

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/6673580>

# Chemical Potential of a Nonionic Surfactant in Solution

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY B · DECEMBER 2006

Impact Factor: 3.3 · DOI: 10.1021/jp0641987 · Source: PubMed

---

CITATIONS

13

---

READS

36

## 3 AUTHORS:



Thomas Krebs

FMC Technologies Inc.

21 PUBLICATIONS 165 CITATIONS

SEE PROFILE



Gunther G Andersson

Flinders University

80 PUBLICATIONS 813 CITATIONS

SEE PROFILE



Harald Morgner

University of Leipzig

131 PUBLICATIONS 1,804 CITATIONS

SEE PROFILE

# Chemical Potential of a Nonionic Surfactant in Solution

Thomas Krebs,\* Gunther Andersson, and Harald Morgner

University of Leipzig, Wilhelm-Ostwald-Institute of Physical and Theoretical Chemistry, Linnéstraße 2, 04103 Leipzig, Germany

Received: July 4, 2006; In Final Form: September 11, 2006

The chemical potential of a surfactant in solution can be calculated from the Gibbs adsorption equation when the surface excess of the surfactant and the surface tension of the solution as a function of surfactant concentration are known. We have investigated a solution of the nonionic surfactant 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine (POPC) in the polar solvent 3-hydroxypropionitrile at concentrations below and above the critical micelle concentration (cmc). Neutral impact collision ion scattering spectroscopy was applied for the direct measurement of the surface excess of POPC as a function of concentration. The Gibbs adsorption equation was applied in conjunction with surface tension measurements to evaluate the chemical potential and the activity coefficients of POPC, respectively. We find that the solution shows ideal behavior up to the cmc and that the chemical potential remains constant at concentrations larger than the cmc.

## Introduction

The Gibbs equation is one of the most commonly used relationships in the thermodynamics of liquid interfaces.<sup>1</sup> It offers a simple method to determine the surface excess concentration of components in a liquid mixture from surface tension measurements if the thermodynamic activities of the components are known. At constant temperature and pressure the Gibbs adsorption equation is given by:

$$d\sigma = -\sum_i \Gamma_i d\mu_i \quad (1)$$

where  $d\sigma$  is the change in surface tension of the solution and  $d\mu_i$  the change in chemical potential of the  $i$ th component. At a liquid surface the quantity  $\Gamma_i$  is defined as:<sup>1</sup>

$$\Gamma_i = \int_{-\infty}^{z_0} c_i(z) dz + \int_{z_0}^{\infty} (c_i(z) - c_i^b) dz \quad (2)$$

where  $c_i(z)$  denotes the concentration at depth  $z$  of the  $i$ th component,  $c_i^b$  is the bulk concentration of the  $i$ th component, and  $z_0$  is the position of the Gibbs dividing plane. In eq 2, the liquid phase is located at  $z \geq z_0$ . Via the Gibbs Duhem equation

$$\sum_i x_i d\mu_i = 0 \quad (3)$$

one can eliminate the chemical potential of one component, e.g., of the solvent. In the case of a binary system, e.g., a solution of one surfactant, the Gibbs equation turns into

$$d\sigma = -\Gamma_{\text{surf}}^e d\mu_{\text{surf}} \quad (4)$$

where the suffix indicates the surfactant. The surface excess  $\Gamma_{\text{surf}}^e$  is defined as

$$\Gamma_{\text{surf}}^e = \Gamma_{\text{surf}} - \frac{x_{\text{surf}}}{1 - x_{\text{surf}}} \Gamma_{\text{solvent}} \quad (5)$$

where  $x_{\text{surf}}$  indicates the surfactant molar fraction. In contrast to the quantities  $\Gamma_{\text{surf}}$  and  $\Gamma_{\text{solvent}}$ , the surface excess  $\Gamma_{\text{surf}}^e$  is independent of the position of the Gibbs dividing plane. In the special case of a mixture between a surfactant and a solvent usually the position of the Gibbs dividing plane is chosen so that  $\Gamma_{\text{solvent}} = 0$ .

As modern surface spectroscopic techniques allow the determination of the surface excess directly, we are in the position to follow an entirely different scheme. We have previously shown for the solution of an ionic surfactant<sup>2</sup> that the combination of experimental values for the surface excess with surface tension data allows us to determine the surfactant activity  $a_{\text{surf}}$  via

$$d\sigma = -\Gamma_{\text{surf}}^e RT d(\ln a_{\text{surf}}) \quad (6)$$

It is noteworthy to state that eq 6, which is equivalent to eq 4, can be employed for the determination of the chemical potential in the concentration range above and below the cmc provided the surface excess is known from experiment. The conventional use of eq 6 for determining the surface excess is restricted to concentrations below the cmc.

