JOURNAL OF
CHEMICAL &
ENGINEERING
DATA

ARTICLE

pubs.acs.org/jced

Activity Coefficients at Infinite Dilution and Critical Micelle Concentrations of Poly(oxy-1,2-ethanedyil), α-Tridecyl-ω-hydroxy Ethers ($C_{13}E_{i=6,10,18}$) in Aqueous Media by the Volmer Surface Equation of State and Group Contributions

Alejandra Pardo-Cervantes, Josefina Viades-Trejo, and Jesús Gracia-Fadrique*

Facultad de Química, Departamento de Fisicoquímica, Universidad Nacional Autónoma de México (UNAM),
Ciudad Universitaria, 04510, Coyoacán, México D.F., México

ABSTRACT: Activity coefficients at infinite dilution and the critical micelle concentration of three different poly(oxy-1,2-ethanedyil), α-tridecyl-ω-hydroxy ethers (POEs) (6, 10, and 18 mol) were determined from surface tension data in aqueous solution at 20 °C. Measurements were made with the ring tensiometer. As is the case for other members of the polyethoxylated alcohols family, experimental data obey the Volmer surface equation of state which contains either the critical micelle concentration or the activity coefficient at infinite dilution among its constitutive parameters. As expected, it was found that the critical micelle concentration values increased (cmc $\times 10^6$ = 2.15, 2.87, and 6.08) and the activity coefficients at infinite dilution decreased ($\gamma^\infty \times 10^{-5}$ = 4.7, 3.5, and 1.6) when the ethylene oxide content increased. The individual contributions of the ethoxy, hydroxide, and methylene groups found for other polyethoxylated surfactants were used to calculate the critical micelle concentration; the calculated values agree with the experimental values obtained by the Volmer surface equation of state.

INTRODUCTION

The chemical industry of surfactants plays an important role in a large number of manufacturing processes including foaming, wetting, solubilization, detergency, particle suspension, emulsifiers, surface coating products, and emulsion polymerization.[1,2] The most commonly used commodities for this purposes are the nonyl and ter-octyl phenol ethoxylates (NPEOs). Recent studies[3] have shown that some products derived from NPEOs are not successfully removed from treated water, and they can harm aquatic organisms.[4−7] Poly(oxy-1,2-ethanedyil), α-tridecyl-ω-hydroxy ethers (POEs) have the surface properties that make them viable candidates as substitutes in these manufacturing processes; additionally they have low toxicity and a biodegradable structure, are easy to obtain, and have lower production costs compared with natural alcohols.[8] POEs are synthetic linear nonionic surfactants, constituted by a hydro carbonated and an ethoxylated chain[9] produced by the hydrogenation of aldehydes derived from α-olefins, which are transformed by oligomerization synthesis.[10] Mixtures of olefins[2,11] of chains between 11 and 15 carbon atoms can be found; more than 70 % of the mixture corresponds to linear alcohols, and less than 30 % are iso-alcohols.[10−13]

The calculation and evaluation of activity coefficients represents the central part of the thermodynamics in fluid phase equilibria. The activity determination in aqueous and nonaqueous mixtures demands the use of activity coefficients. For low vapor pressure solutes, as nonionic surfactants, it is a difficult experimental task as shown in the seminal and thorough work of Clunie et al.[14] who made experimental water activity determinations in the entire concentration range by sophisticated techniques for the $C_{12}E_6$ system and indirect determinations of surfactant activities by the Gibbs−Duhem equation. These data show that the deviation from ideality of the thermodynamic activity of water is remarkably low almost over the entire composition range, despite the several phases that exist along this range.[15] The surface-solution equilibrium option presented in this work provides an alternative for direct surfactant activity determination in the premicellar region, where deviations from ideality are negligible, by means of the Volmer surface equation of state.

Theory. The surface activity and the ability of surfactants to aggregate to form micelles are determinant in their technical performance. The surface tension dependence on surfactant concentration enables a thorough analysis of micelle formation thermodynamics; additionally it is one of the most complete methods of critical micelle concentration cmc determination. The Volmer surface equation of state (SEOS) reported by this group in a previous paper,[16] used for the calculus of the interfacial parameters presented in this work, comes from the coupling of Gibbs and Volmer equations and from the equality of the bulk and surface chemical potentials. The surface chemical potential μ^S was derived from Volmer SEOS $[\pi(A - A_0 = RT)]$[16,17]

$$\int_{\mu^{0S}}^{\mu^S} d\mu^S = RT \int_{\pi_{cmc}}^{\pi} d\ln\pi + A_0 \int_{\pi_{cmc}}^{\pi} d\pi \qquad (1)$$

where $\pi = (\sigma_0 - \sigma)$ is the surface pressure, σ_0 is the surface tension of pure water ($72.57\ \text{mN}\cdot\text{m}^{-1}$) at 20 °C, σ is the surface tension of the solution, π_{cmc} is the surface pressure at the critical micellar concentration, R is the gas constant, T is the absolute temperature, and A_0 is a correction term analogous to the three-dimensional factor ν_o in the van der Waals equation.

Received: November 30, 2010
Accepted: April 28, 2011
Published: May 11, 2011

dx.doi.org/10.1021/je1012795 | J. Chem. Eng. Data 2011, 56, 2812–2817

Table 1. Number of Carbon Units *m*, Number of Ethoxy Units *n*, Calculated Average Molecular Mass M_w, at Temperature T = 293.15 K

surfactant[a]	m[b]	n[b]	M_w[c]/g·mol^{-1}
$C_{13}E_6$$^{\pm}$	$C_{11}-C_{14}$	6	464.77
$C_{13}E_{10}$$^{\pm\pm}$	$C_{11}-C_{14}$	10	641.01
$C_{13}E_{18}$$^{\pm\pm}$	$C_{11}-C_{14}$	18	993.49

[a] Data provided by product manufacturers ($^{\pm}$ICI, $^{\pm\pm}$Sigma-Aldrich). [b] General formula for POE: C_mE_n. [c] M_w as $C_{13}E_n$ with n = 6, 10, and 18, respectively, used for mole fraction calculations.

