The Physicochemical Properties of a Nonaqueous Microemulsion: Cyclohexane/Triton® X-100/Dimethylformamide at 40 °C

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The phase diagram of a nonaqueous microemulsion system containing cyclohexane/Triton® X-100/DMF was determined at 40 °C. The one-phase microemulsion area increased in the presence of a cosurfactant. Physical properties like viscosity, adiabatic compressibility, specific conductance, and contact angle are discussed at a surfactant concentration of 15% to explain the microstructure. A cyclohexane/TX 100+1-propanol/DMF system shows percolation, though not high, with ca. 0.15 mole fraction of DMF. Contact angle measurements of cyclohexane/TX 100/DMF at various cyclohexane/DMF ratios show a DMF continuous system. In the presence of a cosurfactant, the contact angle values show a continuous change indicating an 0/DMF to bicontinuous to DMF/0 structure. NaI does not introduce a three-phase liquid system.

As a continuation of our interest in the properties of microemulsions,[1—4] it was decided to study the properties of a system where water is replaced by a polar organic liquid. It is well-known that microemulsions are generally obtained by mixing water (w), oil (o), and an amphiphile (s), either ionic or nonionic. These are spontaneously forming, transparent, isotropic, homogeneous, and thermodynamically stable colloidal systems. They can be classified as w/o, o/w, and bicontinuous systems.[5] Aqueous microemulsions have gained considerable importance due to their potential applications in tertiary oil recovery. It should be noted, though, that not as many studies have been done on nonaqueous microemulsions. Rico and co-workers[6,7] have studied chemical reactions in nonaqueous microemulsion systems where water was replaced by formamide. Friberg and Liang[8] used glycerol with anionic surfactants and Holmberg et al.[9] studied chemical reactions using a mixture of water and glycerol as the polar solvent. Recently, Schubert and co-workers[10—12] studied nonaqueous microemulsions of formamide with ionic and nonionic surfactants. The present study involves Triton® X-100 (TX 100) as the amphiphile and dimethylformamide (DMF) as the polar liquid. Cyclohexane is the nonpolar liquid. By studying the physicochemical properties one can understand the microstructure in a microemulsion system. Hence we decided to study phase diagram, conductance, viscosity, adiabatic compressibility, and contact angles to get valuable information on the microstructure of the cyclohexane/TX 100/DMF nonaqueous microemulsion system. We have also studied the effect of the presence of 1-propanol on the properties of the above system.

Experimental

Dimethylformamide was obtained from Qualigens, India. It was distilled just before use. Triton® X-100 was obtained from Kochlight Laboratories U.K., and was used as received. Cyclohexane and 1-propanol (E. Merck, India) were distilled before use.

i) Phase Diagrams. Ternary phase diagrams of the microemulsion stabilized by TX 100 were constructed at 40±0.05 °C. The microemulsion was prepared in a stoppered glass test tube. A known amount by weight of surfactant and cyclohexane were added to the test tube and this was then placed in a thermostated bath. After the sample attained the temperature of the bath, it was titrated with DMF kept in a burette in a dry atmosphere. Such titrations were also done when the effect of 1-propanol was determined. In this case, TX 100, 1-propanol (two times by weight of TX 100), and cyclohexane were placed in the test tube, which was stoppered and placed in the thermostat. The stopper was always taped with Teflon® tape to minimize the escape of the liquid vapor. This was then titrated with DMF. The process was repeated with different weight ratios of surfactant and oil (the surfactant–propanol ratio always being two) to cover the entire phase diagram and to determine the phase boundaries. The end point of the titration was the disappearance of turbidity and was visually obtained.

ii) Physical Properties. The viscosities of these systems were measured at 40±0.05 °C with an Ubbelohde viscometer placed in a thermostated bath assuming Newtonian behavior. The flow time was determined visually with the help of a hand-held stopwatch. The viscosity of water (at 40 °C) was taken to be 0.06529×10^{-2} Pas[13] and this was used for the calculation of the viscosity of the microemulsions. The error in the flow time was less than ±0.1 s.

Conductance was measured with a Mullard conductivity bridge at 40 °C. NaI was used as the added electrolyte for the conductivity studies of the system. The concentration of NaI was kept at 0.01 M under all conditions (1 M=1 mol dm^{-3}). The phase diagram of the system did not change markedly with such a small amount of NaI.

