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# Direct Determination of the Distribution Coefficient of Tridecyl Dimethyl Phosphine Oxide between Water and Hexane

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**Abstract:** Drop profile analysis tensiometry is applied to determine the distribution coefficient of a nonionic surfactant for a water/hexane system. The basic idea is to measure the interfacial tension isotherm in two configurations: a hexane drop immersed in the surfactant aqueous solutions at different bulk concentrations, and a water drop immersed into a hexane solution of the same surfactant. Both types of experiments lead to an isotherm for the equilibrium interfacial tensions with the same slope but with a concentration shift between them. This shift refers exactly to the value of the distribution coefficient.

**Keywords:** adsorption kinetics; nonionic surfactant; diffusion-controlled adsorption; water-oil interface; distribution coefficient; surfactant partitioning; drop profile analysis tensiometry

## 1. Introduction

Many studies have paid attention to the adsorption behaviour of various surface-active substances at liquid/liquid interfaces from the viewpoints of basic sciences as well as practical applications. This problem was considered in various books, such as [1–4]; also, a number of studies were published in which both adsorption (equilibrium and kinetic) and rheological characteristics at the surfactant aqueous solution/alkane (oil) interface are analysed [5–20].

One of the most important problems arising during the analysis of experimental results obtained for a liquid/liquid interface is the determination of the coefficient of surfactant distribution between the adjacent phases. Several methods were proposed earlier to solve this problem. In particular, the method used in [9–11] to determine the distribution coefficient for various surfactants between water and hexane was as follows. First, the surface tension isotherm at the interface between the aqueous solution of the surfactant and air was measured. Then, certain volumes of the aqueous solution and pure hexane were brought into contact for sufficiently long times, and the surface tension of the aqueous solution at its interface with air was then measured. Finally, from the analysis of the obtained adsorption isotherm, the hexane distribution coefficient was calculated based on the surfactant mass balance. Using this

method, it was determined in [9–11] that the solubility of the nonionic surfactant tridecyl dimethyl phosphine oxide ( $C_{13}DMPO$ ) in hexane is 34 times higher than in water. Besides methods based on interfacial tension methods, there are also chemical procedures in which the aqueous solution is brought into contact with the oil phase, and after reaching the distribution equilibrium, the amount of surfactant is determined by a suitable analytical method. Such protocols are specific for each surfactant and not further discussed here (see for example the discussions in [7,9,11] and the references therein).

This method described in [9–11], however, suffers from certain deficiencies. In particular, the influence of hexane which remains dissolved in water after its prolonged contact with hexane on the surface tension of the aqueous solution of the surfactant remains unaccounted for. Also, the pendant drop shape method, used to measure the surface tension of the surfactant solution, could yield an incorrect value of the surfactant concentration within the drop if the depletion of the solution caused by the adsorption of the surfactant at the drop surface is not considered correctly [15].

In this study, the interfacial tension isotherms at the hexane/water interface were measured for hexane drops formed in the  $C_{13}DMPO$  aqueous solution and for water drops formed in  $C_{13}DMPO$  solutions in hexane using the drop profile analysis method. From these isotherms, the interfacial distribution coefficient could be easily and precisely determined as the ratio of concentrations at the same interfacial tension. Note, the volumes of the  $C_{13}DMPO$  aqueous solution and the  $C_{13}DMPO$  solution in hexane are about 1000 times larger than the volume of the used drops. Thus, any variation of concentration caused by the adsorption of  $C_{13}DMPO$  onto the drop surface and the diffusion of  $C_{13}DMPO$  into the drop could be neglected.

## 2. Experiment

The experimental protocol employed for equilibrium surface tension measurements (bubble/drop profile analysis tensiometers PAT-1 and PAT-2P from SINTERFACE Technologies, Berlin, Germany) was described in detail elsewhere [21]. These methods were used to measure the dynamic surface tension in the time range from seconds up to the equilibrium of the system over 1 to 10 h, depending on the surfactant concentration.

Tridecyl dimethyl phosphine oxide ( $C_{13}DMPO$ ) was synthesized and purified as described earlier [18,19]; the purity of the surfactant exceeded 99%. The temperature of the measuring cell was kept constant at 25 °C. The hexane of spectroscopic grade was purchased from Labscan (Bangkok, Thailand); its purity was above 99% and was used without further purification. The aqueous solutions were prepared using Milli-Q water. The surface tension of the water was  $72.0 \pm 0.2$  mN/m at 25 °C and kept constant in the time interval of up to 20,000 s.

The experimental procedure was as follows. The buoyant (sessile) drop and pendant drop techniques were employed for the measurements of the water/hexane interfacial tension. The studied  $C_{13}DMPO$  aqueous solutions and its solutions in hexane were put into the measuring cell of 25–30 mL in volume. The drops were formed at the bottom tip of a vertical steel capillary with a conical internal profile and internal diameter of 3.0 mm. The profile of the hexane drops was slightly oblate, while the water drop was prolate. The surface areas of the drops were chosen to be 31–34 mm<sup>2</sup> and were automatically kept constant to this value during the experiments. The initial volume of the drops (21–23 mm<sup>3</sup>) was also approximately the same for all measurements. Note that the decrease of interfacial tension, if the drop surface area is kept constant, leads to the decrease of the drop volume (in our case by 1–6%).

