

A SYSTEMATIC STUDY OF FORMATION OF MICRO-EMULSION WITH THE HELP OF TERNARY PHASE DIAGRAM IN THE PRESENCE OF DIFFERENT CO-SURFACTANTS AND HYDROCARBONS

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ABSTRACT

This paper comprises the studies of micro-emulsion. 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. The role of alcohol in particular is interpreted by means of its auto association in the organic pseudo-phase and its position between core, membrane, and continuous phase of micro-emulsion. Main role of alcohol addition is not only increase interfacial pressure to a level where final interfacial tension could reach zero or below by penetration of alcohol into interfacial layer by means of alcohol-surfactant association but also cause initial reduction of oil-water interface. Two effects would be expected on addition of hydrocarbon to the system (i) Solubility region may be changed (ii) Association concentration within the solubility region may be altered.

ABBREVIATIONS: Micro-emulsion, co-surfactants, ternary phase diagram. Surfactant, Water-alcohol system, Tween20, TTAB, NaDeS.

Introduction

Micro-emulsions are clear, stable, isotropic liquid mixtures of oil, water and surfactant, frequently in combination with a co-surfactant. In ternary systems such as micro-emulsions, where two immiscible phases (water and oil) are present with a surfactant, the surfactants molecules may form a mono layer at the interface between the oil and water, with the hydrophobic tails of the surfactant molecules dissolved in the oil phase and the hydrophilic head groups in the aqueous phase (1). Numerous experiments have been cited (2,3) on micro-emulsions which provide information regarding their formation, properties, structure and stability. Micro-emulsions are isotropic, optically transparent, stable dispersions of oil-in-water or water-in oil. Li and Kunieda (4) reported the micro-emulsion formation and solubilization in presence of cationic surfactants. Schulman et al, (5) have reported that such dispersions occur spontaneously by mixing two immiscible liquids and different types of surfactants in specific proportions. According to Danielsson and Lindman (6), a system of water, oil and amphiphile which is single optically isotropic and thermodynamically stable liquid solution is called micro-emulsion. In recent years, micro-emulsion have attracted a great deal of attention of researchers in academic circles as well as in industrial era as they possess tremendous potentials for many applications in several industries viz. detergents, pharmaceuticals, cosmetics, lubricants, in enhanced oil recovery, in solar energy storage, nutrition industries in biochemistry, in artificial blood and many more.

Seang and coworkers (7) 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 (8). Moilliet et al., (9) 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. (5). The second class by Shinoda and Friberg (10) includes the solubilization theories and third principle includes thermodynamics treatments by Ruchenstein and Chi (11). 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 (12) recently. The factor responsible for micro-emulsion stability are (10-13) 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 (14). 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

Materials

Following surfactants, oils and aqueous phase were used in formulating micro-emulsions.

(i) Surfactant

- (a) Nonionic surfactant - Tween 20.
- (b) Anionic surfactant - Sodium decylsulfate (NaDeS).

(c) Cationic surfactant - Tetradecyltrimethylammonium bromide (TTAB).

(ii) Alcohols - Methanol, Propanol-1, Butanol-1,

(iii) Oil phases - Toluene, Xylene, Benzene, n-haptane, n-decane.

(iv) Aqueous phase - Double distilled water.

Method

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.

Results and Discussion:

(i) Effect of Alcohols

The influence of co-surfactant (alcohols) for the formation of micro-emulsions has been studied and is reported in **Table-1, 2, and 3**. Amount of co-surfactant necessary to give rise of micro-emulsion is dependent of order in which components are added. The role of alcohol in particular is interpreted by means of its auto association in the organic pseudo-phase and its position between core, membrane and continuous phase of micro-emulsion. Main role of alcohol addition is to;

- (i) Increase interfacial pressure to a level where final interfacial tension could reach zero or below by penetration of alcohol into interfacial layer by means of alcohol-surfactant association.
- (ii) Cause initial reduction of oil-water interface.

