



Studies of Optimal Salinity of Nonionic Microemulsions

ANIL KUMAR

Post-Graduate Centre of Chemistry, College of Commerce, Patna-800 020, India

*Corresponding author: E-mail: anilcoc2005@yahoo.co.in; anilkc@hotmail.com

(Received: 20 October 2010;

Accepted: 15 June 2011)

AJC-10049

The optimal salinity of non-ionic microemulsions containing Triton X-100+ 1-hexanol (1:5 molar ratios)/dodecane/water was studied in presence of different types of electrolytes at various temperatures. The volume measurement with increasing salinity reveals three types of Winsor formation (Winsor I, II and III). The optimal salinity determined by plotting solubilization parameters of oil, V_o/V_m and that of water, V_w/V_m against electrolyte concentration decreases with increase in temperature in presence of strong electrolyte. However, it does not change much with increase in temperature in presence of weak electrolyte. At constant temperature optimal salinity was found higher in presence of weak electrolyte as compared to strong electrolyte.

Key Words: Surfactant, Co-surfactant, Microemulsion, Optimum salinity, Interfacial tension, Triton X-100, 1-Hexanol.

INTRODUCTION

Microemulsions are optically transparent, thermodynamically stable, nano-structured mixture of oil and water stabilized by surfactant, either ionic or nonionic¹⁻³. They are classified as w/o, o/w and bicontinuous microemulsion. They have attracted great interest³⁻⁵ because of their unique physicochemical characteristics such as large solubilization capacity, ultra low interfacial tension, a very large interfacial region and because of their potential industrial applications such as enhanced oil recovery, biotechnology, nanotechnology, cosmetics, agriculture, beverages and chemical reaction⁶⁻¹⁷.

The phase behaviour and structural organization of microemulsion are highly dependent on the elastic properties of surfactant monolayer, along with different field variables such as temperature, pressure, ionic strength of water, nature of oil and co-surfactant¹⁻⁴. For a given surfactant, a change in the natural curvature from curve water (positive) to towards oil (negative) or *vice-versa* can be achieved by changing one or more field variables. The most pronounced effect is temperature for nonionic surfactant and salts for ionic surfactant¹⁸. In microemulsion systems, increasing salinity usually induces a variety of phase changes and various different forms, *i.e.*, Winsor I, II and III are possible as function of salt concentration¹⁹. These types of transitions are possible by increase of temperature involving nonionic surfactants²⁰. It has been observed that the three-phase microemulsion formation (Winsor III) is always accompanied by ultra low interfacial tension (*ca.* 10^{-3} mN/m) between microemulsion layer and oil

and/or water layer²⁰. This ultra low interfacial tension is the promising factor for the employment of these formulations in the oil recovery processes⁷. At the optimal salinity, interfacial tension (IFT, γ o/m) between oil (o) and microemulsion (m) becomes equal to that of interfacial tension (IFT, γ w/m) between water (w) and microemulsion (m). Several studies involving the optimal salinity and various factors influencing optimal salinity such as nature of oil, nature of co-surfactant *etc.*, have been reported in the literature^{21,22}. In this paper, the optimal salinity (OS) of nonionic microemulsions comprising a well known surfactant, Triton X-100 plus co-surfactant (1-hexanol)/dodecane/water in presence of different electrolytes at various temperatures are reported.

EXPERIMENTAL

The nonionic surfactant, Triton X-100 (poly-oxyethylene tetramethyl butyl phenyl ether, molecular weight *ca.* 624) was obtained from SRL, India. Anhydrous dodecane and 1-hexanol were procured from Merck Schuchardt, Germany. Sodium chloride (AR) was purchased from SD Fine Chemical Ltd., India. Oxalic acid (AR) was purchased from Speckpure, India. Double distilled water was used for all sample preparation.

Salinity studies: An equal volume of oil and water (10 mL each) and 5 g of surfactant plus co-surfactant (1:5 molar ratios) was taken in a flat-bottle graduated tube and kept at desired temperature. Solid sodium chloride was added in installment of 10 mg at a time and the volume of the different phases *i.e.*, water, oil and microemulsions were measured from the calibration of the graduated test-tube. The ratio of volume

of water (V_w) to the volume of microemulsion (V_m) and the ratio of volume of oil (V_o) to the volume of microemulsion (V_m) were calculated and plotted together against the molar concentration of electrolytes. The intersection point of V_w/V_m and V_o/V_m denotes the optimal salinity of the microemulsion at constant temperature.

