



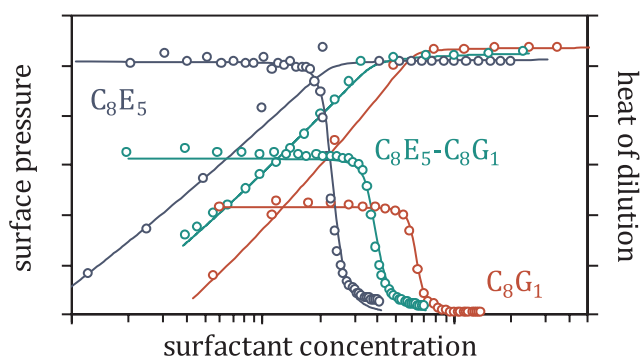
Micellization and adsorption modeling of single and mixed nonionic surfactants

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GRAPHICAL ABSTRACT



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ABSTRACT

The surface tension and heats of dilution of aqueous solutions of octyl- β -D-glucopyranoside (C₈G₁), tetraethylene glycol monoethyl ether (C₈E₄), pentaethylene glycol monoethyl ether (C₈E₅) and C₈E₅-C₈G₁ mixtures at 298.2 K were studied by tensiometry (ST) and isothermal titration calorimetry (ITC). Single surfactant micelle formation and growth were modeled using a multiple chemical equilibrium approach under the assumption that micelles are spherocylinders that can be thermodynamically described by three parameters, namely spherical and cylindrical contributions to the micelle molar Gibbs energy and the enthalpy of micellization. The two-dimensional virial equation of state was employed to correlate the surface tensions, which required two additional parameters: a 2D second virial coefficient and a reference monomer concentration. For the binary surfactant solutions, combining and mixing rules were suggested with no further parameters. For the single surfactants, the model correlated very well both ITC and ST experimental data. For mixed surfactants, ST data were also very well predicted, but this was not the case for ITC data. For the critical micelle concentrations, the model enthalpograms presented both positive and negative deviations from the experimental results, depending on the surfactant relative concentrations. Very low C₈G₁ concentrations promoted the demicellization of C₈E₅, which suggests strong interactions between monomer hydrophilic heads and the possible formation of small aggregates.

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List of symbols

A	surface area	R	calorimetry step
b, b_i	2D second virial coefficient for mixtures and for substance i , respectively	r	gas constant
b_{AB}	2D cross second virial coefficient for amphiphiles A-B interactions	r_i	intermolecular distance
F	Helmholtz energy	S	hydrophilic head hard-disk radius of surfactant i
F_{ITC}, F_{ST}	objective function for ITC and ST curve fitting, respectively	S_A	entropy
g_A^0	molar Gibbs energy of free amphiphile A	S_A	monomeric form of surfactant A
g_ω, g_b	micellization parameters defined in Eq. (6)	\bar{s}	micelle weight-average aggregation number
g_{cyl}	molar Gibbs energy contribution from amphiphiles in the cylindrical body	T	absolute temperature
g_{sp}	molar Gibbs energy contribution from amphiphiles in the spherical end caps	u_{ii}	tail-tail intermolecular energy
g_s^0	molar Gibbs energy of micelle of size s	v	aggregation number variance
$g_{s\beta}^0$	molar Gibbs energy of micelle of size s and composition β	x_A	free monomer mole fraction of amphiphile A
Δg_s^0	standard molar Gibbs energy of micellization of s sized micelle	x_s	mole fraction of s sized micelles
$\Delta g_{s\beta}^0$	standard molar Gibbs energy of micellization of s sized micelle with composition β	$x_{s\beta}$	mole fraction of s sized micelles with composition β
H	enthalpy	x_i^∞	free monomer concentration of substance i when the surface pressure is Π^∞
h_A^0	molar enthalpy of free amphiphile A	y	variable defined in Eq. (9)
$h_{s\beta}^0$	molar enthalpy of micelle of size s and composition β	z	total surfactant concentration
Δh_A^0	standard molar enthalpy of micellization of surfactant A	<i>Greek</i>	
$\Delta h_{s\beta}^0$	standard molar enthalpy of micellization of s sized micelle with composition β	α	bulk mole fraction of surfactant A
K_a, K_b	equilibrium constants defined in Eq. (8)	β	micelle composition
K_s	equilibrium constant for s sized micelle formation	$\bar{\beta}$	average micelle composition
$K_{s\beta}$	equilibrium constant for s sized micelle formation with composition β	γ	surface tension
m	number of amphiphiles in micelle spherical end cap	η_i	surface excess of substance i
M_s	micelle with s amphiphiles	μ_i	chemical potential of specie i
$M_{s\beta}$	micelle with s amphiphiles and composition β	μ_i^∞	chemical potential of specie i in the reference diluted solution
N_w, N_s	number of moles of water and surfactant, respectively	$\Delta_{ads}\mu_i$	molar Gibbs energy of adsorption of substance i , defined in Eq. (45)
Q, q	heat and molar heat absorbed in isothermal titration	Π	surface pressure
		Π^∞	reference surface pressure, 0.01 mN.m ⁻¹
		Ω	vector of adjustable parameters
		σ	standard deviation of a measurement
		ξ_A	surface mole fraction of amphiphile A

