

# THE EFFECT OF ANIONIC (NaDeS) , CATIONIC (TTAB) AND NONIONIC (TWEEN-20) SURFACTANTS IN OIL+ H<sub>2</sub>O+ALCOHOL (MEOH, PROH, BUOH ) SYSTEMS ON MICRO EMULSION

Dr. MAYANK\*

\*Associate Professor, Department of chemistry, Multanimal Modi College, Modinagar

## ABSTRACT

Micro-emulsions are clear, stable, isotropic liquid mixtures of oil, water and surfactant, frequently in combination with a co-surfactant. The aqueous phase may contain salt(s) and/or other ingredients, and the `oil` may actually be a complex mixture of different hydro- carbons and olefins. In contrast to ordinary emulsions, micro-emulsions form upon simple mixing of the components and do not require the high shear conditions generally used in the formation of ordinary emulsions. The two basic types of micro-emulsions are direct (oil dispersed in water, o/w) and reversed (water dispersed in oil, w/o). The comparative effects of surfactants in formulation of micro-emulsions have been summarized and show the reduction of interfacial tension of oil and water. Dispersion of surfactant leads to increase in entropy and decrease in free energy. Nonionic surfactants could give a more expanded film and allows rapid transportation of alcohol. Cationic and anionic surfactants reduce interfacial tension of water and oil in almost same amount as both the surfactants have C-12 structures. Tetradecyltrimethylammonium bromide shows more effective micro-emulsion formulation if propanol-1 as co-surfactant was used. The amount of co-surfactants used for the formulation of micro-emulsion decreases with increasing amount of the surfactants in all the systems. The influence of all the above factors depends upon phase continuity and composition of micro-emulsion.

**ABBREVIATIONS:** Micro-emulsification, co-surfactants, ternary phase diagram. Surfactant (Tween-20, TTAB, NaDeS.), Water-alcohol system,

## Introduction

Seang and coworkers (1) studied the formation of micro-emulsion with branched tail polyoxyethylene sulfonate surfactants. Formation of micro-emulsions with mono and dialkyl amic acid surfactants has been reported by Blum and coworkers (2). Moilliet et al., (3) reported `self emulsifiable oils` used in agricultural and horticultural sprays, are w/o at the concentrated stage. A completely different kind of application is found in pure science, where the mono dispersity is important.

The formation and stability of micro-emulsion have been explained in terms of theories which are widely classified on the basis of three principles. The first theory includes the interfacial or mixed film principle introduced by Schulman et al. (4). The second class by Shinoda and Friberg (5) includes the solubilization theories and third principle includes thermodynamics treatments by Ruchenstein and Chi (6). The separation and sweeping of flavonoids by micro-emulsion of mixed anionic and cationic surfactants by electrokinetic chromatography have been reported by Cao and Liang (7) recently. The factor responsible for micro-emulsion stability are (5-8) van der Waals attraction force compression of diffused electrical double layer and eutropic contribution to the free energy from the space position combinations of the dispersed droplets. Stabilization of micro-emulsion using alcohols as co surfactant has been reported by Bahadur and Chand (9).

The droplets diameter for micro-emulsion particles ranges between 100A<sup>0</sup> (0.01μ) to 2000A<sup>0</sup> (0.20 μ). Droplets are stabilized by a mixed interfacial film of surfactant and alcohol. Penetration of interfacial film with

oil as well as interaction of water with polar groups is essential for the formation of micro-emulsions. Micro-emulsion has also been reported as mono disperses droplets of water-in-oil or oil-in-water. They may be in equilibrium with excess oil, excess water or both(10) Accumulation of surfactants and cosurfactants at the interface of one phase in micro-emulsion not only causes significant reduction in the interfacial tension but also results in the reduction of chemical potential of surfactant and co surfactant in bulk solution and sometimes it reduces up to negative values.

Both nonionic and ionic surfactants can be used to obtain micro-emulsion. The studies with nonionic surfactants avoid additional complication due to columbic ion bonding. Large micelles and clouding phenomenon show by nonionic surfactants are advantageous for their use (11). In micro-emulsion of nonionic surfactants; the advantage is that there is sometimes no need to add co surfactant.