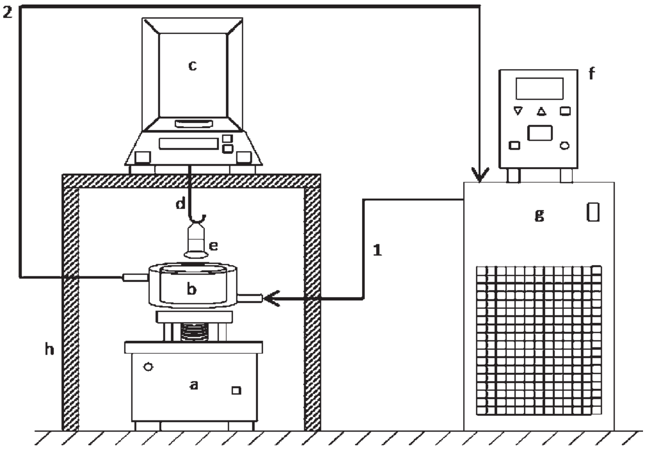

Figure 1. Scheme of apparatus used in this work: a. automatic elevator; b. jacketed glass vessel; c. analytical balance; d. hook; e. Pt−Ir ring; f. electronic unit; g. thermal bath; h. support; 1. fluid inlet (20 °C); 2. fluid outlet.

Writing the integrated form of eq 1 in terms of the reduced surface pressure π^*

$$\mu^S = \mu^{oS} + RT\ln\pi^* - (1-\pi^*)A_0 \tag{2}$$

where π^* is defined as $\pi^* = (\pi\cdot\pi_{cmc}^{-1})$. The reference state for the surfactant is π_m; the maximum surface pressure attained at x_{cmc} $\pi(x_{cmc}) = \pi_m$; thus $\pi^* = 1$.

Under the symmetrical convention and very low surfactant concentrations, $x \to 0$, $\gamma(x) \to \gamma^\infty$ = constant, the nonideal bulk chemical potential for the amphiphile at infinite dilution is

$$\mu^b = \mu^{ob} + RT\ln x + RT\ln\gamma^\infty \tag{3}$$

From eqs 2 and 3

$$\ln\left(\frac{\pi^*}{x}\right) = \frac{\pi_{cmc}A_0}{RT}(1-\pi^*) + \ln\gamma^\infty \qquad x \le x_{cmc} \tag{4}$$

The reference state and the boundary conditions for eq 4 at the cmc ($x\to x_{cmc}$; $\pi\to\pi_{cmc}$; $\pi^*\to 1$) lead to the fundamental thermodynamic equation

$$-\ln x_{cmc} = \ln\gamma^\infty \tag{5}$$

From eq 5, eq 4 may be expressed as

$$\ln\left(\frac{\pi^*}{x}\right) = \frac{\pi_{cmc}A_0}{RT}(1-\pi^*) - \ln x_{cmc}; \qquad x \le x_{cmc} \tag{6}$$

The critical micelle mole fraction x_{cmc} and the activity coefficient at infinite dilution γ^∞ calculated from eq 6 give a complete outlook about surfactant and solvent interactions; it is one of the few cases of SEOS which includes either the activity coefficient at infinite dilution (γ^∞) or the cmc among its constitutive parameters. It is a linear expression valid in the premicellar region $0 \le x \le x_{cmc}$; $0 \le \pi \le \pi_{cmc}$ with the intercept in $-\ln x_{cmc}$.

Table 2. Experimental Values of Surface Pressure π and Reduced Surface Pressure $\pi^* = \pi\cdot\pi_{cmc}^{-1}$ at Surface Tension σ and Mole Fraction x, for the POE $C_{13}E_6$ at the Temperature T = 293.15 K

