Asian Journal of Chemistry Vol. 22, No. 9 (2010), 7347-7352

Effect of Different Emulsifiers on the Surface Properties of 2-Hydroxypropylmethacrylate

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The application areas of micelle-forming surfactants largely depends on surface properties of their aqueous solutions and on their emulsifying and stabilizing abilities. In this study, the effect of 2-hydroxypropylmethacrylate (2-HPMA) on the stability of emulsion system with different emulsifiers and its distribution on toluene-water system, surface tension, surface enthalpy, surface entropy and half-decay time have been investigated. Results showed that:

$$\tau_{1/2(\text{lecithin})} > \tau_{1/2(\text{DTAB})} > \tau_{1/2(\text{DTAB/CTAB})} > \tau_{1/2(\text{CTAB})}$$

$$\gamma_{(\text{DTAB})} > \gamma_{(\text{CTAB})} > \gamma_{(\text{DTAB/CTAB})} > \gamma_{(\text{lecithin})}$$

$$H^{s}_{(\text{DTAB})} > H^{s}_{(\text{CTAB})} > H^{s}_{(\text{DTAB/CTAB})} \cong H^{s}_{(\text{lecithin})}$$

$$S^{s}_{(\text{DTAB})} > S^{s}_{(\text{CTAB})} > S^{s}_{(\text{DTAB/CTAB})} \cong S^{s}_{(\text{lecithin})}$$

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

INTRODUCTION

In a solution of water and surfactant, the surfactant concentration is higher than critical micelle concentration, apolar organic molecules solve like oil. If the quantity of oil is not much, their apolar molecules are placed beside alkyl chain of surfactant, with addition of oil. In such a case, oil is too emulsified with surfactant. Unless the mixture does not forms spontaneously, it will be turbid and phases do not separate from each other and the system will be thermodynamically stable. This mixture is known as microemulsion. It is not specified when change from dissolved oil to microemulsion occurs. But the property of mixture will change. Further use of oil in microemulsion formation needs energy. This energy can be in the form of fast mixing for oil distribution into the aqueous phase. With the addition of oil, drops will grow so big that the mixture becomes turbid. This position is macroemulsion or normal emulsion. If the rate of aggregation of disperse phase is low, emulsion can be kinetically stable for a long time. Distinguishing microemulsion from macroemulsion is difficult, but microemulsions are thermodynamically stable and limpid[1-5].

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Emulsifiers are important factors for stabilizing emulsions. 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 mixture of emulsifiers could be decreased interfacial tension of oil and water by 200 time. The importance of the CMC has led to its measurement by many researchers, for a wide range of surfactants and under different solvent conditions. Experimental determination of CMC could be performed rather accurately often within a range of uncertainty of just a few percent. There are several reports published on surfactant experiments in which the critical micelle concentration is determined[6-12]. In this study CMC variations in the presence of 2-HPMA lecithin, dodecyltrimethyl ammonium bromide (DTAB), cetyltrimethyl ammonium bromide (CTAB), mixture of (DTAB-CTAB) and some of physical properties of them such as surface entropy, surface enthalpy and half-decay time have been compared.

EXPERIMENTAL

2-Hydroxypropylmethacrylate as monomer has been used after distilled under reduced pressure in inert atmosphere (23 mmHg, T_{BP} = 372 K). Dodecyltrimethyl ammonium bromide (DTAB) and cetyltrimethyl ammonium bromide (CTAB) were provided from Merck and were recrystallized from 50/50 (v/v) = acetone/ethanol mixture. 40 % Ethanol solution egg of lecithin was used after complete evaporation of the alcohol. All of solvents were supplied by Merck and doubly distilled water has been used in all experiments.

The conductivity comparison of the emulsifiers in the absence or presence of monomer investigated by (Crison GLP 32) conductometer and varying of log molar conductivity against concentration identified CMC. Surface tension, surface enthalpy, surface entropy and half-decay time were measured in ($v_{toluene}/v_{water}$ = 1/2) for three different temperature (25, 30 and 50 ºC) by drop method.

RESULTS AND DISCUSSION

Distribution of monomer in toluene-water system (emulsion stability): Table-1 shows the variation of the half-decay time (emulsion stability) in the presence of monomer in different emulsifiers. Results showed that in the presence of monomer and lecithin, half-decay time more than the cationic emulsifiers increased.