1. Introduction

Surfactants are used as individual components in aqueous solution or in other solvents in only a few cases in many applications and in industrial practice. In most cases, they are employed as mixtures of two or more surfactants. For example, in the case of emulsifiers, it is known that two emulsifiers operate better than one. In liquid detergents, personal care preparations and other applications, it is common to find more than one surfactant in commercial formulations. In the field of pharmacy, improved oil recovery and the production of water-based paints require mixtures of surfactants to reach emulsification, wetting and dispersion. In general, the industrial and biological use of surfactants corresponds to mixtures of amphiphiles [1,2], their individual use being scarce. Thus, the prediction of the properties of surfactant mixtures is crucial for the determination of the optimum composition to meet the application requirements.

Usually, when experimental data are available, the mass action law with one chemical equilibrium reaction is employed to correlate the measurements and to describe the thermodynamics behind micelle formation [2–4]. For single surfactant solutions, this model assumes that the micelle size distribution is monodisperse. Accordingly, this approach cannot explain the experimentally observed micelle growth, because it assumes that all formed micelles have the same aggregation number. Nevertheless, it relates the Gibbs energy of micellization (normally, an adjustable parameter of the model) to the critical micelle concentration (cmc), i.e., the concentration when a sudden change of

an observable property occurs. The extension of this model to describe mixed surfactant micellization is not straightforward; it requires the aggregation number of mixed micelles which is not a trivial function of the pure surfactant micelle sizes. For surfactant mixtures, the cmc and micelle composition can be estimated by the pseudo-phase separation model of Holland and Rubingh [5] which considers micelles as a macroscopic phase in equilibrium with the free monomers solution; the amphiphiles activity coefficients in the micelles is described by the regular solution theory. This model has one binary parameter for non-ideal mixing. However, as in the monodisperse mass action law, the pseudo-phase model does not allow for the estimation of micelle size distributions; a pseudo-phase is equivalent to micelles with infinite aggregation numbers. In the lack of experimental information, the molecular thermodynamic theories of Puvvada and Blankshtein [6] and of Nagarajan and Ruckenstein [7] provide a methodology to estimate the micellization Gibbs energy. In these predictive models, the micelle size distribution is considered, and it is consistent with the multiple chemical equilibrium approach. The required equilibrium constants are estimated from the geometrical and molecular characteristics of the amphiphiles. On the other hand, for low surface coverage, air-liquid surface tension (ST) data can be correlated by many two-dimensional gas-like equations of state (SEoS). It is known that ST data can be easily correlated by several SEoSs with two or three adjustable parameters [8]. For mixed surfactant monolayers, however, it is very important to have a solid theoretical ground for the mixing and combining rules to estimate mixed surface parameters from the single

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