Interaction Studies of Nonionic Emulsifiers and Carboxymethylstarch and Polymerization of Vinyl Acetate

[a]I. CAPEK, [a]S. JANÍČKOVÁ, [b]P. CAPEK, [c]J. KOVÁČIK, and [d]P. KOŠTIAL

[a]*Polymer Institute, Slovak Academy of Sciences, SK-842 36 Bratislava*
e-mail: upolign@savba.sk

[b]*Institute of Chemistry, Slovak Academy of Sciences, SK-845 38 Bratislava*

[c]*VUCHT a.s., Duslo Group, Duslo, a.s., 927 03 Šaľa*

[d]*Faculty of Industrial Technologies, Trenčín University of A. Dubček, SK-020 32 Púchov*

The organized association of amphiphilic nonionic emulsifiers in the aqueous phase with and without hydrophilic additive (starch) was investigated. The surface tension and conductivity were used to study the association behaviour of amphiphiles. The surface tension of the aqueous solutions of hydrophilic nonionic emulsifiers Slovasol 2520, Slovasol 2430, Slovanik 1070/7, and Sloviol P88-08 (hydrophilic-lipophilic balance, HLB > 15) and anionic emulsifier Slovafos 1M is described by a curve with two straight lines and the break at the critical micellar concentration. Some deviation from the ideal behaviour was observed with Tween 20. The nonideal micellar behaviour was observed with the hydrophobic emulsifier Tween 85 where the surface tension *vs.* conversion curve was described by a curve with minimum at the critical micellar concentration. The addition of polysaccharide – carboxymethylstarch – does not influence the shape of surface tension curve but increases the surface tension. The noncooperative interaction between the hydrophilic polysaccharide and nonionic emulsifier shifts the critical aggregation concentration to the higher emulsifier concentrations.

Solutions of surface-active materials exhibit special and useful property called the critical micelle concentration (CMC), at which micelles first appear in the solution. At the CMC abrupt changes in some physical properties, such as conductivity, surface tension, turbidity, osmotic pressure, *etc.* take place [1]. The surface tension and conductivity are the most popular methods for the characterization of micellar colloidal solutions [2, 3]. The surface tensiometer is easy to operate and the break in the surface tension – concentration curve is clear and shows strong change in the physical properties. Besides, the surface tension method is suitable for solutions of ionic, nonionic, zwitterionic, and mixed emulsifiers. The electrical conductivity method is a widely employed method for characterizing the ionic emulsifier solutions.

The micelles solubilize oil or water in the micelle volume, thereby introducing a heterogeneity in the local concentration of the reactants. Likewise, polymer micelle-like aggregates start to form along the polymer chain at a critical aggregation concentration (CAC). The CAC is thus an analogue of the CMC, but in the solution with an added polymeric compound. A characteristic feature of this parameter is that it is always lower than the CMC of the corresponding emulsifier (surfactant) [4—6]. The lower CAC is particularly pronounced in solutions of polyelectrolytes with an opposite charge to the emulsifier. The emulsifier often interacts cooperatively with polymers at the CAC, forming micelle-like aggregates within the polymer. Noncooperative association between emulsifier and polymer is characterized by the simple partitioning of emulsifier between polymer and the aqueous phase. The addition of emulsifiers to aqueous solution of amphiphilic polymers can either induce or break up interpolymer aggregation [7]. The emulsifier can interact cooperatively with polymers at the CAC, forming micelle-like aggregates within the polymer. Emulsifiers with a relatively long tail bind to the amphiphilic copolymers by simple partitioning between the aqueous phase and the polymer (noncooperative association) [8].

Polymer/emulsifier systems are commercially important in a number of applications. At higher concentration, the micelles are bridged by the polymer chains, forming a network that exhibits interesting rheological behaviour. The interaction between emulsifiers and polymers thus can be described by two critical aggregation concentrations. The first concentration, CAC, corresponds to the emulsifier concen-

tration when binding interaction between emulsifiers and polymer molecules first occurs, which represents the onset for the formation of polymer/emulsifier aggregation complex [4—6]. The second critical concentration, C_2, is more obscure. It is commonly used to represent the emulsifier concentration when the polymer becomes saturated with emulsifier aggregates in polymer/emulsifier aggregation complexes. In addition, another critical concentration, C_m, representing the formation of free emulsifier micelles in the polymer solution, was previously reported in the literature [9]. For some of polymer/emulsifier systems, free emulsifier micelles start to form after the saturation concentration, C_2. Under this condition, C_m is analogous to C_2. However, for other polymer/emulsifier systems, the formation of free emulsifier micelles precedes C_2 or C_m is less than C_2. In this case, there is a competition between the formation of free emulsifier micelles and that of polymer/emulsifier aggregation complexes at emulsifier concentrations between C_m and C_2 [9].

