A Correlation for the Estimation of Critical Micellization Concentrations and Temperatures of Polyols in Aqueous Solutions

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ABSTRACT: An empirical correlation is presented for the estimation of critical micellization concentrations (CMC) and critical micellization temperatures (CMT) for poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) copolymers in aqueous solutions. The CMC and CMT are expressed as a function of the polyol molecular weight, composition, and temperature (for CMC determination) or concentration (in the case of CMT). The correlation was developed from experimental CMT data for a set of 12 polyols that covered a wide range of molecular weights (2900–14600) and poly(ethylene oxide) contents (30–80 wt%) and is based on a simple expression for the standard free energy of micellization. Such a correlation should be useful to practitioners of the field as it allows easy prediction of CMC and CMT for a wide range of polyols with a minimal number of input parameters.
JAOCS 72, 823–826 (1995).

KEY WORDS: Block-copolymers, correlation, critical micellization concentration, micelles, nonionic surfactants, poly(ethylene oxide), polyols, poly(propylene oxide).

Poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) (PEO–PPO–PEO) copolymers are nonionic macromolecular surface-active agents, available commercially as Poloxamers, Synperonic (ICI Chemicals Ltd., Cleveland, United Kingdom), or Pluronic® (BASF Corp., Parisippany, NJ) polyols. Variation of the polyol molecular weight and composition leads to compounds with hydrophilic–lipophilic properties that meet specific requirements in different applications, such as detergency, dispersion stabilization, foaming, emulsification, or lubrication (1–3). A number of PEO–PPO–PEO polyols have been shown to associate in water in the form of micelles with a core composed mainly of the hydrophobic PPO and a corona dominated by the hydrated PEO (hydrophilic) blocks (3). The critical micellization concentration (CMC), i.e., the surfactant concentration at which micelles start forming [which is a strong function of temperature for aqueous polyol solutions

(3)], is a parameter of great fundamental and practical value (4). For common surfactants, a considerable amount of CMC data has been collected and summarized (4), whereas for polyols, only scarce and nonsystematic CMC data are available in the literature so far.

In the context of an ongoing investigation on the micellization behavior (3,5) and solubilization efficacy (6) of PEO–PPO–PEO copolymers in aqueous solutions, we have measured (7) CMC and critical micellization temperatures (CMT) for twelve Pluronic polyols. An empirical correlation for estimating CMC and CMT for PEO–PPO–PEO polyols in aqueous solutions is presented here. The correlation allows easy prediction of CMC and CMT for a wide range of polyols, with a minimal number of input parameters.

EXPERIMENTAL PROCEDURES

Molecular weights and compositions are listed in Table 1 (3). Solubilization of a hydrophobic dye was employed to detect the formation of micelles (CMC and CMT) in the polyol aqueous solutions (7). Surface tension measurements (8) and other techniques [such as pyrene fluorescence emission (9), light scattering (10), differential scanning calorimetry (10),

TABLE 1
Constants of the $1/T_{CMT}$ vs. log (% C) Correlation (Eq. 3) for Various Pluronic Polyols[a]

Pluronic polyol	Molecular weight	wt% PEO	Slope (S) ($\times 10^5$)	Intercept (I) ($\times 10^3$)
L64	2900	40	8.423	3.283
P65	3400	50	10.70	3.240
F68	8400	80	8.919	3.097
P84	4200	40	9.132	3.315
P85	4600	50	8.415	3.302
F88	11400	80	10.96	3.215
P103	4950	30	5.666	3.418
P104	5900	40	6.506	3.392
P105	6500	50	5.782	3.392
F108	14600	80	7.246	3.307
P123	5750	30	5.852	3.460
F127	12600	70	7.629	3.365

[a]Pluronic polyols from BASF Corp. (Parsippany, NJ). T_{CMT}, critical micellization temperature in Kelvin; PEO, poly(ethylene oxide).

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density (10), and proton nuclear magnetic resonance (11) corroborated the CMC and CMT data obtained from the dye solubilization experiments.