π_{cmc}[a] = 45.98 mN·m^{-1}						
x	σ/mN·m^{-1}	$u(\sigma)$[b]/mN·m^{-1}	π/mN·m^{-1}	π^*	time[c]/s	f_i
$1.09\cdot10^{-5}$	26.53	0.07	46.04	1.00	600	0.8792
$9.70\cdot10^{-6}$	26.51	0.08	46.06	1.00	600	0.8792
$8.53\cdot\cdot\,10^{-6}$	26.55	0.11	46.02	1.00	600	0.8792
$7.76\cdot10^{-6}$	26.56	0.09	46.01	1.00	600	0.8792
$6.98\cdot10^{-6}$	26.69	0.06	45.88	1.00	600	0.8792
$6.40\cdot10^{-6}$	26.69	0.06	45.88	1.00	600	0.8792
$5.82\cdot10^{-6}$	26.89	0.07	45.68	0.99	600	0.8792
$5.24\cdot10^{-6}$	26.94	0.04	45.63	0.99	600	0.8792
$4.85\cdot10^{-6}$	27.05	0.01	45.52	0.99	600	0.8792
$4.54\cdot10^{-6}$	27.14	0.04	45.43	0.99	600	0.8792
$4.31\cdot10^{-6}$	27.22	0.04	45.35	0.99	600	0.8792
$3.86\cdot10^{-6}$	27.37	0.04	45.20	0.98	1800	0.8792
$3.69\cdot10^{-6}$	27.52	0.07	45.05	0.98	1800	0.8792
$3.41\cdot10^{-6}$	27.61	0.04	44.96	0.98	1800	0.8792
$3.86\cdot10^{-6}$	27.37	0.1	45.20	0.98	1800	0.8792
$3.10\cdot10^{-6}$	27.79	0.05	44.78	0.97	1800	0.8822
$2.72\cdot10^{-6}$	28.08	0.07	44.49	0.97	1800	0.8822
$2.42\cdot10^{-6}$	28.46	0.07	44.11	0.96	1800	0.8822
$2.21\cdot10^{-6}$	28.64	0.04	43.93	0.96	1800	0.8822
$1.94\cdot10^{-6}$	28.96	0.06	43.61	0.95	1800	0.8822
$1.67\cdot10^{-6}$	29.90	0.04	42.67	0.93	1800	0.8850
$1.40\cdot10^{-6}$	30.95	0.11	41.62	0.91	1800	0.8888
$1.21\cdot10^{-6}$	32.06	0.04	40.51	0.88	1800	0.8900
$1.11\cdot10^{-6}$	33.24	0.07	39.33	0.86	1800	0.8920
$1.01\cdot10^{-6}$	34.10	0.06	38.47	0.84	1800	0.8938
$9.31\cdot10^{-7}$	35.23	0.04	37.34	0.81	1800	0.8956
$8.53\cdot10^{-7}$	36.11	0.06	36.46	0.79	1800	0.8970
$7.76\cdot10^{-7}$	37.09	0.04	35.48	0.77	1800	0.8994
$6.98\cdot10^{-7}$	38.19	0.06	34.38	0.75	1800	0.9011
$6.06\cdot10^{-7}$	39.50	0.04	33.07	0.72	1800	0.9030
$4.05\cdot10^{-7}$	41.75	0.04	30.82	0.67	1800	0.9050
$3.10\cdot10^{-7}$	44.98	0.04	27.59	0.60	1800	0.9092
$1.94\cdot10^{-7}$	49.04	0.32	23.53	0.51	1800	0.9164
$1.55\cdot10^{-7}$	51.69	0.18	20.88	0.45	1800	0.9192
$1.16\cdot10^{-7}$	53.94	0.01	18.63	0.41	1800	0.9224
$7.76\cdot10^{-8}$	56.63	0.15	15.94	0.35	1800	0.9252
$3.88\cdot10^{-8}$	61.57	0.07	11.00	0.24	1800	0.9314

[a] Standard uncertainty $u(\pi_{cmc})$ = 0.08 mN·m^{-1}. [b] Standard uncertainties. [c] Time between measurements. Shaded rows show the constant π values.

In a previous paper of this research group,[18] the calculation of γ^∞ for simple liquids, the reference state for the bulk and the surface phase, was the pure solute: $x = 1\pi = \pi_m$; thus, the reference surface pressure is $\pi_m = (\sigma^0{}_1 - \sigma^0{}_2)$, that is, the difference between the surface tensions of the pure components

Table 3. Experimental Values of Surface Pressure π and Reduced Surface Pressure $\pi^* = \pi \cdot \pi_{cmc}^{-1}$ at Surface Tension σ and Mole Fraction x, for the POE $C_{13}E_{10}$ at the Temperature T = 293.15 K

$\pi_{cmc}{}^{a}$ = 46.28 mN·m^{-1}						
x	σ/mN·m^{-1}	$u(\sigma)^{b}$/ mN·m^{-1}	π/mN·m^{-1}	π^*	time^{c}/s	f_i
$2.81 \cdot 10^{-4}$	26.41	0.06	46.16	1.00	600	0.8770
$1.41 \cdot 10^{-4}$	26.34	0.05	46.23	1.00	600	0.8770
$2.81 \cdot 10^{-5}$	26.30	0.06	46.27	1.00	600	0.8770
$1.41 \cdot 10^{-5}$	26.25	0.06	46.32	1.00	600	0.8770
$1.13 \cdot 10^{-5}$	26.22	0.06	46.35	1.00	600	0.8770
$7.03 \cdot 10^{-6}$	26.24	0.04	46.33	1.00	600	0.8770
$5.91 \cdot 10^{-6}$	26.44	0.06	46.13	1.00	600	0.8792
$5.06 \cdot 10^{-6}$	26.68	0.06	45.89	0.99	600	0.8792
$4.22 \cdot 10^{-6}$	26.66	0.04	45.91	0.99	600	0.8792
$3.52 \cdot 10^{-6}$	26.85	0.1	45.72	0.99	600	0.8792
$3.29 \cdot 10^{-6}$	26.89	0.07	45.68	0.99	600	0.8792
$3.12 \cdot 10^{-6}$	27.39	0.04	45.18	0.98	600	0.8792
$2.80 \cdot 10^{-6}$	27.29	0.04	45.28	0.98	1800	0.8822
$2.73 \cdot 10^{-6}$	27.48	0.05	45.09	0.97	1800	0.8822
$2.67 \cdot 10^{-6}$	27.45	0.49	45.12	0.97	1800	0.8822
$2.48 \cdot 10^{-6}$	27.84	0.04	44.73	0.97	1800	0.8822
$2.25 \cdot 10^{-6}$	28.74	0.09	43.83	0.95	1800	0.8822
$1.97 \cdot 10^{-6}$	29.58	0.04	42.99	0.93	1800	0.8850
$1.76 \cdot 10^{-6}$	30.25	0.06	42.32	0.91	1800	0.8888
$1.60 \cdot 10^{-6}$	31.17	0.07	41.40	0.89	1800	0.8888
$1.41 \cdot 10^{-6}$	32.43	0.04	40.14	0.87	1800	0.8900
$1.21 \cdot 10^{-6}$	33.47	0.07	39.10	0.84	1800	0.8920
$1.01 \cdot 10^{-6}$	34.99	0.06	37.58	0.81	1800	0.8950
$9.56 \cdot 10^{-7}$	35.73	0.16	36.84	0.80	1800	0.8950
$8.79 \cdot 10^{-7}$	36.88	0.13	35.69	0.77	1800	0.8990
$7.31 \cdot 10^{-7}$	38.55	0.07	34.02	0.74	1800	0.9010
$6.19 \cdot 10^{-7}$	39.68	0.1	32.89	0.71	1800	0.9025
$2.93 \cdot 10^{-7}$	45.48	0.01	27.09	0.59	1800	0.9122
$2.25 \cdot 10^{-7}$	47.91	0.06	24.66	0.53	1800	0.9142