TABLE-1
HALF-DECAY TIME FOR DIFFERENT EMULSIFIERS,
([2-HPMA] = 1.19 M, T/W = 1/2, T = 25 ºC)

	$\tau_{1/2}$ (min)	$\tau_{1/2}$ (min)	$\tau_{1/2}$ (min)
Emulsifier/water (g/mL)	0.25 %	0.5 %	0.5 % + monomer
CTAB	7	15	30
DTAB	12	35	75
DTAB/CTAB = 1/1	5	12	40
Lecithin	18	60	90

$$\tau_{1/2(\text{lecithin})} > \tau_{1/2(\text{DTAB})} > \tau_{1/2(\text{DTAB/CTAB})} > \tau_{1/2(\text{CTAB})}$$

Effect of monomer on the stability of emulsiuon system and CMC determination in different emulsifiers: Electroconductivity for determination of variation of CMC in the presence of 0.237 M monomer for different emulsifiers has been used. log molar conductivity *versus* concentration of emulsifier and observation of break point in graphs identified CMC. Results tabulated in Table-2 and Figs. 1-8.

TABLE-2
VARIATION OF log MOLAR CONDUCTIVITY *versus* CONCENTRATION

C × 10^3 (M)	log K/C (lecithin)	log K/C (lecithin + monomer)	log K/C (CTAB)	log K/C (CTAB + monomer)	log K/C (DTAB)	log K/C (DTAB + monomer)	log K/C (DTAB/ CTAB = 1/1)	log K/C (DTAB/ CTAB = 1/1 + monomer)
1	4.604	5.070	5.100	5.430	5.055	5.320	5.050	5.348
2	4.442	4.996	5.000	5.260	5.019	5.250	4.980	5.144
3	4.350	4.828	4.889	5.100	4.997	5.200	4.917	5.091
6	4.180	4.548	4.850	5.010	4.936	5.036	4.900	4.983
8	4.098	4.485	4.765	4.950	4.930	5.006	4.780	4.937
10	4.046	4.334	4.710	4.900	4.921	4.960	4.770	4.897
12	4.043	4.280	4.670	4.860	4.877	4.930	4.700	4.869
15	3.990	4.193	4.630	4.830	-	-	-	-

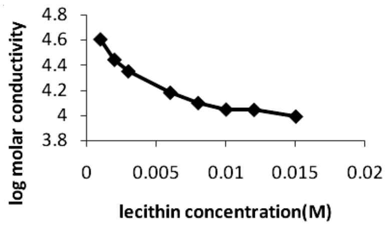

Fig. 1. log molar conductivity-lecithin concentration in the absence of monomer

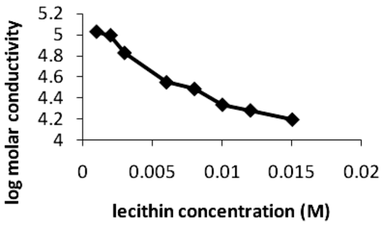

Fig. 2. log molar conductivity-lecithin concentration in the presence of 0.237 M monomer

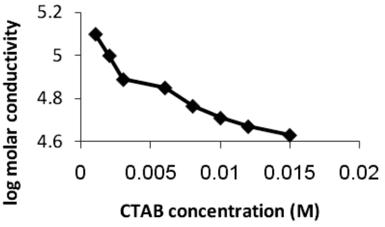

Fig. 3. log molar conductivity-CTAB concentration in the absence of monomer

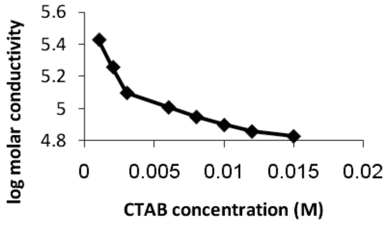

Fig. 4. log molar conductivity-CTAB concentration in the presence of 0.237 M monomer

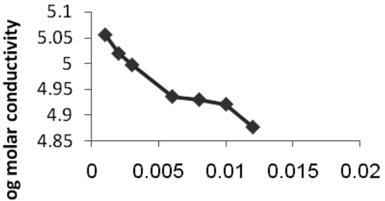

Fig. 5. log molar conductivity-DTAB concentration in the absence of monomer

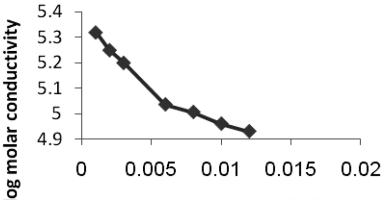

Fig. 6. log molar conductivity-DTAB concentration in the presence of 0.237 M monomer

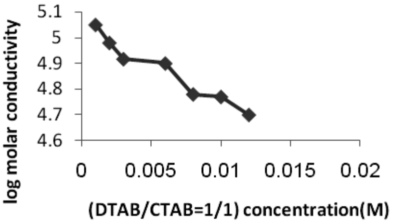

Fig. 7. log molar conductivity-(DTAB/CTAB) concentration in the absence of monomer