RESULTS AND DISCUSSION

Fig. 1 shows the plot of optimal salinity for the pseudo-ternary system, Triton X-100 + 1-hexanol (1:5 molar ratio)/dodecane/water at various temperatures. In Fig. 1, the solubilization parameter of oil, V_o/V_m and that of water, V_w/V_m have been plotted together against NaCl concentration. The concentration at which these two curves intersect is termed as optimal salinity (OS). During the course of investigation, it was observed that the ternary system was biphasic in absence of electrolyte at 25 °C in which water continuous microemulsion equilibrates with excess oil phase. With addition of electrolyte, biphasic system changes into three-phase system in which middle phase microemulsion equilibrates with excess oil and aqueous phase. It is very interesting to note that with progressive addition of electrolyte, the volume of excess water increases and that of oil decreases. As a result solubilization parameters of water, V_w/V_m increases and that of oil, V_o/V_m decreases at constant temperature. This is probably due to the fact that Triton X-100 is hydrophilic in nature at low temperature in absence of electrolyte²³. With the addition of sodium chloride, hydrophilicity of Triton X-100 decreases. That is, Triton X-100 turns hydrophobic in presence of sodium chloride. As a result solubilization of Triton X-100 increases in oil phase and decreases in aqueous phase and this apparently causes an increase in V_w/V_m and a decrease in V_o/V_m and this finally leads to a phase inversion from a lower phase microemulsion (Winsor I) to an oil continuous upper phase microemulsion (Winsor II) *via* a middle phase (Winsor III).

Influence of temperature: It is clear from the Fig. 1 that optimal salinity (OS) of the pseudo-ternary system, Triton X-100 + 1-hexanol (1:5 molar ratio)/dodecane/water system is 0.60 mol dm⁻³ at 25 °C. When temperature is increased from 25-30 °C, optimal salinity decreases drastically and has been found 0.28 mol dm⁻³. With further increase in temperature from 30 to 35 °C, optimal salinity decreases slightly and is equal to 0.25 mol dm⁻³. The optimal salinity-temperature plot (Fig. 2) shows a decrease in optimal salinity with increase in temperature. That is, optimal salinity of a microemulsion system is a function of temperature.

Optimal salinity of nonionic microemulsion composed of Triton X-100 decreases with increase in temperature in the present investigation. Similar results were reported for ionic surfactant, sodium dodecyl sulfate (SDS)²⁴. By comparing these results it is observed that optimal salinity for nonionic surfactant, Triton X-100 is lower than ionic surfactant, SDS and the corresponding temperature at which the solubilization curves intersect are found to be higher in ionic surfactant than nonionic surfactant. Optimal salinity was 0.80 mol dm⁻³ at 80 °C in presence of NaCl for SDS + Brij 35 system and whereas it is 0.60 mol dm⁻³ for Triton X-100 + 1-hexanol at 25 °C in the present investigation. These results clearly indicate that

