



STABILIZATION OF O/W EMULSIONS BY POLYMER SURFACTANT MIXTURE

**SHAILENDRA KUMAR PARIHAR, ASHOK K. GOSWAMI*
and A. M. RAINA**

Department of Chemistry, K. R. (P. G.) College, MATHURA - 281 001 (U. P.) INDIA

ABSTRACT

Mixed emulsifiers consisting of a nonionic (PVP) or cationic polymer (JR-400) and ionic surfactant (anionic sodium dodecylsulphate, SDS and cationic dodecyltrimethylammonium bromide, DTAB) have been found to produce greater stabilizing effects than single polymer or surfactant taken separately as emulsifiers. Greater emulsion stability of such systems is ensured by the presence of a protective layer formed by the polymer and charged species resulting from polymer/surfactant interaction. This result is of significant practical importance. The combination of surfactant and polymers improved the desired properties of the products because addition of a polymer enhances the adsorption of surfactants to a surface.

Key words: Polymer, Surfactant, Emulsion, Stabilization.

INTRODUCTION

The adsorption and orientation of polymer/surfactant complexes at various interfaces and their effect on the stability of emulsion is a subject of great importance in the major areas of formulation of dye stuffs, pesticides, pharmaceuticals etc. Emulsion paints, which at present, have gained much importance, involve the use of polymers (polyvinyl acetate) and surfactants. It is a common practice to use more than one dispersing agent to formulate emulsions, which in many cases could be a combination of a surfactant and a polymer^{1,2}.

In recent years, much attention has been paid to the behaviour of polymers at interfaces. When polymer is adsorbed on the surface of the particles of a colloidal dispersion, the stability of the dispersion is usually affected. Polymers at low concentrations bring flocculation of the system, whereas at high concentrations, the system

* Author for correspondence; Dr. Ashok Kumar Goswami, Radha Raman Street, Vrindavan – 281121 (U.P.)

may be strongly stabilized³. Szelag et al.⁴ investigated properties of emulsion systems stabilized by mixtures of monoacyl glycerols and ethoxylated methyl esters of fatty acids. The behaviour of emulsions stabilized by polyelectrolytes has been studied by Bohm and Lyklema⁵. Tadros⁶ investigated the stability of O/W emulsion stabilized by a mixture of polymer and surfactant and found that the stability of the emulsion increases with an increase in the surfactant concentration. Becher⁷ has reviewed the stability of emulsions stabilized by low molecular weight surfactants. In the present paper, an attempt has been made to study the mechanisms that unfolds and explains the process of stabilization of emulsions using high molecular weight polymers and their mixture with surfactant.

EXPERIMENTAL

Materials

- (i) Sodium dodecylsulphate (SDS) was specially pure material obtained from Sigma, Chemical Co., U.S. A.
- (ii) Dodecyltrimethylammonium bromide DTAB (Aldrich Chemical Company, Inc, Wisconsin, U,8A) was recrystallized from ethanol – acetone mixture.
- (iii) Polymer JR-400; Quaternary nitrogen substituted cellulose ether (mol. weight 400,000) is a product of Union Carbide Corporation, New York, USA.
- (iv) Polyvinyl pyrrolidone (PVP, Wako Pure Chemical Ind., Co. Japan) was used as such.

The oil phase xylene was used without further purification, Solutions were prepared using doubly distilled water in a glass apparatus and were prepared fresh, whenever needed for experiments.

All glasswares were thoroughly cleaned and steamed before use.

Preparation of emulsion

The xylene in water emulsions were prepared by suspending 30% by volume of xylene in 70% by volume of the aqueous phase containing surfactant, polymer or mixture. The emulsion was first shaken for about 15 minutes and then homogenized by double pass through a laboratory hand homogenizer. The time of emulsification was kept constant.

Haemocytometric and microelectrophoretic studies

The particle concentration of the diluted emulsion was determined by manual

technique using haemocytometer cell. Counts were taken in 64 squares of a calibrated graticule fitted in the eye piece with a hand tally counter under an Olympus microscope using 15 x 40 times magnification, A duplicate counting was always carried out and the average of the two was taken to calculate the number of particles. The zeta potential of emulsion was determined by microelectrophoretic technique.