The adiabatic compressibilities of the microemulsions with various weight fractions of DMF were obtained by measuring the ultrasonic velocities, u, with a multifrequency interferometer (MX 3, Mittal Enterprises, New Delhi, India). The densities, ρ, of the solutions at 40 °C were determined with the help of a pycnometer. The compressibility, β, was computed from the relation $\beta=1/\rho u^2$. The average of 5 different independent readings were taken as β. The error in β was computed to be less than 1%.

The contact angles of the microemulsions with a poly(tetrafluroethylene) (Teflon®, obtained from samson India) surface were determined by using a contact θ meter obtained as a gift from the Department of Color Chemistry, Leeds University, Leeds, U.K. The surface was treated with chromic acid and then with copious quantities of water, and acetone and dried before use. At least 10 different drops on various parts of the Teflon® surface were made for a particular microemulsion and the contact angles were determined. The average of these readings are reported. The error in these values was ±2°. The contact angles were studied at room temperature (ca. 25 °C).

Results and Discussion

The phase diagram of the DMF/TX 100/cyclohexane system is shown in Fig. 1a. Above the boundary line, the system exists as a one-phase microemulsion and below it, there is a biphasic region. The surfactant apex shows a single phase region and this gradually extends to the DMF corner. At higher concentrations of cyclohexane, the solubility decreases and a liquid–liquid biphasic region exists where the microemulsion is in equilibrium with excess oil. Formation of a one-phase micellar system in a cyclohexane–DMF mixed solvent is possible. However, the concentration is low and cannot be shown in the phase diagram at this scale.

Figure 1b shows the effect of 1-propanol on the phase diagram. The one-phase microemulsion area covers almost 90% of the phase diagram. Below 10% surfactant concentration, there exists a liquid–liquid biphasic region around the 50% cyclohexane concentration range.

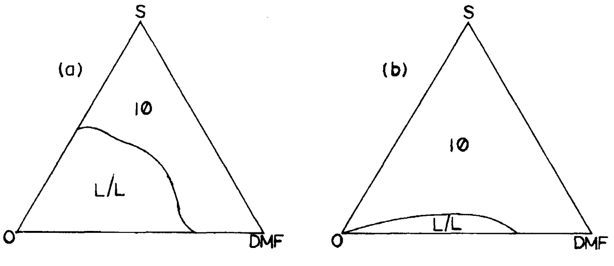

Fig. 1. a) Pseudoternary phase diagram of cyclohexane (O)/Triton® X 100 (S)/DMF system at 40 °C. b) Pseudoternary phase diagram of cyclohexane (O)/Triton® X 100+1-propanol (S)/DMF system at 40 °C.

As the cyclohexane concentration increases and that of DMF decreases, more monophasic microemulsion area becomes available. Addition of a short chain alcohol increases the efficiency of the amphiphile. It enters the amphiphilic monolayer and reduces the interfacial tension between cyclohexane–DMF further[14] which results in a larger one-phase area.

In Fig. 2, the viscosity variation with varying DMF composition (and hence cyclohexane) is shown. The surfactant[15] concentration was kept constant at 15%. It is clear that the viscosity remains almost constant indicating that the change in DMF content does not have any observable effect on the microstructure of the microemulsion. This suggests that the microemulsion is bicontinuous in nature. In the presence of 1-propanol, the viscosity is somewhat lower. This may be due to the use of less Triton® X-100 (ca. 5%) whereas 1-propanol was ca. 10%. In this case, there is a continuous decrease in the viscosity with the addition of cyclohexane. It was mentioned earlier that in the case of an aqueous microemulsion,[16,17] a decrease in viscosity was generally due to a decrease in the size of the water conduit. However, in this case the decrease in viscosity may be due to structural changes of the microemulsion as the O/D ratio increases. It is not prudent to make more specific comments as the changes in viscosity are not large. The dilution effect brings the viscosity down in the case of an aqueous system,[16] though this was not observed here within the concentration range studied.