It has been already proved that association between molecules of interfacial film and hydrocarbon in dispersed or continuous phase is very important in forming micro-emulsions. Micro-emulsions can be prepared by titrating coarse emulsion of oil, water and surfactant with alcohol. It is not essential to add the components in a particular order. This fact indicates that phases are in equilibrium with each other. In micro-emulsion alcohol is distributed between oil, interface and water, while surfactant is entirely in interface. Homogeneous, transparent and low viscous solutions can be formed with considerable amounts of water and oil dispersed (12).

Theoretical and experimental aspects of formation and stabilization of micro-emulsion have been investigated by studying properties of micro-emulsion by electrical conductivity and viscosity (13, light scattering (14), ultracentrifugation (15), X-ray diffraction, NMR, electron microscopy techniques. Stable oil-water emulsions were formed by using nonionic, anionic and cationic surfactants as emulsifier. Micro-emulsions were formed by titration methods using different surfactants, oils and different alcohols.

## Experimental aspects

### Method and Materials:

The surfactants, oil and water were mixed together to form milky emulsion, which was then titrated with the fourth component (alcohol) till mixture became transparent clear. Generally, fixed amount of surfactant was added into oil-water mixture to produce coarse emulsions. Mixture was shaken intermittently for few minutes and alcohol was added to this emulsion in 0.5 ml portions with continuous shaking where coarseness gradually diminishes. The addition of alcohol was reduced to 0.1 ml portion near end point. The micro-emulsion thus formed were kept in Stoppard Pyrex glass tubes for overnight and a few drops of alcohol were added if any separation of oily layer appeared on the top. The micro-emulsions finally obtained, remained isotropic and were found to have long term storage stability. Viscosities of the liquids and solutions were measured with modified Ubbelohde viscometer .Following surfactants, oils and aqueous phase were used in formulating micro-emulsions.

Anionic surfactant [Sodium decylsulfate (NaDeS)].Cationic surfactant [Tetradecyltrimethylammonium bromide (TTAB)]. Nonionic surfactant –(Tween 20),Methanol, Propanol-1, Butanol-1, Toluene, Xylene, Benzene, n- haptane, n-decane are used in formulating micro-emulsion.

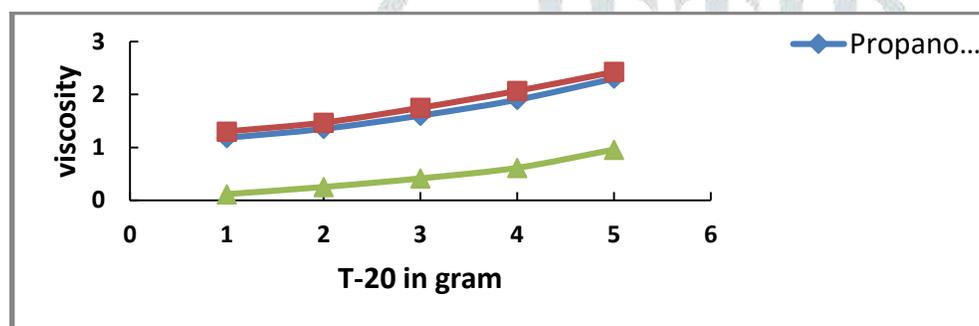
## Results and Discussion:

The composition of micro-emulsion described in terms of the amount of toluene, water and methanol ,propanol-1, butanol-1 for a definite concentration of surfactants are reported in **Table-1** .Data reveals that the percentage composition of water, toluene, and co surfactant in presence of fixed amount of different surfactants was almost same for sodium decylsulfate (NaDeS) and tetra decyltrimethylammonium bromide .However relativity more amount of T-20 was required for the solubilization of same amount of alcohol. The effect of different amount of surfactants with difference surfactants on micro-emulsion is shown in **Table 2, 3 and 4**.

