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P.C. Schulz
R.M. Minardi
M.E. Gschaider de Ferreira
B. Vuano

The interface air/water of *n*-dodecanephosphonic acid solutions

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P.C. Schulz (✉) · R.M. Minardi
M.E. Gschaider de Ferreira · B. Vuano
Universidad Nacional del Sur
Departamento de Química e
Ingeniería Química
Avda. Alem 1253
8000 Bahía Blanca
Argentina

Abstract The air/water interface of the system *n*-dodecanephosphonic acid (H_2DP)–water was studied by surface tension, ion-selective electrodes and evaporation in an electrobalance. The combination of surface tension and ion-selective electrodes measurements enables to study the adsorption of soluble surfactants above the cmc using the Gibbs' equation. H_2DP formed a nonideal monolayer at the air/water interface with $A_{\text{molec}} = 0.995\ \text{nm}^2$ below the cmc. Above the cmc there was a reduction in adsorption giving $A_{\text{molec}} = 6.32\ \text{nm}^2$, which remained almost constant in the explored concentration range. This adsorption reduction may be due to a change composition on micellization, or to a thermodynamic advantage of micellization on adsorption. The reduction in the evaporation rate of water was mainly due to the reduction of the water activity, caused by the presence of solutes in bulk. This is because the strong changes in the surface coverage did not have significant influence on the evaporation rate.

Key words Dodecanephosphonic acid – soluble monolayer – air/water interface – evaporation – adsorption – ion-selective electrodes

Introduction

Although most of the technological applications of surfactant solutions imply their use at concentrations above the critical micelle concentration (cmc), there are much more works about the state of the interface air/water on soluble surfactant solutions below the cmc than above this concentration. This is partly because the experimental technique which gives structural information about such surfaces (surface neutron reflectivity) is recent and limited to very few specialized laboratories, and partly because it is difficult to apply the Gibbs' equation to surface tension data. The main problem in this case is that the surfactant activity is not related simply to the total concentration, and it is experimentally somewhat inaccessible [1]. The only direct measurements of surface excess above the cmc are radiotracer measurements [2], which suffer from the uncertain assumptions that have to be made about scaling and background subtraction; and neutron reflectivity experiments, which give not only the surface excess but the surface structure. In particular, the work of the group of Lu, Penfold and Thomas in England is very interesting and of great significance. Some of these articles will be cited in this work. This technique is very useful but implies the use of noncommon equipment and very expensive chemicals.

It has been recently asserted that surface pressure cannot be applied directly to the adsorbed layer of soluble amphiphiles, which is in thermodynamic equilibrium with the underlying solution [3, 4]. However, there was a pioneering work in using a combination of surface tension and ion-selective electrodes to study the air/water interface of SDS solutions above the cmc by Sasaki et al. [5]

published in 1975. We used the same method to study the surface state of *n*-dodecanephosphonic acid–water.

The presence of insoluble surfactant monolayers at the air/water interface affects the rate of transfer of solute gas molecules through the interfaces [6]. The evaporation of water through insoluble monolayers is also reduced [7, 8]. The reduction in mass transfer through an insoluble surfactant monolayer may be 5–25% of that from of a clean surface of water [9]. Because surfactants reduce the rate of vaporization of small drops, their use has been proposed to reduce evaporation of fogs that protect crops from frost damage [10]. The effect has been explained by solubility of water in the surfactant film and diffusion through it to the air/liquid interface [11]. As far as we know, the effect of soluble monolayers has not been studied so far. We studied the evaporation rate through a soluble surfactant monolayer to determine the influence of the monolayer state on this phenomenon.

Experimental

n-Dodecanephosphonic acid (H_2DP) has been synthesized by the method of Roos and Toet [12] and Kossolapoff [13], and recrystallized four times in petroleum ether (fraction 60–80 °C) until a constant melting point was reached. The acid was extremely pure. This ensured that no impurities were present in the solution.

The solutions were prepared by weighing the solid acid in vials and adding the appropriate amount of double-distilled CO_2-free water. The vials were hermetically sealed and heated to 90 °C for about 20 min. Finally, they were left for 2 days before being used.

The statistical treatment of data was performed by the least-squares method, using Student's *t*-distribution and a confidence level of 0.90.

The surface tension measurements were performed with a Du Noüy (Krüss) tensiometer, thermostatted to 25.0 ± 0.1 °C.

