

## 14. On the Activity of Water and the Concept of the Interfacial Free Energy in W/O-Microemulsions

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### Summary

The water activity and its temperature dependence as a function of the amount of water in the  $L_2$ -phase of the (water/Aerosol OT/isooctane)-system (s. *Exper. Part*) was determined with the help of a differential pressure gauge and a precision cathetometer. A theoretical approach based essentially upon a solution of the *Poisson-Boltzmann* equation with appropriate boundary conditions led to a description of the activity plot in excellent agreement with experimental results.

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**Introduction.** – Stability considerations are central for distinguishing true and apparent so-called microemulsions in the  $L_1$ - and  $L_2$ -phases. The frequently discussed transient region between thermodynamically stable water-in-oil (w/o)- and oil-in-water (o/w) emulsions depends essentially on their stability domains. In spite of the importance of this fact, there have been only a few attempts [1] [2] to determine the stability region of, for example, a thermodynamically stable water-in-oil emulsion.

The most direct procedure appears to be the measurement of the partial pressure of the water vapor above an equilibrated water-in-oil microemulsion ( $L_2$ -phase). This kind of experiment yields straightforwardly the water activity, for example, as a function of the solubilized amount of water. A sensitive experimental set-up should allow one to detect the stability limit of such microemulsions.

Parallel to these investigations theoretical considerations with particular emphasis on the electrostatic contributions to the free energy of the system were carried out quite recently by one of us [5] [6] on reversed micellar aggregates containing solubilized water which surprisingly well support the present experimental results. Hence, this study is believed to contribute some more fundamental results to our knowledge on water-in-oil thermodynamically stable emulsions formed by ionic surfactants.

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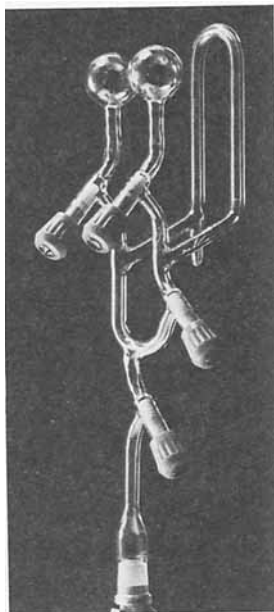


Fig. 1. Differential vapor pressure gauge

**Experimental Part.** – *Material.* Sodium di(2-ethylhexyl)sulfosuccinate (= AOT = Aerosol OT) from *Fluka AG* (Switzerland) of pharmaceutical quality was purified according to the procedure suggested by *Denss* [3]. Isooctane (= 2,2,4-trimethylpentane), *Fluka*, of highest grade purity was used following cyclic distillation over  $\text{CaH}_2$ . Deionized and doubly distilled water was used as solubilizate.

*Equipment.* The differential vapor pressure gauge constructed in this laboratory is shown in *Figure 1*. The spherical bulbs were filled with 3 ml of  $0.1 \text{ mol dm}^{-3}$  (AOT/isooctane)-solution and pure solvent, respectively, with the help of a syringe and a thin flexible teflon tube. Each bulb is closed by a *Rotaflo* teflon valve just after the filling operation; they are connected, however, via a Hg-filled U-shaped tube (cf. *Fig. 1*). It is essential to degas the solution and solvent very carefully. This could be achieved, independently for each bulb, with the teflon valves. The samples were slowly frozen at liquid  $\text{N}_2$ -temperature while they were degased at  $4 \times 10^{-2}$  Torr. The freeze-pump-thaw cycle was repeated three times, the residual gas pressure being monitored with a *Pirani* gauge. The differential pressure gauge was mounted in a precision water thermostat (*Lauda*) with windows to enable readings to be taken with the gauge completely immersed. The selected temperature could be maintained constant at  $T (\pm 0.01 \text{ K})$  for an unlimited time. The readings of the Hg-menisci differences were taken with a precision cathetometer (*Wild, KM-231*). Pure isooctane was used instead of the (AOT/isooctane)-solution as a reference for the vapor pressure measurements. It is known [4] to be difficult to completely desiccate the AOT. The dried AOT-sample was rather hygroscopic and would take-up, at each new preparation, stoichiometrically different amounts of water from the solvent. Also, solubilization would contribute to this effect. Hence irregular pressure variations of the reference system would be observed. Fortunately, the absolute values of the pressure values of the AOT-solution were small ( $< 0.1$  Torr). Thus the error introduced by taking isooctane as reference was small compared with the over-all errors of this method.