The aim of this study is to investigate the organized agglomeration of hydrophilic and hydrophobic nonionic emulsifiers in both aqueous and nonaqueous solutions containing a water-soluble carboxymethylstarch (CMS). One can find a cooperative interaction between the emulsifier and reactive polymers bearing the hydrophobic chains. There is no information on the interaction between the amphiphilic nonionic emulsifier and a polar hydrophilic carboxymethylated starch. This is the reason why we intend to study the solubilization of starch in the micellar solutions. The solubilization of both the hydrophilic starch and hydrophobic monomer(s) can favour the preparation of composite particles (dispersions) with nontraditional mechanical properties by the dispersion polymerization.

EXPERIMENTAL

Cyclohexane (CH, Fluka) was purified by distillation. Nonionic emulsifiers used were the reagent-grade Tween 20 (nonionic emulsifier, polyoxyethylene sorbitan monolaurate, provided by Serva in the form of a 97 % aqueous solution, Tw 20, hydrophilic-lipophilic balance (HLB) = 16.7), Tween 85 (nonionic emulsifier, polyoxyethylene sorbitan trioleate, provided by Serva, Tw 85, HLB = 11.0), Slovasol 2430 (alkyl polyoxyethylene ether type: $C_{24}H_{49}O(CH_2CH_2O)_{29}$-$CH_2CH_3$) (NCHZ Nováky), Slovasol 2520 ($C_{25}H_{51}O$-$(CH_2CH_2O)_{20}CH_2CH_3$) (NCHZ Nováky), Slovafos 1M (anionic emulsifier, NCHZ Nováky), Slovanik 1070/7 (ethyleneoxide/propyleneoxide copolymer) (NCHZ Nováky), and Sloviol P88-08 (10.2 mass % aqueous solution, poly(vinyl acetate)) (NCHZ Nováky). Sodium hydroxide, isopropyl alcohol, sodium salt of monochloroacetic acid, and acetic acid were reagent-grade. Doubly distilled water used for preparation of aqueous solutions of emulsifiers was deprived

of oxygen by heating to boiling point and cooling under a stream of argon. Commercially available vinyl acetate (VAc, Fluka) was purified by distillation under reduced pressure. Extra pure ammonium peroxodisulfate (APS, Fluka), NaHCO$_3$, and native wheat starch (NWS) were used as supplied. The polymerization technique, the preparation of polymer latex for particle size measurements, and the particle number estimation were the same as described earlier [10, 11].

The apparatus for determination of relative molecular mass used (Shimadzu, Wien, Austria) comprised a high-pressure pump LC-10AD, a membrane degasser GT-104, an injector Reodyne 77251 equipped with 0.02 cm^3 sample loop, a differential refractometer RID-6A, and a UV VIS detector SPD-10AV. Chromatographic experiments were performed using a tandem of two columns HEMA-BIO 100 followed by HEMA-BIO 40 column (Tessek, Prague, Czech Republic) of dimensions 8 mm × 250 mm and particle size 10 μm. As a mobile phase 0.02 M-phosphate buffer of pH 7.2 containing 0.1 M-NaCl was used at flow rate 0.8 cm^3 min^{-1}. Samples and calibration dextrans (within the range of $M_{r,m}$ from 1 000 to 100 000) were injected at 1 mg cm^{-3} concentration. Output signals from the differential refractometer as well as from the UV detector (280 nm) were processed on-line using a Class-VP-chromatography software package. CMC for the nonionic emulsifiers was measured by means of surface tension and conductivity measurements. The aqueous and nonaqueous solutions were prepared by diluting a stock solution of emulsifier by mole concentration ranging from 10^{-6} to 10^{-2} mol dm^{-3}. The surface tension was determined by the stalagmometric method [12]. An all-jacketed stalagmometer with a watch glass was used. Constant temperature (30 ℃) was maintained by connection of the jacketed stalagmometer to an adjustable temperature water-bath pump.