Monoprotic *n*-dodecanephosphonate (HDP^-) activity measurements were performed with an HDP^- ion-selective electrode which has been described elsewhere [14], and was calibrated with NaHDP solutions. H^+ activity determinations were made with an Orion glass electrode. A CRIBBAB pH-meter and millivoltmeter were employed. The treatment of potentiometric data has been described elsewhere [14].

The evaporation rate measurements were performed in a CAHN 1000 electrobalance, operating in a register range of 1000 mg and an output potential of 10 mV. The pressure was 101.325 kPa. The samples were measured at 25.0 ± 0.1 °C, thermostatted with water circulation. Known volumes of the solutions were poured into Pyrex cylindrical containers with a 2.9 cm internal diameter. To avoid secondary Archimedes' effects, a compensator container was hung on the other arm of the electrobalance. The thermocouple (Fe–constantan) was in contact with the solution through a thin glass sheath. The evaporation rate was followed by the loss of weight of the containers.

To determine the surface excess at the air/water interface (Γ) the Gibbs adsorption isotherm in its general form for multicomponent systems has been employed:

$$d\sigma = -\sum_i \Gamma_i \, d\mu_i \, , \tag{1}$$

where μ_i is the chemical potential of component *i* and σ the surface tension (mN/m). This system had two components in the phase rule sense: water and *n*-dodecanephosphonic acid. The adsorbable species H_2DP, HDP^- and H^+ are related to the H_2DP equilibrium of dissociation. Since the temperature is constant, the system had only one degree of freedom, i.e., the concentration of one of their components. We have taken the acid concentration as the degree of freedom. This gives

$$d\sigma = -\Gamma \, d\mu \tag{2}$$

with $d\mu = RT \, d(\ln a)$, in which a is the activity of the adsorbable component in bulk. Only the monomeric (non-micellized) form of the surfactant contributes to the surfactant activity or chemical potential, and hence to the surface tension reduction [15]. In the studied system, only free (nonmicellized) H_2DP molecules and HDP^- ions may adsorb at the air/water interface. Micelles are not surface-active [16], and are excluded from the interface region, as it was found by Lu et al. [1]. H_2DP is a weak acid, so the following equilibrium is produced in aqueous solutions:

$$H_2DP \leftrightarrow H^+ + HDP^- \tag{3}$$

with $pK_1 = 3.98$ [17]. The amount of di-ionized species ($DP^=$) was not significant because $pK_2 = 8.42$ [17]. The equilibrium (3) involves only free (nonmicellized) species, which enabled us to compute the activity of free H_2DP ($a_{\text{unionised acid}}$) both in the pre-cmc solutions and in equilibrium with micelles by using the activities of H^+ and HDP^- ions determinated by glass and surfactant ion-selective electrodes. Then we used the activity of the unmicellized species, $a_{\text{unmicellized species}}$, in Eq. (2). Notice that in fully ionized, nonmicellized salts,

$$a_{\text{salt}} = a_+ a_- = (a_\pm)^2 \tag{4}$$

and $\ln a_{\text{salt}} = \ln(a_\pm)^2 = 2 \ln a_\pm$. This is the origin of the coefficient used in the Gibbs equation when the adsorbable species is ionized. But the use of $\ln a_{\text{salt}}$ is completely equivalent to that of $2 \ln a_\pm$. In the usually studied systems, $c = c_+ = c_-$, and this situation leads to the use of the form 2 ln c. Due to the partial dissociation of the acid in the system studied in this work the unmicellized (and adsorbible) species are H_2DP, HDP^- and H^+. These species are not thermodynamically independent. Besides, $[HDP] \neq [H^+]$ at concentrations above the cmc. In this system:

$$\begin{aligned}\mu_{\text{unmicellized species}} &= \mu_{\text{unionised acid}} + \mu_{\text{ionised acid}}\\ &= \mu^{\circ}_{\text{unionised acid}} + RT\ln a_{\text{unionised acid}}\\ &\quad + \mu^{\circ}_{\text{ionised acid}} + RT\ln a_{\text{ionised acid}}\\ &= \mu^{\circ}_{\text{unionised acid}} + \mu^{\circ}_{+} + \mu^{\circ}_{-}\\ &\quad + RT\ln a_{\text{unionised acid}}a_{+}a_{-} \ .\end{aligned}$$

Then the Gibbs equation was put in the form

$$\Gamma = -\frac{1}{RT}\frac{d\sigma}{d\ln a_{\text{unionised acid}}a_{+}a_{-}} \ , \tag{5}$$

where $a_{\text{unionised acid}}a_{+}a_{-}$ is the bulk activity of the adsorbible species. Notice that $a_{\text{unionised acid}} = a_{+}a_{-}/K_1$, then $= d\ln c_{\text{unionised acid}}a_{+}a_{-} = d[\ln(a_{\pm})^4 - \ln K_1] = 4d\ln(a_{\pm})$. We did not use this form because $a_{+} \neq a_{-}$ at concentrations above the cmc. The free H_2DP activity coefficient was taken as unity. a_+ and a_- are the activities of free H^+ and HDP^- ions.

