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Alkyl (C_{10}, C_{12}, C_{14} and C_{16}) triphenyl phosphonium bromide influenced cloud points of nonionic surfactants (Triton X 100, Brij 56 and Brij 97) and the polymer (Polyvinyl methyl ether)

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Abstract The clouding points (CP) of the nonionic surfactants *p-tert*-octyl phenyl polyoxyethylene ether (Triton X 100), Brij-56 and Brij-97, and the water soluble polymer polyvinylmethylether (PVME) have been measured in the presence of the ionic surfactants alkyl (C_{10}, C_{12}, C_{14} and C_{16}) triphenyl phosphonium bromides (ATPBs). The threshold additive concentrations required for efficient CP enhancement of the systems that were studied have been determined. Considering CP as the threshold state of phase separation, the energetics of the process at different additive concentrations has been evaluated. The spontaneity of free energy of the clouding process (ΔG_c^0) at the transition concentrations followed the order PVME $>$ TX 100 $\approx$ Bj 56 $>$ Bj 97. The clouding process has been found to be energetically endothermic with fairly large enthalpy and entropy changes that nicely compensate each other. The compensation temperature has been evaluated and compared with different types of the clouding agents.

Keywords Triphenyl phosphonium bromides · TX 100 · Brij · PVME · Cloud point · Thermodynamics

Introduction

The clouding of nonionic surfactants and water-soluble polymers is an interesting phenomenon, which has attracted the attention of scientists dealing with chemical and physical processes involving surfactants and polymers. Under the condition of increased temperature, the clouding species surfactants and polymers (CS) undergoes desolvation. At a threshold temperature, the compound phases out from the medium normally in an aggregated form imparting cloudiness to the system [1, 2]. The point of such a transition is called cloud point (CP), the knowledge of which is required in dealing with aqueous solutions of nonionic surfactants and polymers under the condition of elevated temperature [3–5].

It is imperative to state that environmental variations may have a striking influence on the CP. Thus, altered solvent medium as well as added salt have the ability to either decrease or increase the CP by way of modification of solvent structure and/or the extent of solvation of the clouding species. The effect of additives (electrolytes and nonelectrolytes) on the CP has been extensively studied [6–11]. In this context, the activity of ionic surfactants has been less explored [12–14]. The ionic surfactants themselves do not show clouding and are known to increase the CP of nonionics and polymers. They may thus act as clouding preventors (or CP enhancers). Results of such studies may also have relevance in chemical processes where clouding of compounds constituting the system is not wanted.

In recent years, the clouding of nonionic surfactants (Triton X 100, Brij 56, Igepal), polymers (block copolymers, methyl cellulose, polyvinylmethyl ether, etc.), and alkyl phenyl ethoxylates alone and in the presence of different additives has been investigated [12, 15–22] and correlative analysis of the results based on molecular structure, polarity of the medium, interaction with solvent, etc. has been attempted [23–25].

In the present work, we have considered the nonionic surfactants Triton X 100, Brij 56, and Brij 97 as well as the polymer PVME as the clouding species and ionic surfactants, and the alkyl triphenyl phosphonium bromides having carbon numbers 10, 12, 14, and 16 in the chain as the clouding preventors (or CP enhancers). Their activities have been explored in detail in terms of their influence on the CP and the thermodynamics of the physicochemical process. As far as the behavior is concerned, the polymer PVME has shown a difference from the nonionic surfactants (TX 100, Bj 56, and Bj 97).

Experimental section

Materials

The nonionic surfactants, Triton X 100 [*p-tert*-octyl phenoxy polyoxy ethylene (9.5) ether], Brij 56 [polyoxyethylene (10) cetyl ether], and Brij 97 [polyoxyethylene(10) oleyl ether] were obtained from Sigma, USA. The polymer PVME (polyvinyl methyl ether, mol wt. 52,000) was obtained from Aldrich, USA. The alkyl triphenyl phosphonium bromides (C_{10}TPB, C_{12}TPB, C_{14}TPB, and C_{16}TPB) were 99% pure products of Caledon Laboratories LTD of Canada (Distributors for Lancaster Synthesis of England) and were the same compounds as used earlier [26]. All the chemicals were used as received. The molecular structure of the clouding species and the additives are represented in Fig. 1.

Method

The experimental procedure for CP measurements previously studied was followed [11]. A known concentration of the clouding species with a desired concentration of the additive (ATPB) was taken in a securely stoppered test tube and placed in a heating mantle, where temperature was increased under a controlled condition of constant stirring. The point of clouding was visually observed and noted at the start of the phenomenon. The heating was then stopped and the system was allowed to cool. The temperature at the clearance of turbidity was again noted. The mean of the two temperatures was considered as the CP of the system.

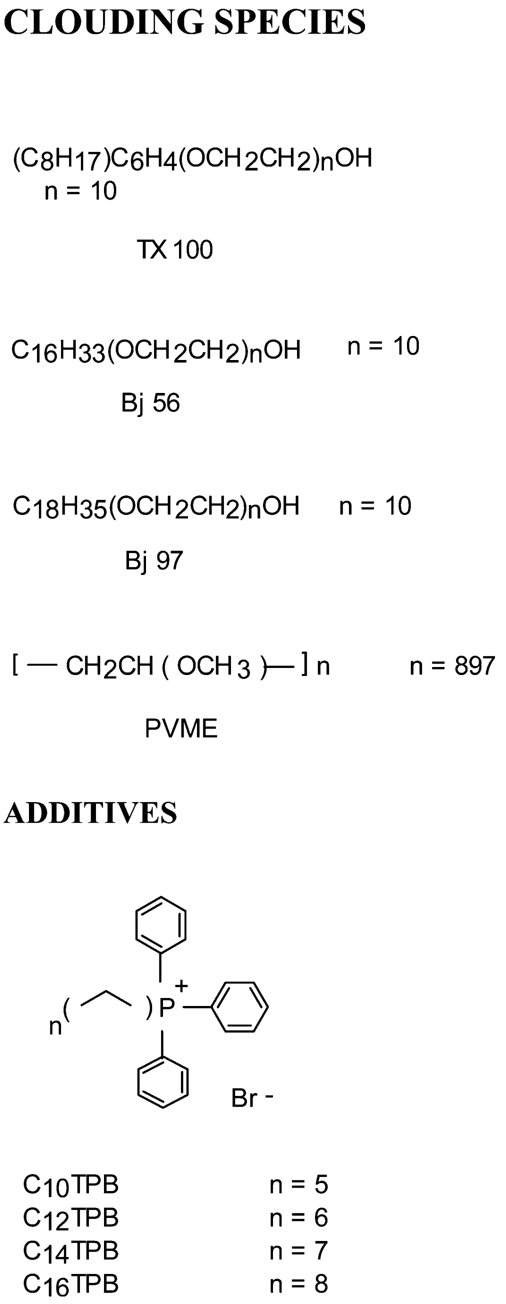


Fig. 1 Molecular structures of the clouding agents and additives

The error in CP measurements was within ±0.1°C. Four different concentrations of each clouding species at several ATPB concentrations were studied.