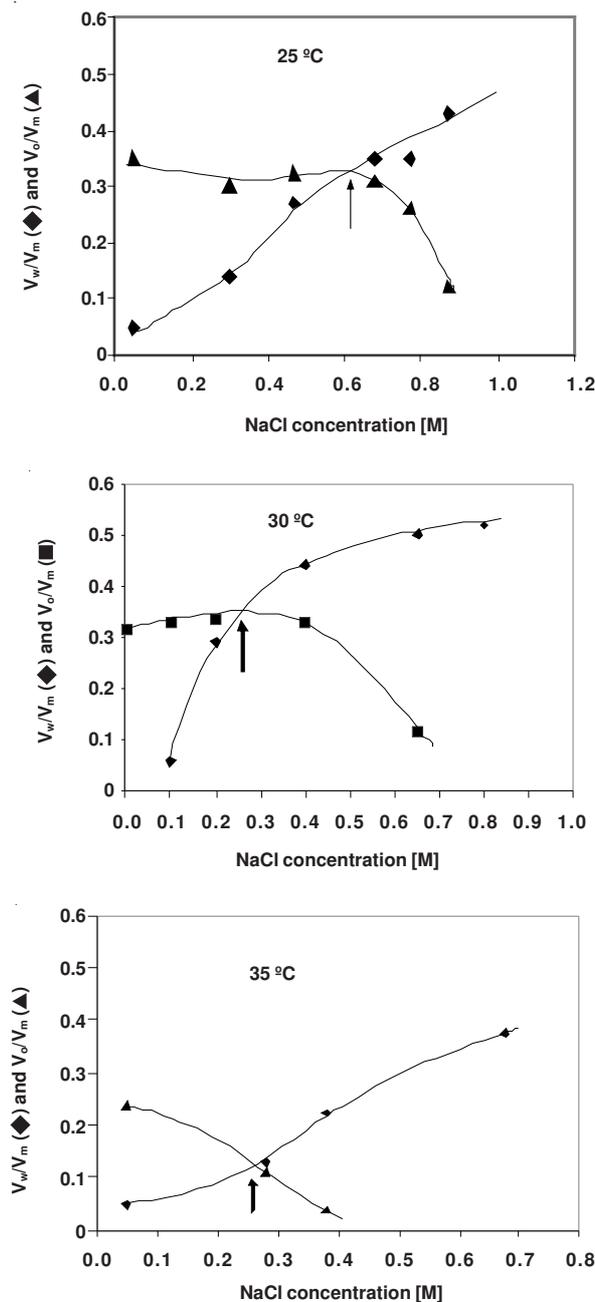


Fig. 1. Plot of V_w/V_m and V_o/V_m against NaCl concentration to determine optimal salinity for the system Triton X-100 + 1-hexanol (1:5 molar ratio)/dodecane/water at different temperatures. V_w , V_m and V_o are the volume of water, microemulsion and oil, respectively

a little change in temperature of nonionic surfactant changes hydrophilicity of the surfactant to a greater extent that induces phase transitions even at very low temperature. It is known that temperature induces phase transition Winsor I \rightarrow III \rightarrow II in the microemulsion where nonionic surfactants are present and this is due to increase in hydrophobicity with increase in temperature^{23,24}. As a result, solubilization of the surfactant (Triton X-100) in water decreases and in non-aqueous medium increases. At low temperature Triton X-100 is hydrophilic in nature. So to turn Triton X-100 hydrophobic in nature at lower temperature, higher concentration of NaCl is required. This is the reason for higher optimal salinity value

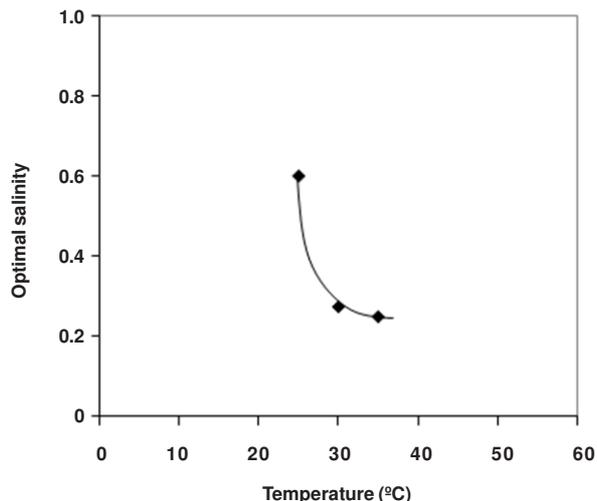


Fig. 2. Plot of optimal salinity vs temperature.

at comparatively lower temperature. When temperature is increased, Triton X-100 turns hydrophobic due to conformational changes in poly-oxethylene moiety of the surfactant²³ and this leads to phase inversion from Winsor I to Winsor II *via* middle phase at higher temperature at comparatively lower salt concentration.

The effect of salinity on the various microemulsion systems have been reported earlier^{21,22}. In ionic microemulsion, increasing salinity usually induces a variety of phase changes. Various different forms *i.e.*, Winsor I, II and III are possible as a function of NaCl concentration. These types of transitions are possible by increase of temperature in the system involving nonionic surfactants¹⁹. It is known that ionic surfactant does not form a three-phase microemulsion due to its high hydrophilicity. The presence of electrolyte, like NaCl, decreases the hydrophilicity of the surfactant system and hence the possibility of formation of a three-phase microemulsion increases. The presence of electrolyte reduces the repulsive force between the charged surfactant molecules and hence affects the phase diagram¹⁹. Addition of electrolytes eventually causes an inversion to an oil continuous upper phase microemulsion (Winsor II) from a lower phase microemulsion (Winsor I) *via* middle phase. That is, an inversion occurs from a lower phase microemulsion to an upper phase microemulsion *via* a middle phase.