Γ was defined as the excess amount of a given component actually present in the system over that present in a reference system of the same volume as the real system and in which the bulk concentration in the two phases remain uniform up to the Gibbs dividing surface [18]. In a simplified form, Γ may be defined as

$$\Gamma = (c_s - c_b)\delta \ , \tag{6}$$

c_s and c_b being the concentration of the active species in the interfacial layer and bulk per unit area, and δ the thickness of the interfacial layer [19]. This means that the surface excess is related to the actual concentration of active species in the interface and bulk phases. Then, the total surface concentration was computed using

$$c_s = ([H_2DP]_{\text{free}} + [HDP]_{\text{free}})\delta + \Gamma \ , \tag{7}$$

where δ is the monolayer thickness. The value of $\delta = 3.75$ nm was taken for dodecyl trimethyl ammonium bromide, which was determined from neutron reflectivity measurements by Lu et al. [20]. The surface area per adsorbed molecule is

$$A_{\text{molec}} = \frac{1}{C^s N_A} \ , \tag{8}$$

N_A being the Avogadro's number.

Results

Surface monolayer

The activities of the various species in solution are shown in Fig. 1, together with the total activity of adsorbable species. In Fig. 2, the surface tension vs. the activity of the adsorbable species has been plotted. The straight lines were computed by the least-squares method giving:

$$\sigma = \begin{cases} 70.5 \pm 4.1 - (3.87 \pm 0.13)\ln a_{\text{unionised acid}}a_{+}a_{-} \ , \\ \quad r = -0.9967 \ , \quad \text{below the cmc} \ , \\ 14.1 \pm 1.1 - (0.7373 \pm 0.050)\ln a_{\text{unionised acid}}a_{+}a_{-} \ , \\ \quad r = -0.8956 \ , \quad \text{above the cmc} \ , \end{cases}$$

r being the correlation coefficient.

By using Eq. (5) Γ was computed, giving the constant values $(1.561 \pm 0.050) \times 10^{-10}\,\text{mol cm}^{-2}$ below the cmc, and $(2.997 \pm 0.020) \times 10^{-11}\,\text{mol cm}^{-2}$ above the cmc.

The values of A_{molec} have been plotted in Fig. 3. Figure 4 shows the plot of ΠA_{molec} vs. Π, where $\Pi = \sigma_0 - \sigma$ is the surface pressure. The ideal value $kT = 4\,\text{mN nm}^2/\text{m}$ was also shown.

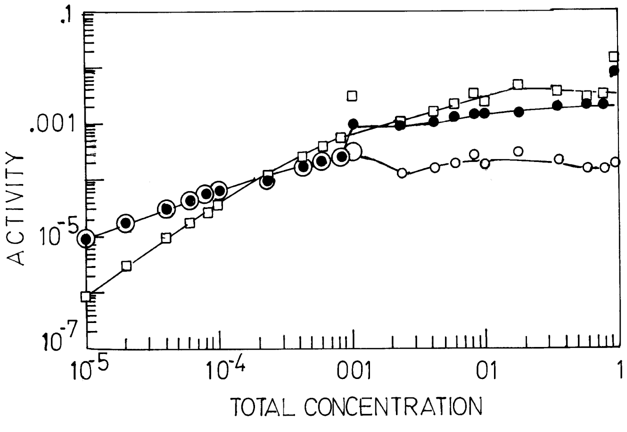
Evaporation

The loss of weight (in kg/(m^2 s)) with time followed a parabolic equation with the general form [22]

$$v = v_0 - Kt^{1/2} \ , \tag{9}$$

where v and v_0 are the rate of evaporation at time t and the initial evaporation, measured as loss of mass per square meter per second. The values of v_0 and K were

Fig. 1 Activity of free H_2DP (□), free HDP^- (○) and free H^+ (●) vs. total concentration of surfactant (mol dm^{-3})