In the first step, film will be expanded and its pressure will be low. While in the second step, the higher alcohol concentration reduces electrostatic repulsion so that liquid condensed film of high spreading pressure will develop. Alcohol molecules will be in excess and although the film will remain condensed, the strong electrostatic, repulsive forces will weaken so that pressure will be lower than in second stage in addition to specific interaction present between hydrocarbon and surfactants. Schulman and Montague (18) first introduced the concept of negative surface due to addition of alcohol. Prince (19) suggested considering surface tension of hydrocarbon, water and surfactant instead of water hydrocarbon interface. The effect of structure of oil phase, surfactant and co-surfactant on the physicochemical and electrochemical properties of discontinuous has been reported by Sripriya and coworkers (20). The possible mechanism of alcohol addition is that alcohol molecules position themselves in bi layer with their hydroxyl group adjacent to hydrophilic head group of surfactant molecules in the surface zone of lamellae. Alcohol tails undergo rapid motion as to the surfactant tail group in the interior of bilayer. The free energy loss which derives the surfactant from aqueous solution to form lamellar

phase, is probably what derives alcohol to partition in ordinary way in lamellae with sufficient alcohol present. Both in higher water/oil and lower water/oil ratio droplet size of water and oil is smaller, so amount of alcohol required to solubilize dispersed droplet is less. At fixed water/oil ratio, tendency of alcohol at interface increase in order of their miscibility with hydrocarbon and immiscibility with water. The nature of alcohol plays an important role in the formation of micro-emulsion.

In **Figures 1, 2 and 3** are shown schematic phase diagrams of water-alcohol-toluene-surfactant systems. Data reported in **Table-1, 2 & 3** showed that on addition of alcohol to phase equilibrium in ternary systems of water-surfactant-oil reveals that methanol acts as less powerful co-surfactant to give micro-emulsion, which may be attributed due to the higher solubility of methanol in water involving stronger hydrogen bonding and thus less effectively weakening the electrostatic repulsive forces. At fixed water-oil ratio, more amount of methanol is needed for the formulation of micro-emulsions. This is due to its more miscibility with water which provides less tendency of methanol to orient away at interface. The lesser tendency of methanol as co-surfactant for micro-emulsions formation has been noticed in presence of all surfactants used (**Table-1, 2, 3**). Further, in case of tetradecyltrimethylammonium bromide(TTAB)+water+toluene system, the efficiency of methanol to act as co-surfactant is much poorer in comparison to other surfactant systems. This may be attributed due to the negatively charged hydroxyl group possessing its position adjacent to hydrophilic head group of cationic surfactant and thus showing more orientation instead of attraction. It becomes increasingly difficult to make micro-emulsion with alcohol of higher hydrocarbon chain i.e. from butanol and onwards. It is reasonable that surfactant must be able to stabilize the system against coagulation after co-surfactant has lowered interfacial tension sufficiently to cause dispersion. When there is no mutual solubility of solvent (higher alcohol-water) mixture, surfactant is not able to stabilize oil and water. This is why no micro-emulsions could be formed in our systems with higher alcohols. One more reason behind this may be their less hydration capacity over the whole range of water-oil ratio, propanol-1, butanol-1 and methanol in the order proved respectively the best alcohols in micro-emulsion formation.

