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# Interfacial Phenomena and Stability of Oil-In-Water-Emulsions Stabilized by Binary Surfactants

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In the present work, interfacial phenomena and stability of oil-in-water emulsions stabilized by binary surfactants was described.

It is found that two distinct classes of emulsions can be produced (1) dilute emulsions of oil-in-water and (2). more concentrated emulsions of either the oil-in-water (o/w) or water-in-oil (w/o) types. The latter needs the presence of a third substance, the emulsifying agents which confer the stability to the systems[1]. Two types of emulsions either oil-in-water (o/w) or water-in-oil (w/o) was proposed by Ostwald[2]. Now recently third type of emulsion has been prepared and fully studied by Sharma which named as oil-in-oil (o/o)[3, 4] emulsion stabilized by different emulsifying agents in the different conditions by taking two and more immiscible oils. These emulsions are also known as non-aqueous emulsions.

The oil-in-water (o/w) emulsions closely resemple to hydrophobic colloids in all the respects. In these cases the oil globlues have a negative charge due to the preferential absorption of hydroxyl ions from water on the surface of the globules. The opposite compensating ($H^+$) ions forming the diffuse portion of the double layer. Their stability essentially due to the charge, as soon as the charge is removed, the emulsion is broken. Similarly in the cases of coagulation of hydrophobic colloids, specially the addition of different electrolytes in such cases the electrolytes having more charges such as polyvalent cations such as $Al^{3+}$, $Fe^{3+}$etc., which are more effective but bivalent and univalent cations are less effective for coagulation.

When two immiscible liquids are homogenized an unstable emulsion is formed and the dispersed globules after some time coalescence due to surface tension forces which resist increase of interfacial area. If a third substance known as emulsifying agent is taken and homogenized with the two immiscible liquids or oils, in these cases the coalescence may be delayed for more or less indefinite time due to the formation of an interfacial film. The more efficient the emulsifying agent, the slower will be the process of breaking of emulsions. The efficiency of an emuisifying agent is very specific property.

In general, hydrophobic groups in the interfacial film constitute a barrier to the coalescence of oil droplets, where as hydrophobic groups in the interfacial film constitute a barrier to the coalescence of water droplets. Hence an interfacial film that is predominantly hydrophobic tends to form an oil-in-water (o/w) emulsions where as on that is predominantly hydrophilic tends to produce water-in-oil (w/o) emulsions.

It was recognized very earlier that many of the most valuable emulsifying agents were surface active materials, Quinke[5] and Donnon and Potts[6] attached considerable importance to the effects of the emulsifier on the interfacial tension. It is significant that factor can play very important role. The reduction of interfacial tension is a significant effect the emulsion is still thermodynamically unstable and the lowering of interfacial tension, while important can not begin to represent the totality of the effect of the emulsifying agent. Bancroft[7] was the first to point out the significance of the Gibb's equation in this connection. The lowering of interfacial tension carriers with it the correlary the emulsifying is concentrated in the interface and forms some sort of interfacial films which exerts a stabilizing influence.

Studies of the stability of emulsion are of very important in technology, pharmacy, agriculture, medicinal chemistry etc. It has been known for a long time that mixed surfactants often form more stable emulsions in comparison of single surfactant[8, 9]. The role of mixed surfactants in the stability of emulsion has been realized due to their biological significance. The mixture of surfactants such as ionic and non ionic are widely used in practice and studies concerning the interactions between members of these classes have appeared[10–15]. In most of the cases the higher stability accounts for a complex formulation at the interface which results in an interfacial film of greater strength.

In view of both the scientific and applied interest of these problems, we studied the absorption of anionic surfactant multifoam at the oil/water interface as well as to the emulsion droplets of different oil phases as stabilized by non-ionic surfactant Tween-21 at 25°C. The oil phase used were three hydrocarbon, namely cyclohexane, *o*-xylene and *p*-xylene in order to show any differences or similarities among straight, branched and cyclic chains. Electrophoretic experiments were very useful in showing how the charge of droplets stabilized by Tween-21 was affected by gradual addition of multifoam. This change mirrors the absorption of anionic surfactant on an interface fully or partly covered by Tween-21. The stability measurements based on the rates of coagulation have been determined according to Smouuechowski theory and a qualitative correlation between rate constant and potential has been found. The influence of the time of incorporation of the second surfactants the stability of cyclohexane emulsion was also studied.

In the study of electrokinetic behavior and stability properties of the hydrocarbons-in-work emulsions, we studied the adsorption behavior of mixtures Tween-21 and multifoam at the water paraffin interfaces. The stability of emulsions is very much related to the interfacial phenomena and the surface behavior of the surfactants used reveals interesting parameters such as the amount of the anionic surfactant adsorbed per unit area of the interface and the area per molecule at the interface which were calculated with the help of Gibbs's euqation.