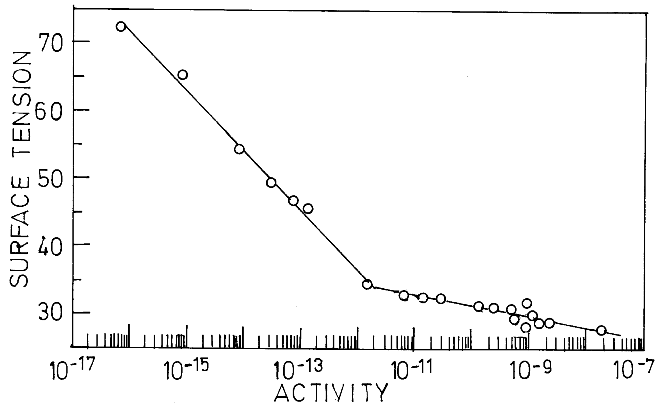


Fig. 2 Surface tension ($mN\,m^{-1}$) vs. total activity of monomeric species

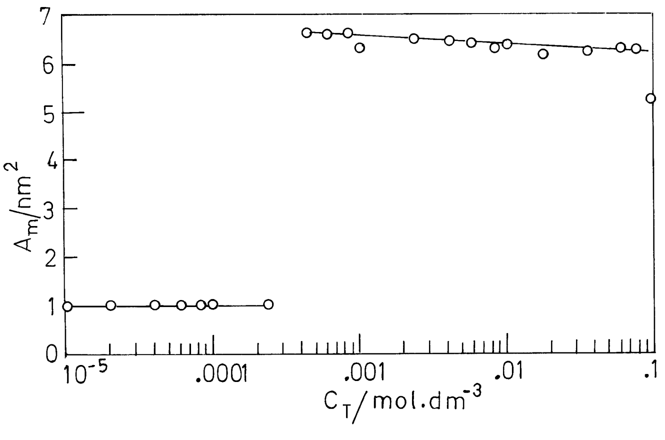


Fig. 3 Area per molecule vs. total concentration of surfactant

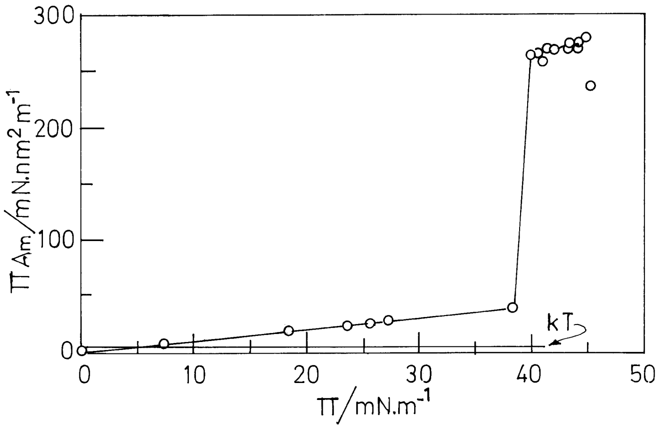


Fig. 4 Plot of ΠA_{molec} vs. Π. The horizontal straight line at $kT = 4$ mN(nm^2)/m is the ideal bidimentional gas behavior

found by the least-squares linear regression method using Eq. (9) and the experimental data, and they are shown in Fig. 5.

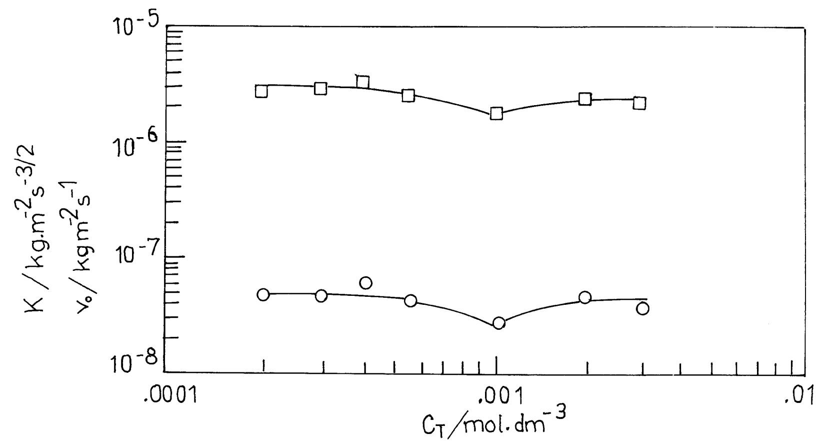
Discussion

Surface monolayer

At very low total concentration ($C_T < 10^{-5}$ M) the surface area per adsorbed molecule is $A_{molec} = 1\ nm^2$ (computed from literature data [21]). Our data below the cmc gave a constant value of $A_{molec} = 0.99526 \pm 0.00012\ nm^2$.