[a] Standard uncertainty $u(\pi_{cmc})$ = 0.09 mN·m^{-1}. [b] Standard uncertainties. [c] Time between measurements. Shaded rows show the constant π values.

Table 4. Experimental Values of Surface Pressure π and Reduced Surface Pressure $\pi^* = \pi \cdot \pi_{cmc}^{-1}$ at Surface Tension σ and Mole Fraction x, for the POE $C_{13}E_{18}$ at the Temperature T = 293.15 K

$\pi_{cmc}{}^{a}$ = 40.45 mN·m^{-1}						
x	σ/mN·m^{-1}	$u(\sigma)^{b}$/ mN·m^{-1}	π/mN·m^{-1}	π^*	time^{c}/s	f_i
$1.09 \cdot 10^{-5}$	32.09	0.07	40.48	1.00	600	0.8900
$9.98 \cdot 10^{-6}$	32.10	0.08	40.47	1.00	600	0.8900
$9.07 \cdot 10^{-6}$	32.20	0.11	40.37	1.00	600	0.8900
$8.17 \cdot 10^{-6}$	32.15	0.1	40.42	1.00	600	0.8900
$7.26 \cdot 10^{-6}$	31.93	0.13	40.64	1.00	600	0.8900
$5.99 \cdot 10^{-6}$	32.25	0.04	40.32	1.00	600	0.8888
$5.08 \cdot 10^{-6}$	33.22	0.07	39.35	0.97	600	0.8920
$4.54 \cdot 10^{-6}$	34.36	0.1	38.21	0.94	1800	0.8938
$3.99 \cdot 10^{-6}$	34.86	0.09	37.71	0.93	1800	0.8950
$3.27 \cdot 10^{-6}$	36.13	0.07	36.44	0.90	1800	0.8970
$2.72 \cdot 10^{-6}$	37.44	0.04	35.13	0.87	1800	0.8990
$2.27 \cdot 10^{-6}$	38.73	0.04	33.84	0.84	1800	0.9010
$2.12 \cdot 10^{-6}$	39.41	0.04	33.16	0.82	1800	0.9030
$2.00 \cdot 10^{-6}$	39.68	0.12	32.89	0.81	1800	0.9030
$1.81 \cdot 10^{-6}$	40.22	0.04	32.35	0.80	1800	0.9030
$1.72 \cdot 10^{-6}$	40.86	0.04	31.71	0.78	1800	0.9050
$1.45 \cdot 10^{-6}$	41.69	0.07	30.88	0.76	1800	0.9050
$1.27 \cdot 10^{-6}$	42.53	0.04	30.04	0.74	1800	0.9050
$1.13 \cdot 10^{-6}$	43.60	0.17	28.97	0.72	1800	0.9092
$1.03 \cdot 10^{-6}$	44.06	0.07	28.52	0.70	1800	0.9092
$9.07 \cdot 10^{-7}$	44.87	0.07	27.70	0.68	1800	0.9122
$7.80 \cdot 10^{-7}$	45.46	0.04	27.11	0.67	1800	0.9122
$6.53 \cdot 10^{-7}$	46.85	0.21	25.72	0.64	1800	0.9122
$5.67 \cdot 10^{-7}$	47.80	0.11	24.77	0.61	1800	0.9142
$4.72 \cdot 10^{-7}$	49.04	0.16	23.53	0.58	1800	0.9164
$3.63 \cdot 10^{-7}$	50.16	0.09	22.41	0.55	1800	0.9164
$2.84 \cdot 10^{-7}$	51.66	0.04	20.91	0.52	1800	0.9192

[a] Standard uncertainty $u(\pi_{cmc})$ = 0.11 mN·m^{-1}. [b] Standard uncertainties. [c] Time between measurements. Shaded rows show the constant π values.

which corresponds to the maximum surface pressure. This condition is not attainable, for surfactants because it is not possible to measure the surface tension of the pure surfactant as, in general, they are either solids or very viscous liquids so the constrained reference state for this materials is the corresponding maximum surface pressure $\pi_m = \pi_{cmc}$. On the other hand, the Volmer SEOS when linear in the premicellar region: $0 \le x \le x_{cmc}$, $0 \le \pi^* \le 1$ the activity coefficient is constant and is equal to γ^{∞}. When the mole fraction reaches the cmc (x_{cmc}) the surface pressure becomes maximum ($\pi_{cmc} = \pi_m$) thus concentrations above the cmc do not result in measurable[18] surface pressure changes, nonetheless the Volmer SEOS only describes the premicellar region $x \le x_{cmc}$. The agreement between cmc values from $\pi - \ln x$ plot (Gibbs isotherm), Volmer SEOS, and the theoretical values from group contributions assures the quality and validity of the method.