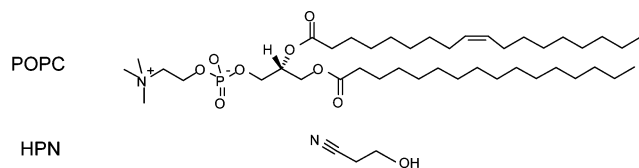
In the present paper we evaluate the chemical potential rather than the activity via eq 4. The variation of the chemical potential between two bulk compositions  $x_1, x_2$  with corresponding surface tension values  $\sigma_1, \sigma_2$  is given by

$$\Delta\mu_{\text{surf}} = -\int_{\sigma_1}^{\sigma_2} \frac{d\sigma}{\Gamma_{\text{surf}}^e(\sigma)} \quad (7)$$

The corresponding variation of the activity can be calculated according to

$$\Delta \ln a_{\text{surf}} = -\frac{1}{RT} \int_{\sigma_1}^{\sigma_2} \frac{d\sigma}{\Gamma_{\text{surf}}^e(\sigma)} \quad (8)$$

\* Corresponding author. Phone: +49 341 9736217. Fax: +49 341 9736090. E-mail: thomaskrebs@gmx.de.



**Figure 1.** Structures of the employed substances.

The surfactant activity and the surfactant activity coefficient  $f_{\text{surf}}$  are related via

$$a_{\text{surf}} = f_{\text{surf}} x_{\text{surf}} \quad (9)$$

For nonionic surfactant solutions it has been argued that any solution behaves ideally with respect to the chemical potential up to the cmc.<sup>3–5</sup> This assumption is often explained with the argument that surfactant concentrations below the critical micelle concentration (cmc) are usually too small to cause a deviation from ideal behavior. However, there is reason to challenge the general validity of this assumption. It has been observed that for certain surfactant systems a premicellar aggregation can occur.<sup>6,7</sup> This behavior would consequently give rise to an activity coefficient changing with concentration. Even if no premicellar aggregation occurs it has been argued that the activity coefficient of the surfactant should change as the concentration approaches the cmc.<sup>8</sup>

For ionic surfactant solutions sometimes activity coefficients calculated from the Debye–Hückel equation are employed.<sup>9,10</sup> The Debye–Hückel theory of electrolyte solutions does not include behavior such as premicellar aggregation. Moreover, it treats the ions as point charges showing only electrostatic interactions. Due to their size this assumption is too simplified for surfactant molecules. For these reasons the Debye–Hückel theory cannot be applied for the prediction of surfactant activity coefficients.

One probable reason surfactant activity coefficients are usually neglected or crudely approximated in the thermodynamic treatment of surfactant solutions is the lack of experimental access to the activity coefficient. Typical methods to determine solute activity coefficients rely on the measurements of colligative properties such as vapor pressure<sup>11</sup> or freezing point depression.<sup>12</sup> When dealing with surfactant solutions these methods are too insensitive at low concentrations to allow the evaluation of activity coefficients.

In the present work we have investigated a solution of the nonionic surfactant POPC in the polar solvent HPN. The direct measurement of the POPC surface excess with neutral impact collision ion scattering spectroscopy (NICISS) was used in conjunction with surface tension measurements to determine the chemical potential and the activity coefficients of POPC, respectively.

## Experimental Methods

**Reagents.** The phospholipid 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine (POPC) was chosen as surfactant. POPC was purchased from Avanti Polar Lipids Inc. and was dried in a vacuum before the solutions were prepared. 3-Hydroxypropionitrile (HPN) was used as a solvent. HPN is a polar liquid (dipole moment of the order  $\sim 3.5$  D) and has a low vapor pressure ( $< 10^{-2}$  mbar at 20 °C) facilitating the handling in a vacuum. HPN was obtained from Merck and was purified by vacuum distillation. The boiling temperature was 80 °C at 2 mbar of pressure. The concentration of the solutions ranged from  $1.20 \times 10^{-5}$  to  $1.48 \times 10^{-3}$  mol·kg<sup>-1</sup>. Figure 1 shows the structures of the solute and the solvent.

**Surface Tension Measurements.** Surface tension measurements were performed with a Kruss K12 Wilhelmy Plate Tensiometer at a temperature of  $(267.15 \pm 0.3)$  K. To avoid condensation of water, the sample was isolated from the surrounding atmosphere, and nitrogen was passed through the sample vessel.