The value of A_{molec} in the monolayer is a typical value for bidimensional expanded liquids [23–25]. Its constancy indicates surface saturation [19]. When surface saturation is reached at very low concentrations and surface pressures, a nonideal surface behavior is

Fig. 5 Vaporization data for H_2DP aqueous solutions, (□) v_0, (○) K



present [26]. Frumkin [27] found this type of nonideality in a series of fatty acid monolayers. The behavior of the ΠA_{molec} vs. Π plot is also typical of nonideal interfacial monolayers, showing attraction among adsorbed molecules at very low Π values, and a strong repulsion among them at higher surface pressures [19]. The sudden increase in ΠA_{molec} at the cmc indicates a strong change in molecular lateral interaction in the two-dimensional system [28].

The radius of the micellized phosphonate headgroup is 0.235 ± 0.092 nm [29]. Using the model of the hard disk bidimensional gas [30] the excluded area per surfactant molecule was computed using

$$A_0 = 2\pi r^2 \tag{10}$$

giving $A_0 = 0.35 \pm 0.13\ \mathrm{nm}^2$. The comparison with $A_{\mathrm{molec}} = 0.9953\ \mathrm{nm}^2$ indicates that about 65% of the pre-cmc surface was water.

The surface per polar headgroup in H_2DP crystals is $S = 0.2501 \pm 0.0023\ \mathrm{nm}^2$ [31]. The comparison of S, A_0 and A_{molec} values suggested that the polar headgroups remained hydrated in the adsorbed state, as it has been found in other systems [4].

The dependence of ΠA_{molec} on Π (Fig. 4) indicates a strong nonideality [19].

At the cmc ($\Pi \approx 40$ mN/m) a change in the state of the monolayer happened. The A_{molec} value increased to $6.32 \pm 0.16\ \mathrm{nm}^2$ and remained almost constant.

The strong decrease in the surface concentration at the cmc may indicate a competition between the adsorbed and the micellized states, with an energetic advantage of the micelles with respect to the adsorbed monolayer. If it is supposed that the state of the polar headgroup does not differ significantly in the micellized and the adsorbed states, the energetic advantage must be due to the hydrocarbon tails. The free energy of adsorption per methylene group for n-alkylphosphonic acids is $\Delta\mu^{\circ}_{\mathrm{CH2,ads}} = -54.3 \pm 3.6$ J/mol [21], whereas that for micellization is $\Delta\mu^{\circ}_{\mathrm{CH2,mic}} = -161.3 \pm 1.5$ J/mol [32]. In consequence, there is an energetic advantage of 2.97 times in transfer the H_2DP molecules from the surface to the micelles. It must be noticed that this is not a common phenomenon. In most surfactant systems, $|\Delta\mu^{\circ}_{\mathrm{CH2,mic}}| < |\Delta\mu^{\circ}_{\mathrm{CH2,ads}}|$ [33, 34]. This is probably due to the much more effective elimination of hydrocarbon–water interphase in micelles, compared to the situation at the air/water interphase.

The pre-cmc value of A_{molec} is 5.5 times the hydrocarbon chain cross section ($0.18\ \mathrm{nm}^2$) [35]. This means that the hydrocarbon chains are not very close to each other and there is a considerable amount of hydrocarbon/air interface at the adsorbed monolayer. In contrast, the hydrocarbon chains form an oil drop in micelles. Since the polar headgroups probably interact through hydrogen bonds between them in the micelle surface, the hydrophobic core must be compact. In contrast, there is some immersion of the hydrocarbon chains into the water layer in soluble monolayers, ranging from 10% to 30% of the total chain length [3, 4, 20, 34–40].

In addition, the adsorbed molecules are far enough to prevent the formation of intermolecular hydrogen bonds. There are intermolecular hydrogen bonds in the polar surfaces of H_2DP mesophases [41], and in the polar surface of H_2DP micelles [42]. This situation may be an extra advantage of the micellar state against the adsorbed one.

The above facts may be the cause of the energetic advantage of the micellization in comparison with the adsorption in this system, thus explaining the desorption of molecules at concentrations larger than the cmc.