EXPERIMENTAL SECTION

Materials. POE_{10} and POE_{18} were purchased from Sigma-Aldrich and POE_6 (RENEX 36) from ICI. All materials were used without further purification. Table 1 summarizes the main information about the surfactants used in this work.

Apparatus. The ring method was used to determine superficial tension data with a noncommercial tensiometer designed in the laboratory, constituted by a digital analytical balance OHAUS (± 0.3 mg) with a hook adapted to the inferior part that carries a Pt–Ir ring, and an automatic elevator from Orbisphere Laboratories which supported a jacketed glass vessel connected to a thermal bath Haake K20 equipped with an electronic unit Thermo Haake DC30 (± 0.01 K). Figure 1 shows a schematic illustration of the apparatus used in this work. The designed tensiometer used provides the possibility of constant sample ascending/descending velocities which sets the method independent of the experimenter manipulating error. Surfactants were weighed on a Shimadzu AW220 digital analytical balance (± 0.2 mg).

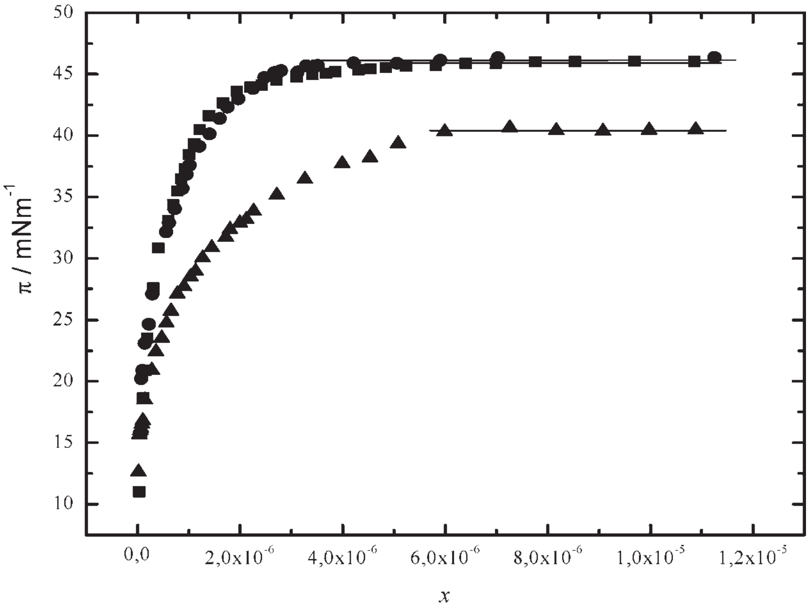

Figure 2. Surface pressure π of POEs in aqueous solutions as a function of mole fraction x at the temperature T = 293.15 K. Saturated regions are marked with lines. ■, $C_{13}E_6$; ●, $C_{13}E_{10}$; ▲, $C_{13}E_{18}$.

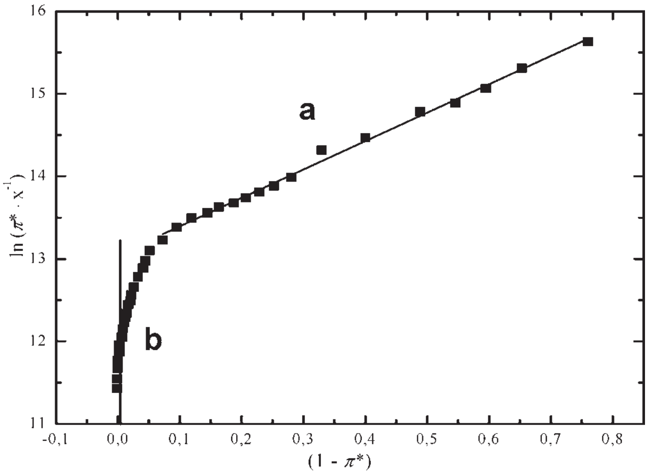

Figure 3. Volmer representation of experimental data of POEs ($C_{13}E_6$) in aqueous solution at the temperature T = 293.15 K, fitted to eq 5. The line marks the $0 \leq (1 - \pi^*) \leq 1$ $(0 \leq x \leq x_{cmc})$ interval (zone a), where the intercept corresponds to $-\ln x_{cmc}$. Zone b corresponds to the constant surface pressure region (π_{cmc}). Experimental data in the region between zones a and b for this system are attributed to a high molecular weight dispersion in these materials as a consequence of the variation in the chain lengths of both the hydrophobic and the hydrophilic chains; thus apparently zone **a** does not include $x = x_{cmc}$.

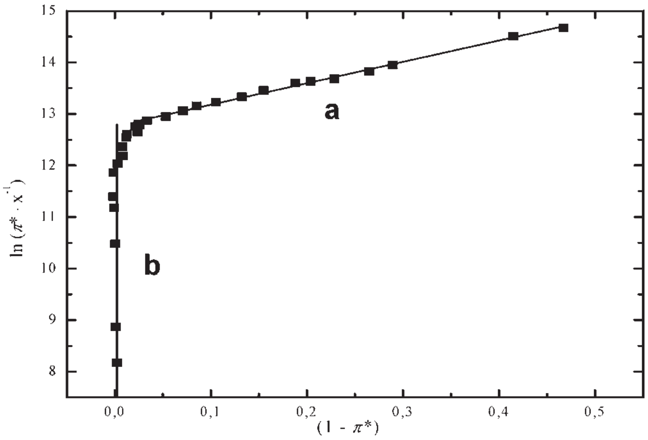

Figure 4. Volmer representation of experimental data of POEs ($C_{13}E_{10}$) in aqueous solution at the temperature T = 293.15 K, fitted to eq 5. The line marks the $0 \leq (1 - \pi^*) \leq 1$ $(0 \leq x \leq x_{cmc})$ interval (zone a), where the intercept corresponds to $-\ln x_{cmc}$. Zone b corresponds to the constant surface pressure region (π_{cmc}). Experimental data in the region between zones a and b for this system are attributed to a high molecular weight dispersion in these materials as a consequence of the variation in the chain lengths of both the hydrophobic and the hydrophilic chains; thus apparently zone a does not include $x = x_{cmc}$.