In Fig. 3, the adiabatic compressibilities of various microemulsion systems with different DMF–cyclohexane ratios at a constant surfactant concentration (15% w/w) are shown. It is obvious that the adiabatic compressibility decreases with an increase in the DMF concentration. DMF is a relatively more structured sol-

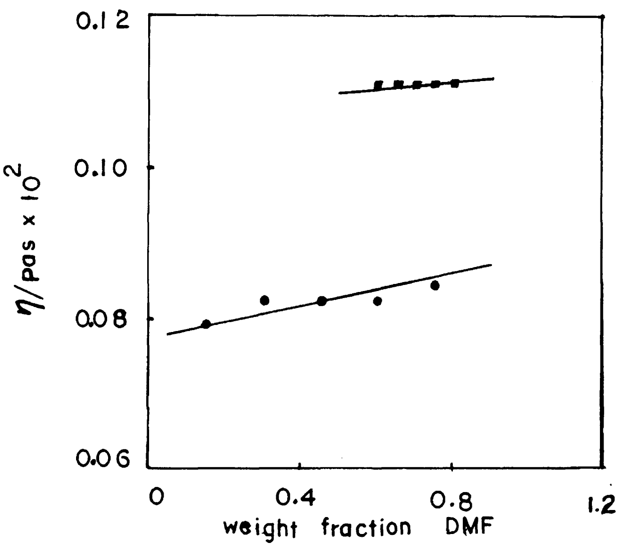

Fig. 2. Plot of viscosity (η) versus weight fraction of DMF. ● Cyclohexane/TX 100+1-propanol/DMF. ■ Cyclohexane/TX 100/DMF.

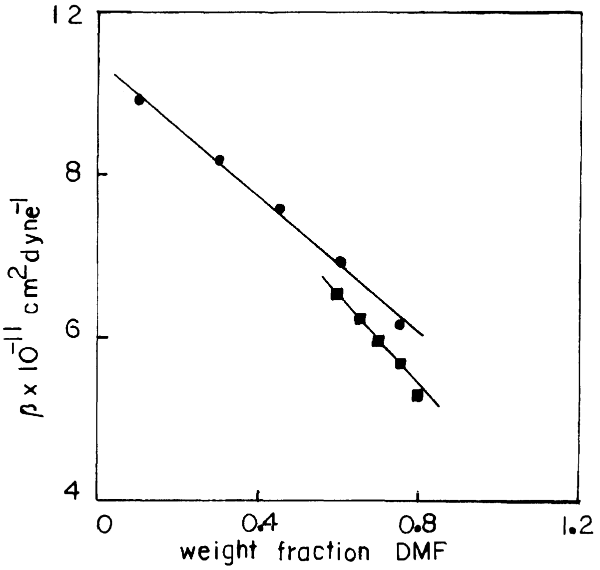

Fig. 3. Plot of adiabatic compressibility (β) versus weight fraction of DMF. ● cyclohexane/TX 100+1-propanol/DMF. ■ cyclohexane/TX 100/DMF.

vent than cyclohexane and hence the compressibility decreases. This is basically a gross property[2,16] and it does not give much indication of the microstructural nature of the medium.

Figure 4 shows the specific conductances increase from a low DMF content to a high DMF content with 15% S. NaI (0.01 M) was used as the electrolyte. The systems do not show any percolation behavior which suggests a single structured form at the different compositions studied. The specific conductance increases gradually as the DMF concentration is raised. This suggests the absence of percolation. The increase is much sharper in the systems where a cosurfactant, 1-propanol, was present. This indicates that percolation cannot be totally neglected when 1-propanol was also present. However, we did not observe any percolation in an Alkane/Brij 35+1-propanol/water nonionic aqueous microemulsion.[3] The steady increase in conductance with the addition of DMF suggests a similar type of structure over the entire cyclohexane/DMF range studied. In the aqueous microemulsion[3] mentioned above, percolation was observed at high w/s ratios. We have not studied a system with a higher DMF/surfactant wt. ratio. However in the presence of 1-propanol, the DMF/TX 100 ratio becomes much higher. When NaI is the electrolyte, it resides in the DMF pool of the microemulsion. The structure is bicontinuous [and a DMF continuum]. At a high cyclohexane concentration, a change [to a cyclohexane continuum] also seems to occur as the O/D ratio becomes very high.

It was suggested by Ninham et al.[18,19] that the specific conductance of a microemulsion, k, is proportional to the volume fraction of the polar solvent DMF, ϕ_{D}, i.e. $k \propto (\phi_{\mathrm{D}} - \phi_{\mathrm{D}}^{\mathrm{P}})^t$ where $\phi_{\mathrm{D}}^{\mathrm{P}}$ is the percolation threshold, i.e. the concentration above which percolation can be seen. It was also suggested that for a bicontinuous system $t=8/5$, i.e. $k \propto (\phi_{\mathrm{D}} - \phi_{\mathrm{D}}^{\mathrm{P}})^{8/5}$ or $k^{5/8} = A(\phi_{\mathrm{D}} - \phi_{\mathrm{D}}^{\mathrm{P}})$ where A is the proportionality constant. Thus a plot of $k^{5/8}$ versus ϕ_{D} should meet the X-axis at $\phi_{\mathrm{D}}^{\mathrm{P}}$. Figure 5 presents such a plot. For a system without 1-propanol, a negative $\phi_{\mathrm{D}}^{\mathrm{P}}$ is obtained indicating no percolation at all. However, for a DMF/TX 100+1-propanol/cyclohexane system, a low $\phi_{\mathrm{D}}^{\mathrm{P}}$ is observed at 0.15 mole fraction DMF. This indicates that the percolation threshold does exist in this case though percolation is not very high. This indicates some type of change in the structure from a

