

Surface Properties of Aqueous Solutions of 2-Hydroxypropylmethacrylate

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Some monomers can decrease surface tension and critical micelle concentration. In this study, the effect of 2-hydroxypropylmethacrylate on stability of emulsion system and its distribution into toluene water system, surface tension, surface entropy, surface enthalpy and half-decay time with sodium lauryl sulphate as an anionic emulsifier has been investigated. Results showed that the surface tension and critical micelle concentration in the presence of monomers decreased. The stability and homogeneity of the system in the presence of monomers increased.

Key Words: 2-Hydroxypropylmethacrylate, Emulsifier, Critical micelle concentration, Surface properties, Emulsion.

INTRODUCTION

Diluted emulsions are Newtonian systems, but in concentrated emulsions, drop of disperse phase react with each other and show non-Newtonian behaviour. Substantially, the viscosity of continuous phase has an important role in determining the rheological characteristics. The viscosity of emulsion is always more than the viscosity of the continuous phase, but it is sometimes more than the viscosity of the disperse phase. The areas of application of micelle-forming surfactants largely depend on surface properties of their aqueous solutions and on their emulsifying and stabilizing abilities. In water-oil emulsions, utilization of two emulsifiers one of which is soluble in water and another soluble in oil are effective. In this case, the mixture of emulsifiers can decrease interfacial tension of oil and water by 200 times. Increase of hydrophobic group in surface active agents facilitates micelle formation. Each group of CH_2 can decrease critical micelle concentration in ionic surface active agents 50 % up to C_{16} and in nonionics the decrease is more remarkable. In C_{18} and higher, critical micelle concentrations are constant for the reason that hydrocarbonic chains in liquid phase are skeining. Increase in temperature causes an increase in the critical micelle concentration and micelle formation do difficulty. In ionic surface active agents change of phase are effected by an increase in electrolyte concentration, which decreases repulsion between neighbouring ions in micelle surface and as a result the CMC decreases. Use of co-surfactant can facilitate micelle formation. These are oily alcohol. Small -OH group can be useful especially when they are mixed with big

head. Alcohols with short chains (C_3 - C_5) tend to form oil in water emulsions (o/w) and alcohols with long chains tend to form inverse emulsions (w/o). Organic substances such as sugar with high concentration can affect water structure and decrease CMC. While urea and formamide destroy the structure and increase CMC, so that micelle formation becomes difficult and slow. With decreasing of the sizes of particles in the process of emulsion formation, the surface of disperse phase increases. Therefore, formation of stable emulsions with small particle dispersion needs emulsions are not thermodynamically suitable systems and have minimum stability¹⁻⁷. In the literature several empirical relationships between structural features to the CMC of homologous compounds have been investigated⁸⁻¹³. There are several reports published on surfactant experiments in which the CMC and surface tension measuring as a function of the concentration of a surface active agent is determined¹⁴⁻²¹. In the present paper CMC variations in the presence of 2-hydroxypropylmethacrylate (2-HPMA) for sodium lauryl sulphate as an anionic emulsifier and its distribution into toluene/water system, surface entropy, surface enthalpy and half-decay time have been investigated.

EXPERIMENTAL

Distilled 2-hydroxypropylmethacrylate (2-HPMA) as monomer has been used under reduced pressure in inert atmosphere (23 mm Hg, TBP = 372 K), sodium lauryl sulphate and toluene were supplied by Merck and doubly distilled water used in all experiments.

Methods: For determination of CMC (Crison GLP 32) a conductometer was used and variation of log molar conductivity *versus* concentration was investigated. Surface properties such as surface tension, surface enthalpy, surface entropy and half-decay time were measured in (toluene/water = 1/2) system. The mechanism of dimerization for monomer by three methods (Ubbelohde viscometer-Shimadzu 1208 UV-Vis spectrophotometer-Crison GLP32 conductometer) was investigated.