RESULTS AND DISCUSSION

Emulsion stabilized by nonionic (PVP) or cationic (JR-400) polymer

Since the volume of oil (30% by volume), time and power of emulsification were kept constant, a comparison of the initial counts of oil droplets of different emulsions after an hour of their preparation, using a haemocytometer cell under a microscope gives a measure of their relative stability. Oil droplets in a definite volume of emulsion in the haemocytometer cell were counted within the same number of squares of a graticule. Results of the same are compiled in the Table 1.

Table 1. Initial counts of oil droplets in various emulsifying solutions (a) Polymer stabilized emulsions -

Concentration (%)	Initial no. of oil droplets /mL x 10 ⁻³	
	PVP	Polymer JR-400
0.01	0.42	1.05
0.05	0.50	1.17
0.10	0.68	1.21
0.15	0.71	1.30
0.20	0.83	1.43

Total number of emulsion droplets formed in the presence of PVP is less than the surfactant stabilized emulsion (Table 1). Increasing concentrations of polymer results in an increase in the number of droplets. Emulsions stabilized by cationic polymer JR 400 have appreciably greater number of droplets in comparison to PVP stabilized emulsion. Evidently such emulsion possesses greater stability.

PVP, a high molecular weight emulsifier, is non-polar. Hence, it is incapable or imparting charge to emulsion droplets despite its easy adsorption. Due to the absence of charge on the emulsion droplets, there is every possibility of flocculation. But the thick

protective layer formed by PVP around the droplets minimises the possibility of coalescence surfactants (like SDS and DTAB are polar substances and are more easily adsorbed on the emulsion droplets on account of their high surface activity. All the emulsion droplets carry like charge due to surface active ion on the surfactants. Like charge on the emulsion droplets keeps them away due to repulsion and thus, prevents flocculation. Since the protective films that surfactants form round the emulsion droplets are not as tough as the films by polymers, chances of coalescence are greater in comparison to PVP stabilized emulsions.

Table 2. Counts in HTAB stabilized emulsion in the presence and absence of PVP

Concentration of DTAB (mole/litre)	Initial number of droplets/mL $\times 10^{-8}$	Concentration of PVP (%)
-	0.00	0.10
1.0×10^{-7}	1.73	1.95
1.0×10^{-6}	1.85	2.05
1.0×10^{-5}	1.97	2.17
1.0×10^{-5}	2.16	2.32
1.0×10^{-4}	2.30	2.49
1.0×10^{-4}	2.43	2.58
1.0×10^{-3}	2.68	2.77
1.0×10^{-3}	2.87	3.05
1.0×10^{-2}	3.06	3.33

A cationic polymer JR-400 imparts positive charge to all the emulsion droplets. Thus, it not only rules out the possibility of coalescence but also checks flocculation. Positive charge on the emulsion droplets plays a vital role in stabilizing the emulsion.

As no flocculation occurs in cationic polymer stabilized emulsions, number of droplets is consequently greater as compared to nonionic polymer stabilized emulsion. Since the increased concentration of any polymer improves the thickness of its protective layer, thereby increasing the resistance of droplets to coalescence, greater number of droplets exists in the emulsions. Hence, stability of emulsion also increases.

Stabilization of emulsion by a mixture of nonionic polymer (PVP) and anionic (SDS) or cationic (DTAB) surfactant

Total number of droplets formed in emulsion stabilized by anionic (SDS) and cationic (DTAB) surfactants is shown in the Table 1. Number of droplets formed in such stabilized emulsion is greater than emulsion stabilized by polymers. With increasing concentrations of surfactants, number of emulsion droplets also goes on increasing. Table 1 further shows that nonionic polymer PVP + anionic surfactant SDS stabilized emulsion has greater number of droplets than nonionic polymer PVP + cationic surfactant DTAB stabilised emulsions.