RESULTS AND DISCUSSION

The standard free energy change for the transfer of one mole of amphiphile from solution to the micellar phase (free energy of micellization), $\Delta G°$, is given by (7,12):

$$\Delta G° = R\,T \ln X_{CMC} \qquad [1]$$

where R is the gas law constant, T the absolute temperature, and X_{CMC} is the CMC expressed in mole fraction units. Applying the Gibbs-Helmholtz equation, we can express the standard enthalpy of micellization, $\Delta H°$, as (7,12):

$$\Delta H° = -R\,T^2\,[\partial \ln X_{CMC}/\partial\,T]_P = R\,[\partial \ln X_{CMC}/\partial\,(1/T)]_P \qquad [2]$$

Equation 2 indicates that if $\Delta H°$ is independent of temperature, there should be a linear relationship between $\ln X_{CMC}$ and $1/T$. This was indeed so when the inverse CMT values were plotted as a function of the natural logarithm of polyol mole fraction for a number of Pluronic polyols (7). Figure 1 shows the inverse CMT values plotted vs. concentration expressed in % wt/vol (which are more useful units than mole fraction). The CMT data are described adequately by a straight line when plotted in this manner. Detailed analysis and discussion on the influence of polyol composition and molecular weight on CMC and CMT are presented elsewhere (3,7); the focus here is on using these data to develop tools for predicting the micellization of polyols in aqueous solutions. As a first step, we present the equations that fitted the data of Figure 1:

$$1/T_{CMT} = S \log C + I \qquad [3]$$

where T_{CMT} is the critical micellization temperature in degrees Kelvin, C is the polyol concentration (% wt/vol), and S and I are constants obtained from the fit (S and I values are listed in Table 1 for various Pluronic polyols). Equation 3 al-

lows accurate determination of CMC at a given temperature, or CMT for a given concentration, for each of the twelve PEO–PPO–PEO polyols that we have studied (that there is no unifying correlation for the polyols based on Eq. 3).

$\Delta G°$ values (calculated at the CMT for polyol solutions of the same concentration, and expressed in kJ/mol) decreased (albeit with some scatter) with increasing polyol molecular weight (M_w) (7). When $\Delta G°$ is expressed in kJ per mole of monomer [i.e., ethylene oxide (EO) and propylene oxide (PO)] segments, the data behave in a remarkably concerted way when examined as a function of M_w. $\Delta G°'$ values (expressed in kJ per mole of EO and PO segments and estimated from Eq. 1 at the CMT) for twelve Pluronic polyols are plotted in Figure 2 as a function of polyol inverse M_w. This normalization reduced the rather scattered $\Delta G°$ vs. M_w data (presented in Ref. 7) to a straight line for a wide range of polyols. To enhance the utility of the data set of Figure 2, and to allow for interpolation, the $\Delta G°'$ values were correlated as a function of M_w and C *via* the empirical equation:

$$\Delta G°' = 10^3\,M_w^{-1}\,(0.3670 \log C - 1.2547) - 0.0045 \log C - 0.0070$$