**Results and Discussion.** – The partial pressure ( $P$ ) of the water vapor above the equilibrated and very precisely thermostated  $\text{L}_2$ -phase as a function of the solubilized amount of water ( $w_0 = [\text{H}_2\text{O}]/[\text{AOT}]$ ) is shown in *Figure 2*. The reference pressure ( $P^\ominus$ ) refers to pure water (treated as described in *Experimental Part*) at the

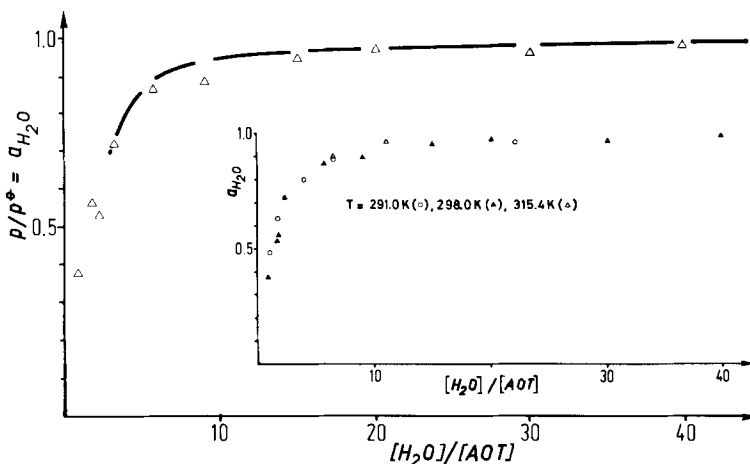


Fig. 2. Vapor pressure of water as a function of  $[H_2O]/[AOT]$ . Solid line: theoretical function according to Eqn. 7 ( $T=298.0\text{ K}$ ,  $E^{el}/A=6.00 \cdot 10^{-3}\text{ J m}^{-2}$ ,  $v_r(H_2O)=78.3$ ). The change of the chemical potential  $\Delta\mu$  is calculated according to Eqn. 4, i.e. neglecting the free energy of mixing. (Insert: exp.  $a_{H_2O}$ -data for different temperatures.)

same temperature. Hence, it refers to the physical situation of separated macroscopic oil and water phases. Around  $w_0 \approx 8$  the activity plot exhibits a pronounced inflection and approaches, with increasing amounts of solubilized water, the value  $P = P^0$ , i.e.  $a_{H_2O} = 1$ . Due to the relatively broad transition region from the  $L_2$ -phase to separated oil and water phases, the determination of the stability is limited. The apparent deviations of the experimental pressure values from the theoretical plot (=solid line) is believed to be due to residual gases which were not eliminated in spite of the very careful degassing procedure. The model cannot be applied to calculate the water activity below  $w_0 \approx 5$  according to the experimental data of Eicke & Rehak [10]. For smaller  $w_0$ -values the experimentally determined surface area covered by one AOT-molecule of a supposed interface between a polar core and the oil phase is smaller than the molecular geometric cross-section. Hence, in this  $w_0$ -region no interface of micellar aggregates can be defined. Actually, the interfacial free energy for one aggregate calculated with the help of Jönsson's model starts to become constant at  $w_0 \approx 5$ .

It is also seen from Figure 2 that the activity of water in these  $L_2$ -phases is apparently temperature-independent within the investigated region of solubilized water. This indicates that the standard chemical potential and the chemical potential of the water in the  $L_2$ -phase have a linear temperature dependence.

