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ORIGINAL CONTRIBUTION

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# Mass transport in Triton X series nonionic surfactant solutions: a new approach to solute–solvent interactions

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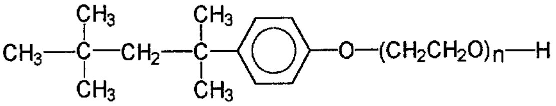
**Abstract** Densities, viscosities and tracer diffusion coefficients for solutions of the nonionic surfactants Triton X-45, X-114, X-100 and X-102 in water (except for Triton X-45) and methanol, and for Triton X-100 in three water–methanol mixtures have been measured at 298.15 K and 308.15 K. The activation energy for viscous flow and the contributions to it from solute and solvent have been calculated. Comparison of the Gibbs energies of these systems shows the roles of polyoxyethylene chains of Triton X molecules in the interactions between solute and solvent, and also the effects of solvents on the interactions for different solutes. The viscosity *B* coefficients are positive for all of the surfactant solutions, and the temperature coefficients of *B* are negative. In the non-micellar solutions in methanol, values of *B* are small and the temperature coefficient of *B* is nearly zero. In water–methanol mixtures the critical micelle concentration becomes larger as the methanol content increases up to 40% w/w; micelles are not formed at higher methanol concentrations. The *B* coefficient decreases with increasing proportion of methanol in the solvent, and the temperature coefficient of *B* changes from a fairly large positive value at low methanol contents to a small negative value at 80% w/w methanol.

**Key words** Mass transport – nonionic surfactant – solutions

## Introduction

The Triton X series polydisperse surfactants are used extensively as detergents, emulsifiers and solvents [1, 2]. The structure of the Triton X surfactants is:



Many studies on aqueous solutions of the surfactants, using NMR, Raman spectrum and light-scattering techniques, have given information on the micellar structure and the association of the surfactants with water [3–11]. Little work has been done on the behaviour of Triton X molecules in solvents such as methanol, and water–methanol mixtures.

The properties of solutions are determined by solute–solute, solvent–solvent, and solute–solvent interactions, and it is quite important to separate these kinds of interactions if possible. In this work we have used the transition-state theory to treat viscosity and diffusion coefficient data for solutions of the surfactants in water, methanol, and water–methanol mixtures, with the objective of quantifying solute–solvent interactions.

The average chain length (*n*), solubilities and critical micelle concentrations (CMC) for solutions in water of the surfactants used in this work are listed in Table 1.

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**Table 1** Physical properties of Triton X surfactants

| | TX-45 | TX-114 | TX-100 | TX-102 |
|---|---|---|---|---|
| $n$ (average number of EO units) | 5 | 7.5 | 9.5 | 12.5 |
| CMC in water ($\mathrm{mol\,L^{-1}}$)[a] | $1.17\times10^{-4}$ | $1.84\times10^{-4}$ | $2.90\times10^{-4}$ | $3.75\times10^{-4}$ |
| Average molar mass[b] | 426 | 536 | 624 | 756 |
| Solubility in water | D | D | M | M |
| Solubility in methanol | D | S | S | S |
| Solubility in benzene | M | M | M | M |

D = Dispersible; M = Miscible; S = Soluble.

[a] From National Standards Reference Data Series, No. 36, U.S. National Bureau of Standards, Washington, 1971.

[b] $\mathrm{g\,mol^{-1}}$.

Increasing the concentration above the CMC changes the size and shape of the micelles from small spheres to large rods, and then a liquid crystalline phase (which can be detected by microscopic examination with crossed polarisers) is formed. Finally the molecules attain a disordered coiled structure at high concentrations.

For Triton X-100 at low concentration in aqueous solution, the micelles have been found to have the following properties (with some variation depending on concentrations, temperature, and the experimental method used):

Aggregation number: 100–140 [3, 11]
Radius: 3–9 nm [9]
Shape: sphere or oblate ellipsoid [1, 3]
Dominant conformation of EO chain: loosely turned helix (coil) [6]
Number of associated water molecules: 3 or 4 per EO unit [3].