Results

The measured CPs for the systems of TX 100, Bj 56, Bj 97, and PVME are illustrated in Figs. 2, 3, 4 and 5. It has been observed that for TX 100 with C_{10}, C_{12}, C_{14},

Fig. 2 The measured CPs of the clouding agent TX 100 versus concentration of the additives **a** TX 100–C_{10}TPB system (*a*, 12.5 mM TX 100; *b*, 15 mM TX 100; *c* 20 mM TX 100; *d* 25 mM TX 100). **b** TX 100–C_{12}TPB system (*a* 12.5 mM TX 100; *b* 15 mM TX 100; *c* 20 mM TX 100; *d* 25 mM TX 100). **c** TX 100–C_{14}TPB system (*a* 10 mM TX 100; *b* 12 mM TX 100; *c* 15 mM TX 100; *d* 20 mM TX 100; e, 25 mM TX 100). **d** TX 100–C_{16}TPB system (*a* 12.5 mM TX 100; *b* 15 mM TX 100; *c* 20 mM TX 100; *d* 25 mM TX 100)

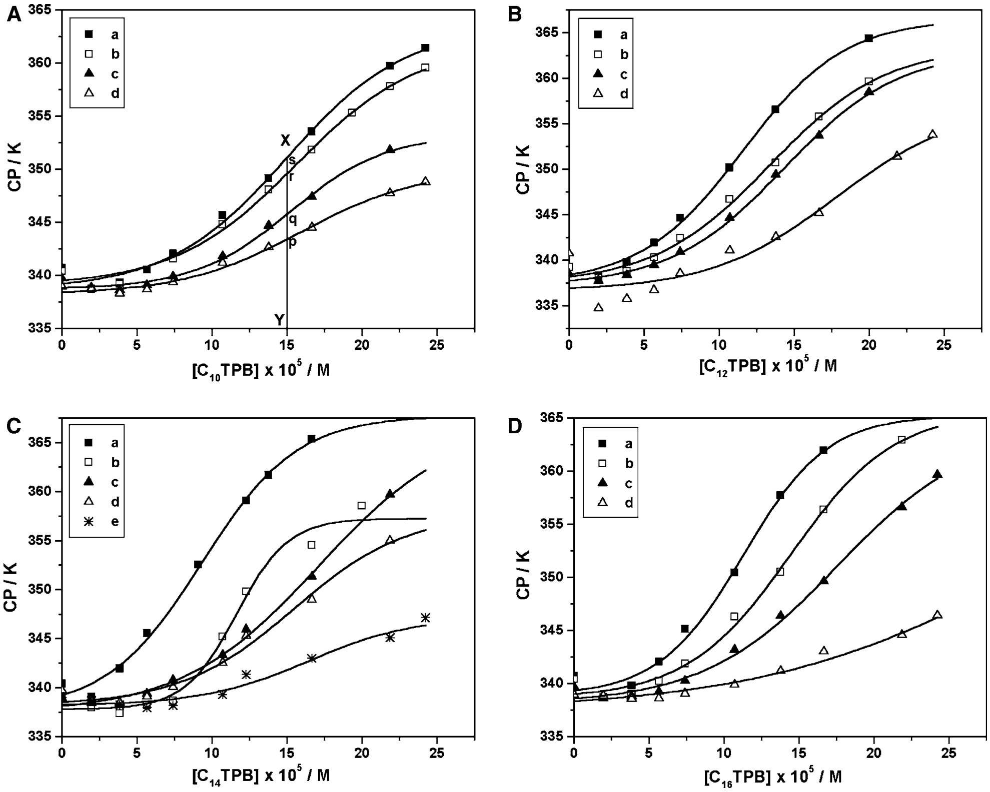


Fig. 3 The measured CPs of the clouding agent Bj 56 versus concentration of the additives. **a** Bj 56–C_{10}TPB system (*a* 15 mM Bj 56; *b* 17.5 mM Bj 56; *c* 20 mM Bj 56; *d* 25 mM Bj 56). **b** Bj 56–C_{12}TPB system (*a* 15 mM Bj 56; *b* 20 mM Bj 56; *c* 25 mM Bj 56; *d* 30 mM Bj 56; e, 35 mM Bj 56). **c** Bj 56–C_{14}TPB system (*a* 20 mM Bj 56; *b* 25 mM Bj 56; *c* 30 mM Bj 56; *d* 20 mM Bj 56; e, 35 mM Bj 56). **d** Bj 56–C_{16}TPB system (*a* 22.5 mM Bj 56; *b* 25 mM Bj 56; *c* 30 mM Bj 56; *d* 35 mM Bj 56)