## 3. Theory

The attempts to calculate the temporal dependence of surface tension at the interface between two phases were undertaken previously; the first practical calculations of adsorption dynamics on a drop or bubble surface based on Fick's equations were performed in 1997 [10]. The approach used in this study was presented in [22]. The diffusion of the surfactant in the system of two concentric phases

which exhibit spherical symmetry (phase 1 of radius  $R_1$  and phase 2 of radius  $R_2$ ) is governed by Fick's law, which in spherical coordinates reads as

$$\frac{\partial c}{\partial t} = D_1 \left( \frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} \right) \quad \text{for } 0 < r < R_1 \quad (1)$$

$$\frac{\partial c}{\partial t} = D_2 \left( \frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} \right) \quad \text{for } R_1 < r < R_2 \quad (2)$$

where  $c = c(r,t)$  is the surfactant concentration at time  $t$  and distance  $r$  from the centre of the cell, and  $D_i$  ( $i = 1$  and  $2$ ) are the diffusion coefficients of the surfactant in the  $i$ th phase. The adsorbed amount  $\Gamma$  is involved in the model via the boundary condition at the drop surface:

$$\frac{d\Gamma}{dt} = -D_1 \frac{\partial c}{\partial r} \Big|_{r=R_1^-} + D_2 \frac{\partial c}{\partial r} \Big|_{r=R_1^+} \quad (3)$$

The boundary conditions at  $r = 0$  and at  $r = R_2$  follow from the symmetry of the system and the fact that the system is closed:

$$\frac{\partial c}{\partial r} \Big|_{r=0} = 0 \quad (4)$$

$$\frac{\partial c}{\partial r} \Big|_{r=R_2} = 0 \quad (5)$$

The initial conditions for the set of Equations (1) and (2) are

$$c(r,0) = c_{10} \quad \text{for } 0 < r < R_1 \quad (6)$$

$$c(r,0) = c_{20} \quad \text{for } R_1 < r < R_2 \quad (7)$$

In the present experiments the surfactant was initially dissolved only in the external liquid phase. Therefore, in Equation (6), the concentration  $c_{10}$  should be set to zero.

Close to the interface an equilibrium distribution of the surfactant exists which relates the two boundary concentrations via the distribution coefficient  $K_p$ . Hence, the distribution coefficient  $K_p$  corresponds to the ratio of subsurface concentrations of the surfactant in hexane to that in water:

$$\frac{c(R_1^+, t)}{c(R_1^-, t)} = K_p \quad \text{for water drop in hexane solution} \quad (8)$$

$$\frac{c(R_1^-, t)}{c(R_1^+, t)} = K_p \quad \text{for hexane drop in water solution} \quad (9)$$

Note, however, that the equilibrium distribution of the surfactant close to the interface can be assumed for any time moment  $t > 0$  but not for the initial time moment  $t = 0$ , as it would contradict the initial conditions, Equation (6). A detailed discussion of the numerical procedure is presented in [22].

To calculate the surface tension  $\gamma$ , which is usually the experimentally accessible quantity, and the adsorption  $\Gamma$ , which enters the boundary condition at the interface, Equation (3), an appropriate equation of state and adsorption isotherm, should be used. The theoretical models used to describe the equilibrium surface tension and adsorption of nonionic surfactants were described in [15,22,23]. The model which is commonly used is the Frumkin model, in which the equations of state and adsorption isotherm take the form

$$\Pi = -\frac{RT}{\omega_0} \left[ \ln(1 - \theta) + a\theta^2 \right] \quad (10)$$

$$bc = \frac{\theta}{(1 - \theta)} \exp[-2a\theta] \quad (11)$$

where  $R$  is the gas law constant,  $T$  is the temperature,  $\Pi$  is the surface pressure ( $\Pi = \gamma_0 - \gamma$ ), and  $\gamma$  and  $\gamma_0$  are the surface tensions of the solution and the solvent, respectively;  $\omega_0$  is the partial molar area of the surfactant at infinite dilution,  $a$  is the intermolecular interaction constant,  $b$  is the adsorption equilibrium coefficient,  $c$  is the subsurface surfactant concentration, and  $\theta$  is the surface layer coverage by the surfactant. The model assumes the compressibility of adsorbed molecules in the surface layer, i.e., the dependence of the partial molar area of the surfactant on the monolayer coverage and surface pressure:  $\omega = \omega_0(1 - \varepsilon_{\Pi}\theta)$ , where  $\varepsilon$  is the compressibility parameter. The surfactant adsorption  $\Gamma$  is calculated from the relation  $\theta = \Gamma\omega$ .