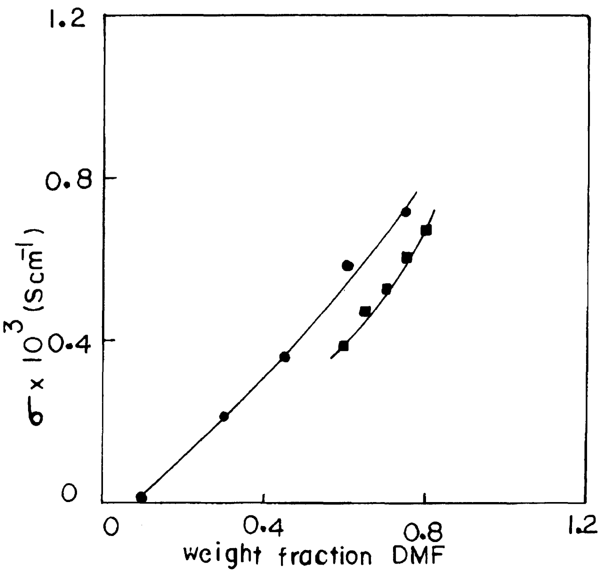

Fig. 4. Plot of specific conductance (k) versus weight fraction of DMF. ● cyclohexane/TX 100+1-propanol/DMF. ■ cyclohexane/TX 100/DMF.

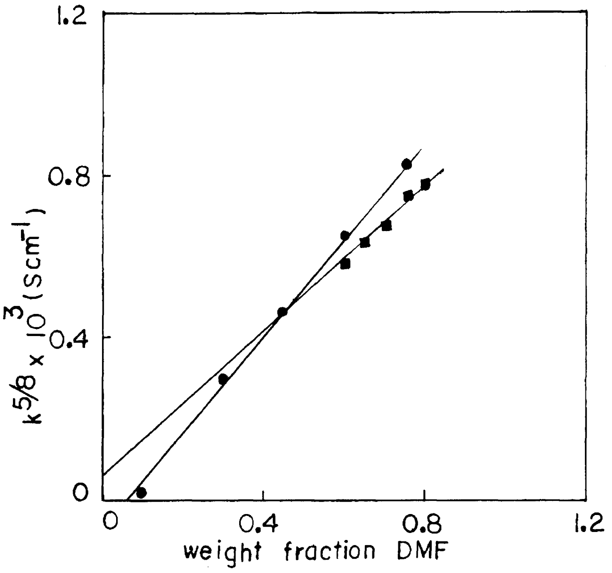

Fig. 5. Plot of (specific conductance, $k^{5/8}$) versus weight fraction of DMF. ● cyclohexane/TX 100+1-propanol/DMF. ■ cyclohexane/TX 100/DMF.

Table 1. Contact Angle (θ) of Microemulsions with Teflon® at Room Temperature

System a Cyclohexane/TX 100/DMF (O) (S)				System b Cyclohexane/TX 100+1-propanol/DMF (O) (S)			
O	S	DMF	$\theta/°$	O	S	DMF	$\theta/°$
0	0	100	132	0	0	100	132
5	15	80	131	10	15	75	121
10	15	75	118	25	15	60	103
15	15	70	117	40	15	45	89
20	15	65	114	55	15	30	86
25	15	60	99	70	15	15	65
100	0	0	56	100	0	0	56

DMF continuum to a cyclohexane continuum through a bicontinuous form. Peyrelesse[20)] et al. also observed percolation in a nonaqueous microemulsion.