The conductivity of aqueous and nonaqueous emulsifier solutions was measured using a Conductometer OK 102/1 (Radelkis, Hungary) according to the method described in [13]. A jacketed glass beaker covered with a watch glass was used. Constant temperature (30 ℃) was maintained by connection of the jacketed beaker to an adjustable temperature water-bath pump. The electrode (type OK 902, Radelkis, Hungary), which directly measures the conductivity, was inserted into a solution of emulsifier.

Carboxymethylstarch

NWS (10 g) was added gradually to a 20 % sodium hydroxide solution (100 cm^3) and stirred for 1 h at room temperature. Isopropyl alcohol (50 cm^3) and sodium salt of monochloroacetic acid (20 g) were added and stirring was continued ($\approx$ 2 h) till the reaction mixture was completely homogeneous. The reaction mixture was neutralized with 4 M-acetic acid, di-

alyzed and the product was recovered by freeze-drying [14].

Potentiometric Titration

The carboxyl content in carboxymethylstarch was determined by potentiometric titration. The accurately weighed amount of carboxymethylstarch in sodium form was dissolved in deionized water, passed through cation exchanger and titrated with 0.1 M-potassium hydroxide solution, free of carbonate upon continuing stirring. The pH titration was carried out using a combined Radelkis electrode (Budapest, Hungary). The degree of substitution (DS = 0.6) of carboxymethylstarch was calculated according to a reported method [15].

RESULTS AND DISCUSSION

The dependence of surface tension (γ) *vs.* emulsifier (Tw 85) concentration is described by the curve with a minimum at *ca.* 1.0×10^{-6} mol dm^{-3} (Fig. 1). First the surface tension of the aqueous solution decreases with increasing the emulsifier (Tw 85) concentration up to *ca.* 1.0×10^{-6} mol dm^{-3} and then it starts to increase above *ca.* 3.0×10^{-6} mol dm^{-3}. The dependence of the conductivity *vs.* emulsifier concentration, on the contrary, is described by a curve with the maximum at *ca.* 5.0×10^{-7}—3.0×10^{-6} mol dm^{-3}. From these dependences the critical micelle concentration (CMC) was estimated to be *ca.* 1.0×10^{-6} mol dm^{-3}. The aqueous phase behaviour of hydrophobic emulsifier (Tw 85, HLB = 11.0) strongly deviates from the classical behaviour of hydrophilic emulsifiers [16]. The classical behaviour is, however, observed for a somewhat more hydrophilic PEO-type nonionic emulsifier, such as Triton X-100 (HLB = 13.5) [17].

Two straight lines and the break on the tension *vs.* conversion plot were observed in the aqueous solutions of Slovasol 2520 and Slovasol 2430 (the classical behaviour) (Fig. 2). The CMC is estimated to be 2.1×10^{-4} mol dm^{-3} for Slovasol 2520 and 2.3×10^{-4} mol dm^{-3} for Slovasol 2430, respectively. The increase in the CMC going from Slovasol 2520 to Slovasol 2430 results from the increased hydrophilicity. The shape and the values of surface tension, however, differ much more for both emulsifiers. For example, the surface tension at the CMC is *ca.* 43 mN m^{-1} for Slovasol 2520 and 48 mN m^{-1} for Slovasol 2430, respectively.

The addition of hydrophilic polysaccharide CMS (DS (degree of substitution) = 0.6; $M_{r,m}$ = 620 000) does not influence the shape of the surface tension *vs.* emulsifier concentration curve but shifts the curve to the higher concentration of emulsifier, *i.e.* the CMC of the aqueous solution of Slovasol 2430 increases (Fig. 3). The absence of the first distinct transition
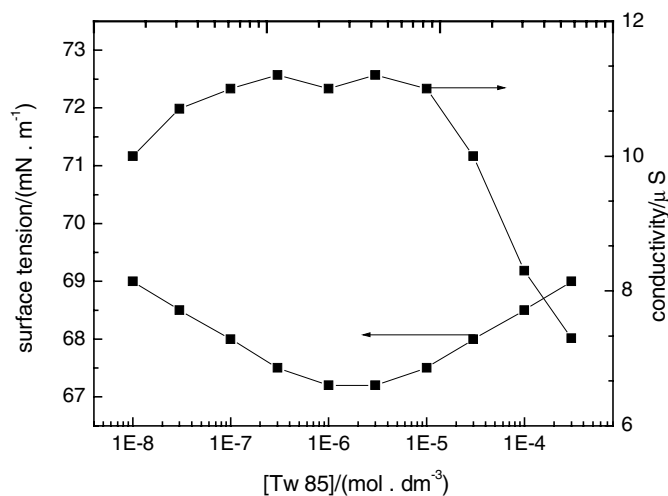