For the processing of the experimental isotherms, the reorientation model was also used. This model assumes that the adsorbed surfactant molecule can have two orientations (states), referred to by subscripts 1 and 2, each characterised by its partial molar area  $\omega_i$ ; for definiteness,  $\omega_2 > \omega_1$ . Compressibility is assumed for the state with the lower molar area  $\omega_1$ :  $\omega_1 = \omega_{10}(1 - \varepsilon_{\Pi}\theta)$ , where  $\omega_{10}$  is the maximum molar area in state 1, corresponding to zero adsorption. The resulting equation of state reads as

$$-\frac{\Pi\omega_0}{RT} = \ln(1 - \Gamma\omega) + \Gamma(\omega - \omega_0) + a(\Gamma\omega)^2 \quad (12)$$

where  $\omega = (\omega_1\Gamma_1 + \omega_2\Gamma_2)/\Gamma$  is the average molar area with  $\theta = \omega\Gamma = \omega_1\Gamma_1 + \omega_2\Gamma_2$  being the surface coverage, and  $\Gamma = \Gamma_1 + \Gamma_2$  being the total adsorption. The adsorption isotherms for the adsorbed states 1 and 2 read as

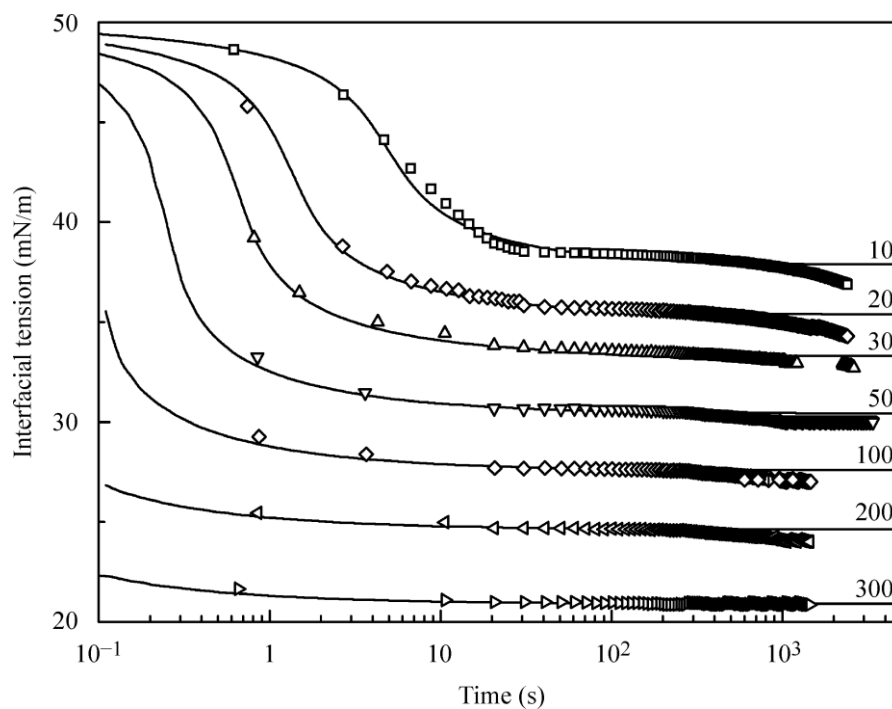
$$bc = \frac{\Gamma_1\omega_0}{(1 - \Gamma\omega)^{\omega_1/\omega_0}} \exp\left(-2a\Gamma\omega\frac{\omega_1}{\omega_0}\right) \quad (13)$$

$$bc = \frac{\Gamma_2\omega_0}{(\omega_2/\omega_1)^\alpha(1 - \Gamma\omega)^{\omega_2/\omega_0}} \exp\left(-2a\Gamma\omega\frac{\omega_2}{\omega_0}\right) \quad (14)$$