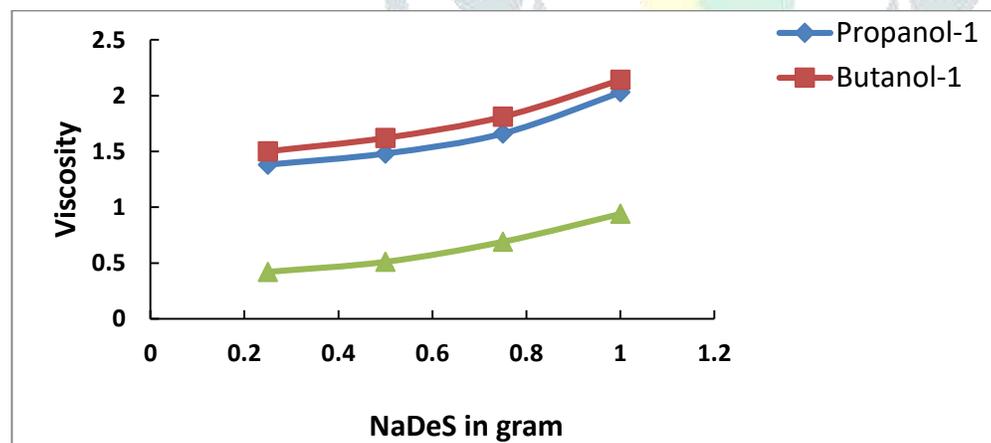
The viscosity (**Fig.1, 2, 3**) of micro-emulsion change when hydrophobic moieties of surfactants are changed. Similar observation has also been noticed in densities of micro-emulsions (**Fig.4, 5, 6**) for different

surfactants used in order to formulate oil-water-alcohol systems. **Fig.7** shows the phase diagram formed by sodium decylsulfate in water-propanol-1-(benzene, toluene, xylene) systems.

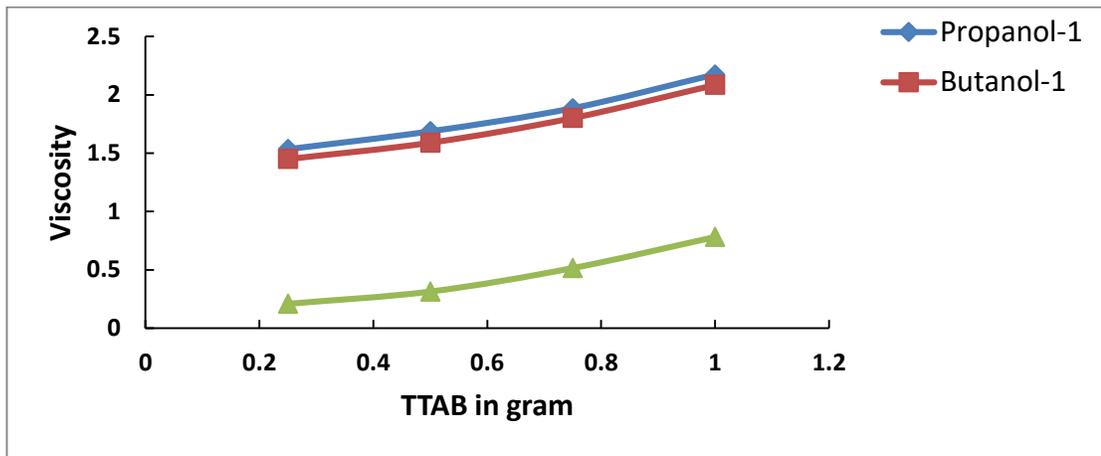
Lawrence and Pearson (16) studied the phase diagram of cationic surfactants and explained isotropic liquid, anisotropic liquid crystal and solid phase. Ekwall et al., (17) have determined phase diagrams for anionic surfactants. Investigations on effect of the surfactant on micro-emulsion have been made by Fendler and Fendler (18). Result of above mentioned studies reveals that surfactants play the role to separate oil rich and water rich part of microstructure in thermodynamically stable way which probably involves surfactant rich, multiply connected sheet like region. In presence of surfactant, interfacial tension of oil/water interface decreases appreciably. On addition of co surfactant, besides the surfactant, interfacial tension is further lowered due to penetration of surfactant film at interface by co surfactant molecules. It has been suggested that when amount of surfactant and co surfactant at interface is to sufficiently large, the spreading pressure may be large enough to produce small or even negative values of interfacial tension. It has been proposed that two interfaces, one between water and hydrophilic part of surfactant have distinct interfacial tension and sum of these interfacial tensions, determine curvature and phase continuity of micro-emulsion. Miller and Seriven (19) pointed out that the entropy effect which causes the interface to become unstable while interfacial tension is still positive and small. At small but positive interfacial tension, interface becomes unstable due to sufficiently large increase of entropy by dispersion.