The suggested model [5] [6] which will be considered here with respect to its applicability to activity measurements of water in the  $L_2$ -phase is essentially an electrostatic model based upon the solution of the Poisson-Boltzmann equation for a particular geometry. The physical situation is depicted by a sphere (=reversed micellar aggregate) suspended in oil. The oil volume attributed to each sphere is determined by the concentration of the spheres. The spherical aggregate is described

by a semi-diffuse electrical double layer, where the negative charges are anchored in the (o/w)-interface represented by a surface charge density  $\sigma$ . The positive counter-ions are non-uniformly distributed in the aqueous core of the aggregate. The whole system, of course, is electroneutral.

The primary aim is to calculate from the total *Gibbs* free energy which is composed of the free energy of all reversed micellar aggregates and that of the mixing of these aggregates in solution

$$G = N G_o + G_{\text{mix}} \quad (1)$$

the chemical potential of the water in the  $L_2$ -phase. In particular

$$G_o = n_{\text{am}} \mu_{\text{am}}^{\ominus, s} + \frac{1}{N} \sum_i n_{i, \text{aq}} \mu_{i, \text{aq}}^{\ominus} + G^{\text{el}} - T S^{\text{id}} + G^s \quad (2)$$

and

$$G_{\text{mix}} = k T N \ln(x_m - 1).$$

$G_o$  is the free energy per reversed aggregate including its proportionate amount of oil,  $N$  the number of aggregates,  $n_{\text{am}}$  the number of surfactant molecules per micelle,  $\mu_{\text{am}}^{\ominus, s}$  the standard chemical potential of surfactant in the interface,  $\mu_{i, \text{aq}}^{\ominus}$  that of the component in the aqueous core of the aggregate. The *Gibbs* electrostatic free energy  $G^{\text{el}} = E^{\text{el}} - T S^{\text{el}}$  comprises the total ion-ion interaction  $E^{\text{el}} = 1/2 \int \rho_T \Phi \, dV = 1/2 z_{\text{am}} n_{\text{am}} e \Phi^s + 1/2 \int \rho_i \Phi \, dV$  where  $\rho_T$  is the total charge distribution including the  $n_{\text{am}}$  charges  $z_{\text{am}} e$  of the amphiphile on the surface of the aggregate where the potential is  $\Phi^s$ ,  $\rho_i$  is the counter-ion density and  $\Phi$  the potential inside the polar core. The entropic contribution due to the non-uniformly distributed ions is described by a decrease of the entropy relative to the entropy  $S^{\text{id}}$  of the uncharged system [7], *i.e.*  $S^{\text{el}} = (S - S^{\text{id}}) = R \sum \{ c_i (\ln x_i - 1) dV - n_i / N \ln(\bar{x}_i - 1) \}$  where  $c_i$  is the counter-ion concentration in  $\text{mol dm}^{-3}$  and  $x_i$  and  $\bar{x}_i$  are the mol-fraction and average mol-fraction of the  $i$ -th ion.  $G^s = \gamma A$  is a surface free energy with  $\gamma$ , the interfacial free energy, and  $A$  the interfacial area per aggregate. Finally,  $x_m$  denotes the mol-fraction of reversed aggregates.

From physical considerations it is apparent (and this will be confirmed later on) that  $G^{\text{el}}$  and  $G^s$  are the most relevant terms in view of our present considerations.  $G^{\text{el}}$  is accessible *via* a solution of the *Poisson-Boltzmann* equation with suitable boundary conditions for reversed aggregates [5]. Hence, the overall *Gibbs* free energy  $G$  has to be differentiated with respect to  $n_{\text{H}_2\text{O}}$  to yield

$$\mu_{\text{H}_2\text{O}} = \mu_{\text{H}_2\text{O}}^{\ominus} + \frac{v_{\text{H}_2\text{O}}}{\sum_i n_i v_i} \left[ E^{\text{el}} + \frac{\sigma A R T}{F} + 2 N k T \ln \left( 1 + \frac{n_{\text{solv}}}{N} \right) \right]. \quad (3)$$