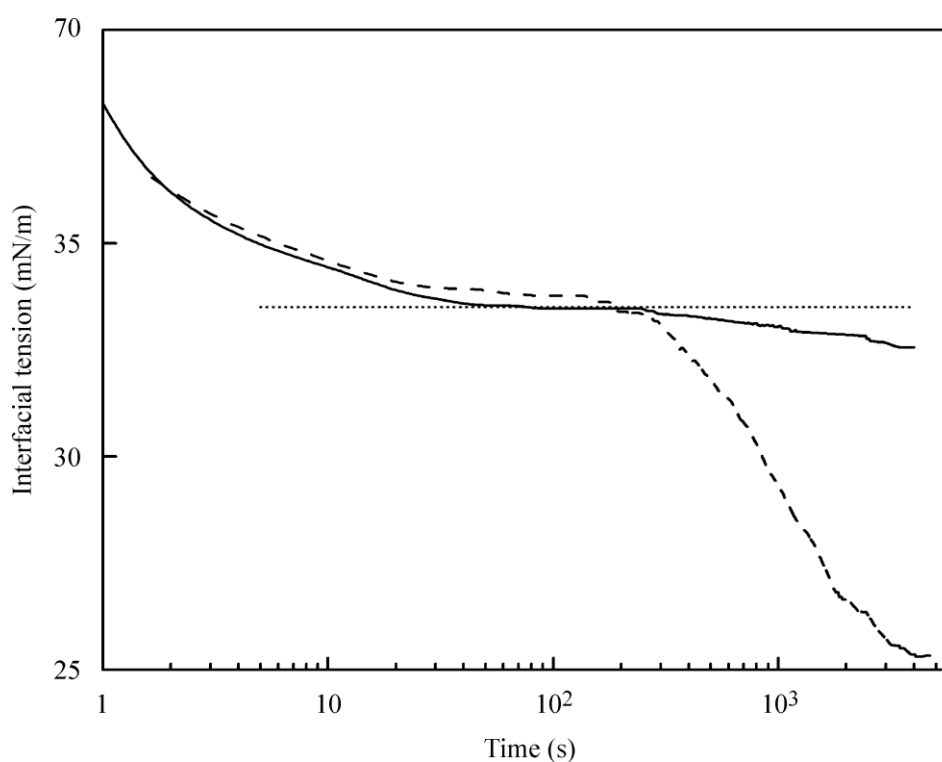
where  $\alpha$  is the exponent of a power law which accounts for different surface activities of the molecules in the two adsorption states. As the surfactant is dissolved in a large volume of liquid into which the drop is immersed, the depletion of the surfactant concentration caused by its adsorption on the drop surface is negligible.

#### 4. Results and Discussion

Figure 1 illustrates the dynamic interfacial tension at the interface between water drop and the solution of  $C_{13}$ DMPO in hexane at various concentrations of the surfactant. It is clearly seen that for the solutions with surfactant concentrations of 10 and 20  $\mu\text{mol/L}$ , the dependencies exhibit a plateau at times above 20–30 s, while at times above 500–700 s, some decrease of interfacial tension is observed. For the solutions with higher concentrations, the dependencies turn into a plateau at times below 10 s, while a small decrease of the interfacial tension exists at times beyond 200–300 s and later. This decrease of the surface tension at high times could be obviously attributed to some unknown impurities present in hexane. As the concentration of hexane in the measuring cell is about 8 mol/L, the presence of 1% of impurities would yield a concentration of 0.08 mol/L, which is four orders of magnitude higher than the surfactant concentration for the highest dilution (10  $\mu\text{mol/L}$ ) among those shown in Figure 1. The supposition that the surface tension decrease at high adsorption times is caused by the impurities present in hexane is supported by the data shown in Figure 2, where the kinetic dependencies for the  $C_{13}$ DMPO concentration of 30  $\mu\text{mol/L}$  in hexane are shown for its solutions in hexane of 99% purity and hexane of 95% purity. It is seen that the surface tension decrease in the solution at times above 300 s for the surfactant solution in the less purified hexane is drastically higher than that in the solution using hexane of high purity.



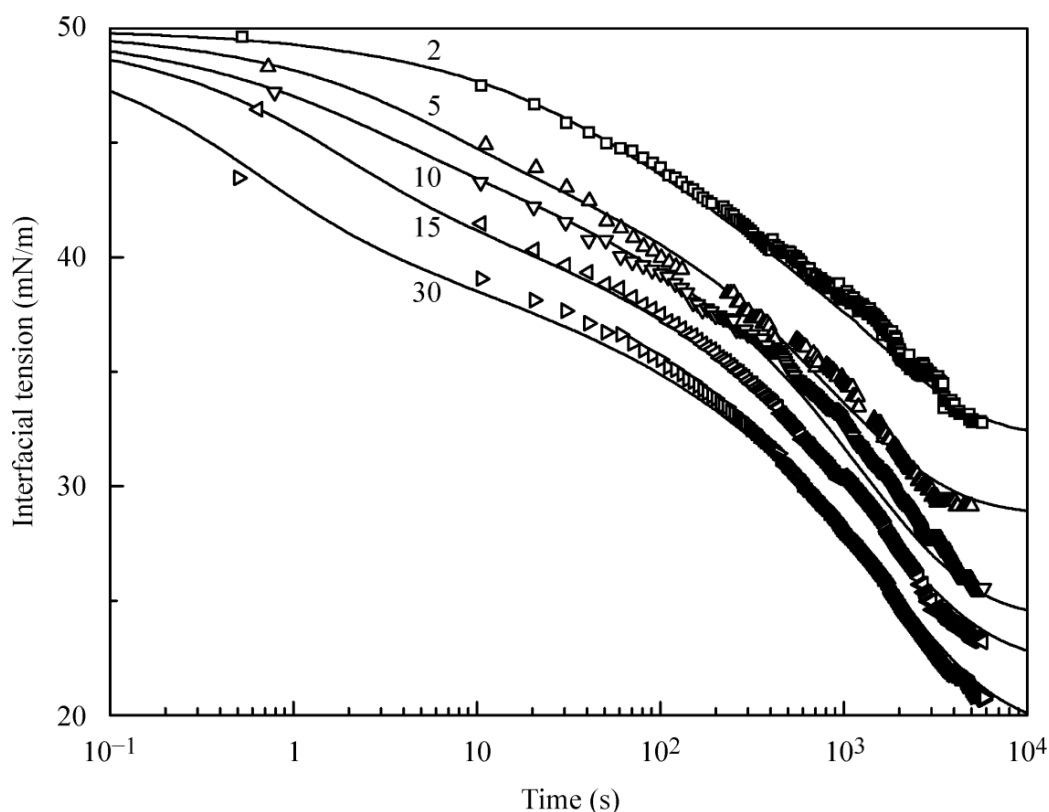
**Figure 1.** Tension at the interface between a water drop and solutions of  $C_{13}DMPO$  in hexane at various concentrations of the surfactant as labeled in  $\mu\text{mol/L}$ . Points—experimental data; lines—theoretical calculations.