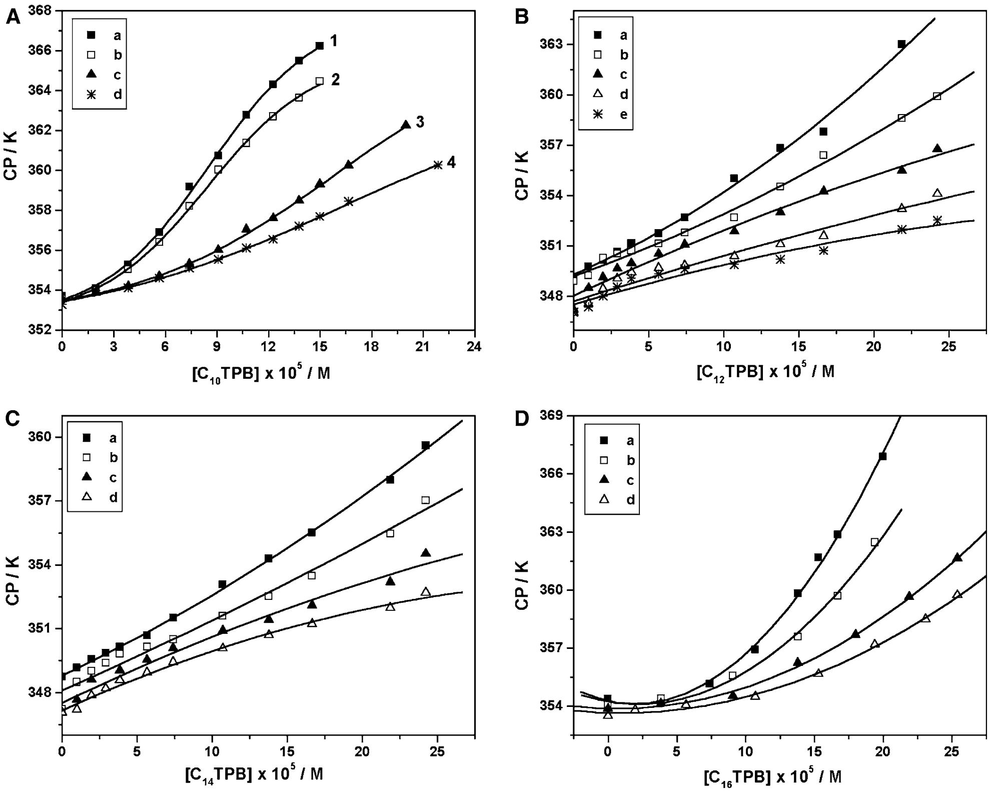


Fig. 4 The measured CPs of the clouding agent Bj 97 versus concentration of the additives. **a** Bj 97–C_{10}TPB system (*a* 15 mM Bj 97; *b* 20 mM Bj 97; *c* 25 mM Bj 97; *d* 30 mM Bj 97). **b** Bj 97–C_{12}TPB system (*a* 15 mM Bj 97; *b* 20 mM Bj 97; *c* 25 mM Bj 97; *d* 30 mM Bj 56). **c** Bj 97–C_{14}TPB system (*a* 15 mM Bj 97; *b* 20 mM Bj 97; *c* 25 mM Bj 97; *d* 30 mM Bj 97). (Inset shows the point of transition from the crossing C of the two straight lines for 25 mM Bj 97.) **d** Bj 97 – C_{16}TPB system (*a* 22.5 mM Bj 97; *b* 25 mM Bj 97; *c* 30 mM Bj 97; *d* 35 mM Bj 97)

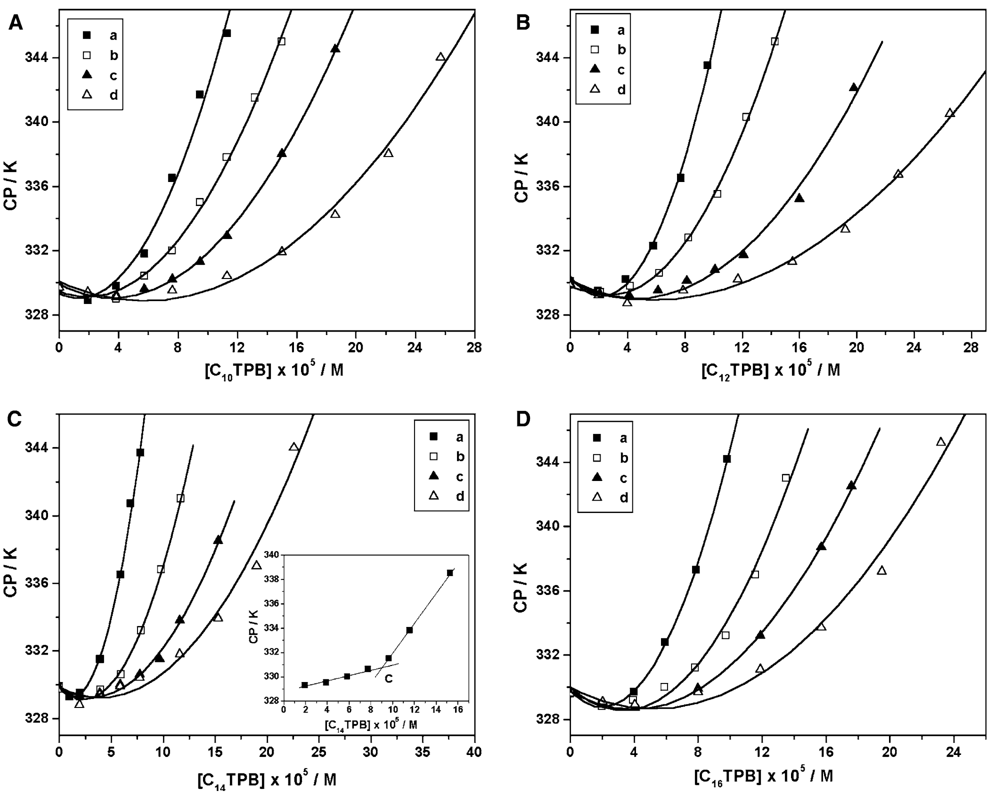
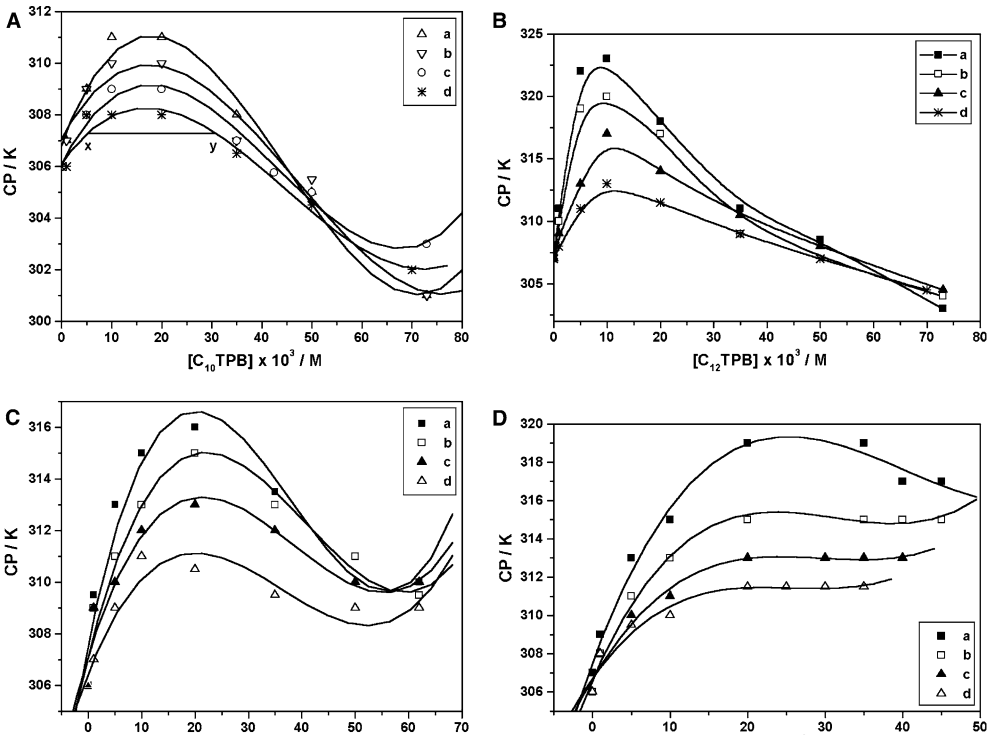