**NICISS Measurements.** We have previously investigated surfaces of several pure liquids and surfactant solutions with NICISS.<sup>2,13,14</sup> The method is used to determine elemental concentration depth profiles up to a depth of 300 Å with a depth resolution far below 10 Å. The details are described elsewhere.<sup>13</sup> The target is bombarded with a pulsed beam of inert gas ions with a kinetic energy of several kiloelectronvolts. The energy of the projectiles backscattered from the atoms in the target is determined by their time-of-flight (TOF) from the target to the detector.

The projectiles lose energy during the backscattering process that can be described to a good approximation as classical collision between two collision partners.<sup>15</sup> The extent of energy transfer depends on the mass of the target atom. Additionally, the projectiles lose energy on their trajectory through the bulk with a magnitude proportional to the depth of the target atom. The energy loss in the bulk is calibrated with self-assembled monolayers of alkanethiolates on gold and silver single crystals.<sup>16</sup> The depth that can be investigated with this method is limited by the broadening of the beam in the bulk due to low-angle scattering. The dose of the He ions for this investigation was about  $10^{10}$  ions/cm<sup>2</sup>. Thus damage of the surface and the influence of the impinging ions on the surface structure can be neglected.

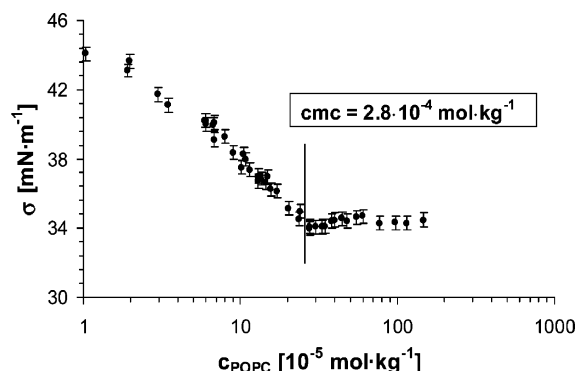
An additional inelastic energy loss occurs during the central scattering event between the projectile and the target atom. This additional energy loss has to be known to gauge the zero point of the depth scale.<sup>17</sup> Gas-phase NICISS measurements have been performed with trimethylphosphine to gauge the zero point of the depth scale of phosphorus. For the elements nitrogen, oxygen, and carbon, respectively, the zero point of the depth scale was determined from the NICIS spectrum of pure HPN. The zero point of the depth scale for each element is identical with the onset of the corresponding signal provided the molecule does not have a preferential orientation at the surface along the surface normal. It has been shown by means of metastable induced electron spectroscopy that the HPN molecules are randomly oriented at the surface of the pure substance.<sup>18</sup>

The liquid surface is generated as a liquid film with a thickness of several tenths of a millimeter on a rotating disk that is partially immersed into a reservoir filled with the investigated liquid. He<sup>+</sup> was used as a projectile. The scattering angle was 168°. The primary energy of the ion beam in our experiments was chosen to be 4.5 keV. The energy spread of the ion beam is approximately 10 eV. The temperature of the solution was set to  $(267.15 \pm 0.2)$  K. The pressure in the vacuum chamber in the presence of the solution ranged from  $2 \times 10^{-4}$  to  $8 \times 10^{-5}$  mbar during the measurements.

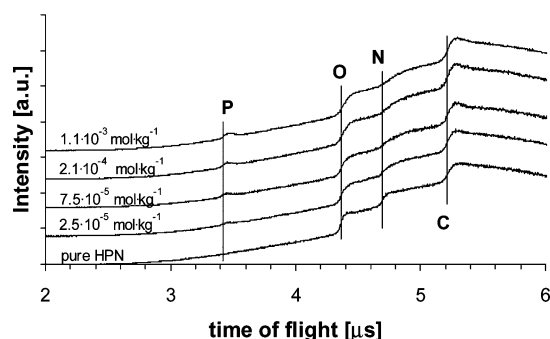
## Results

**Surface Tension Measurements.** Figure 2 shows the surface tension  $\sigma$  of the POPC solution as a function of POPC concentration  $c_{\text{POPC}}$ . The curve shows a discontinuity at a concentration of  $2.8 \times 10^{-4}$  mol·kg<sup>-1</sup> indicating the cmc. At the cmc the curve shows a slight but reproducible minimum. The influence of this minimum on the evaluation will be discussed later.

**NICISS Results.** Figure 3 shows NICIS spectra of solutions with different POPC concentrations and of the pure solvent.