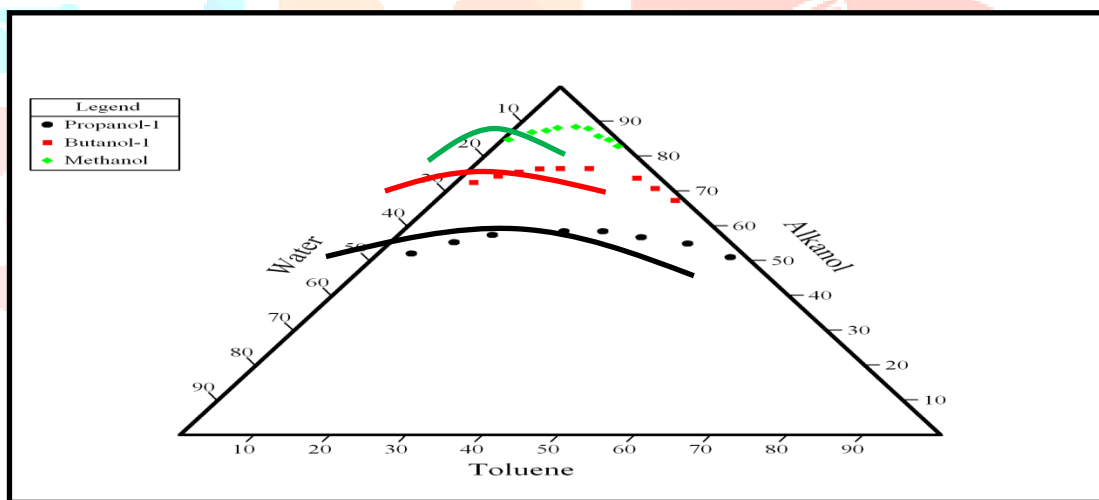


Fig.1: Ternary Phase diagram for the micro-emulsions of water-toluene-propanol-1, butanol-1 and methanol for fixed tetradecyltrimethylammonium bromide.

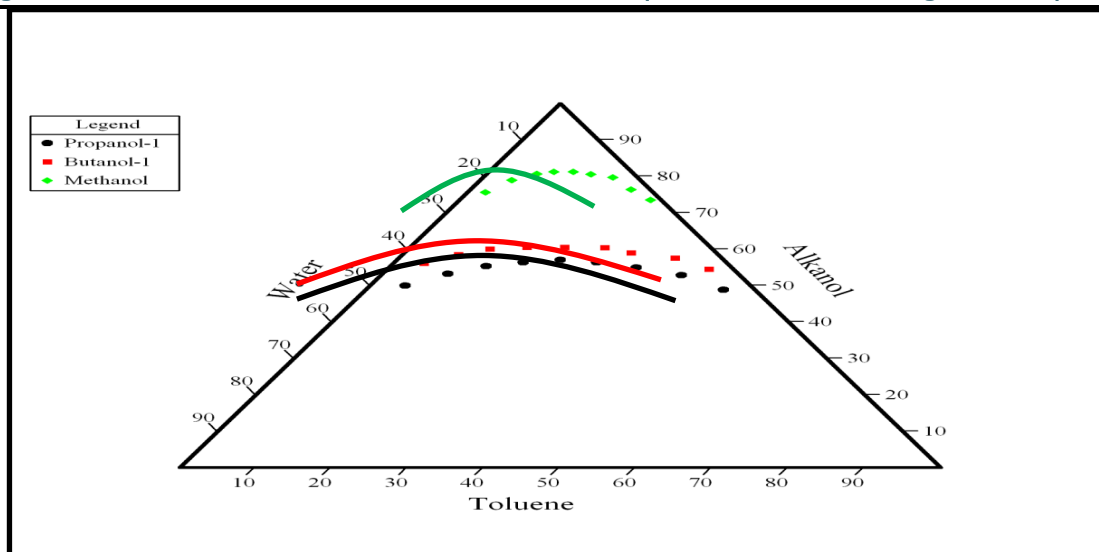


Fig.2: Ternary Phase diagram for the micro-emulsions of water-toluene-propanol-1, butanol-1 and methanol for fixed sodium decylsulfate.