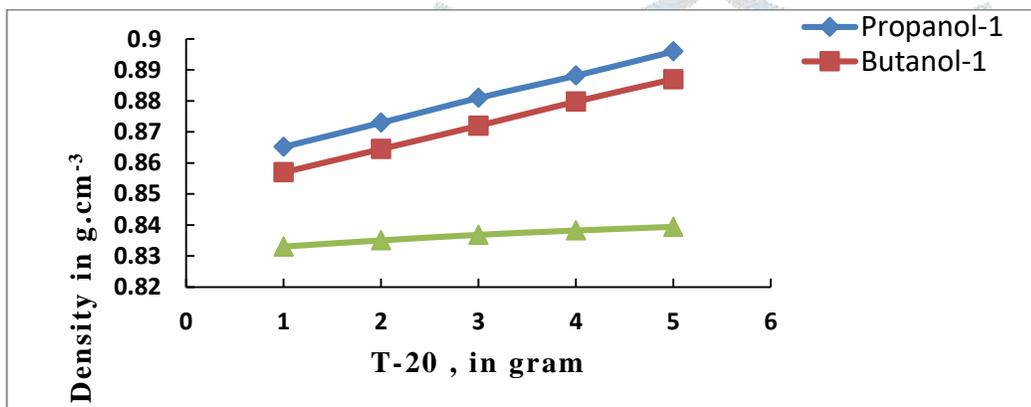
**Fig.1:** Plots of viscosity of micro-emulsion formed with different concentrations of Tween-20 surfactant in propanol-1, butanol-1 and methanol.



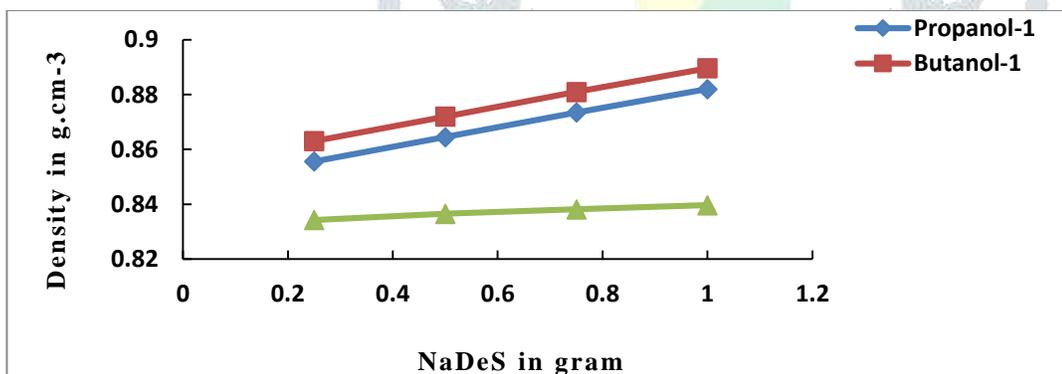
**Fig.2:** Plots of viscosity of micro-emulsion formed with different concentrations of sodium decylsulfate surfactant in propanol-1, butanol-1 and methanol.



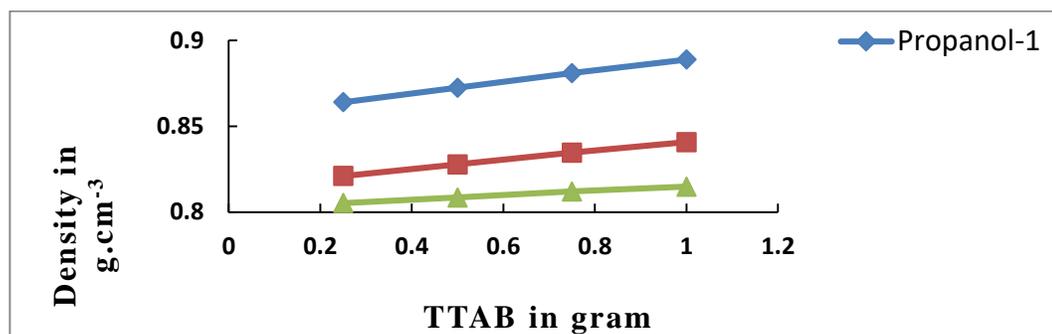
**Fig.3:** Plots of viscosity of micro-emulsion formed with different concentrations of tetradecyltrimethylammonium bromide surfactant in propanol-1, butanol-1 and methanol.