## Transition-state theory

Eyring and co-workers [12] suggested that every molecule in viscous flow must pass through a transition-state in which the molecule has a different structure and thermodynamic properties from those of the ground-state molecule. The following relationships were proposed. For pure liquids:

$$\eta_1 = (hN_A/V_1^0)\exp(\Delta\mu_1^{0\#}/RT) \tag{1}$$

and for solutions:

$$\eta_{1,3} = (hN_A/V_{1,3})\exp(\Delta G_{1,3}^{\#}/RT)\,, \tag{2}$$

where 1 and 3 denote solvent and solute respectively, $N_A$ and $h$ are the Avogadro constant and Planck constant, $V_1^0$ is the molar volume of component 1, $\Delta\mu_1^{0\#}$ and $\Delta G_{1,3}^{\varnothing}$ are Gibbs energy of activation for viscous flow of pure solvent and solution, respectively, and $V_{1,3}$ is the molar volume of the solution, given by

$$V_{1,3} = x_1V_1^0 + x_3V_3^{\varnothing}\,,$$

where $x$ is mole fraction and $V_3^{\varnothing}$ is the molar volume of the solute. When the solvent is a mixture a variant of Eq. (1) can be used:

$$\eta_{1,2} = (hN_A/V_{1,2})\exp(\Delta G_{1,2}^{\#}/RT)\,. \tag{1'}$$

In Eq. (1′) $V_{1,2}$ is the mean molar volume of the mixture given by

$$V_{1,2} = x_1V_1^0 + x_2V_2^0$$

and $\Delta G_{1,2}^{\#}$ is the mean Gibbs energy of activation for viscous flow of the mixed solvent.

Feakins and co-workers [13–15] extended the theory by combining Eqs. (1) and (2) with the Jones–Dole equation

$$\eta_r = 1 + Ac^{1/2} + Bc \approx 1 + Bc\,.$$

The activation energy term in Eq. (2) is replaced by

$$\Delta G_{1,3}^{\#} = x_1\Delta\mu_1^{0\#} + x_3\Delta\mu_3^{\varnothing\#}\,, \tag{3}$$

where $\Delta\mu_3^{\varnothing\#}$ is the solute contribution to $\Delta G_{1,3}^{\#}$. The viscosity $B$ coefficient is

$$B = (V_1^0 - V_3^{\varnothing}) + (V_1^0/RT)(\Delta\mu_3^{\varnothing\#} - \Delta\mu_1^{0\#})\,, \tag{4}$$

where $V_3^{\varnothing}$ is the molar volume of the solute.

It is now possible to determine $\Delta\mu_3^{\varnothing\#}$ (a partial thermodynamic function of the transition state for viscous flow of the solution) from measurable properties of the solution. However, $\Delta\mu_3^{\varnothing\#}$ is not solely determined by solute–solvent interactions since it includes a contribution from the changes in solute–solute interactions which result from addition of solute to solvent. $\Delta\mu_3^{\varnothing\#}$ can be divided into two parts

$$\Delta\mu_3^{\varnothing\#} = \Delta G_3^{\varnothing}(1 \rightarrow 1') + \Delta G_3^{\varnothing}(3 \rightarrow 3')\,, \tag{5}$$

where $\Delta G_3^{\varnothing}(1 \rightarrow 1')$ is the difference in Gibbs energy for a ground-state solute dissolved in a transition state solvent and a ground-state solvent, and $\Delta G_3^{\varnothing}(3 \rightarrow 3')$ is the Gibbs energy difference for a solute transferring from its ground state to its transition state, in a ground state solvent. Solution of a transition state solute in a transition state solvent has an extremely small probability and the corresponding Gibbs energy difference is therefore neglected. To evaluate $\Delta G_3^{\ominus}(3 \rightarrow 3')$, we suppose that the transport mechanism is similar for surfactant molecules undergoing diffusion and viscous flow. Then

$$D = (kT\lambda^2/h)\exp(-\Delta G_D^{\#}/RT) \,, \tag{6}$$

where $\lambda$ is a constant related to intermolecular distance [16], and $\Delta G_D^{\#}$ is the Gibbs energy of activation for diffusive transport. We adopt the strategy of calculating $\Delta G_D^{\#}$ from experimentally determined diffusion coefficients, substituting $\Delta G_D^{\#}$ for $\Delta G_3^{\ominus}(3 \rightarrow 3')$ in Eq. (5) and hence evaluating $\Delta G_3^{\ominus}(1 \rightarrow 1')$.

Feakins and co-workers developed the theory for solution systems of simple molecules, such as aqueous methanol solutions. In the present work we are extending the methodology to surfactant–solvent systems, in which the surfactant may be present as single molecules (in methanol solutions) or as micellar aggregates (in aqueous solutions). We do not at present take into account explicitly the molecular form of the surfactant.