$$[4]$$

The accuracy of the fit is excellent ($R^2 > 0.999$); the solid lines in Figure 2, results of the fit, attest to this. $\Delta G°'$ values predicted from Equation 4 differ less than 2.5% from those determined experimentally. The validity of a relatively simple relationship (Eq. 4) for the determination of the free energy of micellization, $\Delta G°$, for PEO–PPO–PEO polyols points to the relative importance of polyol composition and M_w on the micellization process. For a given polyol concentration, it appears as if the differences between PEO and PPO are either not important or cancel out at the CMT, and $\Delta G°$ depends only on the polyol M_w and the total number of EO and PO segments. Note that the intercepts of the $\Delta G°'$ vs. $1/M_w$ lines are approximately zero; the contribution to $\Delta G°$ per segment diminishes as the number of segments increases.
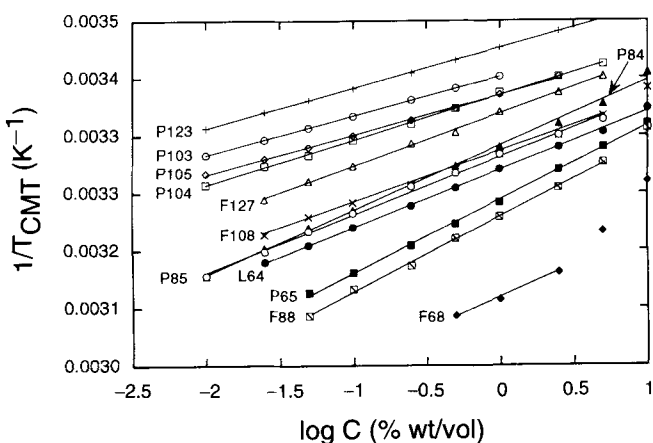

FIG. 1. $1/T_{CMT}$ (critical micellization temperature in Kelvin) vs. log (C) plots for various Pluronic (BASF Corp., Parsippany, NJ) polyols; the solid lines are fits to the experimental data.
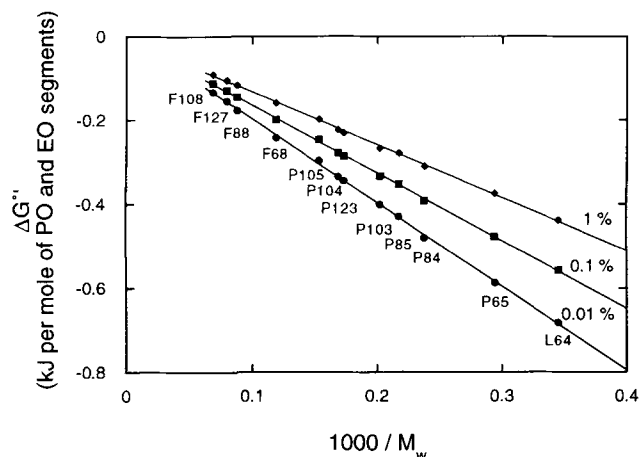
FIG. 2. $\Delta G°'$ [expressed in kJ per mole of propylene oxide (PO) and ethylene oxide (EO) segments] as a function of polyol inverse molecular weight (M_w). The solid lines are the results of fit by using Equation 4.

Equation 4 now can be used as a tool to estimate the micellization properties for PEO–PPO–PEO polyols in the 2900–14600 M_w range and for 30–80 wt% PEO content. The standard free energies ($\Delta G°$) can be determined directly from Equation 4, whereas enthalpies ($\Delta H°$) and entropies [$\Delta S° = (\Delta H°–\Delta G°)/T$] of micellization for various polyols can be derived from Equation 2 by utilizing CMT and CMC data obtained from the correlations presented below. Values for the critical micellization temperature (T_{CMT}) in °K can be obtained from $\Delta G°'$ (Eq. 4) through Equation 1:

$$T_{CMT} = N_{PO+EO} \, (R \ln X)^{-1} \, [M_w^{-1} \, 10^3 \, (0.3670 \log C - 1.2547)$$
$$- 0.0045 \log C - 0.0070 \,] \qquad [5]$$

where N_{PO+EO} is the number of PO and EO segments in the polyol molecule and $R = 0.008314$ kJ K^{-1} mol^{-1}. The natural logarithm of the polyol mole fraction, X, can be expressed as a function of M_w and C (assuming that C is much smaller than 100):