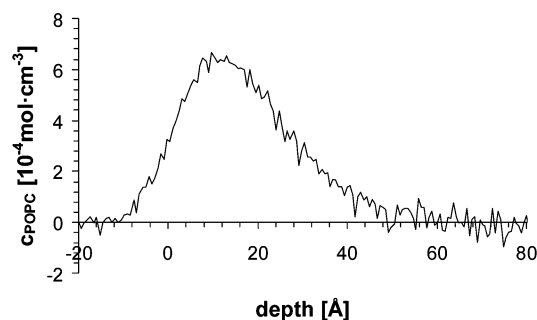
**Figure 2.** Surface tension  $\sigma$  of the POPC solution as a function of POPC concentration  $c_{\text{POPC}}$ . The vertical line indicates the position of the cmc.



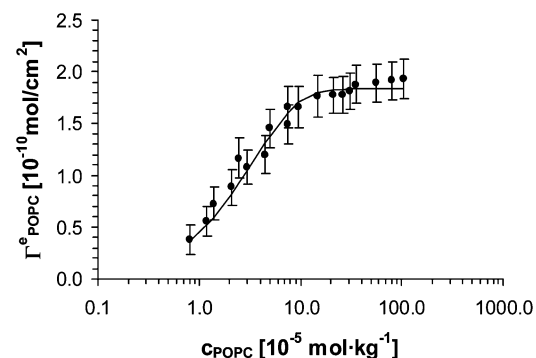
**Figure 3.** NICIS time-of-flight spectra of POPC solutions for different concentrations of POPC and of the pure solvent. Spectra are vertically offset for clarity.

The spectra are vertically offset for clarity. Several signals corresponding to different elements can be identified. The peak-like signal starting at  $3.42 \mu\text{s}$  in the spectra of the POPC solutions can be assigned to the phosphorus atom in the POPC molecule. The steplike signals can be assigned to oxygen ( $4.36 \mu\text{s}$ ), nitrogen ( $4.69 \mu\text{s}$ ), and carbon ( $5.21 \mu\text{s}$ ). All of these latter elements are abundant in both the POPC and HPN molecules. With increasing POPC concentration the phosphorus signal increases for the concentrations shown in the diagram. Furthermore, the onset of the oxygen and nitrogen steps becomes less steep while the carbon signal shows a peak near the onset of the step. These changes can be ascribed to the adsorption of POPC at the solution surface whereas HPN is depleted at the surface. All signals are superimposed by a background signal. This signal is caused by sputtered hydrogen atoms that are also detected.

From the time-of-flight spectra the depth profiles can be extracted. The procedure to remove the hydrogen background has been described in detail.<sup>2</sup> To determine the phosphorus depth profiles a polynomial was fitted to the background signal at times of flight higher and lower than the phosphorus signal. The polynomial was then subtracted from the spectrum to yield the phosphorus signal without the background signal. This procedure presumes that the bulk concentration of POPC is negligibly small compared to the statistic error of the signal, so that the homogeneous bulk distribution is not visible as a step following the peak in the spectrum. The maximum POPC bulk concentration investigated in this work is  $1.1 \times 10^{-3} \text{ mol}\cdot\text{kg}^{-1}$ , therefore this assumption is justified. Since the concentration of POPC is very small the HPN bulk concentration can be assumed to be constant for all solutions. The height of the steplike signals corresponding to oxygen, nitrogen, and carbon, respectively, is a relative measure for the HPN concentration. Since the HPN concentration is known and constant for all



**Figure 4.** Phosphorus depth profile of a  $1.1 \times 10^{-3} \text{ mol}\cdot\text{kg}^{-1}$  POPC solution.



**Figure 5.** Surface excess of POPC  $\Gamma_{\text{POPC}}^e$  as a function of POPC concentration  $c_{\text{POPC}}$ . The solid line is an exponential fit to the data points.

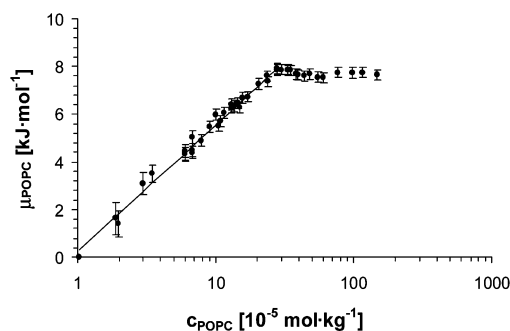
POPC concentrations to a very good approximation, the ratio between a step height and the HPN concentration is the conversion factor between intensity and concentration for a given spectrum. The oxygen signal was used to determine the conversion factor for all spectra. This factor was used to convert the intensity scale of the phosphorus signal to the concentration scale.