## Experimental

The Triton X series (–45, –114, –100 and –102) surfactants were provided by the Union Carbide Corporation, and were dried with molecular sieve (0.3 nm) before use. Methanol (Rhone Poulenc AR grade material) was used without further purification. Deionised water with conductivity 0.2 $\mu$S was used.

Viscosity was measured using factory calibrated Cannon Instrument Company Ubbelohde-type viscometers, and densities were determined with an Anton Parr model DMA 02C digital densimeter using water and aqueous sucrose as calibration fluids. Viscosity and density measurements were done at the same time using a thermostated water bath whose temperature (298.15 K or 308.15 K) was constant to within ±0.02 K, on solutions with surfactant concentrations in the range $1 \times 10^{-3}$–$7 \times 10^{-2}$ mol L$^{-1}$. The solvents used were water, methanol and water–methanol mixtures containing 20, 50 and 80% w/w methanol. Densities were measured with precision $1 \times 10^{-5}$ g cm$^{-3}$ and accuracy $3 \times 10^{-5}$ g cm$^{-3}$. The accuracy of the measured viscosities is ±0.5%.

The tracer diffusion coefficient of $^3$H-labelled Triton X-100 was measured at a single surfactant concentration (0.01 mol L$^{-1}$) in water and methanol, at 298.15 K and 308.15 K, using glass diaphragm cells that were calibrated using KCl solution, and associated standard procedures [17]. Mixtures of radioactive solutions with Biofluor scintillator were made up by weight, and several hundred thousand counts were recorded for each solution. The counting procedures are described in detail elsewhere [17]. The measured diffusion coefficients are accurate to within ±1%.

## Results and discussion

The experimental density and viscosity data (relative to pure water) are recorded in Tables 2, 3 and 4, and the tracer diffusion coefficients in Table 5. The Jones–Dole equation was obeyed accurately by all solutions, and viscosity $B$ coefficients for the solutions are listed in Table 6 together with values for $\Delta\mu_3^{\ominus\#}$ calculated using Eq. (4).

**Table 2** Relative densities and viscosities for Triton X surfactants in water

| Surfactant | $10^3$ c/mol L$^{-1}$ | 298.15 K | | 308.15 K | |
|---|---|---|---|---|---|
| | | $\rho_r$ | $\eta_r$ | $\rho_r$ | $\eta_r$ |
| TX-114 | 4.97 | 1.00024 | 1.024 | 1.00016 | 1.017 |
| | 7.17 | 1.00030 | 1.053 | 1.00031 | 1.028 |
| | 10.9 | 1.00044 | 1.099 | 1.00041 | 1.062 |
| | 15.5 | 1.00050 | 1.122 | 1.00058 | 1.099 |
| | 20.0 | 1.00073 | 1.260 | 1.00070 | 1.150 |
| | 54.3 | – | – | 1.00076 | 1.239 |
| TX-100 | 1.65 | 0.99993 | 1.018 | 0.99972 | 1.014 |
| | 7.24 | 1.00031 | 1.043 | 1.00003 | 1.034 |
| | 17.0 | 1.00082 | 1.114 | 1.00060 | 1.065 |
| | 32.6 | 1.00159 | 1.128 | 1.00132 | 1.141 |
| | 50.9 | 1.00261 | 1.218 | 1.00221 | 1.292 |
| TX-102 | 4.96 | 1.00032 | 1.018 | 1.00038 | 1.028 |
| | 7.28 | 1.00058 | 1.019 | 1.00053 | 1.022 |
| | 10.0 | 1.00076 | 1.034 | 1.00070 | 1.039 |
| | 14.9 | 1.00120 | 1.066 | 1.00108 | 1.059 |
| | 20.2 | 1.00159 | 1.087 | 1.00114 | 1.092 |
| | 49.9 | 1.00386 | 1.237 | 1.00359 | 1.230 |