Methodology. Surfactant solutions were prepared in concentrations from $1 \cdot 10^{-6}$ to $1 \cdot 10^{-3}$ m. Each solution was placed in the glass vessel and taken to 20.0 ± 0.1 °C. The container was raised with the elevator until the ring lay flat on the surface solution. Once the balance lecture was constant, the vessel was descended until the ring separated from the surface, and the maximum mass lecture was registered; this procedure was repeated four or five times to reduce experimental uncertainty. A time of ten minutes between measurements was taken to ensure surface equilibrium conditions; for more diluted solutions, the time was 30 min; as indicated in Tables 2 to 4. After each measurement, the ring was washed twice with acetone and dried in an alcohol lamp flame. Surface tension (σ) values, presented in Tables 2 to 4, were calculated with the DuNoüy equation (eq 7) applying the Harkins-Jordan correction factors f_i,[20] (the values used are included in Tables 2 to 4)

$$\sigma = \frac{Mg}{4\pi R} f_i \tag{7}$$

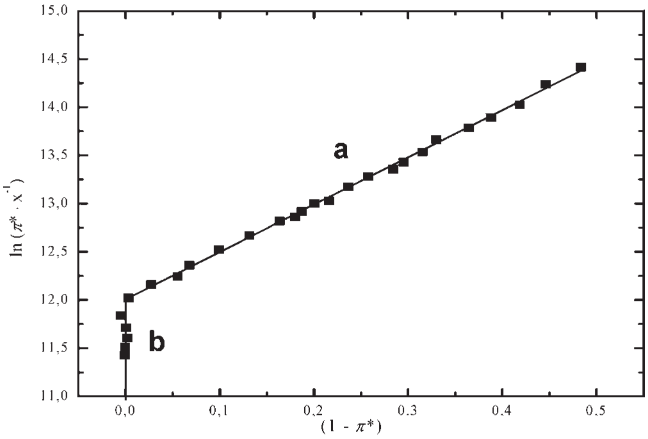

Figure 5. Volmer representation of experimental data of POEs ($C_{13}E_{18}$) in aqueous solution at the temperature $T = 293.15$ K, fitted to eq 5. The line marks the $0 \leq (1 - \pi^*) \leq 1$ ($0 \leq x \leq x_{cmc}$) interval (zone a), where the intercept corresponds to $-\ln x_{cmc}$. Zone b corresponds to the constant surface pressure region (π_{cmc}). For this system there is an abrupt change of slope between zones a and b; thus it is evident that zone a includes $x = x_{cmc}$.

Table 5. Experimental Values of Activity Coefficients at Infinite Dilution γ^∞ and Mole Fraction at Critical Micelle Concentration x_{cmc} from Volmer's SEOS for POEs at the Temperature $T = 293.15$ K

surfactant	γ^∞	x_{cmc}
$C_{13}E_6$	$4.70 \cdot 10^5$	$2.15 \cdot 10^{-6}$
$C_{13}E_8$[a]	$4.95 \cdot 10^5$	$2.02 \cdot 10^{-6}$
$C_{13}E_{10}$	$3.50 \cdot 10^5$	$2.87 \cdot 10^{-6}$
$C_{13}E_{12}$[a]	$4.74 \cdot 10^5$	$2.11 \cdot 10^{-6}$
$C_{13}E_{18}$	$1.60 \cdot 10^5$	$6.08 \cdot 10^{-6}$

[a] Ref 25.

where M is the maximum mass solution raised by the ring, g is the local gravity value at México City equal to 977.94 cms^{-2}, R is the ring's radius, and f_i[20] is the correction factor.