Fig. 1. Variation of surface tension and conductivity (μS) of the aqueous micellar solution with increasing the Tween 85 concentration.
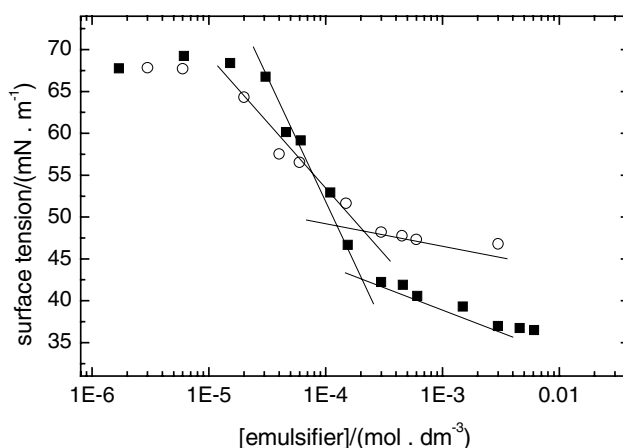

Fig. 2. Variation of surface tension of aqueous emulsifier solution with the emulsifier type and concentration at 25 °C (■ Slovasol 2520, ○ Slovasol 2430).

below *ca.* 2×10^{-4} mol dm^{-3} of emulsifier disfavours the formation of strong polymer/emulsifier complexes. Fig. 3 shows that the values of surface tension for the CMS/emulsifier system are much higher than that for the emulsifier alone, especially below *ca.* 2×10^{-4} mol dm^{-3}. This results from the interaction between some groups of CMS and emulsifier. The loosely organized CMS/emulsifier associates increase the CMC and the surface tension. The increased CMC does not favour the cooperative interaction, *i.e.* the micelles do not accumulate along the chain of polysaccharide but rather the single emulsifier molecules accumulate along the chain of polysaccharide *via* the hydrogen bonding between PEO chains of emulsifier and carboxymethyl groups of starch. In the aqueous solution, the emulsifier (ethylene oxide (EO) groups) layer curvature is strongly hydrated and so positively charged
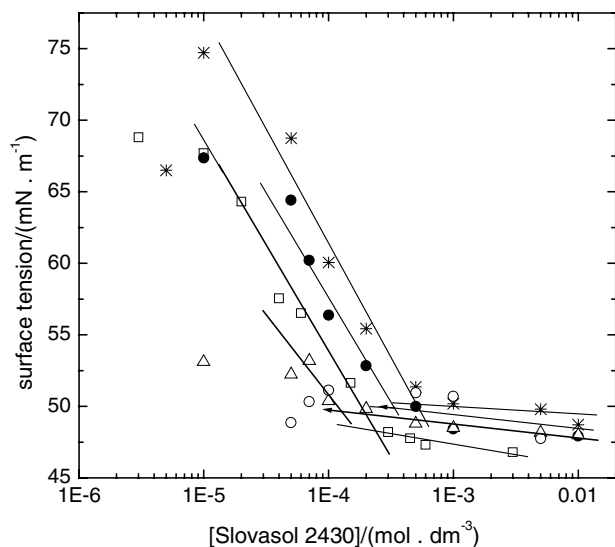
Fig. 3. Variation of surface tension of aqueous emulsifier Slovasol 2430 solution with the emulsifier and starch contents at 25 °C. □ Without starch, ● 0.1 mass % starch, ∗ 0.25 mass % starch, △ 0.5 mass % starch, and ○ 0.75 mass % starch. $CMC/(10^{-4}$ mol $dm^{-3})$: □ 2.36, ● 3.12, ∗ 4.4, △ 1.3, ○ none.