The third term in the bracket is the free energy of mixing of reversed aggregates with oil molecules.  $v_{\text{H}_2\text{O}}$  is the partial molecular volume of water in the  $L_2$ -phase,  $\sum_i n_i v_i$  is the total volume of one polar core composed of  $i$  components.  $F$  denotes the *Faraday* constant and  $n_{\text{solv}}$  the number of oil molecules in the system. The

second term in the bracket has a positive sign since  $\sigma$  refers to a negatively charged interface.  $\sigma$  is defined by  $z_{am} e / f_{am}$ , where  $f_{am}$  is the area of the interface covered by one surfactant molecule. Since  $\sum_i n_i v_i$  is proportional to  $R_o$  (the 'mean charge surface radius'<sup>2</sup>), which is a measure of the aqueous core of the aggregate, it can be shown [5] that with increasing  $R_o$  the absolute value of the second term in the bracket of Eqn. 3 decreases if  $E^{el}$  and  $\sigma$  do not increase simultaneously with droplet size. This, however, is not the case as can be inferred from an experimental verification of another important relation, *i.e.*:

$$\left(\frac{\partial G}{\partial A}\right)_{T,P,eq.} = -\left(\frac{2E^{el}}{A} - \gamma\right)_{eq.} = 0. \quad (4)$$

This equation is rather general [8] in the case of a semi-diffuse double layer and states that the interfacial free energy ( $\gamma$ ) of the (w/o)-interface in the presence of surfactant is twice the electrostatic potential energy. If the free energy of mixing is to be considered in Eqn. 4, the relation may be modified to yield

$$\left(\frac{\partial G}{\partial A}\right)_{T,P} = -\left\{\frac{2E^{el}}{A} - \gamma + \frac{3kT}{A} \ln\left(1 + \frac{n_{solv}}{N}\right)\right\}_{eq.} = 0 \quad (5)$$

*Calibration of the model.* An essential feature of the model is its property to contain experimentally describable parameters which can be fitted to literature data. In this way  $E^{el}/A$  was adjusted to earlier data of this laboratory [9] [10] describing  $f_{AOT} = f(R_o)$  and the radius of the aggregate as a function of  $w_o$ . These values had been derived from molecular weights determined by light-scattering experiments. This yielded, together with Eqn. 4, a very interesting result (*cf. Fig. 3*). It is thus seen that the interfacial free energy is constant, *i.e.*  $\gamma = 12.0 \pm 0.2 \cdot 10^{-3} \text{ J m}^{-2}$ , over the entire experimentally investigated microemulsion region. This is a remarkable finding with consequences for other investigations of thermodynamically stable emulsions. Also interesting is a comparison of the value of the interfacial free energy with corresponding data found for other mesophase structures: for the lamella phase

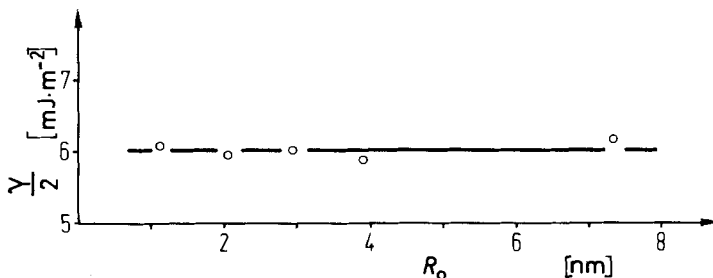


Fig. 3. Interfacial free energy  $\gamma$  of a single microemulsion droplet calculated for different radii according to Eqn. 4 ( $T = 298.0 \text{ K}$ ,  $\epsilon_r(\text{H}_2\text{O}) = 78.3$ ). Exper. data are taken from [10].