**Figure 2.** Tension at the interface between a water drop and a  $30 \mu\text{mol/L}$  solution of  $C_{13}DMPO$  in hexane of high (99%, solid curve) and low (95%, dashed curve) purity. The dotted line corresponds to the equilibrium surface tension at this concentration.

The theoretical calculations (solid lines in Figure 1) were performed using the basic Equations (1)–(7), with the adsorption isotherm calculated either via the Frumkin model, Equations (10) and (11), or via the reorientation model, Equations (12)–(14). The equilibrium surface tension values used for the calculations were taken to be those which correspond to the onset of the surface tension decrease due to the presence of impurities. Both these models provide a quite satisfactory correspondence between the observed data and calculated values. This is because for these models, at high  $C_{13}\text{DMPO}$  concentrations, the most significant differences would be observed in the initial range of temporal dependencies, where experimental data are not available. The parameters of the reorientation model and the  $C_{13}\text{DMPO}$  diffusion coefficient in hexane estimated from the correspondence between the observed data and calculated values of surface tension are:  $\omega_{10} = 5.5 \times 10^5 \text{ m}^2/\text{mol}$ ;  $\omega_2 = 10.0 \times 10^5 \text{ m}^2/\text{mol}$ ;  $b = (3.5\text{--}4.7) \times 10^2 \text{ m}^3/\text{mol}$ ;  $\alpha = 0.0$ ;  $a = 1.0$ ;  $\varepsilon = 4.0 \times 10^{-3} \text{ m/mN}$ ; and  $D_2 = (3.2\text{--}4.5) \times 10^{-9} \text{ m}^2/\text{s}$ . The corresponding parameters for the Frumkin model are listed below. The ranges of coefficients  $b$  and  $D_2$  listed above correspond to the best fit of the experimental data by the calculated surface tension values for all  $C_{13}\text{DMPO}$  concentrations—10–300  $\mu\text{mol/L}$ . As the distribution coefficient of  $C_{13}\text{DMPO}$  is high (its solubility in hexane is approximately by a factor of 30 higher than that in water), and the water drop volume is much lower than the cell volume, the calculated temporal dependencies of interfacial tension are almost independent of the variations of the diffusion coefficient of  $C_{13}\text{DMPO}$  in water within a quite wide range, i.e., in the range of  $10^{-9}\text{--}10^{-10} \text{ m}^2/\text{s}$ . The values of the  $C_{13}\text{DMPO}$  diffusion coefficient in hexane are approximately one order of magnitude higher than those in water. This difference is quite reasonable because (i) the viscosity of hexane is three times lower than that of water, and (ii) a convective diffusion of the surfactant towards the drop located in the middle of the cell can possibly occur.

Figure 3 illustrates the dynamic interfacial tension at the interface between a hexane drop and  $C_{13}\text{DMPO}$  aqueous solutions at various surfactant concentrations. The shape of curves is essentially different from that shown in Figure 1. It is seen that, in contrast to the solutions of the surfactant in hexane at its interface with a water drop, where the adsorption process is very fast, the adsorption of  $C_{13}\text{DMPO}$  from its aqueous solution onto the hexane drop is slow, and the time of 6000–8000 s is insufficient to attain the adsorption equilibrium. The equilibrium is achieved at the earliest after 20,000 s. This behaviour can be explained by two facts: (i) the concentration for the aqueous surfactant solution having the same interfacial tension as that observed in the hexane solution is very low; and (ii)  $C_{13}\text{DMPO}$  passes from the water phase into hexane where its solubility is higher. Note that the surfactant concentration in hexane for both types of experiments is higher (by a factor equal to the distribution coefficient) than in water. Therefore, in the experiments with a water drop immersed into the  $C_{13}\text{DMPO}$  solution in hexane, the adsorption rate is correspondingly increased, while for the hexane drop immersed into the  $C_{13}\text{DMPO}$  aqueous solution, the adsorption rate is correspondingly decreased. Thus, the difference in the adsorption rates could be estimated approximately as the square of the distribution coefficient. On the other hand, it follows from the experimental curves shown in Figures 1 and 2 and the calculations of the interfacial tension dynamics, which yield the equilibration time duration of 10–20 and 10,000–20,000 s, respectively, for the two types of studied solutions, the difference in the adsorption rates is by a factor of about 1000. This agrees rather well with the distribution coefficient value estimated in this work (about 30, see below) and also agrees with the value of 34 reported in [9].