The nonionic surfactant Tween-21 of HICO product, Bombay and Multifoam was also from the HICO product. Cyclohexane, *o*-xylene and *p*-xylene were of BDH grade. Water was of double distilled form and NaCl was also of BDH grade.

(a) *Preparation of Emulsion:* The emulsion were prepared by taking 0.5% by volume of the oil phase in water containing Tween-21 (0.01 g). The solution for the emulsions was first hand shaken for about 15 min. The emulsion were then prepared by the homogenizer. The appropriate quantity of anionic surfactant multifoam was added simultaneously with Tween-21. The pH of the solution was determined and found to remain stable depending upon concentration of multifoam.

(b) *Interfacial Tension Measurements:* The interfacial tension between the dispersed and the aqueous phase containing 0.01M NaCl solution was measured. The non ionic surfactant concentration *i.e.*, Tween-21 was kept constant while the concentration of anionic surfactants multifoam was varied. The addition of sodium chloride in high concentrations compared to that of the anionic surfactant results in an easier application of the Gibb's equation to the multicomponent solution. The interfacial tension values were the study values obtained after a period of contact (1h) between the oil and the aqueous phases.

The interfacial tension values obtained with variation of multifoam concentration and taking Tween-21 concentration constant. In the low concentration of multifoam the interfacial tension values increase on increasing multifoam concentration and are slightly higher compare to the interfacial tension of a single Tween-21 micellar solution. The number of oil droplets per unit volume is taken as a measure of the dispersivity of each oil phase (80 mins) after the preparation of emulsions and is represented in the Table 1.

TABLE 1
*NUMBER OF DROPLETS PER UNIT VOLUME N × $10^{-3}$(cm$^3$). 80 mins.
AFTER THE PREPARATION OF EMULSION

| Multifoam Conc.(M) | Cyclohexane | Xylene | Ethylene glycol |
|---|---|---|---|
| 0.25 | 70 | 60 | — |
| $5 \times 10^{-6}$ | 28 | 70 | 60 |
| $9.5 \times 10^{-6}$ | 28 | 70 | 61 |
| $1.9 \times 10^{-5}$ | 28 | 71 | 60 |
| $4 \times 10^{-5}$ | 29 | 70 | 64 |
| $8 \times 10^{-5}$ | 31 | 70 | 62 |
| $4 \times 10^{-4}$ | 28 | 85 | 70 |
| $6.4 \times 10^{-4}$ | 34 | 84 | 75 |

The concentration of Tween-21 is $7.5 \times 10^{-3}$.

From the data given in the Table 1, we observed that the greater the number of droplets per unit volume the smaller are the specific rates of flacculation, which means the greater stability of the emulsions. Accordingly the cyclohexane emulsions prepared with $7.5 \times 10^{-3}$% Tween-21 have a lower stability than those of respective xylene and ethylene glycol emulsions. These may be attributed to the greater solubility of cyclohexane in water than other two organic compounds in water. The addition of low concentrations of multifoam in these emulsion after preparation lightly increases their stability. The higher concentration of multifoam about $5 \times 10^{-5}$M increases their stability.

## REFERENCES

1. I.P. Pandey, *J. Indian Chem. Soc.*, **56,** 221 (1988).
2. Wo. Ostwald, *Z. Chem. Ind. Kolloid,* 8103 (1910).
3. M.K. Sharma, *J. Colloid Interface Sci.*, **53,** 340 (1977).
4. ________, *Curr. Sci. (India),* **46,** 181 (1977).
5. G. Qunike, *Pogg Ann.*, **139,** 1 (1870).
6. F.G. Donnon, and H.E. Potts, *Kolloid-Z,* **7,** 28 (1910).
7. W.D. Bancroft, *J. Phy. Chem.*, **17,** 501 (1913); **19,** 275 (1915).
8. E.G. Cockbain and T.S. McRobberts, *J. Colloid Sci.*, **8,** 440 (1956).
9. Gan-Zue Li and S.E. Fribarg, *J. Am. Oil Chem. Soc.*, **59,** 569 (1982).
10. D.A. Haydon, *Proc. Soc. London, Ser. A,* **258,** 319 (1960).
11. G.G. Jayson and G. Thomson, *J. Colloid Interface Sci.*, **111,** 65 (1986).
12. E.A. Lissi and E. Abuin, *J. Colloid Interface Sci.*, **105,** 1 (1985).
13. J.H. Clint, *J. Chem. Soc. Faraday Trans,* **171,** 1327 (1975).
14. P. Bahadur and S.N. Srivastava, *Collid Polym. Sci.*, **253,** 315 (1975).
15. X.Y. Hau and M.J. Rosen, *J. Colloid Interface Sci.*, **87,** 469 (1982).

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