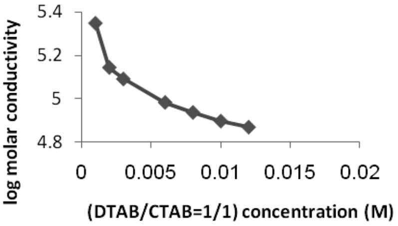

Fig. 8. log molar conductivity-(DTAB/CTAB) concentration in the presence of 0.237 M monomer

We observed a change in CMC for lecithin from 0.01 to 0.006 M in the presence of monomer. While no change has been observed for DTAB and CTAB in the absence or the presence of monomer and CMC for DTAB and CTAB were determined 0.006 and 0.003 M, respectively. The break point of the curve of (DTAB/CTAB = 1/1) in the presence of monomer abserved in 0.003 M.

Increasing of the electroconductivity at the presence of monomer showed that:

$$EC_{(\text{lecithin})} > EC_{(\text{DTAB/CTAB=1/1})} > EC_{(\text{CTAB})} > EC_{(\text{DTAB})}$$

Investigation of the surface properties: Surface properties such as surface tension, surface enthalpy and surface entropy were investigated by drop method for different emulsifiers in 25, 30 and 50 ºC. Results tabulated in Table-3 and Fig. 9-16. We used from the equation of:

$\gamma = G^S = H^S - TS^S$ for determination of above parameters.

Surface tension, surface enthalpy and surface entropy measurements in the presence of 1.19 M monomer showed a decreasing in all of emulsifiers:

$$\gamma_{(\text{DTAB})} > \gamma_{(\text{CTAB})} > \gamma_{(\text{DTAB/CTAB})} > \gamma_{(\text{lecithin})}$$

$$H^s_{(\text{DTAB})} > H^s_{(\text{CTAB})} > H^s_{(\text{DTAB/CTAB})} \cong H^s_{(\text{lecithin})}$$

$$S^s_{(\text{DTAB})} > S^s_{(\text{CTAB})} > S^s_{(\text{DTAB/CTAB})} \cong S^s_{(\text{lecithin})}$$

TABLE-3
SURFACE PROPERTIES FOR DIFFERENT EMULSIFIERS
([2-HPMA] = 1.19 M, T/W = 1/2, T = 25, 30 AND 50 °C)

	$\gamma_{(25\,°C)}$ (J/mol)	$\gamma_{(25\,°C)}$ + monomer (J/mol)	$\gamma_{(30\,°C)}$ (J/mol)	$\gamma_{(30\,°C)}$ + monomer (J/mol)	$\gamma_{(50\,°C)}$ (J/mol)	$\gamma_{(50\,°C)}$ + monomer (J/mol)	H^S (J)	H^S + monomer (J)	S^S (J/°C)	S^S + monomer (J/°C)
Lecithin (1 %)	22.73	21.41	23.00	21.80	24.10	23.30	21.36	19.50	-0.055	-0.076
CTAB (1 %)	27.00	23.56	27.80	24.50	30.19	27.54	23.95	19.70	-0.125	-0.157
DTAB (1 %)	27.50	21.60	27.75	22.90	28.60	25.95	26.42	17.61	-0.044	-0.168
(DTAB/CTAB=1/1) (1%)	24.75	23.86	24.82	24.10	25.10	24.89	24.40	22.86	-0.014	-0.041

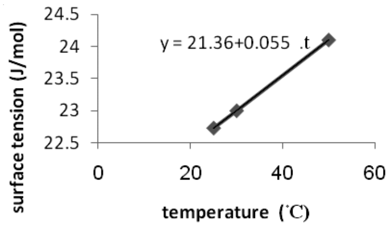

Fig. 9. Surface tension-temperature (T/W = 1/2 lecithin = 1 %)

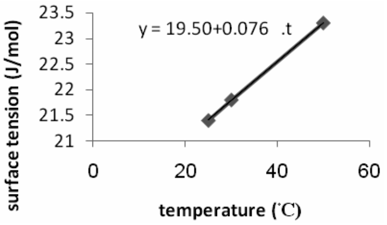

Fig. 10. Surface tension-temperature in the presence of 1.19 M monomer (T/W = 1/2 lecithin = 1 %)

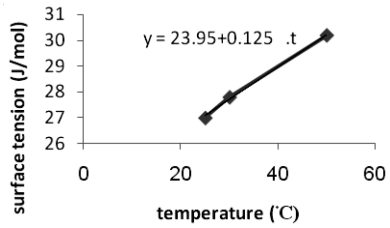

Fig. 11. Surface tension-temperature (T/W = 1/2, CTAB = 1 %)