Neglecting the POPC bulk concentration, eq 2 is simplified when applied to the concentration depth profile of phosphorus  $c_P(z)$ :

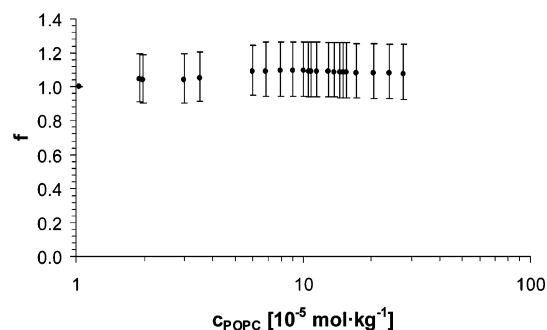
$$\Gamma_P^e = \int_{z_1}^{z_2} c_P(z) dz \quad (10)$$

In eq 10,  $z_1$  and  $z_2$  denote reasonable upper and lower boundaries of integration (e.g.,  $z_1 = -100 \text{ Å}$  and  $z_2 = 100 \text{ Å}$ ). Figure 4 shows the phosphorus concentration depth profile of a  $1.1 \times 10^{-3} \text{ mol}\cdot\text{kg}^{-1}$  POPC solution. This depth profile does not represent the actual phosphorus depth profile. All spectral signals are convoluted with the energy distribution of the backscattered projectiles. This convolution leads to a broadening of the depth profiles. The depth profiles can be deconvoluted to yield the actual depth profile, if desired.<sup>14</sup> However, for the evaluation of the surface excess it is not necessary to conduct a deconvolution, since the area under the curve is the same for the convoluted and deconvoluted depth profile.

Since the POPC molecule contains one phosphorus atom, the phosphorus surface excess is equal to the POPC surface excess. Figure 5 shows the POPC surface excess as a function of the POPC concentration calculated from the phosphorus depth profiles. The error bars are composed of two components. The first contribution is caused by the uncertainty in the determination of the oxygen step height that is used to determine the conversion factor between intensity and concentration. The second contribution is the uncertainty in the calculated scattering cross sections. To evaluate the chemical potential from eq 7 an



**Figure 6.** Chemical potential  $\mu$  of POPC as a function of POPC concentration  $c_{\text{POPC}}$ . The solid line is a logarithmic fit to the data points below the cmc.



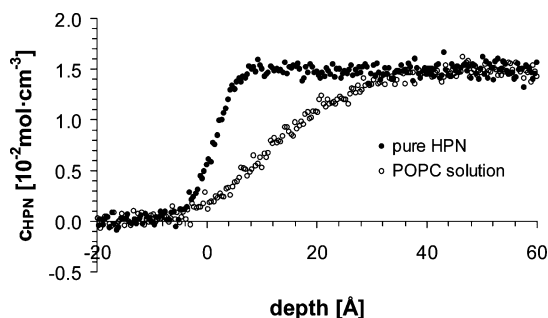
**Figure 7.** Activity coefficient  $f$  of POPC as a function of POPC concentration  $c_{\text{POPC}}$ .

exponential function was fitted to the surface excess values for interpolation between the data points.

The chemical potential was calculated from the surface tension and the surface excess data with eq 7 for the investigated concentration range below and above the cmc. The lowest investigated concentration was chosen as the standard state with  $\mu = 0$ . Figure 6 shows the chemical potential of POPC as a function of POPC concentration. The solid curve in the diagram is a logarithmic fit to the data points below the cmc. The POPC activity coefficients were calculated up to the cmc with eqs 8 and 9. Figure 7 shows the activity coefficients of POPC as a function of POPC concentration. The activity coefficient at the lowest concentration was set equal to 1, which implies that this concentration is chosen as the standard state. The activity coefficient can be evaluated only up to the cmc. Because of micelle formation the bulk concentration of monomeric units is not known above the cmc thus the activity coefficient cannot be evaluated from the activity.

It has been argued that a minimum in the surface tension curve indicates the presence of impurities.<sup>19,20</sup> From the surface tension data single-handedly this possibility cannot be excluded. However this information can be obtained from the NICIS spectra to a certain extent. As can be seen from the spectra the only elements present in the sample are phosphorus, nitrogen, oxygen, and carbon. As a consequence the possible impurity cannot be composed of other elements. The HPN spectrum is composed only of the signals from oxygen, nitrogen, and carbon. The signals are homogeneous steps with no peaks appearing at the onsets. For that reason it is evident that HPN is free of surface-active impurities. The impurity, if any, then has to be present in the surfactant. Eligible candidates are either the double-chain phospholipids 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine or 1,2-dioleoyl-*sn*-glycero-3-phosphocholine, their single-chain analogues, or the corresponding fatty acids as they are all possible residues from the POPC synthesis.