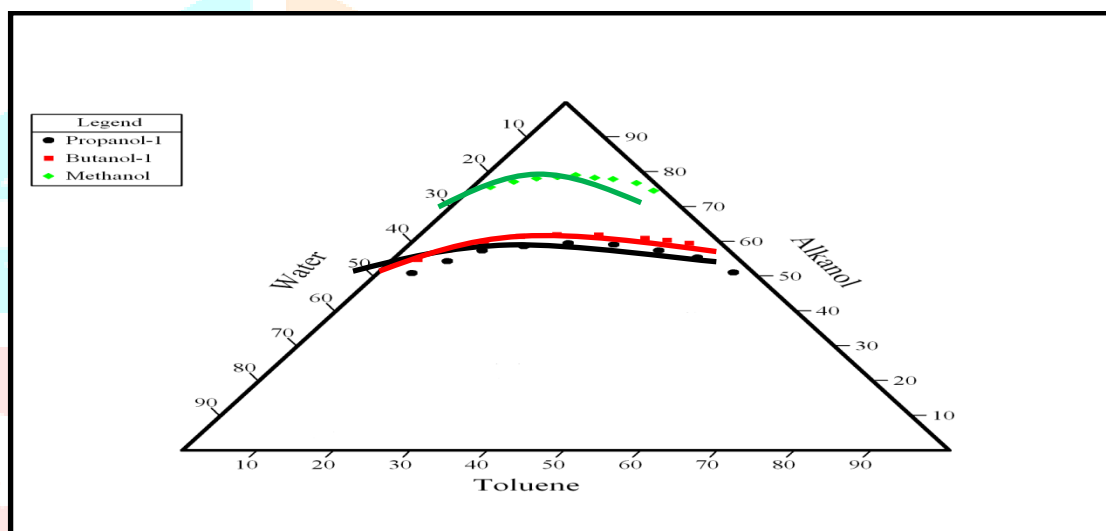


Fig.3: Ternary Phase diagram for the micro-emulsions of water-toluene-propanol-1, butanol-1 and methanol for fixed Tween-20.

The values reported in **Table-4** are the volume percentage of alcohol used, densities and viscosities of micro-emulsions formed. The lower values of viscosities and densities of micro-emulsions formed in presence of methanol also confirm the finding that methanol acts as relatively poor co-surfactant for these systems.

(ii) Effect of Hydrocarbon

The influence of oil phase on micro-emulsion formulation has been studied by varying oil phase. Different aromatic and aliphatic hydrocarbons were used as oil phase. However, no stable micro-emulsion formulation could be obtained in case of aliphatic hydrocarbon used (i.e. n-heptane, n-octane, n-decane). The case of micro-emulsion formation in case of aromatic hydrocarbon may be explained by the fact that no progressive aggregation occurs in case of benzene, like non-polar media. Also, the intersection of electrons of the benzene ring and the hydroxyl group of alcohol give rise to the formation of micro-emulsion. In **Table-5**, the results of volume percentage composition for micro-emulsion systems using toluene, benzene, and xylene as oil phase in the presence of 1% sodium decylsulfate are reported. A substitution reaction in an oil-in-water micro-emulsion catalyzed by a phase transfer catalyst was observed by Hager and Holmberg (20). Data reveals that formulation of micro-emulsion in case of aromatic hydrocarbon used as oil phase shows almost closer values and thus confirms similar formulation of micro-emulsion.

The oil influences phase continuity of emulsion. Relative wet ability of interfacial film by oil and water determines phase continuity. Behaviour of oils in micro-emulsion formation can be summarized to be based on following factors:

- (i) Molecular volume of hydrocarbon.
- (ii) Polarity effect of hydrocarbon.
- (iii) Interfacial tension values at oil/water interface.
- (iv) Distribution of alcohol between oil phase and interface.

TABLE-1

Volume percentage composition of water, toluene, propanol-1, butanol-1 and methanol in micro-emulsion formed by 1% tetradecyltrimethylammonium bromide (**TTAB**) surfactant.