Fig. 4. Variation of surface tension of aqueous and non-aqueous emulsifier Tween 20 solution with the emulsifier concentration and additive (starch) at 25 °C. ■ 0.5 mass % starch, in water, $CMC = 1.34 \times 10^{-4}$ mol dm^3; ○ without starch, in water, $CMC = 1.0 \times 10^{-4}$ mol dm^3; ▲ cyclohexane (starch insoluble).

[18]. The competition between water and CMS for EO groups leads to the presence of both the water/PEO aggregates and CMS/PEO ones. The slight interaction between emulsifier and CMS molecules does not lead to the formation of water-insoluble aggregates as it is in the case of strong interaction between oppositely charged polyelectrolytes. The larger the water-solubility of emulsifier, the larger the CMC and the aggregation number of emulsifier. The incorporation of emulsifier molecules into the polysaccharide skeleton decreases the fraction of free emulsifier available for the formation of micelles. The formation of mixed CMS/emulsifier micelles, however, cannot be ruled out. This includes the incorporation of the CMS macromolecules into the micellar aggregates due to which the micelle structure and the value of CMC vary. The hydrophilic nature of CMS excludes any changes in the hydrophobic core of colloidal nanoparticles. When amphiphiles with different chain length are mixed, the long chain has more space than that in pure polymer system. The depressed aggregation of amphiphiles or the formation of less compact aggregates can result from the location of CMS chains at the micelle surface [19].

Fig. 3 shows that the CMC of mixed emulsifier (Slovasol)/starch system increases with increasing the mass fraction of starch up to a certain critical concentration of starch: {CMC $\times 10^4$/(mol dm^{-3})}/{w(starch)/mass %}: 2.36/0, 3.12/0.1, 4.4/0.25, 1.3/0.5, −/0.75. At 0.5 mass % of starch the CMC decreased and at 0.75 mass % of starch the micellar aggregation does not appear. The increase of the starch concentration increases the viscosity of the
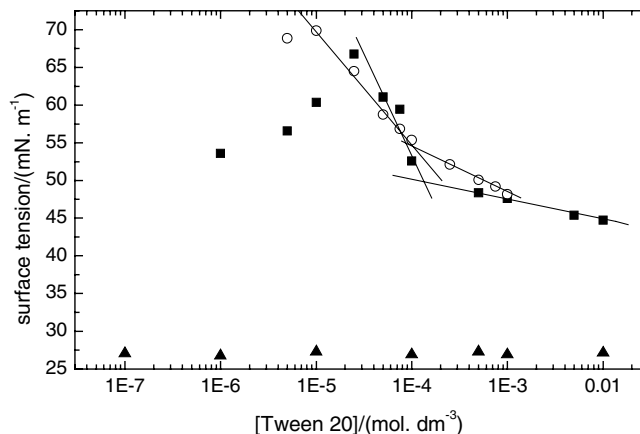
reaction systems. The deviation of the CMC from linearity at 0.5 mass % and 0.75 mass % of starch can be attributed to the very high viscosity of the reaction system. The increased immobilization of emulsifier molecules in the viscous starch gel depresses the aggregation of emulsifier molecules.

A somewhat different behaviour was observed in the aqueous solution of Tw 20 and starch (Fig. 4). The addition of 0.5 mass % of starch slightly increased the CMC. Under the same condition the strong decrease in the CMC of Slovasol appears. The self-aggregation of emulsifier molecules, thus, is much stronger in the Tw 20 solution than in the Slovasol one or the interaction between emulsifier and starch is stronger in the latter. This indicates that Slovasol is more hydrophilic than Tw 20. The addition of hydrophobic methyl group (as oxypropylene) into the polymer (PEO) shifts the formation of polymer (PEO)/emulsifier (sodium dodecyl sulfate, SDS) aggregates to the lower emulsifier concentration [20]. In both Slovasol and Tw 20 systems the values of surface tension at very low emulsifier concentrations (much below the CMC) do not keep the classical plateau but increase with increasing the emulsifier concentration. This can result from the interaction between emulsifier and polymer or some kind of pre-micelle formation. In the nonaqueous solution (cyclohexane) there is no variation in the surface tension with the CMS concentration. This can result from the low oil-solubility of CMS.