Fig. 5 The measured CPs of the clouding agent PVME versus concentration of the additives. **a** PVME–C_{10}TPB system (*a* 0.058 mM PVME; *b* 0.096 mM PVME; *c* 0.192 mM PVME; *d* 0.288 mM PVME). **b** PVME–C_{12}TPB system (*a* 0.096 mM PVME; *b* 0.144 mM PVME; *c* 0.192 mM PVME; *d* 0.288 mM PVME). **c** PVME–C_{14}TPB system (*a* 0.160 mM PVME; *b* 0.192 mM PVME; *c* 0.240 mM PVME; *d* 0.288 mM PVME). **d** PVME–C_{16}TPB system (*a* 0.192 mM PVME; *b* 0.240 mM PVME; *c* 0.288 mM PVME; *d* 0.336 mM PVME)



and $C_{16}TPB$, and Bj 56 with $C_{10}TPB$, the CP versus [ATPB] plots were sigmoidal in nature. The rest of the combinations, save those with PVME, were different, of which Bj 97-related combinations rose steeply after an initial mild change in CP. For the PVME–ATPB combinations, the plots produced distinct maxima with C_{10}, C_{12}, and $C_{14}TPB$. The maxima were shallow with $C_{16}TPB$. For the PVME–$C_{10}TPB$ and PVME–$C_{14}TPB$ combinations, distinct minima were also observed at higher concentrations of C_{10} and $C_{14}TPB$.

For all the nonionic surfactants that were studied, it was observed that at a constant [ATPB], the CP was directly proportional to the [Surfactant]. However, for the PVME–ATPB system, due to its dome-shaped pattern, a single CP was bounded by two [ATPB] concentrations (as indicated by the line *xy* in Fig. 5a) except for the PVME–$C_{16}TPB$ combination. Thus, the PVME–ATPB interaction was in direct contrast with the nonionics (TX 100, Bj 56, and Bj 97)–ATPB interaction.

The transition points (A_t) of the sigmoidal curves for TX 100 (Fig. 2) and for Bj 56 (Fig. 3a, curves 1, 2) with the concentration of the clouding agent are presented in Table 1. The A_t has been evaluated by using the Sigmoidal Boltzman Fitting procedure [27] of the CP versus [ATPB] according to the relation,

$$\mathrm{CP} = \mathrm{CP_f}\left[1 + \left(\frac{\mathrm{CP_i} - \mathrm{CP_f}}{\mathrm{CP_f}}\right)\{1 + \exp(A_c - A_t)/\Delta A_c\}^{-1}\right] \qquad (1)$$

where A_c is the concentration of the ATPB in the system, A_t is its concentration at the transition point, ΔA_c is the constant interval of A_c, and the subscript i and f denote the initial and final stages of CP respectively.

For the nonsigmoidal CP versus [ATPB] plots [with Bj 56, Fig. 4a (curves 3, 4), b–d) and Bj 97 (Fig. 5)], the point of transition was determined from the intersection point C of the two straight lines as shown in the inset of Fig. 5c. In the case of PVME–ATPB combinations, the maxima of the curves were considered as the transition points.

The effect of the additive chain length as well as the concentration of the clouding agents on the transition concentration (A_t) was mild (Table 1). In this respect the PVME–ATPB system was most inert; the TX 100–ATPB system was inert towards $C_{10}TPB$ but was responsive with the other ATPBs. The other two systems Bj 56–ATPB and Bj 97–ATPB were responsive both towards the ATPB type and the concentration of the clouding species. The mild variation of the transition points observed in this study can be considered as a special feature of the systems that were studied.

Table 1 Dependence of transition concentration (TP) of ATPB on the concentration of the clouding species (CS)

TP/mM				
[CS]/mM	$C_{10}TPB$	$C_{12}TPB$	$C_{14}TPB$	$C_{16}TPB$
TX 100				
10	–	–	0.09	–
12.5	0.15	0.12	0.12	0.11
15	0.16	0.13	0.17	0.14
20	0.15	0.14	0.15	0.18
25	0.16	0.18	0.16	0.15
Bj 56				
15	0.09	0.167	–	–
17.5	0.08	–	–	–
20	0.10	0.107	0.190	0.095
25	0.12	–	0.200	0.120
30	–	0.160	0.095	0.110
35	–	0.170	0.110	0.140
Bj 97				
15	0.08	0.09	0.06	0.09
20	0.12	0.12	0.10	0.095
25	0.16	0.15	0.09	0.10
30	0.22	0.25	0.16	0.15
PVME				
0.0961	18	9	–	–
0.144	–	9	–	–
0.16	–	–	20	–
0.192	17	11	21	24
0.24	–	–	21	21
0.288	17	10	19	20
0.336	–	–	–	20

Discussion

Taking the CP as the point of phasing out of the clouding species (CS) from the solution, the standard free energy of the clouding process, $\Delta G_c{}^0$, has been obtained in terms of the relation used earlier [11],

$$\Delta G_c^0 = RT \ln X_c \qquad (2)$$

where X_c is the mole fraction of the clouding species, and the other terms have their usual significance.

The standard state considered was the hypothetical standard state of unit mole fraction. The rationale for the determination of the enthalpy of the clouding process ($\Delta H_c{}^0$) given in earlier studies has been followed. At a fixed concentration of an additive, different concentrations of the clouding agent produced different CP values. Those were the temperature for phase separation of the clouding species (herein, the nonionic surfactants and PVME). A representative illustration of the $\Delta H_c{}^0$ determination procedure is shown with reference to Fig. 2a with crossing points along the vertical line *XY* cutting the CP curves at p, q, r, and s. The CP values corresponding to p, q, r, and s points were used as the clouding temperatures of the clouding agent (here, TX 100) at concentrations of 12.5, 15, 20, and 25 mM respectively. The $\Delta G_c{}^0$ values corresponding to these concentrations (obtained from Eq. 2) were processed according to Eq. 3 to derive the enthalpy of clouding (ΔH_c^0) at the additive concentration denoted by the base point of the vertical line *XY* on the abscissa. Thus,

$$\frac{d\Delta G_c^0/T}{d(1/T)} = \Delta H_c^0 \tag{3}$$

The entropy of clouding (ΔS_c^0) was then computed from the Gibbs-Helmholtz relation,

$$\Delta S_c^0 = (\Delta H_c^0 - \Delta G_c^0)/T \tag{4}$$

Representative linear plots of $\Delta G_c^0/T$ against $1/T$ at different additive concentrations are depicted in Fig. 6. ΔH_c^0 and ΔS_c^0 values obtained at different [ATPB] are given in Tables 2, 3, 4 and 5.