It must be noted that this situation is not common. There are some determinations of adsorption at concentrations above the cmc, obtained by neutron reflectivity. For SDS, A_{molec} is constant and amounts to $0.415\ \mathrm{nm}^2$ [43]. The same result was obtained by radioactive tracers [44]. Sasaki et al. [3] found that this situation remains unchanged up to about 20 mM and above this concentration A_{molec} increased. Tetradecyltrimethyl ammonium bromide solutions showed a decrease in A_{molec} above the cmc [1], but other measurements indicated an increase of about 15% between the cmc and 3 cmc [45].

An alternative explanation may be that the composition of the interface is different below and above the cmc. The less hydrophilic H_2DP molecules may be preferentially solubilized in micelles rather than adsorbed at the interface, thus enriching the latter with HDP^- ions. This situation may produce a stronger repulsion between the adsorbed molecules, giving the sudden rise in A_{molec} which can be seen in Fig. 4.

Evaporation

The reduction in the initial rate of evaporation v_0 may be due to two different factors: one of them may be an effect of reduction of the effective surface of water exposed to evaporation, because of the partial coverage of the air/water interface by surfactant molecules. The other may be the reduction of water activity in the bulk, caused by the presence of solutes.

By use of the hard disc model with $A_0 = 0.35\ \mathrm{nm}^2$, the surface available for water molecules is $0.995–0.35 = 0.65\ \mathrm{nm}^2$ per surfactant molecule, which is about 6.6 times the area per water molecule ($0.097\ \mathrm{nm}^2$) [45–50]. This means that the surface mole fraction of water is 0.87, and the value of v_0 must be 0.87 of that of pure water ($(1.000 \pm 0.028) \times 10^{-5}\ \mathrm{kg\,m^{-2}\,s^{-1}}$). It can be seen in Fig. 5 that v_0 about $3 \times 10^{-6}\ \mathrm{kg\,m^{-2}\,s^{-1}}$ in surfactant solutions. Since the surface composition does not vary in the explored region below the cmc, the extra decrease in v_0 must be due to the reduction in water activity caused by the increase in the solute concentration. This is also the cause for the slight reduction in v_0 with the increase of C_T, having a minimum near the cmc.

At concentrations above the cmc the average surface area per surfactant molecule is 6.32 $\mathrm{nm^2}$. By subtraction of the A_0 value (0.35 $\mathrm{nm^2}$) there will be 5.97 $\mathrm{nm^2}$ of free water per surfactant molecule, which corresponds to 6.15 water molecules per surfactant molecule. The surface mole fraction of water is then 0.98. If the partial coverage of the surface were the main factor in v_0 reduction, the increase above the cmc would be very large. Nevertheless, in Fig. 5 it may be seen that only a slight increase in v_0 occurs. The conclusion is that the main contribution to the decrease in initial evaporation rate is the reduction in the activity of water by the presence of solutes.

The variation in time of the evaporation rate (K) is related to the rate of diffusion of molecules with enough energy to evaporate, from the bulk to the surface, where the initial evaporation created a deficit of molecules with enough energy [22]. The value of K is $(1.63 \pm 0.09) \times 10^{-7}\ \mathrm{kg\,m^{-1}\,s^{-3/2}}$ in pure water. The reduction of K in surfactant solutions must be mainly due to steric hindrance to the diffusion of water in bulk solution. K is about $4 \times 10^{-8}\ \mathrm{kg\,m^{-1}\,s^{-3/2}}$ in surfactant solutions, and there was a gradual reduction up to near the cmc, because of the increase in dissolved species concentration. The slight increase of K above the cmc probably means that there is an energy barrier to the incorporation of water molecules from bulk to the interface, whose height depends on the amount of adsorbed surfactant. The value of the barrier energy must be very low.

Conclusions

- The combination of surface tension and ion-selective electrodes measurements enables to study the adsorption of soluble surfactants above the cmc.
- H_2DP forms nonideal monolayers at the air/water interface with $A_{\mathrm{molec}} = 0.99526\ \mathrm{nm^2}$ below the cmc. Above the cmc there is a reduction in adsorption giving $A_{\mathrm{molec}} = 6.32\ \mathrm{nm^2}$.
- The reduction in the evaporation rate of water is mainly due to the reduction of water activity, caused by the presence of solutes in bulk. The reduction of the effective area available for evaporation has only a slight effect on water evaporation.

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