One necessary condition for purity in the adsorption layer is



**Figure 8.** Depth profiles of pure HPN (full circles) calculated from the nitrogen signal and of HPN in a  $1.1 \times 10^{-3} \text{ mol} \cdot \text{kg}^{-1}$  POPC solution (open circles) calculated from eq 11.

that the surface excess of surface-active species determined from the carbon signal has to equal the surface excess determined from the phosphorus signal. The application of eq 2 to the carbon depth profile permits the determination of the total surface excess  $\Gamma_{\text{C}}^{\text{e}}$  of all molecules containing carbon atoms excluding the solvent. For the determination of the position of the Gibbs dividing plane  $z_0$  the concentration depth profile of the solvent has to be known. The nitrogen depth profile as obtained from the NICIS spectra can be used for this purpose. The nitrogen depth profile  $c_{\text{N}}(z)$  is composed of the nitrogen signal from HPN  $c_{\text{N}}^{\text{HPN}}(z)$  and the nitrogen signal from the choline group in POPC  $c_{\text{N}}^{\text{POPC}}(z)$ . To obtain the depth profile of the solvent, the contribution of the POPC has to be removed. POPC contains one phosphorus and one nitrogen atom. Thus the phosphorus depth profile  $c_{\text{P}}(z)$  can be assumed to be equal to the nitrogen depth profile. Since the positions of the nitrogen atom and the phosphorus atom in the POPC molecule are not the same, the phosphorus depth profile is only an approximation for the description of the choline nitrogen depth profile. The concentration depth profile of HPN  $c_{\text{HPN}}(z)$  results approximately from

$$c_{\text{HPN}}(z) \approx c_{\text{N}}(z) - c_{\text{P}}(z) \quad (11)$$

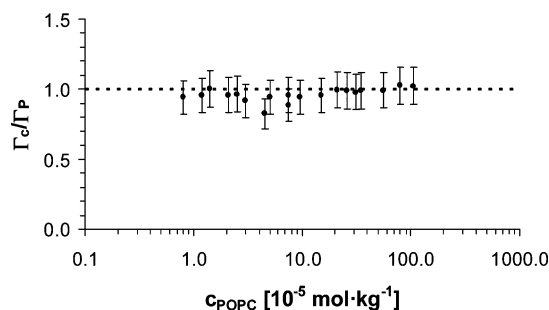
However, the exact shape of the depth profiles is irrelevant for the determination of the Gibbs dividing plane. The areas under the phosphorus and nitrogen depth profiles of POPC are the same. Consequently the value of  $z_0$  calculated from eq 2 will be invariant of whether  $c_{\text{P}}(z)$  is replaced by  $c_{\text{N}}^{\text{HPN}}(z)$  in eq 11. Once  $z_0$  is known, the surface excess of all carbon-containing species  $\Gamma_{\text{C}}^{\text{e}}$  except HPN can be evaluated with eq 2.

Figure 8 shows the depth profile of HPN in a  $1.1 \times 10^{-3} \text{ mol} \cdot \text{kg}^{-1}$  POPC solution and of the pure solvent for comparison. The depletion of solvent at the surface in the POPC solution is clearly visible.

Figure 9 shows the ratio  $\Gamma_{\text{C}}^{\text{e}}/\Gamma_{\text{P}}^{\text{e}}$  as a function of POPC concentration. For comparison the expected value of unity is shown as the dotted line. As can be seen the surface excess ratio is equal to unity within the error bars throughout the investigated concentration range. This result indicates that either the solution is free of surface-active impurities or that the impurity contains phosphorus atoms and has a stoichiometric ratio between carbon atoms and phosphorus atoms that matches the ratio of the POPC molecule. We will return to the question about the presence of impurities in the Discussion section.

From the NICIS spectra not only the surface excess concentrations of all elements can be extracted but also information regarding the molecular structure of the adsorption layer. The depth profile in Figure 4 shows a maximum at a depth of  $(11.7 \pm 2.5) \text{ \AA}$ . This indicates a preferential orientation of the POPC





**Figure 9.** Ratio of the POPC surface excesses  $\Gamma_C^e/\Gamma_P^e$  evaluated from the carbon and phosphorus signals as a function of POPC concentration  $c_{\text{POPC}}$ . The dotted line indicates the value that is expected as a necessary criterion for surface purity.

molecules with the aliphatic carbon chains in the adsorption layer closer toward vacuum than the phosphocholine part of the headgroup. However, the orientation of the POPC molecule is not the subject of this article but shall be discussed in a forthcoming publication.<sup>21</sup>