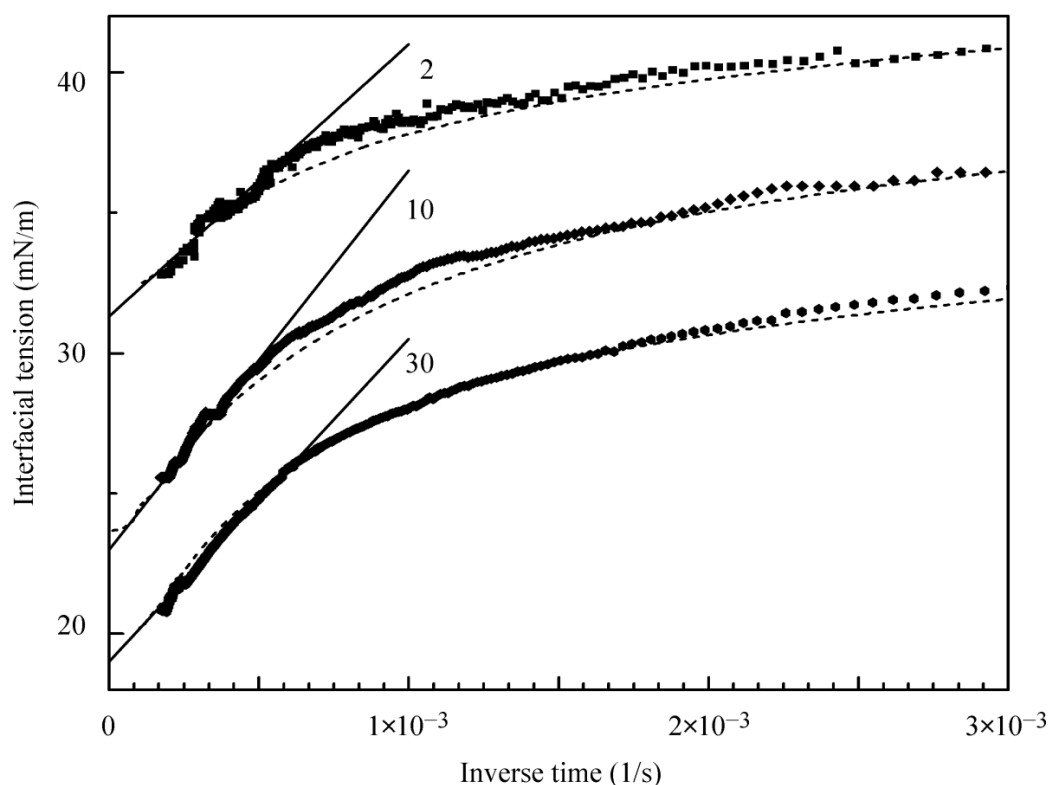


**Figure 3.** Interfacial tension at the interface between a hexane drop and aqueous solutions of  $C_{13}$ DMPO at various concentrations of the surfactant as labeled in  $\mu\text{mol/L}$ . Points—experimental data; lines—theoretical calculations.