RESULTS AND DISCUSSION

Figure 2 shows the π versus x plots of the three alcohols; as expected, surface pressure increases as surfactant concentration rises along the curves depicted in the figure, reaching a maximum value (π_{cmc}), marked by a line for each surfactant, that remains almost constant from thereon, as the change in surface tension and activity is very slow above the cmc to be detected unless the experimental sensitivity is enhanced.[19] Experimental data of the three systems are shown in Tables 2 to 4. The π_{cmc} is an average value calculated from the constant surface pressure region in the π versus x representation. The π_{cmc} value can be observed in Figures 3 to 5 (zone b); it represents the abrupt change of the slope at the cmc between the diluted (zone a) and saturated (zone b) regions when the x_{cmc} is reached. Thus in the interval $0 \leq x \leq x_{cmc}$ (zone **a**) the π_{cmc} value is included, and for $x > x_{cmc}$ π no longer increases (region b) meaning that intermolecular forces at the surface are invested in micelle formation suggesting that the micelization process could occur at the surface followed by their posterior transfer to the bulk.[16] The $\ln(\pi^* \cdot x^{-1})$ versus $(1 - \pi^*)$ representation from eq 5 in Figures 3 to 5 shows a linear behavior (zone a) where the intercept equals the minus logarithm of the critical micelle concentration (thus $\ln \gamma^\infty$). For $C_{13}E_{18}$ zone a marks the interval $0 \leq x \leq x_{cmc}$ as predicted by the Volmer SEOS, while for $C_{13}E_6$ and $C_{13}E_{10}$ the interval in zone a apparently is not the same, that is, does not include $x = x_{cmc}$; thus there is no abrupt change in slope between zones a and b, and this behavior is attributed to a high molecular weight dispersion in these materials as a consequence of the variation in the chain lengths of both the hydrophobic and the hydrophilic chains. For comparison purposes experimental data of POE_8 and POE_{12} taken from the literature[24] are included in Tables 5 and 6. Table 5 presents x_{cmc} and γ^∞, calculated values for all of the systems. It was found that the critical micelle concentration values increased with the ethylene oxide content; this is attributed to the hydrophilic nature of the ethylene oxide (EO), the more EO units in the surfactant molecule the fewer the tendency to migrate to the surface and to form micelles. Thus, the critical micelle concentration increases, and correspondingly the activity coefficients at infinite dilution decreased, as these values mark the surface activity, that is, the tendency of getting adsorbed at the interface of these substances. This is also valid for data from the literature ($cmc_{E8} < cmc_{E12}$ and $\gamma^\infty{}_{E8} > \gamma^\infty{}_{E12}$); the apparent discrepancy with our data may arise from the cmc determination methods and/or to the molecular weight dispersion of the materials. It is worthy of notice that water activity in the system may be ascribed to the interaction of the hydrophilic groups of the micelar solute with water.[19] The hydrophobic and hydrophilic contributions to the critical micelle concentration for the POEs are shown in Table 6, where the cmc was calculated from group contribution values reported in previous works,[14,16] the hydrophobic contribution value from Traube's rule for simple liquids (ln 3),[16] and the hydrophilic contribution values: for the ethylene oxide group (−0.06)[16] and for the hydroxide group (−0.8).[18] The fact that the theoretical (from group contributions) and the experimental (from Volmer's SEOS) values agree with each other in both cases (our data and data from the literature) validates the hydrophilic contribution value previously reported by us.

Table 6. Negative Logarithm of Mole Fraction at the Critical Micellar Concentration, $-\ln x_{cmc}$, Experimental Values (from Volmer SEOS and Gibbs Isotherm) and Values from Group Contribution to the Critical Micelle Concentration, for POEs at the Temperature $T = 293.15$ K

	$-\ln x_{cmc}$		
	experimental[a]		
surfactant	Volmer SEOS	Gibbs isotherm	group[b]
$C_{13}E_6$	13.05	12.917	13.12
$C_{13}E_8$[c]	13.11		13.00
$C_{13}E_{10}$	12.76	12.73	12.88
$C_{13}E_{12}$[c]	12.52		12.76
$C_{13}E_{18}$	12.01	11.97	12.40

[a] Except for $C_{13}E_8$ and $C_{13}E_{12}$ which are taken from ref 25. [b] Individual group values taken for calculation: methylene, ethylene (CH_3, CH_2) = ln 3;[16] ethylene oxide (OCH_2CH_2) = −0.06,[16] hydroxyl (OH) = −0.8.[18] [c] Ref 25.

CONCLUSIONS

The Volmer's SEOS gives an accurate description of the three different POEs used in this work. Important information about the interactions and interfacial activity of the system can be studied, and parameters, such as x_{cmc} and γ^{∞}, can be obtained from experimental data. The linear behavior of the $\ln(\pi^*/x) - (1 - \pi^*)$ relationship in the premicellar interval found for all of the systems studied entails the acceptance of Volmer SEOS data treatment in the determination of γ^{∞} and cmc. The comparison of these two parameters with the corresponding values from the $\pi^* - \ln x$ traditional method for cmc calculations validates the acceptance of the model. Moreover, this data treatment can give an overview of the behavior and the influence of the length of the ethoxylated chain, setting a linear dependence between the ethoxylated number and both the $\ln x_{cmc}$ and the $\ln \gamma^{\infty}$.[15] It is clearly noted a decreasing tendency of x_{cmc} as the ethoxy number increases; on the other hand, it was found that the γ^{∞} follows an opposite behavior. The hydrophobic (ln 3) and hydrophilic contributions (OH −0.8 and OE −0.05 ± 0.01) reported previously[16,17] by this research group for similar materials, to the critical micelle concentration, are also suited for the prediction of cmc values for the different POEs used in this work and for those taken from the literature, the ethylene oxide group the upper limit value (−0.06) from the interval being the one which provided the best agreement with experimental values. Activity and activity coefficient determinations in the premicellar and micellar regions are of capital importance for the knowledge of hydrophilic−hydrophobic interactions in micellar solutions, mesophases, and monomers in aqueous media, as pointed out by Clunie et al.[14]

AUTHOR INFORMATION

Corresponding Author

*Tel.: 00 52 55 56223525. Fax: 00 52 55 56162010. E-mail: alcepace@hotmail.com (A.P.-C.), josefina@unam.mx (J.V.T.), jgraciaf@unam.mx (J.G.-F.).

Funding Sources

The authors wish to thank the Dirección General de Asuntos del Personal Académico (DGAPA) de la Universidad Nacional Autónoma de México for its financial support through the PAPIIT Projects IN103108 and IN100808.

REFERENCES

(1) Huibers, P. D. T.; Lobanov, V. S.; Katritzky, A. R.; Shah, D. O.; Karelson, M. Prediction of critical micelle concentration using a quantitative structure-property relationship approach. 1. Nonionic surfactants. *Langmuir* **1996**, *12*, 1462–1470.

(2) Frank, C.; Frielinghaus, H.; Allgaier, J. Nonionic surfactants with linear and branched hydrocarbon tails: Compositional analysis, phase behavior, and film properties in bicontinuous micro emulsions. *Langmuir* **2007**, *23*, 6526–6535.