For all the systems studied, the ΔH_c^0 values were endothermic and decreased with increasing [ATPB]. The ΔH_c^0 values with C_{10}TPB were higher than the rest of the ATPBs particularly at lower concentrations. The ΔS_c^0 values were also high. High values of both enthalpy and entropy of clouding have been reported earlier with hydrotrope and other additives. For PVME at higher concentrations above 50 mM, the clouding process was reasonably exothermic with a large negative entropy. Such large and exothermic heat changes were also observed for other clouding systems. In view of the modest change in ΔG_c^0 and large changes in ΔH_c^0 and ΔS_c^0, a nice compensation effect between the last two parameters was expected. Such plots corresponding to the transition concentrations of the ATPBs, which were in line with the expectation, are illustrated in Fig. 7. The thermodynamic parameters of clouding at the transition concentration (A_t) of the ATPBs are given in Table 6. The ΔG_c^0 values obtained at the transition concentrations of the ATPBs are plotted against the concentration of the clouding agents in Fig. 8. The plots are fairly linear and the overall spontaneity of the phenomenon followed the order PVME $>$ TX 100 $\approx$ Bj 56 $>$ Bj 97. The values of free-energy change per mole of the clouding agents ($d(\Delta G_c^0)/d$[CA]) obtained from the slope of the plot are presented in Table 8. This has given a comparison of the efficiency of the additives. For Bj 56, Bj 97, and PVME followed the order C_{10}TPB $>$ C_{12}TPB $>$ C_{14}TPB $>$ C_{16}TPB (with the exception of PVME with C_{12}TPB). For TX 100, the order was reversed (again showing an anomaly with C_{12}TPB).

The averaged compensation temperatures (T_{comp}) obtained for the four different systems studied herein (considering results at all concentrations of the additives that were studied) are also presented in Table 8. For the systems that were studied, the compensation temperatures have followed the order

$$(T_{comp})_{Bj\,56} > (T_{comp})_{TX\,100} > (T_{comp})_{Bj\,97} > (T_{comp})_{PVME}$$

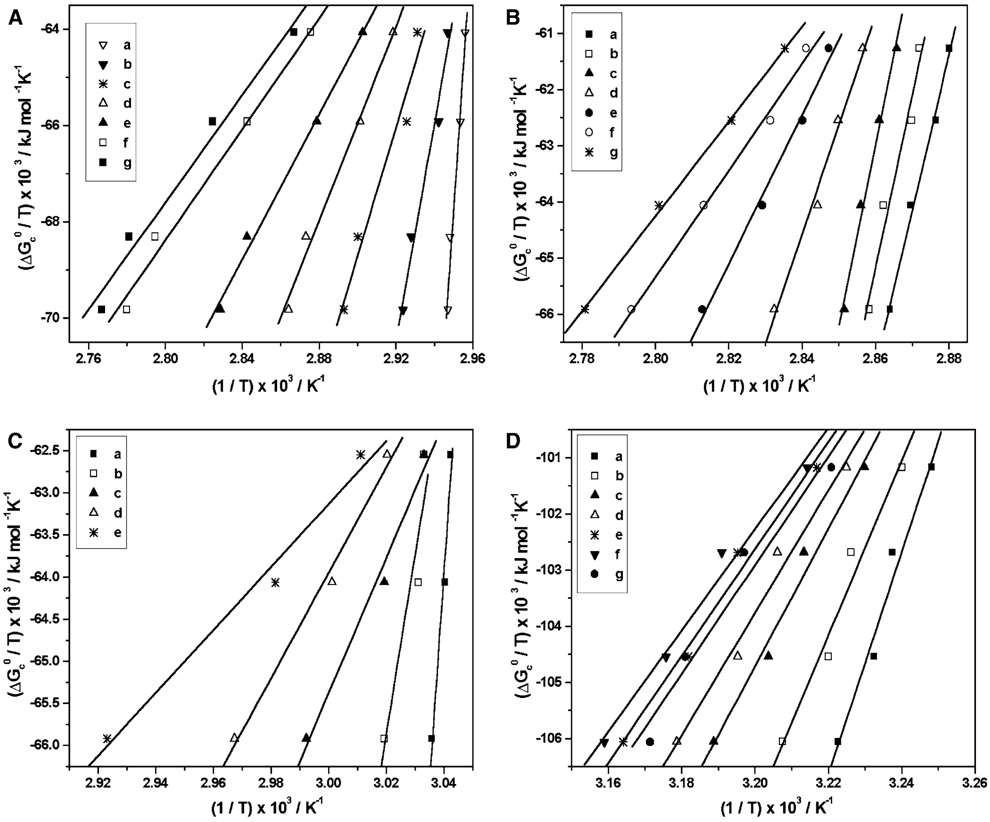


Fig. 6 Plots of $\Delta G_c^0/T$ versus $1/T$. **a** TX 100–C_{10}TPB system. (*a* 0.038 mM; *b* 0.074 mM; *c* 0.107 mM; *d* 0.138 mM; e, 0.167 mM; f, 0.219 mM; g, 0.242 mM). **b** Bj 56–C_{14}TPB system. (*a* 0.010 mM; *b* 0.029 mM; *c* 0.057 mM; *d* 0.107 mM; e, 0.167 mM; f, 0.219 mM; g, 0.242 mM). **c** Bj 97–C_{16}TPB system. (*a* 0.059 mM; *b* 0.079 mM; *c* 0.098 mM; *d* 0.116 mM; e, 0.135 mM). **d** PVME–C_{14}TPB system. (*a* 3 mM; *b* 5 mM; *c* 8 mM; *d* 10 mM; e, 15 mM; f, 20 mM; g, 30 mM)

Table 2 $\Delta H_c{}^0$ and $\Delta S_c{}^0$ of clouding of TX 100 in the presence of ATPBs