$$\ln X = 2.302 \log C - \ln M_w - 1.715 \qquad [6]$$

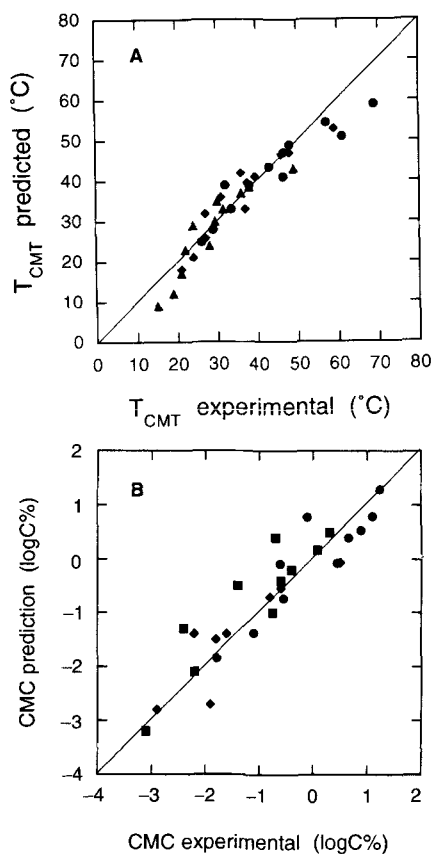The fitting ability of Equation 5 is demonstrated in Figure 3A,

where the estimated T_{CMT} (from Eq. 5) values are plotted as a function of the experimentally determined T_{CMT} for the twelve polyols studied, for a range of polyol concentrations. The experimental and predicted values are in good agreement and distribute evenly along the 45° line for the temperature range 20–60°C. A systematic deviation can be seen at the two temperature extremes, a result of the simple functional form used to fit the data.

A simple expression for the critical micellization concentration, C_{CMC}, expressed in mass units (% wt/vol), can also be obtained from Equations 5 and 6.

$$\log C_{CMC} = \frac{R\,T\left(\ln M_w + 1.715\right) - N_{PO+EO}\left(1254.7\,M_w^{-1} + 0.0070\right)}{2.302\,R\,T + N_{PO+EO}\left(-367\,M_w^{-1} + 0.0045\right)} \qquad [7]$$

The predictive ability of Equation 7 is demonstrated in Figure 3B, where the C_{CMC} values estimated from Equation 7 are plotted as a function of the experimentally determined C_{CMC} for the polyols studied and for a range of temperatures. If the assumption of Equation 6 is not valid, a numerical solution for the system of Equation 5 and the relationship $X = C/[C + (5.55 - 0.055C)M_w]$ is needed. Note that Equations 5 and 7 were derived from experimental data that fell in the temperature range of 10–70°C and concentration range of 0.01–1%. Consequently, the predictions are valid in this range of conditions, which should cover most of the applications of PEO–PPO–PEO polyols.

In addition to their practical utility, the correlations developed here can also prove helpful in evaluating published theories of block copolymer micellization and improving their treatment of polyol–water systems. An expression for $\Delta G°$ that has the same functional form as the experimentally determined $\Delta G°$, can be derived (13) from the Munch and Gast (14) theory, thus providing insight on the interdependence of the micellization parameters for the PEO–PPO–PEO/water system. The micellization theory of Nagarajan and Ganesh (15), developed for diblock copolymers, succeeded in qualitatively predicting the contributions of the polymer composition and the M_w on the micellization of PEO–PPO–PEO polyols; however, the theory overpredicts the experimentally obtained $\Delta G°$ by a factor of 4, and the CMC values (related to $\Delta G°$ via Eq. 1) by orders of magnitude (13). Modification (16) of the Nagarajan theory to account for triblock copolymers was not sufficient to reduce the discrepancy between the experimental data and theoretical predictions (13). This exemplifies the importance of correlations that are based on experimentally obtained data (such as the one presented here) in predicting the micellization properties of polyols.

FIG. 3. A: T_{CMT} values, predicted from Equation 5, plotted as a function of experimentally determined T_{CMT}, and B: C_{CMC} values, predicted from Equation 7, plotted as a function of experimentally determined C_{CMC}. The symbols in Figure 3A are the same as in Figure 2. In Figure 3B, ●, data at 25°C; ■, at 35°C; and ◆, at 45°C. CMC, critical micellization concentration; other abbreviations as in Figure 1.

ACKNOWLEDGMENT

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