Mixed emulsifiers PVP + SDS and PVP + DTAB produce greater stabilizing effects than any surfactant or polymer taken alone. As such, the number of emulsion droplets is greater than number of droplets in emulsion stabilized by a polymer or surfactant alone.

Interaction of nonionic polymers with anionic surfactant (SDS) produces highly charged polyelectrolyte, which is readily adsorbed onto the oil droplets due to which a tough protective film is formed round the oil droplets and a high negative charge is developed. Tough protective film obviously checks coalescence and high negative charge minimizes chances of flocculation.

Though the mixture of nonionic polymer PVP and cationic surfactant DTAB produces the similar effect, their interaction in this case is comparatively weak. Hence, the number of emulsion droplets is less than the emulsion stabilized by a mixture of nonionic polymer PVP and anionic surfactant SDS, and clearly, the stability is also less in this case.

This result is of significant practical importance as it is possible to increase the stability of an emulsion against coagulation by using a mixture of polymer with an ionic surfactant. Thus, the mixture of a nonionic polymer and an ionic surfactant as emulsifier finds more significant utility in preparation of emulsion than simple surfactants or polymers alone.

In the absence of PVP, the oil droplets attain considerable zeta potential of + 60 mV at the lowest DTAB concentration (5×10^{-5} M) after which the zeta potential increases gradually with increase in DTAB concentration reaching a maximum value + 90 mV at and the above 5×10^3 M concentration. The same trend is observed with SDS and the zeta potential reaches a maximum value of - 95 mV at 5×10^3 M concentration of SDS.

In the presence of PVP, the zeta potential of the oil droplets in DTAB solutions at concentration less than 10^{-3} M dropped to a value very close to zero, after which it rises rapidly until a maximum value was reached.

The lowering of the zeta potential on addition of PVP to a given surfactant solution could be accounted for by polymer/ surfactant interaction at the interface. At low surfactant concentration, the interaction is weak and thus, the value of zeta potential is very close to zero and in the intermediate surfactant concentration region, there is strong interaction between the surfactant and polymer, which is accompanied by rapid uptake of surfactant ions and forming highly charged complex. This explains the rapid increase in zeta potential at intermediate surfactant concentrations.

Emulsions stabilized by mixture of cationic polymer (JR-400) and anionic surfactant (SDS)

When the concentrations of anionic surfactant SDS was increased in the mixed emulsifiers SDS + JR-400, keeping the concentration of JR-400 constant, the effect is that the number of droplets decreases rapidly and comes to a minimum when the concentration of SDS is 5×10^{-3} moles/litre. If the concentration of SDS exceeds the above value, number of droplets increases. Thus, the stability of emulsion first decreases, comes to a minimum and then starts increasing with increasing concentration of SDS.

When the concentration of anionic surfactant SDS was increased in the mixture SDS + JR-400, anion DS neutralizes the charge of the cationic polymer JR-400, resulting in the formation of a nonionic complex as a thick precipitate without any emulsifying activity and adsorbability. At this stage, no emulsion is formed.

If the concentration of anionic surfactant SDS was further increased, solubilization of precipitated complex takes place due to excess of DS ions and it is changed into soluble polyelectrolyte, which forms a rigid protective layer round the oil droplets and imparts to them a high negative charge. Protective layer now checks coalescence and the high negative charge on the droplets completely prevents any flocculation.

At very low surfactant concentration, the system SDS + 0.1% JR-400 assume positive charge but as the concentration of SDS increases, the zeta potential first decreases, then reversal of charge takes place and finally the value of zeta potential shows an increase in the reversed direction

In this system, the polymer is positively charged and due to its dominant effect, the

zeta potential of the emulsion at low SDS concentration is positive but as the concentration of surfactant SDS increases, the charge of the polymer is neutralized as a result of which the value of zeta potential becomes zero. On further increasing the concentration of surfactant, the charge of the emulsion is reversed due to the formation of highly negative charged polymer/surfactant complex. The formation of polymer/ surfactant complex imparts greater stability to the emulsion.

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