## Discussion

From Figure 7 it can be seen that the activity coefficient of POPC is essentially constant as a function of concentration, with a slight increase of the activity coefficient above unity when approaching the cmc resides within the error bars. An actual increase of the activity coefficient with concentration would be surprising. In the case of electrolyte solutions an increase of the activity coefficient with concentration is usually observed only at very high salt concentrations.<sup>21</sup> This behavior is explained with an incomplete solvation of the individual ions. Consequently the screening between the ions is reduced and the activity coefficient increases. For the POPC solutions the solute concentrations are far too low to cause a partial breakup of the solvation shell surrounding the molecule. Therefore the possibility of an activity coefficient increasing with concentration is likely to be discarded.

The POPC/HPN surfactant/solvent system behaves ideally throughout the whole concentration range up to the cmc. The assumption to neglect the activity coefficients is justified for this system. The ideal behavior also reveals that no premicellar aggregation of the POPC molecules takes place. Because the activity coefficient can be determined only for bulk concentrations lower than the cmc we shall look at the course of the chemical potential as a function of POPC concentration. The finding that the activity coefficient is constant as a function of concentration implies that the chemical potential changes linearly with the logarithm of the concentration. This behavior is indeed observed as one can see from the logarithmic fit to the pre-cmc data points in Figure 6. The slope of the line is  $2.22 \text{ kJ}\cdot\text{mol}^{-1}$  matching exactly the expected value of  $RT = 2.22 \text{ kJ}\cdot\text{mol}^{-1}$ . As calculated from eq 7 the chemical potential is constant as a function of concentration above the cmc within the error bars. This statement may appear trivial at first sight. However, this result can only be obtained if both the surface excess and the surface tension have been measured and not from surface tension measurements alone.

Disregarding the error bars the chemical potential shows a maximum as a function of concentration at  $0.28 \text{ mol}\cdot\text{kg}^{-1}$ . This maximum is caused by the minimum in the surface tension curve since the surface excess as a function of concentration does not change its sign. A minimum in the surface tension curve is associated in some cases with the presence of a surface-active impurity in the solution.<sup>19,20</sup> By using the Gibbs equation it is

possible to predict the influence of this potential impurity on the evaluation of the POPC activity coefficients and the chemical potential of POPC, respectively. For simplicity we shall assume that there is only one impurity present in the solution. The following considerations can be extended to an arbitrary number of components if desired. The presence of an impurity is noted in the Gibbs equation via the introduction of an additional chemical potential and activity, respectively:

$$d\sigma = -(\Gamma_1^e d\mu_1 + \Gamma_2^e d\mu_2) \quad (12)$$

$$d\sigma = -RT[\Gamma_1^e(d(\ln f_1) + d(\ln x_1)) + \Gamma_2^e(d(\ln f_2) + d(\ln x_2))] \quad (13)$$

If at all, the impurity must be contained in the POPC sample because the purity of HPN was proven experimentally. Thus the molar fractions of both components scale linearly with each other:

$$x_1 = \alpha x_2 \quad (14)$$

where  $\alpha$  is a constant. Inserting (14) into (13) yields after rearranging

$$\frac{d\sigma}{d(\ln x_1)} = -RT(\Gamma_1^e + \Gamma_2^e) - \frac{RT}{d(\ln x_1)}(\Gamma_1^e d(\ln f_1) + \Gamma_2^e d(\ln f_2)) \quad (15)$$

The ratio between the carbon surface excess and the phosphorus surface excess is very close to the stoichiometric ratio between the two elements in POPC. Therefore the impurity contains at least one phosphorus atom. The surface excess of phosphorus determined from the NICIS spectra will then be proportional to the sum of the surface excess of POPC and the impurity,  $\Gamma_P^e = \Gamma_1^e + \Gamma_2^e$ . We have shown in the results section that the following equation is true:

$$\frac{d\sigma}{d(\ln x_1)} = -RT\Gamma_P^e \quad (16)$$

Equation 16 states that, although the two substances containing phosphorus might be present at the surface, the total phosphorus surface excess depends only on the molar fraction of one component. Hence the solution behaves apparently ideally. However, from eqs 15 and 16 it follows:

$$\Gamma_1^e \frac{d(\ln f_1)}{d(\ln x_1)} = -\Gamma_2^e \frac{d(\ln f_2)}{d(\ln x_1)} \quad (17)$$

One solution of eq 17 is that the two derivatives are equal to zero, which would reduce eq 15 to eq 16. POPC and the impurity would then show ideal behavior throughout the whole concentration range up to the cmc. The second possibility is that both derivatives have opposite signs. The activity coefficient of one component then increases with concentration while the activity coefficient of the other component decreases with concentration. Since the surfactant and the impurity probably have a similar chemical structure, one would expect the qualitative dependence of the activity coefficient of both substances to be the same as a function of concentration. For that reason none of the derivatives in eq 17 should be positive. Moreover, it is unreasonable to assume an increase of the activity coefficient at low bulk concentrations of the solute. We conclude from these considerations that a behavior where the derivatives have opposite signs is very unlikely.