RESULTS AND DISCUSSION

All experiments were carried out at 303 K and the emulsion stability and the surface properties determined at 298, 303 and 323 K. The relation of $v_{\text{toluene}} / v_{\text{H}_2\text{O}}$ in emulsions was 1/2.

Study of monomer behaviour in water monomer system: Conductometry, viscometry and UV-Vis spectroscopy in different concentration of the monomer have been used (Figs. 1 and 2). Results of electroconductivity, viscosity and UV-Vis spectroscopy measurements in $\lambda_{\text{max}} = 217$ nm, in different concentration of monomer showed the equilibrium of dimerization of $2(2\text{-HPMA}) \rightleftharpoons (2\text{-HPMA})_2$ between 0.08-0.1 M^{22,23}.

Effect of monomer on the stability of emulsion system and CMC: Molar conductivity measurement of the solution in the presence and the absence of monomer with the concentration of 0.237 M of monomer has been investigated. Figs. 3 and 4

represent log molar conductivity *versus* the concentration of the emulsifier and observation of the break point in graphs identified CMC. Results showed a change in CMC from 0.008 to 0.006 M. In fact, due to presence of -OH functional group in monomer which was discussed in introduction section with the existing references regarding to the effects of alcoholic agents in decrease of CMC, monomer would act as a co-surfactant monomer operated as a co-surfactant.

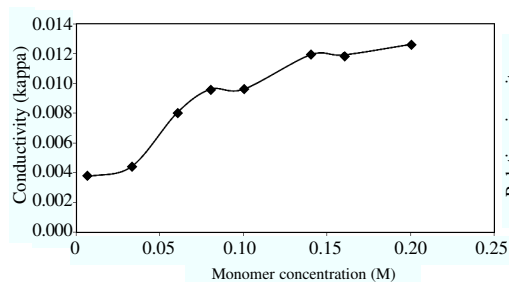


Fig. 1. Conductivity-monomer concentration

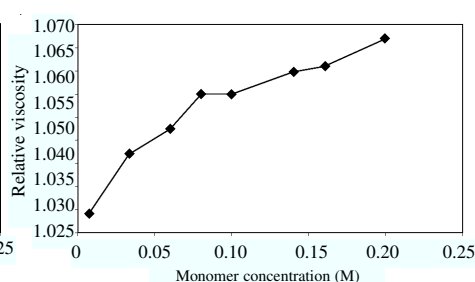


Fig. 2. Relative viscosity-monomer concentration

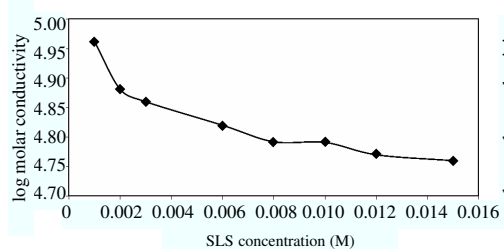


Fig. 3. log molar conductivity-SLS concentration in the absence of monomer

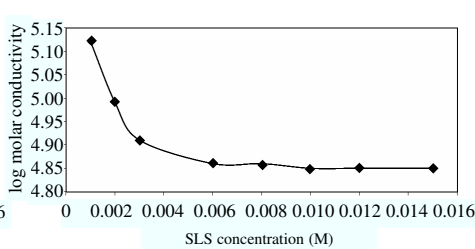


Fig. 4. log molar conductivity-SLS concentration in the presence of 0.237 M monomer

Distribution of monomer into toluene-water system: Surface properties such as surface tension, surface enthalpy and surface entropy investigated with drop method at 25, 30 and 50 °C. Figs. 5 and 6 show on the other hand, we have: $\gamma = G^S = H^S - TS^S$, surface tension measurement in the presence of 1.19 M monomer showed a decrease in the surface tension about 18 %. In these conditions, surface enthalpy and surface entropy changed from 25.91 J to 21.12 J and -0.14 J/°C to -0.13 J/°C, respectively. In addition, half-decay time in the presence of 1.19 M monomer, ($T/W = 1/2$, $T = 25$ °C, sodium lauryl sulphate = 0.5 %) showed an increasing from 35 to 270 min. All these results show that the presence of -OH functional group in monomer 2-HPMA would cause to decrease in the CMC and thermodynamic stability of the system has increased.