The calculations for the dynamic curves shown in Figure 3 were also made with the two models of the surface layer. However, for the reorientation model Equations (12)–(14), to achieve the agreement of theoretical predictions with experimental data, the molar area for each of the two states ought to be decreased by a factor of 2. The most probable explanation for this is that the  $C_{13}$ DMPO molecules do not have sufficient time to undergo reorientation and are rather desorbed from the interface into the hexane drop bulk. Therefore, the calculations using the Frumkin model could be considered as the more adequate approach. The theoretical curves shown in Figure 3 were obtained with the following model parameters:  $\omega_0 = (2.5\text{--}3.0) \times 10^5 \text{ m}^2/\text{mol}$ ;  $b = (2.6\text{--}3.8) \times 10^3 \text{ m}^3/\text{mol}$ ;  $a = 0.0$ ; and  $\varepsilon = 3.0 \times 10^{-3} \text{ m/mN}$ . The calculated adsorption dynamics is strongly dependent on the values of the surfactant diffusion coefficient in the hexane drop  $D_1$  because of the relatively high quantity of  $C_{13}$ DMPO passing to the drop. The values of the diffusion coefficients estimated from the best fit throughout the whole range of concentrations were  $D_1 = (1\text{--}2) \times 10^{-9} \text{ m}^2/\text{s}$  and  $D_2 = (4\text{--}6) \times 10^{-9} \text{ m}^2/\text{s}$ , respectively. The main reason for the high  $D_2$  values is that in the experiments illustrated by Figure 3, convection plays an essential role. The nature of liquid also contributes to this difference. Comparing the data obtained in the experiments with a water drop immersed in the surfactant solution in hexane (Figure 1) with the results obtained for a hexane drop immersed in the aqueous solution (Figure 3), one can see that the coefficient  $D_1$  for the second case is higher than in the first case. It is known that the diffusion coefficient is inversely proportional to the viscosity of liquid. Hence, as the viscosity of hexane is three times lower than that of water, the diffusion coefficient in hexane is three times higher than that in water. Also, the diffusion rate in both phases is higher due to the essential nonsphericity of the oblate hexane drop formed at the vertical capillary. While for spherical drops with a volume characteristic to those in our studies, the surface-area-to-volume ratio is  $3/R_1 = 1.62 \text{ mm}^{-1}$ ; for the actual drop (with account for the area at the capillary tip) this ratio exceeds

$2.0 \text{ mm}^{-1}$ . Among other Frumkin model parameters corresponding to dynamic conditions, one could distinguish the lower area per adsorbed  $\text{C}_{13}\text{DMPO}$  molecule for the hexane drop immersed into the aqueous surfactant solution. This fact could be ascribed to the partial (incomplete) unfolding of the  $\text{C}_{13}\text{DMPO}$  molecules due to their desorption into the hexane drop.

To estimate the equilibrium interfacial tension, the experimental curves shown in Figure 3 were extrapolated vs.  $1/t$  onto the infinite time. This dependence was found to simulate quite well the complicated mechanism of  $\text{C}_{13}\text{DMPO}$  adsorption from its aqueous solution onto the hexane drop; some examples are shown in Figure 4, where the theoretical values recalculated from those presented in Figure 3 are also plotted by dashed lines. Note that the calculations made for the concentration  $10 \text{ }\mu\text{mol/L}$  were performed within the time range up to  $10^5 \text{ s}$ . It is seen that these results agree well with the values obtained by extrapolation of experimental data to the equilibrium as used in Figure 5. It should be noted that the equilibrium surface tension values estimated in this way are approximately by  $1 \text{ mN/m}$  lower than the experimental values obtained at adsorption times of  $5000\text{--}7000 \text{ s}$ , and are by  $0.6\text{--}0.9 \text{ mN/m}$  lower than the values reported in [9]. This latter fact could be caused by the difference in the experimental temperatures—in [9], the temperature was  $20 \text{ }^\circ\text{C}$ . To verify this, we repeated some experiments at  $20 \text{ }^\circ\text{C}$  and found that the interfacial tension becomes higher by  $0.5 \text{ mN/m}$ .



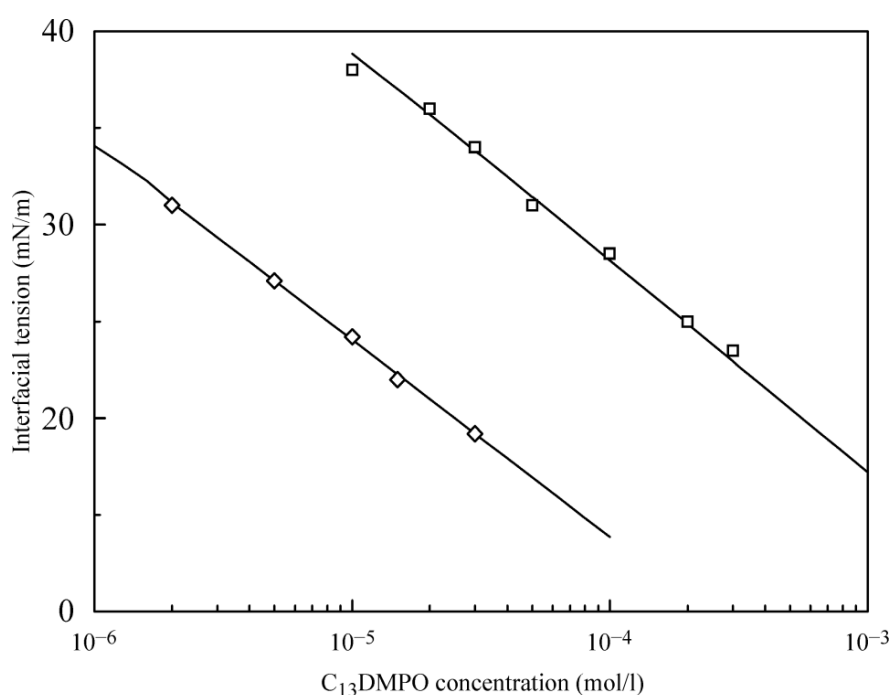
**Figure 4.** Interfacial tension for three values of  $\text{C}_{13}\text{DMPO}$  concentration as labeled in  $\mu\text{mol/L}$  plotted vs. inverse time for the adsorption from the surfactant aqueous solution onto the hexane drop. Points—experimental data replotted from Figure 3; dashed lines—theoretical calculations also replotted from Figure 3; solid lines—extrapolation.