<sup>2</sup>) This surface is defined [5] as the surface characterized by the mean distribution of charges at the interface of the aggregate.

of AOT in water between 8 and 71 wt-% AOT,  $E^{\text{el}}A = \gamma/2$  has been determined to be between  $4$  and  $6 \times 10^{-3} \text{ J m}^{-2}$  for commercial AOT [11] [12]. With Na-salts of *n*-alkyl carboxylates  $\gamma/2$ -value of  $9.2 \pm 0.1 \cdot 10^{-3} \text{ J m}^{-2}$  for the lamella mesophase at 377 K and a thickness of the water/layer between 0.2 and 0.7 nm was found [6]. This value was reported to be only weakly dependent on the alkyl-chain length, on temperature in the range between 318 and 377 K, and the alkali counter-ion type. This very satisfactory agreement is indeed encouraging.

Also, further support of the validity of Eqn. 4 was recently given from surface tension measurements in this laboratory [13]: the drop-volume method was applied for the system water/AOT/isooctane<sup>3</sup>). In this case macroscopic interfaces were investigated and with the help of the relation  $\lim_{1/R_0 \rightarrow 0} (f_{\text{AOT}}) = 2kT \left| \frac{d \ln(c/c_0)}{d\gamma} \right|$  a limiting value of the interface covered by one AOT-molecule ( $f_{\text{AOT}}^0$ ) was determined from a  $\gamma - \ln(c/c_0)$ -plot.  $c$  is the concentration of AOT in the oil phase and  $c_0$  a reference concentration [14]. In this way a  $f_{\text{AOT}}^0$ -value of  $0.562 \pm 0.028 \text{ nm}^2/\text{AOT-molecule}$  was found. This value should be compared with that calculated from the above model, *i.e.* with a constant  $E^{\text{el}}/A$  term =  $6.00 \cdot 10^{-3} \text{ J m}^{-2}$  for large values of  $R_0$  (see Fig. 4). The result is  $f^0 = 0.561 \text{ nm}^2/\text{AOT-molecule}$ . The agreement is certainly striking.

It should be noticed, however, that in the case of hexagonal mesophases of the above mentioned Na-salts of *n*-alkyl-carboxylate surfactants the concept of the constant interfacial tension fails. The calculated  $E^{\text{el}}/A$ -values decrease linearly as a function of the inverse thickness of the water-layer. It is not yet possible to decide with certainty whether energetic parameters were neglected or the numerical solution of the *Poisson-Boltzmann* equation is incomplete [5].

In relation to the above discussion it should be pointed out again that the interfacial free energy of a microemulsion is a quantity which is derived from the above presented theoretical concept. Although it is experimentally not directly accessible, its relevance is established by direct relations to experimentally available quantities.

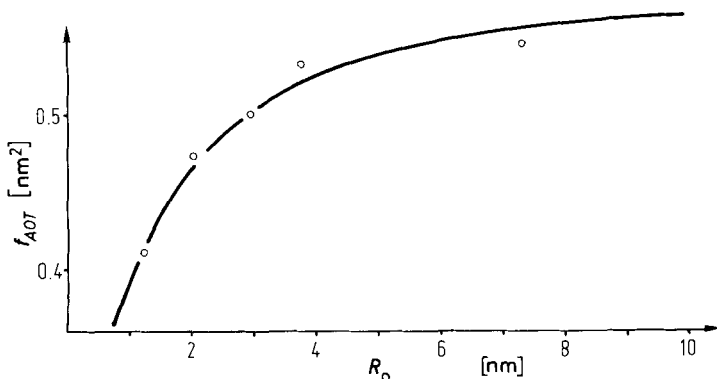


Fig. 4. The area of the oil/water interface covered by one AOT molecule,  $f_{\text{AOT}}$ , as a function of  $R_0$ . The solid line is calculated for  $E^0/A = 6.00 \cdot 10^{-3} \text{ J/m}^2$  ( $T = 298.0 \text{ K}$ ,  $v_r = 78.3$ ). The experimental points are taken from [10].