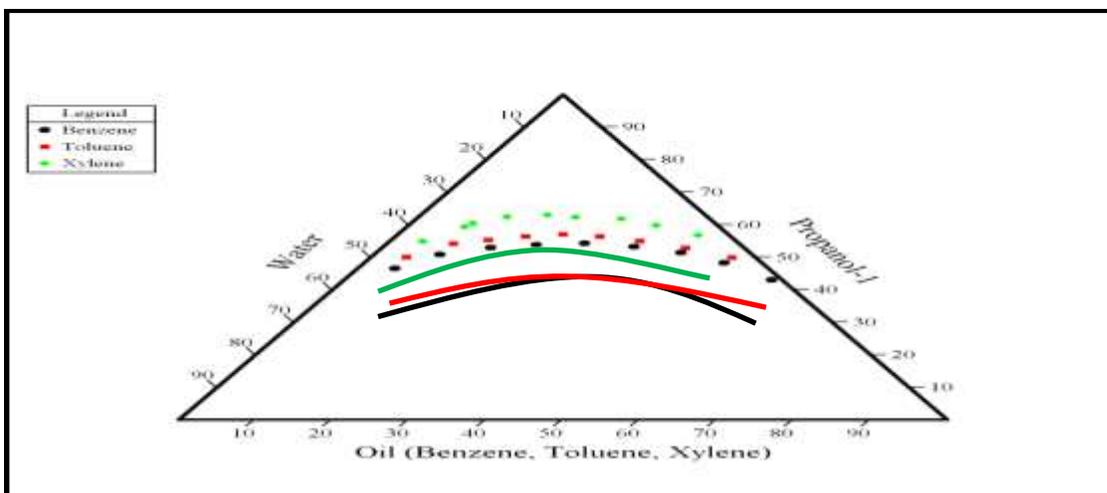
**Fig.4:** Plots of density of micro-emulsion formed with different concentrations of Tween-20 surfactant in propanol-1, butanol-1, and methanol.



**Fig.5:** Plots of density of micro-emulsion formed with different concentrations of sodium decylsulfate surfactant in propanol-1, butanol-1 and methanol.



**Fig.6:** Plots of density of micro-emulsion formed with different concentrations of tetradecyltrimethylammonium bromide surfactant in propanol-1, butanol-1 and methanol.



**Fig.7:** Ternary Phase diagram for the micro-emulsions of water-propanol-1-(benzene, toluene, xylene) for fixed sodium decylsulfate.

The decreasing free energy due to this entropy change may exceed the increase caused by creation of interfacial area and thus resulting in negative free energy change. Liu and coworkers (20) studied the important phase behavior of Taxes/toluene/water micro-emulsion systems for solubilization absorption of toluene recently.

The comparative effects of surfactants in formulation of micro-emulsions have been summarized as follows:

- (i) Reduction of interfacial tension of oil and water.
- (ii) Entropy increase and decrease in free energy by dispersion of surfactant.
- (iii) Nonionic surfactants could give a more expanded film and allows rapid transportation of alcohol.
- (iv) Cationic and anionic surfactants reduce interfacial tension of water and oil in almost same amount as both the surfactants have C-12 structures.
- (v) Tetradecyltrimethylammonium bromide (TTAB) shows more effective micro-emulsion formulation if propanol-1 as co surfactant was used.
- (vi) Amount of co surfactants used for the formulation of micro-emulsion decreases with increasing amount of the surfactants in all the systems.

The influence of all above factors depends upon phase continuity and composition of micro-emulsion.

**TABLE-1**

Volume percentage composition of water, toluene, propanol-1 in micro-emulsion formed by different surfactants.

