



# Thermodynamic properties of anionic surfactant/polymer/water systems with respect to polymer-surfactant interactions and salting-effect of surfactant on polymer in aqueous solutions



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## ABSTRACT

An extensive set of experimental measurements was carried out on several ternary polymer-surfactant aqueous solutions in order to investigation of the binding behaviors between anionic surfactants and water soluble polymers in aqueous solutions. Isopiestic measurements of different ternary polymer (polyethylene glycol 400 (PEG400), polyethylene glycol 2000 (PEG2000), polyethylene glycol 6000 (PEG6000) and polypropylene glycol 400 (PPG400)) + anionic surfactant (sodium *n*-hexyl sulfonate) + water systems indicate that, the constant water activity lines of the investigated systems show three regions with convex, concave and convex slopes respectively in low-, intermediate- and high-solutes concentration region. In the second part of this work, volumetric and compressibility properties of micellization of sodium *n*-hexyl sulfonate in aqueous polymer solutions were studied. Finally, the cloud point measurements of aqueous PPG725 solutions in the absence and presence of various anionic surfactants show that, anionic surfactants with short hydrocarbon chain length decrease the cloud point temperature of PPG725 aqueous solutions (salting-out effect), while anionic surfactants with long hydrocarbon chain length increase that (salting-in effect). Based on the cloud point values, the energetic parameters of the clouding process were estimated and it was found that, entropy is the driving force for biphasic formation. The obtained results were interpreted in term of different interactions existing in aqueous solutions which determine the salting-effects produced by the addition of hydrophilic solutes to aqueous solutions of water soluble polymers.

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## 1. Introduction

In industrial applications, polymer-surfactant systems are commonly encountered, such as in foods, cosmetics, mineral processing, paints, coating, polymer synthesis, adhesives, and pharmaceutical products. Surfactants may bind cooperatively to nonionic water-soluble polymers to form micelle-polymer complexes, and these interactions are largely confined to anionic surfactants. Goddard [1,2] gave an excellent review of the interaction between nonionic polymers and charged surfactants. The interactions between surfactants and polymers in aqueous solutions have been studied by a variety of techniques, including surface tension [3,4], ITC [5–8], conductivity [9–12], laser light scattering [4,11,13], viscosity [9,11,14,15], neutron scattering [16,17], electron

spin resonance [15], zeta potential [11], dialysis equilibrium [18,19], NMR [5,20–22], fluorescence [4,11], UV [15], size exclusion chromatography [23]. However, the structure and morphology of the polymer-surfactant complexes as well as the nature of the interaction involved in the complex have not been well established yet and although this phenomenon is well documented and has been extensively investigated in the literature, their mechanism at the molecular level is still unclear.

In order to study the effect of anionic surfactants on the phase behavior of aqueous polymer solutions and in an attempt to obtain further information about the mechanism of salting-effect of surfactants on aqueous polymer solutions, experimental measurements of vapor-liquid equilibria, liquid-liquid equilibria (cloud point values), volumetric and compressibility properties were performed for ternary aqueous solutions of anionic surfactants in the presence of a large series of water soluble polymers (PEG400, PEG2000, PEG6000, PPG400 and PPG725).

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## 2. Experimental

### 2.1. Materials

The specifications of used chemicals are summarized in Table 1. Double-distilled and deionized water was used.

### 2.2. Experimental procedures

The details of isopiestic method used in this work are similarly to the one used previously [24]. In this method, different solutions with only one common solvent, when connected through the vapor space, approach equilibrium by transferring solvent mass by distillation. At equilibrium, the chemical potential of solvent (and also solvent activity) in each of the solutions in the isopiestic system is identical. From the solvent activity of one or more standard solutions, the activity of solvent for each solution within the isopiestic system can be known. The apparatus used consisted of a multi-leg manifold attached to round-bottom flasks. Two flasks contained the standard pure NaCl solution, one flask contained the pure polymer solution, one flask contained the pure surfactant solution, two or three flasks contained the polymer + surfactant solutions and the central flask was used as a water reservoir. The apparatus was held in a constant-temperature bath at least 5 days (depending on the solutes concentration) for equilibrium. The temperature was controlled at 298.15 K to within  $\pm 0.05$  K. After equilibrium had been reached, the manifold assembly was removed from the bath, and each flask was weighed with an analytical balance with a precision of  $\pm 1 \cdot 10^{-4}$  g. From the weight of each flask after equilibrium and the initial weight of solutes, the mass fraction of each solution was calculated. The osmotic coefficients for the standard NaCl aqueous solutions have been calculated from correlation given in the literature [25].

Density and sound velocity measurements were carried out by an Anton Paar DSA 5000 model high precision vibrating tube digital densimeter and sound velocity measuring device, with automatic viscosity corrections and proportional temperature control that kept the samples at working temperature within  $\pm 10^{-3}$  K. The calibration of the instrument was made with degassed and bidistilled water and dry air at atmospheric pressure according to the instruction manual of the instrument. The uncertainties of measurements were  $\pm 5 \times 10^{-6}$  g cm $^{-3}$  for density and  $\pm 5 \times 10^{-1}$  m s $^{-1}$  for sound velocity. All the solutions for density and sound velocity measurements were prepared by mass on a Sartorius CP225D balance precisely within  $\pm 1 \times 10^{-5}$  g.