<sup>3</sup>) Macroscopic water droplets covered by AOT in the continuous oil-phase.

*Calculation of vapor pressures.* It was shown above that the interfacial free energy, derived from experimentally accessible quantities, is independent of the curvature of the droplet interface beyond the micellar region [15]. Hence, the partial pressure of the water above the  $L_2$ -phase can be calculated according to Eqn. 3. Now,  $\sum_i n_i \cdot v_i = R_o A/3$ , can be inserted into Eqn. 3 to give

$$\Delta\mu_{H_2O} = \frac{3v_{H_2O}}{R_o} \left[ E^{el}/A + \frac{\sigma RT}{F} + \frac{kT}{2\pi R_o^2} \ln \left( 1 + \frac{n_{solv}}{N} \right) \right] \quad (6)$$

(with  $v_{H_2O}$  the average partial molecular volume of water, *i.e.*  $29.9 \cdot 10^{-3} \text{ nm}^3$  at 298 K) if also  $A$  in the third term within the bracket is replaced by  $4\pi R_o^2$ .

Eqn. 6 is easily transformed into a relation for the water activity or the ratio of the partial vapor pressure and a reference pressure by considering the relation between activity and difference in the chemical potentials, *i.e.*:

$$\frac{P_{H_2O}}{P_{H_2O}^\ominus} = \exp \left( \frac{\Delta\mu_{H_2O}}{kT} \right). \quad (7)$$

It should be noted that according to Eqn. 6  $\gamma$  involves an entropy term and might therefore change slightly. The effect, however, is rather small and vanishes with increasing  $w_o$ . A consideration of this entropy term to calculate  $\Delta\mu_{H_2O}$  changes the plot insignificantly and only at  $w_o < 7$ . In order to calculate  $n_{solv}/N$  of the last term in the bracket one can approximately equate this ratio to  $(c_{solv}/c_{AOT})n_{AOT}$ , where  $c_{solv}$  is, in the present case, the constant concentration of the isoctane, *i.e.*  $6.06 \text{ mol dm}^{-3}$ ,  $c_{AOT}$  the AOT concentration and  $n_{AOT} = 4\pi R_o^2/f_{AOT}$ , the number of AOT-molecules per droplet.

*Computational procedures.* In order to calculate  $P_{H_2O}/P_{H_2O}^\ominus$  explicitly, individual points of the function  $\Delta\mu = \Delta\mu(R_o)$  were calculated according to a procedure [5] of an iterated solution of the *Poisson-Boltzmann* equation for a constant value of  $E^{el}/A = 6.00 \cdot 10^{-3} \text{ J m}^{-2}$ . For the following computational procedure it appeared suitable to approximate the curve obtained by plotting the calculated points by a mathematical function. Another point of importance is the relation between  $R_o$  and  $w_o = [H_2O]/[AOT]$ , *i.e.*:

$$w_o = \frac{1}{3} \frac{f_{AOT} R_o}{v_{H_2O}} \quad (8)$$

if one assumes that all AOT-molecules are within the interface.

As mentioned earlier,  $R_o$  is the 'mean charge surface radius' which is not necessarily identical with the geometric radius of the polar core of the aggregate. From molecular considerations it appears plausible that water may penetrate the interfacial region due to the steric arrangement of the hydrophilic groups of the surfactants [16]. A non-linear least squares fit with data taken from the vapor pressure plot shows that the difference between the geometric radius and  $R_o$  is about 0.25 nm, *i.e.* 1.5 water molecules are bound to one AOT-molecule which apparently do not contribute to the vapour pressure of water.

The agreement between the experimental and theoretical vapor pressure or activity plots is surprisingly good. The usual assumptions, as, for example, point charges, macroscopic dielectric constant, or the neglect of the ion-ion correlation in the aqueous core [5] of the reversed aggregates are apparently of only second order. In view of this result it is to be expected that this model will be appropriate to predict other properties of reversed, thermodynamically stable (W/O)-emulsions from ionic surfactants.

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