It is well known fact that the maximum solubilization can be achieved by varying the factors, which increases the packing parameters of the surfactant molecules. The packing parameters can be increased by reducing the effective area of the head group by dehydrating the head group of a nonionic surfactant either by increasing temperature or by addition of salt²⁵. It is clear from the Fig. 1 that optimum salinity decreases with increase in temperature and this is due to decrease in hydrophilicity of TritonX-100 when temperature is increased or NaCl is added because both have similar effect.

Influence of nature of electrolytes: Fig. 3 shows the optimal salinity of the pseudo-ternary system, Triton X-100 + 1-hexanol (1:5 molar ratio)/dodecane/ water in presence of oxalic acid at 25 and 35 °C. By comparing the results shown

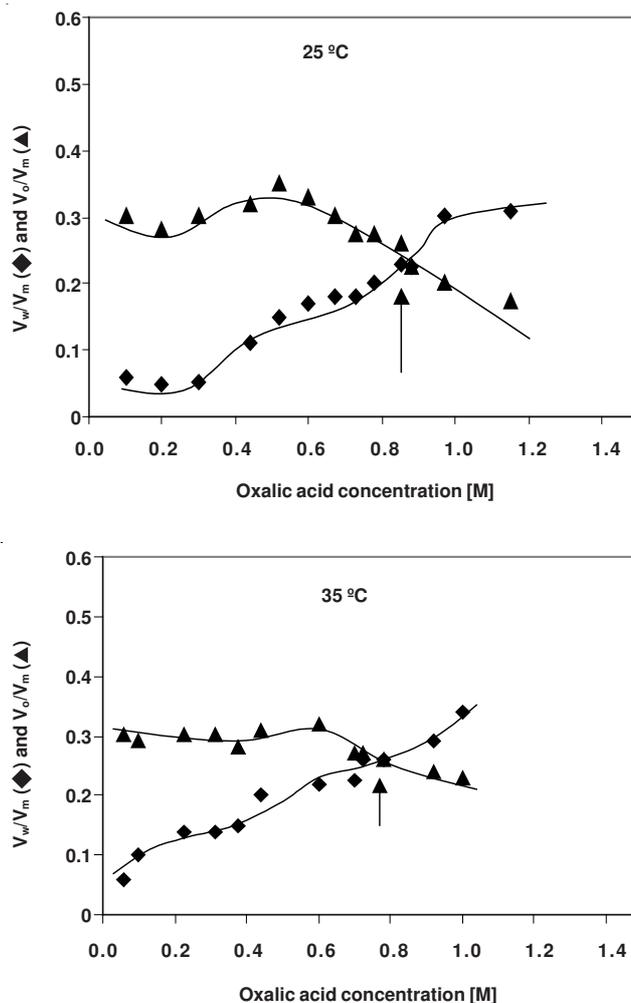


Fig. 3. Plot of V_w/V_m and V_o/V_m against oxalic acid concentration to determine optimal salinity for the system Triton X-100+1-hexanol (1:5 molar ratio)/dodecane/water at different temperatures. V_w , V_m and V_o are the volume of water, microemulsion and oil, respectively

in Figs. 1 and 3, it is evident that optimal salinity decreases with increase in temperature in presence of both types of electrolytes, strong as well as weak. But the decrease in optimal salinity is higher in presence of sodium chloride as compared to oxalic acid. In presence of sodium chloride, optimal salinity is 0.60 mol dm^{-3} at 25 °C and 0.25 mol dm^{-3} at 35 °C. That is, optimal salinity becomes less than half in presence of strong electrolyte (NaCl). Whereas optimal salinity is 0.88 mol dm^{-3} at 25 °C and 0.82 mol dm^{-3} at 35 °C in presence of weak electrolyte (oxalic acid) (Fig. 3). That is, optimal salinity does not change much with change in temperature in presence of weak electrolyte. Furthermore, at 25 °C optimal salinity is higher in presence of weak electrolyte (oxalic acid) than strong electrolyte (NaCl). This is probably due to the fact that strong electrolyte (NaCl) decreases hydrophilicity of Triton X-100 to a greater extent than oxalic acid. As a result, phase inversion occurs from Winsor I to Winsor II *via* middle phase at comparatively lower salt concentration. That is why optimal salinity is observed less in presence of sodium chloride as compared to oxalic acid. Alternatively, oxalic acid is a weak electrolyte and furnishes fewer ions as compared to NaCl and decreases hydrophilicity of the surfactant system (TX-100 + 1-hexanol)

to lesser extent than sodium chloride. That is, higher concentration of oxalic acid is required to decrease the hydrophilicity of the surfactant system for the phase inversion from Winsor I to Winsor II *via* middle phase. As a result optimal salinity is observed higher in presence of oxalic acid than sodium chloride.