The experimental apparatus employed for determination of liquid-liquid equilibria phase diagrams (cloud point curves) is a glass vessel with an external jacket. A Julabo thermostat with a precision of  $\pm 0.05$  K was used to circulate water at a certain

temperature in the external jacket around the vessel. The cloud point temperatures for solutions of PPG725 in water and in aqueous solutions with the same molality of anionic surfactants were determined by visual observation. Temperature of the stirred sample in stoppered glass vessel was slowly increased by increasing temperature of circulated water around the vessel until the sample clouded or got turbid. The sample temperature was then slowly decreased until the turbidity was vanished. The heating-cooling cycle was repeated three times for a given sample, to check the reproducibility of the measurements. The mean value of the temperature for appearance and the temperature for disappearance of clouding was considered as the cloud point temperature ( $T_C$ ). The samples for cloud point measurements were prepared on a Sartorius CP124S balance precisely within  $\pm 1 \times 10^{-4}$  g.

## 3. Results and discussion

In this work, three part of experimental measurements have been carried out on several ternary polymer-surfactant aqueous solutions: (i) isopiestic equilibrium measurements for the ternary {PEG400, PEG2000, PEG6000, PPG400 + C $_6$ SO $_3$ Na + water} systems at  $T = 298.15$  K, (ii) volumetric and compressibility properties measurements for solutions of C $_6$ SO $_3$ Na in aqueous solutions of 0.03 w/w PEG6000 at  $T = 298.15, 303.15, 308.15, 313.15$  and  $318.15$  K and (iii) the cloud point measurements for PPG725 in water and in aqueous solutions of anionic surfactants including C $_8$ SO $_4$ Na (0.011 mol kg $^{-1}$ ), C $_{12}$ SO $_4$ Na (0.002, 0.005, 0.008 and 0.011 mol kg $^{-1}$ ), C $_6$ SO $_3$ Na (0.011 mol kg $^{-1}$ ) and C $_{12}$ SO $_3$ Na (0.011 mol kg $^{-1}$ ) as a function of PPG725 concentration. The measured vapor-liquid equilibria, cloud point, density and sound velocity data are presented in the [Supplementary Material](#) of this manuscript.

### 3.1. Vapor-liquid equilibria properties

For a certain polymer-surfactant aqueous solution which is in isopiestic equilibrium with a sodium chloride solution with molality  $m_{\text{NaCl}}$  and osmotic coefficient  $\Phi_{\text{NaCl}}$ , the water activity,  $a_w$ , and vapor pressure,  $p$ , were obtained according to:

$$a_w = \exp[-2M_w m_{\text{NaCl}} \Phi_{\text{NaCl}}], \quad (1)$$

$$\ln a_w = \ln \left( \frac{p}{p_w^\circ} \right) + \frac{(B_w^\circ - V_w^\circ)(p - p_w^\circ)}{RT}, \quad (2)$$

where  $M_w$  is the molar mass of water,  $B_w^\circ$  is the second virial coefficient of water vapor,  $V_w^\circ$  is the molar volume of liquid water, and  $p_w^\circ$  is the vapor pressure of pure water.

The Zdanovskii-Stokes-Robinson (ZSR) rule, proposed by

**Table 1**  
Specification of chemicals used in this work.

Chemical name (abbreviation)	$10^3 \cdot$ Molecular weight (kg mol $^{-1}$ )	Source	Lot number	Purification method	Final mass fraction purity <sup>a</sup>
sodium <i>n</i> -hexyl sulfonate (C $_6$ SO $_3$ Na)	188.22	Merck	K35876705613	None	$\geq 99$
sodium <i>n</i> -dodecyl sulfonate (C $_{12}$ SO $_3$ Na)	272.38	Merck	K37015808722	None	$\geq 99$
sodium <i>n</i> -octyl sulfate (C $_8$ SO $_4$ Na)	232.28	Merck	L55093568635	none	
sodium <i>n</i> -dodecyl sulfate (C $_{12}$ SO $_4$ Na)	288.38	Merck	L55084433728	None	$\geq 99$
polyethylene glycol 400 (PEG400)	400	Merck	S6041783 019	None	
polyethylene glycol 2000 (PEG2000)	2000	Merck	S5415037004	None	
polyethylene glycol 6000 (PEG6000)	6000	Merck	S35317203	None	
polypropylene glycol 400 (PPG400)	400	Fluka	125230420206282	None	
polypropylene glycol 725 (PPG725)	725	Aldrich	06228MD-197	None	
NaCl	58.44	Merck		was dried in an electrical oven at about 110 °C for 24 h prior to use	$\geq 99.95$

<sup>a</sup> Declared by supplier.

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