Table 1 shows the contact angles, θ, of various microemulsions with a Teflon® surface. The microemulsions without 1-propanol (Table 1a) have values almost as high as that of pure DMF with Teflon®. This suggests to us that the DMF of the microemulsion is in contact with the teflon. In presence of 1-propanol (Table 1b), the θ values are similar to those in Table 1a up to 25% cyclohexane. This indicates that both microemulsions have a similar structure up to this composition range. Further addition of cyclohexane changes the contact angle in a gradual fashion (Table 1b). Hence we assume that an O/D to D/O structural change occurs and in the middle composition range a bicontinuous system may be present where the surfactant (i.e. TX 100 with 1-propanol) is 15% by weight.

The addition of an electrolyte generally has a drastic effect on an aqueous microemulsion involving phase inversion and formation of three-phase systems. However, earlier authors have failed to get a three-phase system by addition of electrolytes to nonaqueous microemulsions.[21)] We have confirmed this. The addition of NaI to a one-phase microemulsion, both in the presence and absence of 1-propanol, did not lead to a three-phase system. We also used urea to see whether any effect was observed on the phase. Again, no phase seperation was observed at all. To our knowledge, no nonaqueous microemulsion has shown phase separation by the addition of an electrolyte as is observed in aqueous microemulsions.

Conclusion

Microemulsions can be formed with a polar organic liquid like DMF and show physical properties somewhat similar to those of aqueous systems. The presence of 1-propanol as a cosurfactant changed the area of a one-phase microemulsion drastically, increasing it by almost 2 times. The physical properties changed, but the similarity of the changes in the properties remained the same as a function of the DMF concentration. However, the effect of an electrolyte which shows phase changes in an aqueous microemulsion was not observed in this nonaqueous microemulsion. The presence of 1-propanol as cosurfactant induces the presence of O/D, bicontinuous, and D/O structural patterns.

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References

1) A. C. John and A. K. Rakshit, *J Colloid Interface Sci.*, **156**, 202 (1993).

2) A. C. John and A. K. Rakshit, *Langmuir*, **10**, 2084 (1994).

3) S. Ajith and A. K. Rakshit, *J. Surf. Sci. Technol.*, **8**, 365 (1992).

4) S. Ajith and A. K. Rakshit, "Proc. Natl. Conf. Ph. Chem. Aspects Org. Bio. Assemblies," Jadavpur University, Calcutta (1991), pp. 124—128.

5) M. J. Rosen, "Surfactants and Interfacial Phenomena," John Wiley & Sons, New York (1989), p. 332.

6) A. Lattes, I. Rico, A. DeSavignac, and Z. S. Ahmad, *Tetrahedron*, **43**, 1725 (1987).

7) I. Rico and A. Lattes, *Nouv. J. Chem.*, **8**, 429 (1984).

8) S. E. Friberg and Y. Liang, "Progress in Microemulsions," ed by S. E. Friberg and Y. Liang, Plenum, New York (1989), p. 77.

9) K. Holmberg, B. Lassen, and M. B. Stark, *J. Am. Oil Chem. Soc.*, **66**, 796 (1989).

10) K. V. Schubert, G. Busse, R. Strey, and M. Kahlweit, *J. Phys. Chem.*, **97**, 248 (1993).

11) K. V. Schubert, R. Strey, and M. Kahlweit, *Prog. Colloid Polym. Sci.*, **89**, 263 (1992).

12) K. V. Schubert, R. Strey, and M. Kahlweit, *NATO ASI Seri., Ser. C*, **369**, 841 (1992).

13) "Handbook of Chemistry and Physics," 54th ed, ed by R. C. Weast, CRC Press, Ohio (1973—74).

14) M. Kahlweit, R. Strey, and G. Busse, *J. Phys. Chem.*, **95**, 534 (1991).

15) By Surfactant we mean TX 100 or TX 100 and 1-propanol together when 1-propanol is present in the system.

16) S. Ajith, A. C. John, and A. K. Rakshit, *Pure Appl. Chem.*, **66**, 509 (1994).

17) B. K. Paul, M. L. Das, D. C. Mukherjee, and S. P. Moulik, *Indian J. Chem.*, *Sect. A*, **30A**, 328 (1991).

18) S. J. Chen, D. F. Evans, and B. W. Ninham, *J. Phys. Chem.*, **88**, 1631 (1980).

19) S. T. Hyde, B. W. Ninham, and T. Zemb, *J. Phys. Chem.*, **93**, 1464 (1989).

20) J. Peyrelesse, C. Boned, and Z. Saidi, *Progr. Colloid Polym. Sci.*, **79**, 163 (1989).

21) H. D. Dorfler and E. Norrmeister, *Tenside Deterg.*, **29**, 3 (1992).