In contrast to the isotherm parameters which correspond to the dynamical conditions (calculated assuming diffusional transport and adsorption-related losses), the equilibrium isotherms shown in Figure 5 were calculated based on the  $\text{C}_{13}\text{DMPO}$  concentrations in the volume of its solution in hexane or in water into which the water or hexane drop was immersed, respectively. In both cases, the isotherms were fitted by the Frumkin model with the same values of parameters:  $\omega_0 = 5.3 \times 10^5 \text{ m}^2/\text{mol}$ ;  $a = 0.0$ ; and  $\varepsilon = 3.1 \times 10^{-3} \text{ m/mN}$ . However, because the  $\text{C}_{13}\text{DMPO}$  concentrations in water were different



from those in hexane, the values of  $b$  also were different; for aqueous solution  $b = 3.7 \times 10^4 \text{ m}^3/\text{mol}$ , while for the solution in hexane, we have  $b = 1.3 \times 10^3 \text{ m}^3/\text{mol}$ . It is seen that the thus calculated isotherms are in a good correspondence with the experimental data. In our case, the discrepancy between the experimental and calculated values does not exceed  $\pm 0.2 \text{ mN/m}$ .

From these results it is straightforward to determine quite precisely the distribution coefficient of  $C_{13}$ DMPO between the studied phases. To do this, one should compare the values of concentrations for the two systems (for two isotherms) at equal values of interface tension. This is illustrated by the data shown in Table 1; the deviation from the average value of 30 is seen to be quite small ( $\pm 2$ ). This agrees with the result reported in [9], where the average value was 34. Note also that the ratio between the  $b$  constants corresponding to the  $C_{13}$ DMPO in water and in hexane is 27.5, which almost coincides with the value of the distribution coefficient obtained in this study. Most probably the difference between the values of the distribution coefficients obtained here and in [9] could be ascribed to the difference in the experimental temperatures: the higher is the temperature, the lower is the value of the distribution coefficient.



**Figure 5.** Equilibrium interfacial tension isotherms for  $C_{13}$ DMPO solutions. Experimental values: squares ( $\square$ )—water drop immersed into the surfactant solution in hexane; diamonds ( $\diamond$ )—hexane drop immersed into the aqueous surfactant solution. Lines: calculations as explained in the text.

**Table 1.** Concentrations of  $C_{13}$ DMPO in the two phases at equal interfacial tension values and the coefficients of  $C_{13}$ DMPO distribution between hexane and water determined by direct method using the isotherms 1 and 2.

Interfacial Tension, mN/m	Concentration in Hexane (Isotherm 1), $\mu\text{mol/L}$	Concentration in Water (Isotherm 2), $\mu\text{mol/L}$	Hexane/Water Distribution Coefficient
36	20	0.71	28.2
34	30	1.05	28.6
32	50	1.8	27.8
29	100	3.1	32.2
26	200	6.2	32.1
24.5	300	10.0	30.0

## 5. Conclusions

The buoyant (sessile) drop and pendant drop methods were used to measure the interfacial tension of C<sub>13</sub>DMPO solution at the hexane/water interface. Two types of experiments were performed: adsorption of surfactant from its aqueous solution onto a hexane drop, and adsorption of surfactant from its solution in hexane onto a water drop. Two C<sub>13</sub>DMPO adsorption isotherms were obtained, essentially different from each other with respect to concentration, which is significantly higher for the C<sub>13</sub>DMPO solution in hexane. From the obtained results, the distribution coefficient of the surfactant between the two phases could be directly obtained as the ratio of the surfactant concentrations in the phases at equal interfacial tension values. It is worth noting that, as the volumes of C<sub>13</sub>DMPO solutions are very large as compared with the volumes of the drops, the depletion of the solution caused by adsorption onto the drop surface and transfer of the surfactant into the drop could be safely neglected. The coefficient of C<sub>13</sub>DMPO distribution between water and hexane determined using this method for various values of surface tension is in the range of 28–32, with an average of 30, which is rather similar to the results obtained by the indirect method used in [9].

**Author Contributions:** R.M. conceived the study; V.B.F. and V.I.K. developed the theory; R.M., V.B.F. and S.B.A. designed the experiments; E.V.A. developed the fitting software; A.A.S. performed the experiments; A.V.M. maintained the experimental tools and contributed materials; R.M., V.B.F., V.I.K., S.B.A. analysed the data; R.M., V.B.F. and E.V.A. wrote the paper.

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**Conflicts of Interest:** The authors declare no conflicts of interest.

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