The different behaviour was observed in the aqueous solution of anionic emulsifier Slovafos 1M (Fig. 5). The addition of CMS decreases the critical agglomeration concentration of emulsifier. The slight decrease in CMC (or CAC) can be attributed to the interaction between polymer and emulsifier and the formation of mixed micelles. Most of polysaccharides, such as hy-
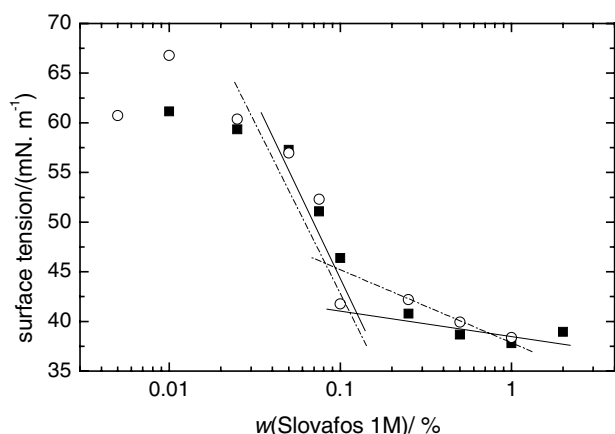
Fig. 5. Variation of surface tension of aqueous emulsifier Slovafos 1M solution with the emulsifier concentration and additive (starch) at 25 °C. ■ 0.25 mass % starch: CMC = 0.085 %, ○ without starch: CMC = 0.12 %.
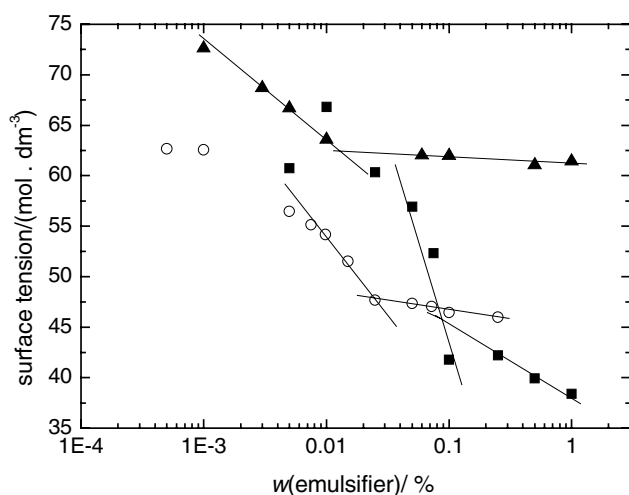

Fig. 6. Variation of surface tension of aqueous emulsifier solution with the emulsifier type and concentration at 25 °C. ■ Slovafos 1M: CMC = 0.085 %, ○ Slovanik 1070/7: CMC = 0.025 %, ▲ Sloviol P88-08: CMC = 0.014 %.

droxyethylcellulose derivatives usually decrease both the CMC and the surface tension of an aqueous solution by the addition of the polymer [21]. When the addition of hydrophobized polysaccharide does not decrease the surface tension and the surface tension was kept unchanged even at the higher concentration, it means that the hydrophobic core of the polysaccharide aggregates is complete and stable and covered by the hydrophilic shell of the polysaccharide skeleton. This is not the case when the surface tension is high and decreases beyond the CMC as presented in some given systems. The very low critical aggregation concentration might indicate the formation of colloidal particles, but the decrease in the surface tension above the CMC can result from some kind of disorganization.

The surface tension of the aqueous solution of

PVAc-type emulsifier decreases with increasing the emulsifier concentration and when the CMC is reached the surface tension remains almost constant (Fig. 6). The similar value of CMC is found with Slovanik but the CMC and plateau in the former case is characterized by much lower surface tension. The CMC of nonionic emulsifier PVAc and Slovanik was smaller than that of the anionic emulsifier Slovafos 1M. The lower water solubility of the former shifts the CMC to lower concentrations of emulsifier.