**Table 3** Relative densities and viscosities for Triton X surfactants in methanol

| Surfactant | $10^3$ c/mol L$^{-1}$ | 298.15 K | | 308.15 K | |
|---|---|---|---|---|---|
| | | $\rho_r$ | $\eta_r$ | $\rho_r$ | $\eta_r$ |
| TX-45 | 7.26 | 1.00076 | 1.003 | 1.00090 | 0.993 |
| | 9.95 | 1.00115 | 1.011 | 1.00126 | 0.992 |
| | 16.7 | 1.00204 | 1.017 | 1.00221 | 0.999 |
| | 29.6 | 1.00382 | 1.033 | 1.00405 | 1.020 |
| | 47.0 | 1.00637 | 1.056 | 1.00646 | 1.033 |
| | 58.2 | 1.00790 | 1.068 | 1.00808 | 1.048 |
| TX-114 | 2.27 | 1.00038 | 0.992 | 0.99936 | 0.988 |
| | 6.24 | 1.00127 | 0.999 | 1.00000 | 0.992 |
| | 12.3 | 1.00255 | 1.009 | 1.00142 | 1.000 |
| | 22.8 | 1.00433 | 1.029 | 1.00335 | 1.017 |
| | 38.5 | 1.00751 | 1.064 | 1.00643 | 1.047 |
| | 53.8 | 1.01044 | 1.087 | 1.00952 | 1.083 |
| TX-100 | 1.31 | 1.00000 | 0.975 | – | – |
| | 1.87 | 1.00013 | 0.980 | 1.00142 | 0.998 |
| | 4.36 | 1.00064 | 0.978 | 1.00206 | 1.008 |
| | 17.4 | 1.00369 | 1.012 | 1.00489 | 1.039 |
| | 37.0 | 1.00815 | 1.064 | 1.00927 | 1.082 |
| | 54.4 | 1.01222 | 1.098 | 1.01351 | 1.135 |
| | 73.5 | 1.01655 | 1.148 | 1.02522 | 1.165 |
| TX-102 | 0.62 | 1.00013 | 0.992 | 0.99910 | 1.003 |
| | 1.14 | 1.00025 | 0.992 | 1.00116 | 1.011 |
| | 9.23 | 1.00255 | 1.015 | 1.00154 | 1.016 |
| | 17.4 | – | – | 1.00399 | 1.051 |
| | 21.5 | 1.00611 | 1.065 | 1.00515 | 1.096 |

**Table 4** Relative densities and viscosities for solutions of Triton X-100 in methanol–water mixtures

| Methanol (% w/v) | $10^3$ c/mol L$^{-1}$ | 298.15 K | | 308.15 K | |
|---|---|---|---|---|---|
| | | $\rho_r$ | $\eta_r$ | $\rho_r$ | $\eta_r$ |
| 20 | 2.78 | 1.00031 | 1.006 | 1.00032 | 1.017 |
| | 5.08 | 1.00041 | 1.013 | 1.00048 | 1.021 |
| | 7.99 | 1.00073 | 1.021 | 1.00072 | 1.026 |
| | 21.4 | 1.00187 | 1.067 | 1.00148 | 1.067 |
| | 43.5 | 1.00342 | 1.159 | 1.00305 | 1.145 |
| 50 | 1.52 | 1.00044 | 1.004 | 1.00051 | 1.004 |
| | 3.71 | 1.00077 | 1.009 | 1.00087 | 1.009 |
| | 7.95 | 1.00121 | 1.017 | 1.00122 | 1.018 |
| | 24.1 | 1.00274 | 1.051 | 1.00271 | 1.052 |
| | 45.1 | 1.00494 | 1.109 | 1.00495 | 1.104 |
| 80 | 1.59 | 1.00047 | 1.007 | 1.00038 | 1.006 |
| | 3.31 | 1.00083 | 1.013 | 1.00084 | 1.009 |
| | 7.81 | 1.00178 | 1.021 | 1.00119 | 1.011 |
| | 21.0 | 1.00368 | 1.050 | 1.00325 | 1.044 |
| | 42.8 | 1.00415 | 1.092 | 1.00859 | 1.094 |

Values of $\Delta G_3^{\circ}(1 \rightarrow 1')$ calculated using Eq. (5) are given in Table 7.

When a solute dissolves it is surrounded by the neighbouring solvent molecules, giving rise to solute–solvent interactions and affecting solvent–solvent interactions. Viscous flow of a solvent molecule involves two kinds of movements. First, it moves from a site near to a solvent molecule to the vicinity of a second solvent molecule. Second, it moves from a site near to a solute to a site adjacent to the next solvent molecule. These general situations can be represented as follows:

$$A - B + C \rightarrow [A - B - C]^{\#} \rightarrow A + B - C\ .$$

In the first case $A$, $B$ and $C$ are all solvent molecules; in the second situation $A$ is a solute particle (specifically, an EO chain), $B$ and $C$ are solvent molecules.