Conclusion

The optimal salinity of nonionic microemulsions consisting of Triton X-100 + 1-hexanol (1:5 molar ratios)/dodecane/water was investigated in presence of different types of electrolytes at various temperatures. It is inferred that optimal salinity of a microemulsion system is a function of temperature. It decreases with increase in temperature due to increase in hydrophilicity of the surfactant system in presence of both types of electrolytes, strong as well as weak. However, the decrease in optimal salinity is higher in presence of strong electrolyte than weak electrolyte. Further, at constant temperature optimal salinity is found higher in presence of weak electrolyte in comparison with strong electrolyte.

REFERENCES

1. S.E. Freiberg, P. Brotherly, *Microemulsions, Structures and Dynamics*, CRC Press: Boca Raton, FL (1987).
2. A.M. Cazabat, In ed.: V. Degiorgio, In *Physics of Amphiphiles: Micelles, Vesicles and Microemulsions*, North Holland, Amsterdam (1985).
3. L.M. Prince, *Microemulsion, Theory and Practices*, Academic: New York (1997).
4. C. Solans, R. Pons and H. Kunieda, In: *Industrial Applications of Microemulsions*, Marcel Dekker, New York (1987).
5. K. Bhattacharya, *Acc. Chem. Res.*, **36**, 95 (2003).
6. A. Kumar, R.R. Rai, R. Sharma, K. Kumar and B.K. Singh, *Ultra Sci.*, **22**, 113 (2010) and references cited therein.
7. D.O. Shah and R.S. Stretcher, *Improved Oil Recovery by Surfactant and Polymer Flooding*, Academic Press, New York (1977).
8. A.M. Rao, H. Ngwjen and V.T. John, *Biotechnol. Prog.*, **6**, 465 (1990).
9. D. Atwood, In ed.: J. Kreuter, In *Colloid Drug Delivery Systems*, Marcel Dekker, New York (1994).
10. A.S. Bommarius, T.A. Hattan and D.I.C. Wang, *J. Am. Chem. Soc.*, **117**, 4515 (1995).
11. J. Estoete, M.J. Hollamby and L. Hudson, *Adv. Colloid Interf. Sci.*, **128**, 5 (2006).
12. C. Destree and J.B. Negy, *Adv. Colloid Interf. Sci.*, **123-126**, 353 (2006).
13. M. Summers, J. Eastoe and S. Devis, *Langmuir*, **18**, 5023 (2002).
14. R. Aboofazeli and M.J. Lawence, *Int. J. Pharm.*, **93**, 161 (1993).
15. P.K. Gosh and R.S.R. Murthy, *Curr. Drug Deliv.*, **3**, 167 (2006).
16. C.-K. Kim and J.-S. Park, *Am. J. Drug. Delv.*, **2**, 113 (2004).
17. A. Kumar, A.K. Moren and K. Holmberg, *J. Dis. Sci. Technol.*, **24**, 89 (2003).
18. K.-V. Schubert and E.W. Kaler, *Ber. Bunsenges Phys. Chem.*, **100**, 190 (1996).
19. A.C. John, A.K. Rakshit, *Langmuir*, **10**, 2084 (1994).
20. M. Kahlweit, R. Strey and G. Busse, *J. Phys. Chem.*, **94**, 3881 (1990).
21. R. Leung and D.O. Shah, *J. Colloid Interf. Sci.*, **120**, 330 (1987).
22. L. Magid, *J. Colloid Interf. Sci.*, **87**, 460 (1982).
23. K. Aramaki, A. Kumar and H. Kunieda, In ed.: A. Hubbard, *Encyclopedia of Surface & Colloid Science*, Marcel Dekker, pp. 3973-3982 (2002).
24. S. Ajith and A.K. Rakshit, *J. Phys. Chem.*, **99**, 14781 (1995).
25. A. Kumar, Ph.D Thesis, University of Delhi, Delhi, India (1998).