($\Delta H_c{}^0$/kJ mol^{-1}) ($\Delta S_c{}^0$/kJ mol^{-1} K^{-1})				
10^5[Additive]/M	C_{10}TPB	C_{12}TPB	C_{14}TPB	C_{16}TPB
3.85	(589) (1.81)	(158) (0.535)	–	(488) (1.51)
5.66	(344) (1.08)	(130) (0.450)	–	(190) (0.624)
7.41	(225) (0.729)	(115) (0.403)	–	(109) (0.386)
10.71	(133) (0.456)	(78) (0.294)	(116) (0.405)	(67) (0.260)
12.3	–	–	(51) (0.215)	–
13.7	(101) (0.359)	(52) (0.215)	–	(44) (0.192)
16.7	(75) (0.282)	(43) (0.187)	(44) (0.192)	(38) (0.176)
21.9	(58) (0.229)		(34) (0.162)	(27) (0.143)
24.2	(56) (0.224)		(20) (0.120)	(17) (0.114)

Table 3 $\Delta H_c{}^0$ and $\Delta S_c{}^0$ of clouding of Bj 56 in the presence of ATPBs

($\Delta H_c{}^0$/kJ mol^{-1}) ($\Delta S_c{}^0$/kJ mol^{-1} K^{-1})				
[Bj 56]/M	C_{10}TPB	C_{12}TPB	C_{14}TPB	C_{16}TPB
0.99	–	(319) (0.979)	(278) (0.861)	–
1.96	–	(319) (0.976)	(335) (1.025)	–
2.91	–	(286) (0.883)	(307) (0.944)	–
3.85	–	(388) (1.17)	(334) (1.021)	–
5.66	(177) (0.562)	(340) (1.04)	(322) (0.985)	–
7.41	(102) (0.352)	(262) (0.811)	(280) (0.863)	–
9.09	(78) (0.285)	–	–	–
10.0	–	–	–	(198) (0.619)
10.71	(67) (0.253)	(169) (0.543)	(195) (0.617)	–
11.6	–	–	–	(151) (0.486)
12.3	(58) (0.226)	–	–	–
13.5	(56) (0.220)	(131) (0.434)	(158) (0.513)	(105) (0.356)
15.0	(55) (0.219)	–	–	(86) (0.302)
16.0	–	–	–	(75) (0.273)
16.7	–	(113) (0.384)	(133) (0.440)	–
17.0	–	–	–	(65) (0.245)
18.0	–	–	–	(57) (0.222)
19.0	–	–	–	(54) (0.213)
20.0	–	–	–	(46) (0.191)
22.0	–	(80) (0.288)	(95) (0.332)	
24.2	–	(78) (0.284)	(84) (0.300)	

In the table, the T_{comp} has been compared with the average of the clouding temperatures T_{ave} (discussed in the next section).

A general comprehension

The A_t values of the ATPBs only modestly differed from one another (Table 1) and the maximum A_t values observed with TX 100, Bj 56, Bj 97, and PVME were 0.18, 0.20, 0.25, and 21 mM, respectively. The cmc values of the ATPBs C_{10}TPB, C_{12}TPB, C_{14}TPB, and C_{16}TPB at 303 K were 6.70, 1.53, 0.690, and 0.095 mM, respectively. Except for PVME, the maximum transition concentrations (A_t) of the additives were appreciably lower than their aqueous cmc values considering the absence of any drastic effect of temperature variation on cmc in the CP range of 325–360 K. The mild dependence of A_t on the ATPB-chain length was a striking phenomenon. Only PVME had shown requirement of ATPBs much in excess of cmc values, and their A_t values remained nonvariant with [PVME]; and the values with C_{12}TPB were much different from those with the other ATPBs. The concentrations of the clouding surfactants used were all much above their cmcs (the Bj 56 and Bj 97 were 15,000–35,000 times and TX 100 was ~50–125 times larger than their respective cmc values). The effect of a minor amount of ATPB (1 mol of ATPB per 50–125 mol of TX 100, and ~60–120 mol of Bj 35 clouding compound) to augment the retardation of clouding demanded a unique mechanism of action. It is normally considered that the hydrophilic center (groups) of the nonionic surfactants and water soluble polymers gets desolvated by the heat energy, and they assemble/aggregate to phase out from the solution. How a very minor quantity of a hydrophobically rich ATPB molecule (having three phenyl rings in the head group) retarded the clouding process required a special

Table 4 ΔH_c^0 of clouding of Bj 97 in the presence of additives

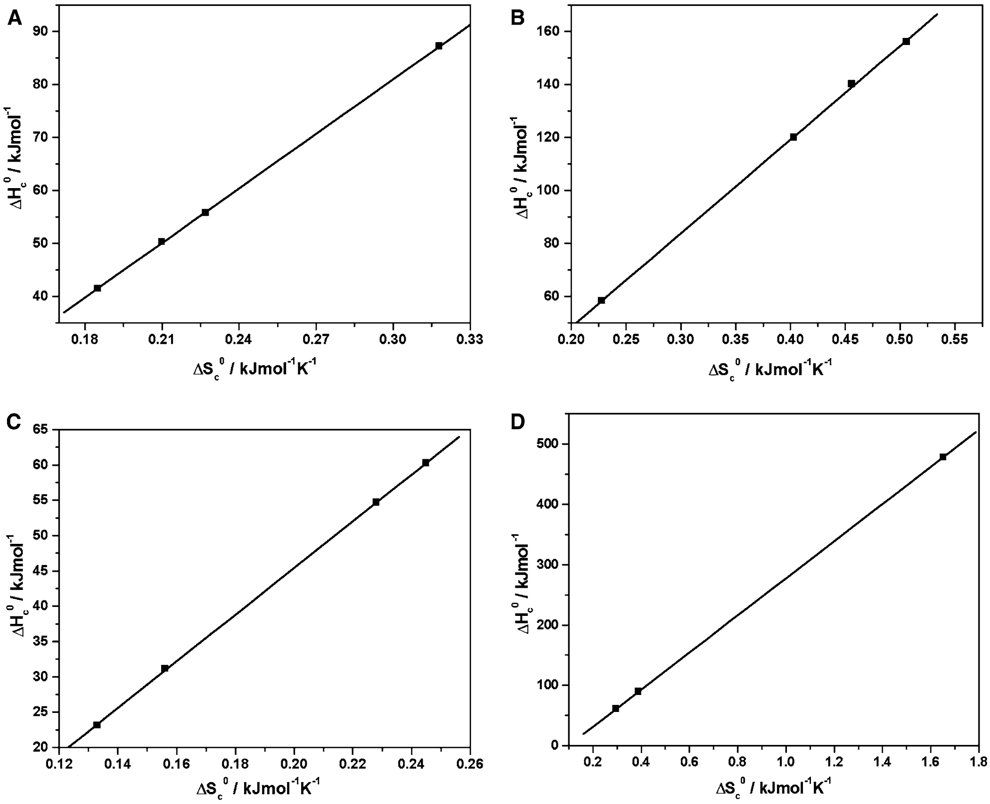
10^5[Additive]/M	C_{10}TPB	C_{12}TPB	C_{14}TPB	C_{16}TPB
	(ΔH_c^0/kJ mol^{-1}) (ΔS_c^0/kJ mol^{-1} K^{-1})			
1.98	–	–	(860) (2.68)	–
3.84	(850) (2.64)	–	–	–
4.2	–	(498) (1.58)	–	–
5.31	–	(203) (0.682)	–	–
5.74	(208) (0.696)	–	–	–
5.90	–	–	(459) (1.46)	(498) (1.58)
6.83	–	(104) (0.379)	(151) (0.521)	–
7.62	(85) (0.320)	–	–	–
7.88	–	–	(109) (0.394)	(213) (0.709)
8.53	–	(57) (0.237)	–	–
9.49	(46) (0.202)	–	–	–
9.81	–	–	(56) (0.233)	(80) (0.307)
9.96	–	(40) (0.186)	–	–
11.5	(42) (0.191)	–	(38) (0.178)	(63) (0.252)
12.1	–	(36) (0.172)	–	–
13.5	–	–	–	(37) (0.175)
14.4	–	(26) (0.140)	–	–
15.0	(29) (0.151)	–	–	–
15.4	–	–	–	(34) (0.165)
17.6	–	–	–	(27) (0.142)
18.6	(17) (0.113)	–	–	–
19.5	–	–	–	(23) (0.131)