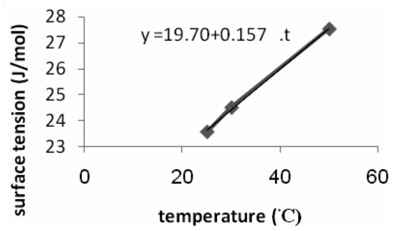

Fig. 12. Surface tension-temperature in the presence of 1.19 M monomer (T/W = 1/2, CTAB = 1 %)

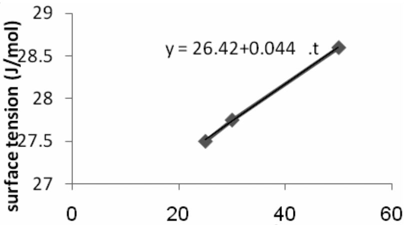

Fig. 13. Surface tension-temperature (T/W = 1/2, DTAB = 1 %)

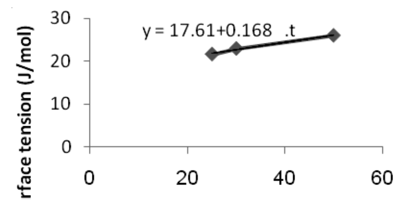

Fig. 14. Surface tension-temperature in the presence of 1.19 M monomer (T/W = 1/2, DTAB = 1 %)

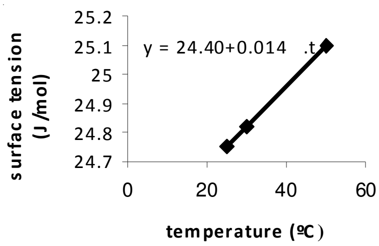

Fig. 15. Surface tension-temperature (T/W = 1/2, DTAB/CTAB = 1/1 = 1 %)

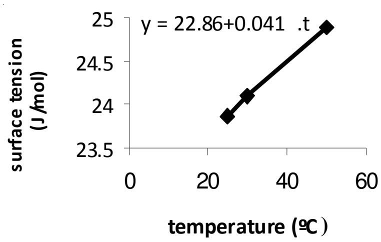

Fig. 16. Surface tension-temperature in the presence of 1.19 M monomer (T/W = 1/2, DTAB/CTAB = 1/1 = 1 %)

Conclusion

A comparison of different emulsifiers effects on the electroconductivity of 2-hydroxypropylmethacrylate in emulsion system, showed that, lecithin is the best emulsifier for the monomer-toluene-water system. When the best results of physical chemical properties is recorded for DTAB and in the (DTAB/CTAB = 1/1) mixture it has a tendency to CMC of CTAB. In general, the monomer for all conditions act as a suitable co-surfactant.

REFERENCES

1. D.O. Shah, V.K. Bansal, K. Chan and W.C. Hsieh, Improved Oil Recovery by Surfactant and Polymer Flooding, Academic Press Inc., pp. 297-337 (1977).
2. H.C. John, Surfactant Aggregation, Blaclie Publication, pp. 223-249 (1992).
3. S.D. Alexander, Comrehensive Polymer Science, 4, Pergamon Press, pp. 219-229 (1989).
4. S. Qutubuddin, E. Haque, W.J. Benton and E.J. Fendler, Polymer Association Structure, ACS, pp. 64-83 (1989).
5. H.J. Butt, K. Graf and M. Kappl, Physics and Chemistry of Interfaces, pp. 246-279 (2003).
6. P. Mukerjee and K.J. Mysels, NSRDS-NBS 36, U.S. Dept of Commerce, Washington, DC (1971).
7. A. Dominguez, A. Fernandez, N. Gonzalez, E. Iglesias and L. Montengro, *J. Chem. Educ.*, **74**, 1227 (1997).
8. K.J. Furton and A. Norelus, *J. Chem. Educ.*, **70**, 254 (1993).
9. X. Huang, J. Yang, W. Zhang and Z. Zhang, *J. Chem. Educ.*, **76**, 93 (1999).
10. P.C. Schulz and D. Clusse, *J. Chem. Educ.*, **80**, 1053 (2003).
11. R.S. Haroutiounian, N.M. Beylerian and A.V. Babakhanian, *J. Surface Sci. Technol.*, **11**, 21 (1995).
12. R.S. Haroutiounian, N.M. Beylerian, E.N. Attanassian and L.Kh. Simonian, *Armyanski Khim. J.*, **31**, 560 (1978).

(*Received*: 20 February 2010; *Accepted*: 26 June 2010) AJC-8838