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
Water	25.03	20.92	17.59	14.38	11.59	7.85	2.95	2.05	1.12
Toluene	2.59	4.92	7.05	9.31	12.00	15.78	23.48	27.33	31.62
BuOH-1	72.38	74.16	75.36	76.31	76.41	76.37	73.57	70.62	67.26
Water	14.24	10.14	7.98	6.19	3.65	2.24	1.94	1.10	0.90
Toluene	1.10	3.10	4.72	5.81	8.07	9.92	12.41	14.35	16.37
Methanol	84.66	86.76	87.30	88.00	88.28	87.84	85.65	84.55	82.73

TABLE-2

Volume percentage composition of water, toluene, propanol-1, butanol-1 and methanol in micro-emulsion formed by 1% sodium decylsulfate (**NaDeS**) surfactant.

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
Water	40.61	34.03	29.09	24.04	19.08	13.88	11.14	6.09	3.09
Toluene	4.32	7.65	11.00	15.65	20.55	25.90	30.05	36.55	42.55
BuOH-1	55.97	58.32	59.91	60.31	60.37	60.22	58.81	57.36	54.36
Water	21.91	16.82	12.69	10.14	7.59	5.61	3.12	2.42	1.28
Toluene	2.62	4.41	6.86	8.85	11.37	13.96	17.39	21.38	25.40
Methanol	75.47	78.77	80.45	81.01	81.04	80.43	79.49	76.20	73.32

TABLE-3

Volume percentage composition of water, toluene, propanol-1, butanol-1 and methanol in micro-emulsion formed by 5% **Tween-20** surfactant.

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
Water	41.74	36.49	30.55	25.09	20.09	14.66	9.12	6.47	4.09
Toluene	3.55	6.06	9.55	13.55	18.05	23.55	30.03	33.27	36.55
BuOH-1	54.71	57.45	59.90	61.36	61.86	61.79	60.85	60.26	59.36
Water	21.90	18.06	14.65	11.7	9.06	6.91	4.76	2.29	1.10
Toluene	2.61	4.91	7.37	9.91	12.03	14.91	17.41	21.03	24.41
Methanol	75.49	77.03	77.98	78.39	78.91	78.18	77.83	76.68	74.49

TABLE-4

Formation of micro-emulsion and their physical properties in different surfactants, different co-surfactants, and oil.

Surfactants, Tween-20 (5%), sodium decylsulfate (1%), tetradecyltrimethylammonium bromide (1%), oil, toluene=10 ml (fixed), water= 90 ml (fixed).

Co-surfactants, propanol-1, butanol, methanol added till turbidity just disappears.

Surfactant(g)	Co-surfactant	Volume (ml)	Density (g cm ⁻³)	Viscosity (cp)
Tween-20	Propanol-1	90.00	0.8960	2.3010
	Butanol-1	96.04	0.8871	2.4262
	Methanol	260.00	0.8394	0.9560
Sodium decylsulfate (NaDeS)	Propanol-1	85.50	0.8821	2.0312
	Butanol-1	106.20	0.8896	2.1401
	Methanol	278.40	0.8396	0.9402
Tetradecyltrimethyl ammonium bromide (TTAB)	Propanol-1	95.40	0.8889	2.1753
	Butanol-1	230.00	0.8408	2.0864
	Methanol	510.50	0.8148	0.7822

TABLE-5

Volume percentage composition of (water, benzene, propanol-1), (water, toluene, propanol-1) and (water, xylene, propanol-1) in micro-emulsion formed by 1% sodium decylsulfate surfactant.

Water	48.45	40.46	32.81	26.44	19.99	14.00	8.87	4.81	1.25
Benzene	5.12	8.85	14.35	19.90	25.88	32.86	39.89	47.08	55.90
PrOH-1	46.43	50.69	52.84	53.66	54.13	53.14	51.24	48.11	42.85
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
Water	42.71	33.00	29.44	26.01	20.45	16.08	10.45	6.88	4.96
Xylene	4.60	7.80	8.27	11.78	16.77	20.77	26.88	32.42	39.37
PrOH-1	54.69	59.20	60.29	62.21	62.78	62.15	61.67	59.70	56.67

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