<b>TTAB</b>									
Water	43.44	36.17	30.09	24.65	19.48	15.05	10.56	5.70	2.09
Toluene	4.64	8.67	12.60	17.01	21.49	26.62	32.48	39.51	47.05
PrOH-1	51.92	55.16	57.31	58.34	59.03	58.33	56.58	54.79	50.86
<b>NaDeS</b>									
Water	45.34	38.07	31.99	26.55	21.38	16.95	12.46	7.60	3.99
Toluene	4.85	8.88	12.81	17.22	21.70	26.83	32.69	39.72	47.26
PrOH-1	49.81	53.05	55.20	56.23	56.92	56.22	54.85	52.68	48.75
<b>T-20</b>									
Water	44.47	38.14	32.06	25.69	19.81	14.09	9.05	5.05	2.53
Toluene	4.75	7.62	10.69	15.45	20.77	26.93	33.69	39.66	46.50
PrOH-1	50.78	54.24	57.25	58.56	59.42	58.98	57.26	55.29	50.97

**TABLE-2**

Micro emulsification using different amount of surfactant, Tween-20 with cosurfactants. oil=10 ml, water=90 ml. co surfactants, propanol-1, butanol-1 and methanol.

Surfactant (g)	Propanol-1 (ml)	Density (g cm <sup>-3</sup> )	Viscosity (cP)
1.0	220.32	0.8652	1.182
2.0	178.22	0.8730	1.351
3.0	145.10	0.8811	1.600
4.0	107.50	0.8882	2.901
5.0	87.00	0.8960	2.301
Surfactant (g)	Butanol-1 (ml)	Density (g cm <sup>-3</sup> )	Viscosity (cP)
1.0	270.22	0.8571	1.300
2.0	213.40	0.8645	1.468
3.0	173.50	0.8722	1.748
4.0	130.20	0.8798	2.067
5.0	93.20	0.8871	2.426
Surfactant (g)	Methanol (ml)	Density (g cm <sup>-3</sup> )	Viscosity (cP)
1.0	570.20	0.8331	0.115
2.0	485.12	0.8352	0.250
3.0	405.10	0.8368	0.412
4.0	333.40	0.8382	0.613
5.0	265.60	0.8394	0.956

**TABLE-3**

Micro emulsification using different amount of surfactant, Sodium decylsulfate (NaDeS) with co surfactants.

oil=10ml, water=90ml, co surfactants= propanol-1, butanol-1 and methanol.

Surfactant (g)	Methanol (ml)	Density (g cm <sup>-3</sup> )	Viscosity (cP)
0.25	245.20	0.8556	1.3802
0.50	180.10	0.8645	1.4811
0.75	130.15	0.8735	1.6613
1.00	83.40	0.8821	2.0312
Surfactant (g)	Methanol (ml)	Density (g cm <sup>-3</sup> )	Viscosity (cP)
0.25	270.40	0.8631	1.5012
0.50	205.00	0.8720	1.6210
0.75	150.10	0.8812	1.8120
1.00	105.10	0.8896	2.1401
Surfactant (g)	Methanol (ml)	Density (g cm <sup>-3</sup> )	Viscosity (cP)
0.25	445.10	0.8342	0.4201
0.50	405.15	0.8365	0.5102
0.75	390.21	0.8381	0.6925
1.00	280.10	0.8396	0.9402

**TABLE-4**

Micro emulsification using different amount of surfactant, tetradecyltrimethylammonium bromide (TTAB) with cosurfactants. oil=10 ml, water=90 ml, co surfactants propanol-1, butanol-1 and methanol.

Surfactant (g)	Methanol (ml)	Density (g cm <sup>-3</sup> )	Viscosity (cP)
0.25	185.10	0.8640	1.526
0.50	140.20	0.8725	1.688
0.75	110.30	0.8810	1.886
1.00	95.10	0.8889	2.175
Surfactant (g)	Methanol (ml)	Density (g cm <sup>-3</sup> )	Viscosity (cP)

0.25	380.10	0.8210	1.4521
0.50	315.55	0.8278	1.5932
0.75	270.40	0.8346	1.8021
1.00	223.10	0.8408	2.0864
Surfactant (g)	Methanol (ml)	Density (g cm <sup>-3</sup> )	Viscosity (cP)
0.25	740.10	0.8052	0.2103
0.50	660.65	0.8085	0.3155
0.75	580.40	0.8121	0.5164
1.00	510.20	0.8148	0.7822

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