Effects of additives on the cloud points of aqueous micellar solutions of triblock copolymers

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An empirical equation based on the mass action law and the core-shell structure of micelles was obtained for the description of the effects of additives upon the cloud points of aqueous micellar solutions of triblock copolymers.

The micelles of polymers, as well as other surface-active subctances, have a hydrophobic core and a hydrophilic shell,[1,2] which provide their ability to solubilize compounds of different polarity.[3–5] The phase behaviour of systems containing block copolymers was extensively studied for triblock copolymers $E_nP_mE_n$ and $P_mE_nP_m$,[2] where E and P are oxyethylene and oxypropylene fragments, respectively. Above a certain temperature known as a cloud point (T_c), polymeric micelles disintegrate with separation into two phases (polymer-diluted and polymer-rich). The T_c magnitude restricts the upper temperature margin of the use of micellar solutions of block copolymers, and it depends on the presence of impurities and additives in the system.

The T_c values of polymeric micellar systems decrease in the presence of salts, such as LiCl, NaCl, NaBr, KF, KCl and KBr, while the additives of NaI, NaSCN and KSCN increase the T_c values.[6–8] Previously,[9] very interesting results were obtained, which give a quantitative feature of the influence of additives upon the cloud temperatures of aqueous $E_nP_mE_n$ and $P_mE_nP_m$ triblock copolymers. Various polar additives, such as urea (Ur), dimethylurea (DU), nicotinamide (NA), and salts, such as sodium thiocyanate (TC), tetrapropylammonium (TP) and tetrabutylammonium (TB) bromides, sodium *p*-toluene (TS) and xylene (XS) sulfonates led to increasing the T_c values.[9]

The aim of this work was to derive a general equation reflecting the relation between the structures of triblock copolymers, such as $E_nP_mE_n$ and $P_mE_nP_m$, and the effects of additives on the T_c values of aqueous micellar copolymer systems. The efficiency of an influence of the additives on the T_c values is characterised by the difference $\Delta T = T_{c,a} - T_c$, where $T_{c,a}$ is the T_c value in the presence of an additive.

The ΔT values were measured at the wide variations of copolymer compositions,[9] which is very important for estimating the coefficients of the equation. Some ΔT magnitudes corresponding to the value $T_{c,a}$ = 90 °C (upper temperature limit of the experiments) were published.[9] Such ΔT values were not employed in calculations because they are wrong. In the cases when double ΔT values were given by da Silva and Loh,[9], the lower value corresponding to the onset of the formation of a second phase was used (all values of ΔT determined in the heating conditions of systems at a heating rate of < 1 K min^{-1}).[9] The calculations were performed by the least squares method. The coefficients of equations and their standard deviations, the multiple correlation coefficient (r) corrected on the number of freedom grades, the standard deviation for subset (s), and the Fisher statistic test (F) were estimated for all equations.

Table 1 Composition of $E_nP_mE_n$ copolymers[a] and the concentrations of E and P fragments for the poly(oxyethylene) and poly(oxypropylene) blocks in aqueous 5% solutions of the copolymers.

Copolymer	T_c	M	M_{2E_n}	M_{P_m}	$2n$	m	C_E	C_P
L31	33	1100	110	990	2	17	0.0909	0.773
L42	24.6	1650	330	1320	8	23	0.242	0.697
L43	55	1900	570	1330	14	23	0.3684	0.6053
L62	24.1	2400	480	1920	10	33	0.2083	0.6875
L64	54.4	2900	1160	1740	26	30	0.4483	0.5172
L121	24.5	4950	1485	3465	34	60	0.1136	0.7727
P103	40.3	4400	440	3960	10	58	0.3434	0.6061
25R2[b]	16.5	3100	620[c]	2480[d]	14[e]	43[f]	0.2258	0.6935

[a]The values of T_c, M, M_{2E_n}, M_{P_m}, n, and m from ref. 9. [b]$P_mE_nP_m$ copolymer. [c]M_{E_n}. [d]M_{2P_m}. [e]n. [f]$2m$.

Possible mechanisms of the influence of additives upon the properties of micellar solutions are frequently discussed.[6–10] Among them are a change of the solvent structure near micelles, a change of the conformation of polymeric chains under the action of additives, the replacement of water molecules by additives in the solvation sphere of E fragments. Recently, the formation of complexes between the additives and polar groups of copolymers has been established.[11,12]

A mechanism of the influence of additives upon the properties of micelles probably consists of several stages. The solubilization of additives leads to a change of the properties of the shell and core of micelles, in particular, their capability to solvation, due to the interaction of additives with polar groups of the E and P fragments. If the binding of additives by micelles plays a significant role in the mechanism, the effect of composition copolymer and the additive concentrations upon the magnitude ΔT may be expressed by the following equation reflecting the mass action law for the core-shell model of micelles:

$$\Delta T = K_E C_E C_A + K_P C_P C_A, \quad (1)$$

where C_E and C_P are the concentrations of E and P fragments in the aqueous copolymer systems, respectively (Table 1), C_A is the concentration of an additive in these systems, K_E and K_P are the coefficients reflecting the efficiency of the additive. For $E_nP_mE_n$ copolymers, the C_E and C_P values were calculated according to the relations $C_E = 2nC$, and $C_P = mC$, where C (mol dm^{-3}) is the concentration of copolymers in the system. The relations $C_E = nC$, and $C_P = 2mC$ have been used for the $P_mE_nP_m$ copolymer.

Equation (1) is statistically acceptable for aqueous micellar solutions of copolymers containing various additives (Table 2). Note that equation (1) was tested for the concentrations of copolymers shown in Table 1 and the concentrations of the additives given in Tables 3 and 4. Additional data are needed to test an adaptation of equation (1) to a wider range of concentrations of copolymers and additives.