Table 5 ΔH_c^0 clouding of PVME in the presence of additives

10^3 [PVME]/M	C_{10}TPB	C_{12}TPB	C_{14}TPB	C_{16}TPB
	(ΔH_c^0/kJ mol^{-1}) (ΔS_c^0/kJ mol^{-1} K^{-1})			
3	–	(125) (0.505)	(198) (0.744)	–
5	(749) (2.54)	(90) (0.391)	(155) (0.604)	(135) (0.537)
7	–	(82) (0.366)	–	–
8	–	–	(123) (0.497)	(100) (0.424)
9	–	(86) (0.378)	–	–
10	(568) (1.94)	–	–	(89) (0.387)
11	–	(92) (0.397)	–	–
13	–	–	–	(79) (0.354)
14	–	(101) (0.425)	–	–
15	(492) (1.69)	–	(95) (0.407)	(74) (0.338)
17	–	(114) (0.467)	–	–
19	–	(135) (0.534)	–	–
20	(475) (1.64)	–	(90) (0.391)	(66) (0.312)
25	(493) (1.70)	(173) (0.658)	(91) (0.393)	(58) (0.287)
30	(551) (1.89)	(235) (0.859)	(97) (0.412)	(59) (0.291)
35	(791) (2.68)	(323) (1.14)	(89) (0.387)	(66) (0.312)
40	(895) (3.025)	–	(100) (0.424)	(72) (0.332)
45	–	–	(119) (0.486)	–
50	–	–	(174) (0.666)	–
60	(−836) (−2.65)	–	–	–
70	(−439) (−1.34)	–	–	–

mechanism for rationalization. In the case of PVME (requiring roughly 1 mol of ATPB per 0.05–0.2 mol of the polymer or 45–180 mol of the repeating unit in the molecule), the required explanation was equally challenging. On the average, the aggregation number of the nonionic surfactants used herein should be around 200 at 300 K [28, 29]. In the temperature range 325–360 K, due to desolvation the micelles should appreciably grow, and values of the aggregation number in the range of 800–1,000 would not be an overestimate. Thus, on the average four ATPB molecules reside in a micelle of the nonionic surfactants. Likewise, with increasing [ATPB], 1 mol of PVME received 5–20 mol of ATPBs at the CP maximum or the transition point. These mixed entities (mixed micelles and surfactant–polymer combines) bearing similar positive charges

Fig. 7 Compensation plots corresponding to transition concentrations. **a** TX 100; **b** Bj 56; **c** Bj 97; **d** PVME



underwent repulsion to manifest aggregation and phase separation at a higher temperature. The [ATPB] required for the transition in CP, therefore, mildly depended on their alkyl-chain lengths. The energetics of the clouding process also supported this feature, whereas on the whole, the magnitudes of the parameters at equal [ATPB] were comparable. The maximization of the CP at an intermediate [ATPB] in the case of PVME could be explained as follows. When the mole ratio of [PVME]/[ATPB] is in the range of 0.05–0.2, the association of the surfactant with the PVME increased repulsion among the polymer molecules and consequently the CP increased. At higher ratios, the ATPB-induced hydrophobicity aided intermolecular association thus significantly lowering the CP, which even went below the CP of the pure polymer. An increasing value of the CP, thereafter, for PVME–C_{10}TPB and PVME–C_{14}TPB indicated complexity of interaction of the ATPB combined systems. The rationalization given herein is only tentative. Further work is warranted for a better understanding of the mechanistic aspect of the phenomenon that was observed.

Like other chemical systems, the clouding processes studied herein have evidenced excellent enthalpy–entropy compensation [11, 30, 31]. The product of T_{comp} and the entropy of clouding (ΔS_c^0) emerges to be equivalent to the nonfree (or nonuseful) part of the process enthalpy. It was expected to correspond to the average of the experimental temperature expressed by the relation [11]. Thus,

$$T_{\mathrm{ave}} = \left(\prod_{i=1}^{n} T_i\right)^{1/n} \tag{5}$$

where T_i is the ith temperature of the total number n. The T_{ave} values (Table 7) obtained were several degrees higher than T_{comp}. Maximum deviation was observed for TX 100–ATPB combinations. In hydrotrope environments, for Bj 56 and PVME, T_{ave} was found [11] to be several degrees lower than the T_{comp}. The ΔH_c^0 and ΔS_c^0 were both found to be appreciably large. Desolvation of a number of oxygen centers of the clouding species together with breakdown of the water structure contributed large shares in the endothermic process. The contribution of the exothermic aggregation process of the micelle or the polymer was relatively small.

Conclusions

1. For all the nonionic surfactants that were studied, at a constant [ATPB], the CP was directly proportional to the [nonionics].
2. The PVME–ATPB interaction was in direct contrast with the nonionics (TX 100, Bj 56, and Bj 97)–ATPB interaction.