SEM: The SEM micrographs of the surface of emulsion systems by a JEOL JSM-5600 scanning electron microscopy have been investigated (Figs. 7 and 8). SEM micrographs showed that in the presence of 1.19 M monomer, the stability

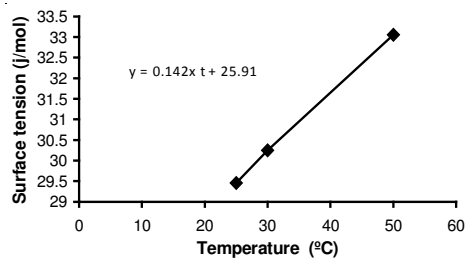


Fig. 5. Surface tension-temperature (T/W = 1/2, SLS 1 %)

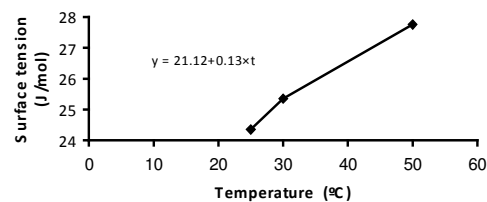


Fig. 6. Surface tension-temperature in the presence of 1.19 M monomer (T / W = 1 / 2, SLS 1%)

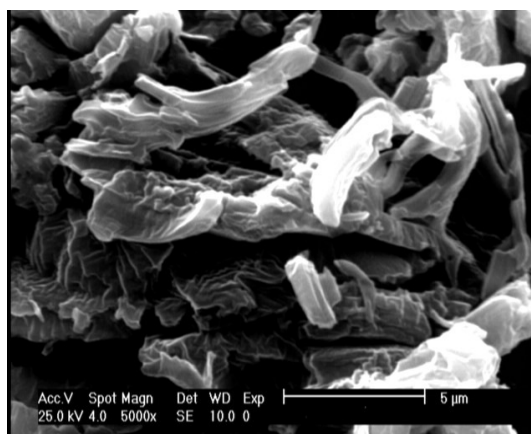


Fig. 7. SEM graphs of (T/W = 1/2), (SLS = 1 %) in the absence of monomer at a magnification of 5000×

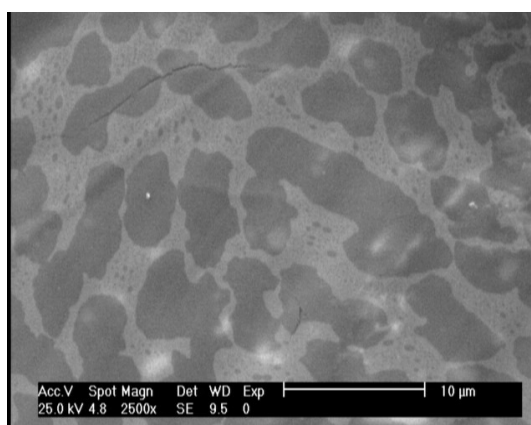


Fig. 8. SEM graphs of (T/W = 1/2)-(SLS = 1 %) in the presence of 1.19 M monomer, at a magnification of 2500×

and homogeneity of the system had increased. However, the size of drops did not change. This emphasized the decrease of surface tension as well as the increase of thermodynamic stability of micelle.

Conclusion

The effect of 2-hydroxypropylmethacrylate on surface properties of toluene-water-emulsifier in the presence of monomer showed decreasing in CMC and surface tension and increasing in half-decay time. On the other hand the size of drops did not change. In fact monomer operated as a co-surfactant. In addition, dimerization possibility observed in 0.08-0.1 M concentration of the monomer.

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