The CMC for two alkylphenol polyethylene glycol ethers Triton X-100 (HLB = 13.5) and Triton X-114 (HLB = 12.4) is 2.77×10^{-7} mol dm^{-3} and 2.12×10^{-7} mol dm^{-3} [16]. The surface tension at the CMC was 30 mN m^{-1} for Triton X-100 and 28.5 mN m^{-1} for Triton X-114. The CMC and the surface tension are larger for the more hydrophilic emulsifier Triton X-100. The CMC for the more hydrophobic emulsifier Tw 85 is estimated to be $ca.$ 1.0×10^{-6} mol dm^{-3} (HLB = 11, Fig. 1), which is somewhat larger than that for Triton even though the former is more hydrophilic. The CMC of two more hydrophilic emulsifiers Slovasol 2430 and Slovasol 2520 is $ca.$ 2×10^{-4} mol dm^{-3}. The CMC $ca.$ 1×10^{-4} mol dm^{-3} was estimated for more hydrophilic Tw 20 with HLB = 16.7. These data indicate that also other factors than the water solubility of emulsifier influence the aggregation of emulsifier. Comparing the water solubilities and HLBs of studied emulsifiers, the HLB for Slovasols can be estimated to be $ca.$ around 16.

The distinct CMC transition occurs in the aqueous micellar systems containing nonionic emulsifiers Slovasols, Slovanik, and Sloviol and anionic Slovafos. Furthermore, the CMCs of all nonionic emulsifiers are smaller than that of anionic emulsifier Slovafos. This results from the lower water solubility of nonionic emulsifiers. The more efficient aggregation and adsorption of anionic emulsifier at the interface is accompanied by the lower values of surface tension. The reverse order for the CMC and surface tension is observed for the following three emulsifiers: {CMC/mass %}/{γ/(mN m^{-1})}: 0.015/62.5 Sloviol; 0.026/47 Slovanik; 1070/7; 0.31/37.5 Slovafos 1M.

Furthermore, the surface tension slightly decreases with increasing the emulsifier concentration above the CMC except of the Slovafos 1M (Fig. 6). The more pronounced decrease in the surface tension beyond the CMC appears in the micellar solutions with Slovasol 2430 and Slovasol 2520. This indicates that the structure of micellar aggregates (the aggregation number of aggregates) varies with increasing the emulsifier concentration.

The value of $(C_2 - \text{CMC})/[\text{CMS}]$ can be used to estimate the amount of emulsifier bound to the polymer chains. For both Slovasol 2430 (Fig. 3) and Tween 20 (Fig. 5), the molar ratios of $(C_2 - \text{CMC})/[\text{CMS}]$ are about 26.2 {2.1×10^{-4} mol dm^{-3}/(8×10^{-4} mol dm^{-3})} and 4.1{0.33×10^{-4} mol dm^{-3}/(8×10^{-4} mol

Table 1. Preparation of Poly(Vinyl Acetate) Dispersions[a]

Sample	Sloviol	Water	CMS	Viscosity	D
	g	g	G	mPa	nm
1	44.1	30	0	340	430
4	36.75	33.97	3.38	117	–
6	29.4	37.95	6.75	140	–
3	22.05	41.9	10.13	958	–
7	14.7	45.9	13.51	Solid	–
5	7.35	49.9	16.88	Solid	–

a) Recipe: 69.6 g VAc, 1.5 g NaHCO$_3$, 14.3 g water, 0.225 g APS.

Table 2. Preparation of Poly(Vinyl Acetate) Dispersions[a]

Sample	Sloviol	NWS	H$_2$O	Viscosity	D
	g	g	g	mPa	nm
1	44.1	0	30	340	430
2	36.75	5	30	4936	412*
3	40.43	2.5	30	1814	470*
4	36.75	0.75	37.35	913	472
5	29.4	1.5	44.7	–	461
6	22.05	2.25	52.05	4790	508*

a) See the legend to Table 1. *Agglomerates.

dm^{-3})}, respectively. These numbers indicate that CMS can bind more hydrophilic Slovasol 2430 than a somewhat less hydrophilic Tw 20 at saturation concentration C_2. The aggregation number of nonionic emulsifiers (Tween 20 and Slovasol 2430) alone is *ca.* 100—150 [22, 23]. In the mixed emulsifier/CMS aggregate there is *ca.* 4—6 CMS molecules for Slovasol 2430 and *ca.* 30 for Tw 20. These data do not seem real. The shift in the CMC, thus, can be attributed to the binding of emulsifier molecules to the CMS skeleton. Furthermore, the cooperative binding of ionic emulsifier (sodium dodecyl sulfate, SDS) monomers to PEO was reported to occur when $M_{r,m,PEO}$ exceeds *ca.* 3000 [20]. For the hydrophilic polymer with EO segments, the exothermic peak was ascribed to the rehydration of the EO segments in the water phase, and these rehydrated segments could form an ion-dipole association with the hydrophilic headgroups of SDS micelles. In the present case, the hydrophilic headgroups of CMS could form an ion-dipole association with the rehydrated EO segments of nonionic emulsifiers. The relative molecular mass of PEO chains is *ca.* 1000 for Slovasol 2430 and 680 for Tw 20. This might be one of the reasons why the loosely-associated aggregates are formed and the differences in C_2 values for both emulsifiers appear.