The energy of the transition-state determines whether the process can proceed easily. On the other hand, the viscosity $B$ coefficient can be interpreted qualitatively by the Einstein equation:

$$B = 2.5\Phi/c ,$$

where $\Phi$ and $c$ are the volume fraction and concentration, respectively, of the solute.

In aqueous solutions, the $B$ coefficient is a measure of the interactions between solute and water. If the solute strengthens the structural network of water $B$ should be positive. For the surfactant solutions, $B$ is always positive (see Fig. 1) so that the addition of the surfactant to water makes the network structure more stable. When surfactants dissolve in water they form micelles if the concentration is above the CMC, but the average size of the micelles will be different for Triton X-114, Triton X-100, and Triton X-102 (Triton X-45 forms a dispersion rather than a solution in water) because of the difference in the average ethylene oxide (EO) chain length. Generally the aggregation number, $N$, of micelles, increases as the chain becomes shorter, and the size of the micelles for a surfactant with a longer EO chain will be smaller because of greater hydration [18]. The larger the average micelle size, the greater should be the effect of the micelles on the water structure, leading to the trend shown in Fig. 1, i.e., $B$ increases with decreasing EO chain length. However, it is also possible that Triton X-114 forms rod-like micelles in water whereas the micelles in Triton X-100 and Triton X-102 are spherical, due to the shorter EO chain. In that case the rod-like micelle solution would show higher viscosities in comparison to solutions with the same concentration containing spherical micelles. In addition, the dependence of $B$ on temperature can be explained by a significant decrease in the length of the rod-like micelles with increasing temperature, whereas spherical micelles should be less affected by temperature.

The data listed in Table 7 show that associated with the enlargement of the EO chains is a decrease in $\Delta G_3^{\circ}(1 \to 1')$. The contribution of the EO unit to $\Delta G_3^{\circ}(1 \to 1')$ is therefore negative (assuming that Triton X molecules with varying chain length have the same activation energy for diffusion).

**Table 5** Tracer diffusion coefficients of Triton X-100 in 0.01 mol L$^{-1}$ solutions in water and methanol

| Solvent | T/K | $10^9$ D/m$^2$ s$^{-1}$ |
|---|---|---|
| water | 298.15 | 0.475 |
| water | 308.15 | 0.813 |
| methanol | 298.15 | 1.033 |
| methanol | 308.15 | 1.381 |

**Table 6** Viscosity $B$ coefficients and values of $\Delta\mu_3^{\circ\#}$ for solutions of Triton X-100 in methanol–water mixtures

| Methanol (% v/v) | 298.15 K | | 308.15 K | |
|---|---|---|---|---|
| | B/L mol$^{-1}$ | $\Delta\mu_3^{\circ\#}$/kJ mol$^{-1}$ | B/L mol$^{-1}$ | $\Delta\mu_3^{\circ\#}$/kJ mol$^{-1}$ |
| 0 | 6.39 | 971 | 5.46 | 868 |
| 20 | 3.67 | 531 | 3.22 | 491 |
| 50 | 2.38 | 306 | 2.28 | 304 |
| 80 | 2.08 | 212 | 2.18 | 205 |
| 100 | 2.38 | 189 | 2.37 | 181 |

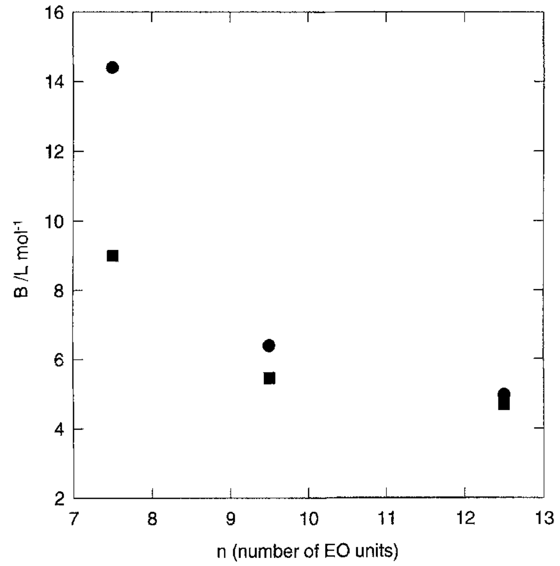

**Fig. 1** The variation of viscosity $B$ coefficients with oxyethylene chain length in water. ●, 298.15 K; ■, 308.15 K

**Table 7** Values of $\Delta G_3^{\circ}(1 \to 1')$ for Triton X surfactant solutions

| Solvent | TX-45 | | TX-114 | | TX-100 | | TX-102 | |
|---|---|---|---|---|---|---|---|---|
| | 298.15 K | 308.15 K | 298.15 K | 308.15 K | 298.15 K | 308.15 K | 298.15 K | 308.15 K |
| water | – | – | 2012 | 1301 | 932 | 829 | 751 | 737 |
| methanol | 88 | 86 | 134 | 128 | 170 | 162 | 232 | 196 |

Units: kJ mol$^{-1}$.