In summary, we cannot exclude the possibility of impurities being present in the solution. However, we have shown that if there are impurities present both the POPC and the possible impurity must behave ideally at concentrations below the cmc.

### Conclusions

We have determined the chemical potential of the nonionic surfactant POPC in the solvent HPN at POPC concentrations below and above the cmc. Neutral impact collision ion scattering spectroscopy was used to determine the surface excess of POPC. The Gibbs equation was used in conjunction with surface tension measurements to calculate the chemical potential of POPC as a function of POPC concentration. POPC activity coefficients were evaluated up to the cmc. The solution behaves as an ideal mixture up to the cmc and the chemical potential remains constant at concentrations higher than the cmc. The ideal behavior also reveals that no premicellar aggregation of the POPC molecules takes place. The possible influence of surface-active impurities was discussed. The finding that the solution behaves ideally up to the cmc is not affected by the presence of those impurities whose presence is compatible with the experimental data.

**Acknowledgment.** We express our gratitude to Dr. Karin Kirmse for performing the surface tension measurements. Financial support from the Deutsche Forschungsgemeinschaft (Grant No. MO 288/34) is acknowledged.

### References and Notes

- (1) Adamson, A. W.; Gast, A. P. *The Physical Chemistry of Surfaces*; Wiley-Interscience: New York, 1997.
- (2) Andersson, G.; Krebs, T.; Morgner, H. *Phys. Chem. Chem. Phys.* **2005**, *7*, 136.
- (3) Rosen, M. J. *Surfactants and Interfacial Phenomena*; Wiley-Interscience: New York, 1989.
- (4) Fainerman, V. B.; Lucassen-Reynders, E. H.; Miller, R. *Colloids Surf., A* **1998**, *143*, 141.
- (5) Prosser, A. J.; Franses, E. *Colloids Surf., A* **2001**, *178*, 1.
- (6) Song, L. D.; Rosen, M. J. *Langmuir* **1996**, *12*, 1149.
- (7) Waengnerud, P.; Joensson, B. *Langmuir* **1994**, *10*, 3542.
- (8) Strey, R.; Viisanen, Y.; Aratono, M.; Kratochvil, J. P.; Yin, Q.; Friberg, S. E. *J. Phys. Chem. B* **1999**, *103*, 9112.
- (9) Penfold, J.; Thomas, R. K.; Lu, J. R.; Staples, E.; Tucker, I.; Thompson, L. *Phys. B* **1994**, *198*, 110.
- (10) Downer, A.; Eastoe, J.; Pitt, A. R.; Penfold, J.; Heenan, R. K. *Colloids Surf., A* **1999**, *156*, 33.
- (11) Randall, M.; White, J. M. *J. Am. Chem. Soc.* **1926**, *48*, 2514.
- (12) Scratchard, G.; Prentiss, S. S.; Jones, P. T. *J. Am. Chem. Soc.* **1932**, *54*, 2690.
- (13) Andersson, G.; Morgner, H. *Surf. Sci.* **1998**, *405*, 138.
- (14) Andersson, G.; Morgner, H. *Surf. Sci.* **2000**, *445*, 89.
- (15) Niehus, H.; Heiland, W.; Taglauer, E. *Surf. Sci. Rep.* **1993**, *17*, 213.
- (16) Andersson, G.; Morgner, H. *Nucl. Instrum. Methods Phys. Res., Sect. B* **1999**, *4*, 357.
- (17) Andersson, G.; Morgner, H.; Schulze, K. D. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2002**, *190*, 222.
- (18) Wulf, M. Ph.D. Thesis, Witten, 1994.
- (19) Miles, G. D.; Shedlovsky, L. *J. Phys. Chem.* **1944**, *48*, 57.
- (20) Brady, A. P. *J. Phys. Chem.* **1949**, *53*, 56.
- (21) Krebs, T.; Andersson, G.; Morgner, H. To be submitted for publication.
- (22) Pitzer, K. S. *Thermodynamics*; McGraw-Hill College: New York, 1995.