The variations of colloidal and rheological properties of polymer dispersions with the concentration and the type of starch are summarized in Tables 1 and 2.

The addition of a small amount of CMS causes the decrease in the viscosity of the polymer dispersion (Table 1). The further addition of CMS strongly increases the viscosity and at a certain concentration of CMS the polymer dispersion becomes solid. The distinct polymer particles were formed in the emulsion system without CMS. The presence of CMS depresses the formation of distinct polymer particles, *i.e.* the light scattering measurements (hydrodynamic size) did not confirm the formation of polymer particles.

The emulsion polymerization of VAc in the presence of native wheat starch leads to the formation of polymer dispersion with the distinct polymer particles (Table 2). The addition of larger amount of NWS induces the particle agglomeration and the formation of coagulum. The viscosity of the polymer dispersion increases with increasing the amount of NWS.

REFERENCES

1. Shaw, D. J., *Introduction to Colloid and Surface Chemistry*, Chap. 4. Butterworth—Heinemann, Oxford, 1992.
2. Mukerjee, P. and Mysels, K. J., *J. Phys. Chem. 59*, 2937 (1955).
3. Ross, S. and Olivier, J. P., *J. Phys. Chem. 63*, 1673 (1959).
4. Yoshida, K., Morishima, Y., Dubin, P. L., and Mizusaki, M., *Macromolecules 30*, 6208 (1997).
5. Liaw, D. J., Huang, C. C., and Kang, E. T., *Curr. Trends. Polym. Sci. 4*, 117 (1999).
6. Winnik, F. M. and Reismond, S. T. A., *Colloids Surf., A 118*, 1 (1996).
7. Halay, S. W., McCormick, C. L., and Butler, B. G. (Editors), *Water-Soluble Polymers*: *Synthesis, Solution, Properties, and Application*. ACS Symposium Series No. 467. American Chemical Society, Washington, D.C., 1991.
8. Winnik, F. M., *Langmuir 7*, 905 (1991).
9. Ghoreishi, S. M., Fox, G. A., Bloor, D. M., Holzwarth, J. F., and Wyn-Jones, E., *Langmuir 15*, 5474 (1999).
10. Capek, I. and Chudej, J., *Polym. Bull. 43*, 417 (1999).
11. Capek, I., *Macromol. Symp. 179*, 153 (2002).
12. Harkins, W. D., *J. Am. Chem. Soc. 69*, 1428 (1947).
13. Grimm, W. L., Min, T. I., El-Aasser, M. S., and Vanderhof, J. W., *J. Colloid Interface Sci. 94*, 531 (1983).
14. Bhattacharyya, D., Singhal, R. S., and Kulkarni, P. R., *Carbohydr. Polym. 27*, 167 (1995).
15. Rinaudo, M. and Hudry-Clergeon, G., *J. Chim. Phys. 64*, 1746 (1967).
16. Capek, I., Mlynárová, M., and Bartoň, J., *Chem. Pap. 42*, 763 (1988).
17. Chang, H. C., Hwang, B. J., Lin, Y. Y., Chen, L. J., and Lin, S. Y., *Rev. Sci. Instrum. 69*, 2514 (1998).
18. Kunieda, H., Uddin, Md. H., Furukawa, H., and Harashima, A., *Macromolecules 34*, 9093 (2001).

19. Kato, T., Katsuki, T., and Takahashi, A., *Macromolecules 17*, 1726 (1984).
20. Dai, S., Tam, K. C., and Li., L., *Macromolecules 34*, 7049 (2001).
21. Londoll, L. M., *J. Polym. Sci., Polym. Chem. Ed. 20*, 443 (1982).
22. Haque, M. E., Das, A. R., and Moulik, S. P., *J. Colloid Interface Sci. 217*, 1 (1999).
23. Streletzky, K. and Phillies, G. D. J., *Langmuir 11*, 42 (1995).