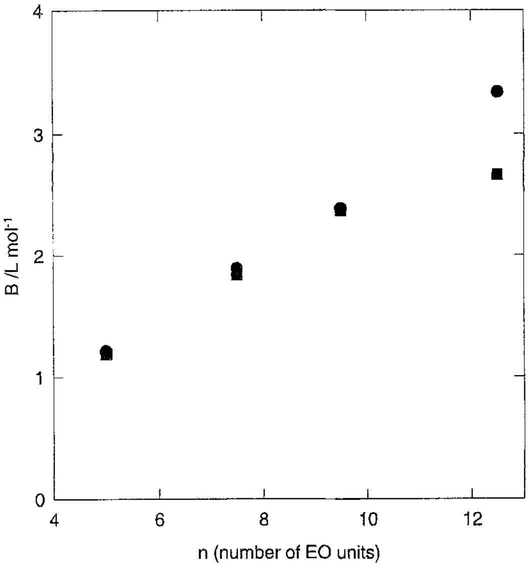

**Fig. 2** The variation of viscosity $B$ coefficients with oxyethylene chain length in methanol. ●, 298.15 K; ■, 308.15 K

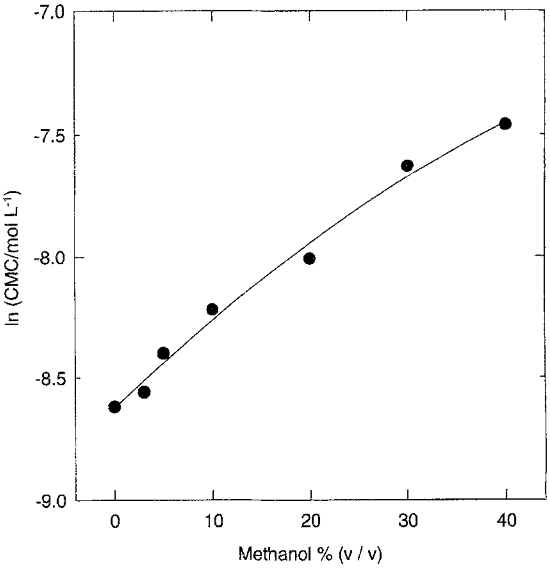

**Fig. 3** The variation of the critical micelle concentration with methanol content in solutions of Triton X-100 in water–methanol mixtures at 298.15 K

In methanol solutions, the surfactants do not form micelles in the concentration range we have studied, because of the polarity and structure of methanol. Solute–solvent interactions are reflected in the $B$ coefficients, shown in Fig. 2, which are all positive indicating that the addition of the surfactant can reinforce interactions between methanol molecules. Since the solute molecules exist individually in the solutions, when the size of the molecule increases the $B$ value should increase according to the Einstein equation, as is observed. Similarly, higher temperature makes $B$ smaller but the effect of temperature is very small except for the longest EO chain surfactant. The temperature coefficient $dB/dT$ is much smaller than that in water since the solute–solvent interaction in methanol is weak compared to that in water where micelles are formed. In contrast to the change of $\Delta G_3^{\circ}(1 \rightarrow 1')$ in water, for methanol solutions the contribution of the EO unit to $\Delta G_3^{\circ}(1 \rightarrow 1')$ is positive (see Table 7).

When Triton X-100 surfactant dissolves in water–methanol mixtures the behaviour of the solute is more complicated. It can form micelles if the methanol content of the solvent is less than 40% v/v, but the CMC increases (see Fig. 3) and the average micelle size may become smaller as the proportion of methanol increases up to 40%. The $B$ coefficient and $\Delta\mu_3^{\circ\neq}$ which represent the interaction between solute and solvent both become nearly independent of solvent composition when micelles cease to be formed. Above 40% methanol the hydrophobic parts of the surfactant molecules which usually form the cores of micelles in polar solvents come into contact with methanol or water molecules that will reduce part of the affinity of the solute for the solvent, and that effect persists until the methanol content reaches 100% (see Table 6).

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