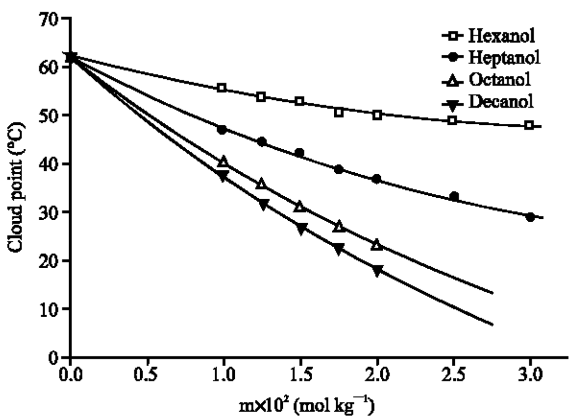

Fig. 6: Cloud point of 4% Triton X-100 solution in the presence of hexanol, heptanol, octanol and decanol of different concentrations

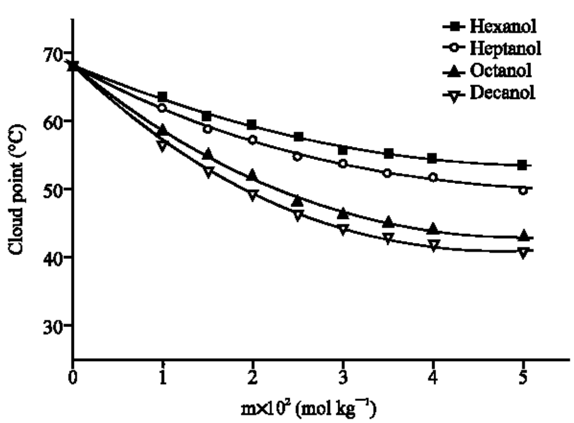

Fig. 7: Cloud point of 10% Triton X-100 solution in the presence of hexanol, heptanol, octanol and decanol of different concentrations

replacement of water molecules in the surface region by alcohols molecules resulting a decrease in the solubility of the micellar aggregates in the solution which decreases the cloud point. It appears that, the decrease in cloud point becomes more pronounced with increasing alcohol content. As well, alcohols of longer chain length are more capable of lowering the cloud point of the TX-100 solution containing the same amount of solubilizate. It indicates that, the depth of penetration of alcohols into the micelle depends on the chain length of alcohols. Alcohols molecules with longer hydrophobic chain penetrate more deep into the palisade layer of micelle weakening the many more EO-water interactions. This results an additional dehydration, which favors the micellar growth thereby showing more decrease in cloud point.

CONCLUSION

In conclusion, we find that cloud point of aqueous solutions of TX-100 sharply increases with increase of surfactant concentration beyond 4%. The clouding of Triton X-100 in water is likely to be due to an increase in aggregation number of Triton X-100 micelle and a decrease in intermicellar repulsions resulting from the decreased dehydration of polyoxyethylene group with increase of temperature. The addition of hexane, heptane, octane and decane to 4 and 10% surfactant solutions results a small but significant decrease in cloud point of the TX-100 solutions. The alkanes of higher chain length are more effective in lowering the cloud point and the extent of depression follows the order: decane>octane>heptane>hexane. The presences of lower alcohols enhance the cloud point while the higher alcohols depress the cloud point of TX-100 solutions remarkably. The magnitude of lowering of cloud point of TX-100 depends largely on the amount and the chain length of alcohol. The depression of cloud point of Triton X-100 solutions with same amount of alcohols follows the order: decanol>octanol>heptanol>hexanol> butanol. It is generally expected that alkanes is solubilized in the inner part of the micelle while the alcohols are solubilized on the micellar surface. The alcohol of higher chain lengths are likely to be solubilized close to the micellar surface with its hydrocarbon part embedded in the inner part of the micelle. It probably decreases the dielectric constant at the micellar interface resulting a decrease in the solubility of the surfactant monomers in solution which reduces the cloud point.

ACKNOWLEDGMENT

The authors are grateful to University Grand Commission (UGC) of Bangladesh for providing financial assistance for this study.

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