(3) Calvo, E.; Bravo, R.; Amigo, A.; Gracia-Fadrique, J. Dynamic surface tension, critical micelle concentration and activity coefficients of aqueous solutions of nonyl phenol ethoxylates. *Fluid Phase Equilib.* **2009**, *282* (1), 14–19.

(4) Hu, J.; Jin, F.; Wan, Y.; Yang, M.; An, L.; An, W.; Tao, S. Trophodynamic behavior of 4-nonylphenol and nonylphenol polyethoxylate in a marine aquatic food web from Bohai Bay, North China: Comparison to DDTs. *Environ. Sci. Technol.* **2005**, *39*, 4801–4807.

(5) Wrenn, B. A.; Virkus, A.; Mukherjee, B.; Venosa, A. D. Dispersability of crude oil in fresh water. *Environ. Pollut.* **2009**, *157*, 1807–1814.

(6) Shao, B.; Hu, J.; Yang, M.; An, W.; Tao, S. Nonylphenol and Nonylphenol Ethoxylates in River Water, Drinking Water and Fish Tissues in the Area of Chongqing, China. *Arch. Environ. Contam. Toxicol.* **2005**, *48*, 467–473.

(7) Chen, T.; Yeh, Y. Ecological risk, mass loading, and occurrence of nonylphenol (NP), NP mono-, and diethoxylate in Kaoping River and its tributaries, Taiwan. *Water, Air, Soil Pollut.* **2009**, *208*, 209–220.

(8) Jansen, L. L. Relation of structure of ethylene oxide ether-type nonionic surfactants to herbicidal activity of water-soluble herbicides. *Agric. Food Chem.* **1964**, *12* (3), 223–227.

(9) Balcan, M.; Anghel, D.; Voicu, A.; Balcan, D. Determination of thermodynamic parameters of ethoxylated nonionic surfactans by beans of reversed-phase high-performance liquid chromatography. *Colloids Surf.* **2002**, *204*, 141–151.

(10) Weissermel, K.; Arpe, H. J. *Química Orgánica Industrial, productos de partida e intermedios más importantes*, 4th ed.; Wiley-VCH: Weinheim, Germany, 2003.

(11) Suradkar, Y.; Bhagwat, S. CMC Determination of an odd carbon chain surfactant (C13E20) mixed with other surfactants using a spectrophotometric technique. *J. Chem. Eng. Data* **2006**, *51*, 2026–2031.

(12) ICI Surfactants. SYNPERONIC. A, K, BD, 91 ranges.

(13) Habrdová, K.; Hovorka, S.; Bartovská, L. Concentration dependence of surface tension for very dilute aqueous solutions of organic nonelectrolytes. *J. Chem. Eng. Data* **2004**, *49*, 1003–1007.

(14) Clunie, J. S.; Goodman, J. F.; Symons, P. C. Phase Equilibria of Dodecylhexaoxyethylene Glycol Monoether in Water. *Trans. Faraday Soc.* **1969**, *65*, 287–296.

(15) Laughlin, R. G. *The Aqueous Phase Behavior of Surfactants*; Academic Press: New York, 1994.

(16) Viades-Trejo, J.; Gracia-Fadrique, J. A new surface equation of state Hydrophobic-hydrophilic contributions to the activity coefficient. *Fluid Phase Equilib.* **2008**, *264*, 12–17.

(17) Viades-Trejo, J.; Amigo, A.; Gracia-Fadrique, J. Activity coefficients at infinite dilution for surfactants. *Fluid Phase Equilib.* **2006**, *250*, 158–164.

(18) Gracia-Fadrique, J.; Brocos, P.; Piñeiro, A.; Amigo, A. *Langmuir* **2002**, *18*, 3604–3608.

(19) Lu, J. R.; Thomas, R. K.; Penfold, J. Surfactant Layers at the Air/water Interface: Structure and Composition. *Adv. Colloid Interface Sci.* **2000**, *84*, 143–304.

(20) Harkins, W. D.; Jordan, H. F. A method for the determination of surface and interfacial tension from the maximum pull on a ring. *J. Am. Chem. Soc.* **1930**, *52*, 1751–1772.

(21) Crook, E. H.; Trebbi, G. F.; Fordyce, D. B. Thermodynamic properties of solutions of homogeneous *p*,*t*-octylphenoxyethoxyethanols (OPE_{1-10}). *J. Phys. Chem.* **1964**, *68* (12), 3592–3599.

(22) Crook, E. H.; Fordyce, D. B.; Trebbi, G. F. Molecular weight distribution of nonionic surfactants. I. Surface and interfacial tension of normal distribution and homogeneous *p*,*t*-octylphenoxyethoxyethanols (OPEs). *J. Phys. Chem.* **1963**, *67* (10), 1987–1994.

(23) Inoue, T.; Ohmura, H.; Murata, D. Cloud point temperature of polyoxyethylene-type nonionic surfactants and their mixtures. *J. Colloid Interface Sci.* **2003**, *258*, 374–382.

(24) Vitagliano, V.; D'Errico, G.; Ortona, O.; Paduano, L. Physicochemical properties of ethoxylated surfactants in aqueous solutions. In *Encyclopedia of Surface and Colloid Science*; CRC Press: Boca Raton, FL, 2002; Vol. 3, pp 4105−4123.

(25) Van Os, N. M.; Haak, J. R.; Rupert, L. A. M. *Physico-Chemical Properties of Selected Anionic, Cationic and Nonionic Surfactants*; Elsevier: New York, 1993.