For the majority of the additives there are both terms in equation (1) which reflect the interaction of the additives with the core and shell fragments. In all cases, the interaction for the E fragments is stronger than that for the P fragments: $K_E > K_P$ (Table 2). The efficiency of the interaction of the additives with the E fragments grows in the following order: Ur < NA < DU < < TC < TP < TB < XS < TS. The interaction of additives with

Table 2 Coefficients in equation (1) for additives in aqueous micellar solutions of triblock copolymers.

Additive	K_E	K_P	N^a	r	s	F
NA	18.3±2.9	16.7±1.2	15	0.995	1.8	685
DU	21.0±3.7	3.4±1.6	16	0.966	2.5	104
Ur	8.9±2.8		16	0.637	3.5	10
TC	26±15	12.8±5.0	14	0.922	6.7	37
TP	57±11	–23.3±4.4	16	0.814	7.0	15
TB	100±12		7	0.961	5.1	72
TS	139±28	–20±10	9	0.946	5.7	35
XS	116±11		5	0.982	4.9	108

[a]Number of values in the subset.

Table 3 The values of ΔT observed[a] and calculated by equation (1) for additives in aqueous micellar solutions of the triblock copolymers $E_nP_mE_n$ and $P_mE_nP_m$.

Copolymer	C_a/mol dm^{-3}	ΔT									
		Ur		DU		NA		TC		TP	
		obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
L31	0.5	0.9	0.4	3.5	2.3	8.5	7.3	3.8	6.1	0.8	–6.4
L31	1.5	2.1	1.2	9.4	6.8	23.0	21.9	9.3	18.4	–13.0	–19.2
L42	0.5	1.6	1.1	–1.6	3.7	9.2	8.0	14.0	7.6	–0.6	–1.2
L42	1.5	–0.9	3.2	12.8	11.2	24.2	24.1	31.8	22.8	–14.6	–3.7
L43	0.5	–5.2	1.6	2.0	4.9	6.8	8.4	8.0	8.7	3.7	3.4
L43	1.5	0.1	4.9	14.3	14.7	13.4[b]	25.3	29.5	26.0	13.1	10.3
L62	0.5	0.7	0.9	1.6	3.4	7.7	7.6	5.2	7.1	–1.1	–2.1
L62	1.5	1.7	2.8	7.7	10.1	19.4	22.9	15.5	21.3	–22.1	–6.3
L64	0.5	0	2.0	3.7	5.6	10.3	8.4	5.9	9.1	7.4	6.7
L64	1.5	7.0	6.0	20.5	16.7	27.3	25.2	7.4[b]	27.4	20.5	20.2
P103	0.5	4.2	1.5	3.2	4.6	6.0	8.2	3.0	8.3	10.6	2.7
P103	1.5	12.5	4.6	12.1	13.9	24.1	24.6	7.8[b]	25.0	16.4	8.1
P121	0.5	1.5	0.5	1.2	2.5	8.9	7.5	8.4	6.4	–0.3	–5.8
P121	1.5	–0.8	1.5	7.2	7.5	24.2	22.5	31.9	19.3	–13.3	–17.3
25R2[c]	0.5	3.2	1.0	5.2	3.6	8.2	7.9	7.7	7.4	3.4	–1.6
25R2[c]	1.5	5.6	3.0	11.2	10.7	21.5	23.6	13.5	22.1	–7.6	–4.9

[a]Taken from ref. 9. [b]Value is not employed in calculations. [c]$P_mE_nP_m$ copolymer.

the E fragments leads to an increase of the $T_{c,a}$ values. The results of the interaction of additives with the P fragments may be different. For some additives, the interaction with the P fragments leads to an increase in the $T_{c,a}$ values, while the other additives (TP and TS) cause a decrease of $T_{c,a}$. For three additives (Ur, TB, and XS) the second term in equation (1) disappeared, probably, their interaction with the P fragments is insignificant. A comparison of the observed and calculated ΔT values (Tables 3 and 4) showed that the influence of additives on the cloud temperatures of the aqueous triblock copolymers $E_nP_mE_n$ and $P_mE_nP_m$ may be adequately described by equation (1). In some cases, the effect of the interaction of additives with P fragments may be larger than the effect of their interaction with E fragments, $(K_EC_EC_A)/(K_PC_PC_A) > 1$. This ratio arises at $C_P >> C_E$.

Based on equation (1), the prediction of the additive influence on the cloud temperatures of aqueous micellar solutions of triblock copolymers can be performed.

Table 4 The values of ΔT observed[a] and calculated by equation (1) for salt additives in aqueous micellar solutions of the triblock copolymers $E_nP_mE_n$ and $P_mE_nP_m$.

Copolymer	C_a/mol dm^{-3}	ΔT					
		TB		TS		XS	
		obs.	calc.	obs.	calc.	obs.	calc.
L31	0.5	6.4	4.6	5.6	–1.4	8.6	5.3
L31	1.5			28.9[b]	–4.2		
L42	1.5	7.1	12.1	5.3	9.8	12.0	14.0
L43	1.5			26.6	19.5	15.1	21.3
L62	1.5	3.6	10.4	4.8	7.6	46.1[b]	12.1
L64	1.5			27.2	26.0		
P103	1.5	21.1	17.2	21.1	17.8	26.4	19.9
P121	1.5	6.6	5.7	6.6	0.2		
25R2[c]	0.5	4.2	11.3	3.7	8.8		
25R2[c]	1.5	37.5	33.9	21.6	26.3	39.6	39.3

[a]Taken from ref. 9. [b]Value is not employed in calculations. [c]$P_mE_nP_m$ copolymer.

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