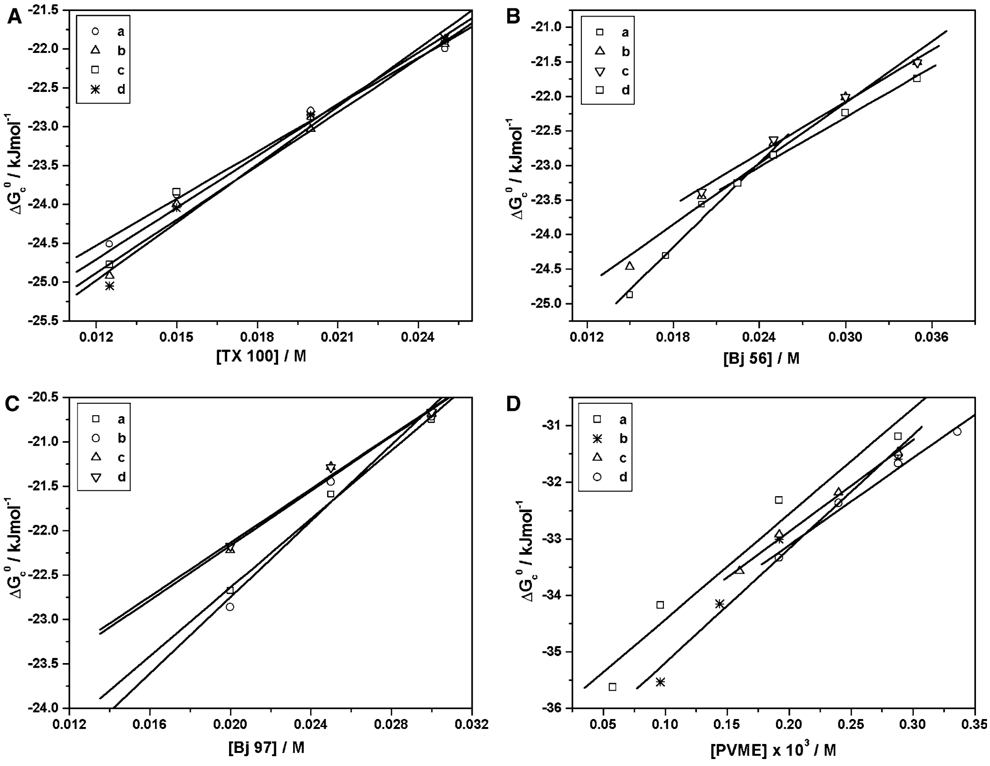


Fig. 8 Plots of ΔG_c^0 values at transition concentrations of the ATPBs versus concentration of clouding agents. **a** TX 100 with (*a* C_{10}TPB; *b* C_{12}TPB; *c* C_{14}TPB; *d* C_{16}TPB). **b** Bj 56 with (*a* C_{10}TPB; *b* C_{12}TPB; *c* C_{14}TPB; *d* C_{16}TPB). **c** Bj 97 with (*a* C_{10}TPB; *b* C_{12}TPB; *c* C_{14}TPB; *d* C_{16}TPB). **d** PVME with (*a* C_{10}TPB; *b* C_{12}TPB; *c* C_{14}TPB; *d* C_{16}TPB)

Table 6 Thermodynamic parameters for clouding at the transition concentration (A_t) of the ATPBs

[CS]/mM	ΔG_c^0/kJ mol^{-1}	ΔH_c^0/kJ mol^{-1}	ΔS_c^0/Jmol^{-1} K^{-1}
	$C_{10}/C_{12}/C_{14}/C_{16}$	$C_{10}/C_{12}/C_{14}/C_{16}$	$C_{10}/C_{12}/C_{14}/C_{16}$
TX 100 (A_t = 15/14/15/14.5)[a]			
12.5	−24.5/−24.9/−24.8/−25.0	87/50/56/41	318/211/227/ 186
15	−23.9/−24.0/−23.8/−24.0		
20	−22.8/−23.0/−22.9/−22.8		
25	−22.0/−21.9/−21.9/−21.9		
Bj 56 (A_t = 12/16/15/12)[a]			
15	−24.9/−24.5/–/–	58/120/156/140	228/403/506/456
17.5	−24.3/–/–/–		
20	−23.6/−23.4/−23.4/–		
22.5	–/–/–/−23.2		
25	−22.8/−22.7/−22.6/−22.8		
30	–/−22.0/−22.0/−22.2		
35	–/−21.5/−21.5/−21.7		
Bj 97 (A_t = 14.5/15/10/11)[a]			
20	−22.7/−22.9/−22.2/−22.2	31/23/55/60	156/133/228/245
25	−21.6/−21.4/−21.3/−21.3		
30	−20.7/−20.7/−20.7/−20.7		
PVME (A_t = 17.2, 10, 20.6, 20)[a]			
0.058	−35.6/–/–/–	478/89/89/61	1652/388/388/296
0.096	−34.2/−35.5/–/–		
0.144	–/−34.2/–/–		
0.160	–/–/−33.6/–		
0.192	−32.3/−33.0/−32.9/−33.3		
0.240	–/–/−32.2/−32.4		
0.288	−31.2/−31.6/−31.5/−31.7		
0.336	–/–/–/−31.1		

[a] The A_t values are in mM unit

Table 7 Compensation temperature and average temperature of clouding for the ATPB combinations—clouding species studied

Additive	TX 100	Bj 56	Bj 97	PVME
C_{10}TPB	337 (345)	353 (358)	328 (334)	306 (307)
C_{12}TPB	330 (346)	348 (352)	329 (333)	308 (315)
C_{14}TPB	337 (345)	347 (351)	329 (332)	306 (312)
C_{16}TPB	338 (346)	354 (358)	328 (334)	308 (313)

Table 8 Free energy-change per unit mole of the clouding species at the transition concentrations of the additives

ΔG^0_{ca}/kJ mol^{-1} mol$^{-1}_{ca}$				
Additive	Bj 56	Bj 97	TX 100	PVME
C_{10}TPB	204	193	201	18,661
C_{12}TPB	147	214	229	20,151
C_{14}TPB	125	154	222	16,215
C_{16}TPB	120	151	248	15,406

3. The ΔH_c^0 values were endothermic and decreased with increasing [ATPB].
4. For Bj 56, Bj 97, and PVME, the efficiency order of the additives was C_{10}TPB > C_{12}TPB > C_{14}TPB > C_{16}TPB (with the exception of C_{12}TPB with PVME). For TX 100, the order was reversed (also showing an anomaly with C_{12}TPB).
5. The maximum transition concentrations (A_t) of the additives were appreciably lower than their aqueous cmcs except for PVME. The A_t depended mildly on the ATPB-chain length.

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