

Chemistry

УДК 541.182+661.185

A. M. TERZYAN, Sh. A. MARKARIAN

DINAMIC SURFACE TENSION MEASUREMENTS OF DIBUTYLSULFOXIDE AQUEOUS SOLUTIONS

A maximum bubble pressure method has been used to study dynamic surface tension, $\gamma(t)$ of dibutylsulfoxide aqueous solutions at 0,0004–0,24 *M* concentration range. The $\gamma(t)$ decays were measured in the range of 30 *ms* to 60 *s* and analyzed in term of asymptotic solutions to the Ward and Tordai equation. The adsorption model provided by diffusion was applied to describe the surface mass transfer process and to predict the dynamic surface tension.

Introduction. The surface tensions of binary mixtures dimethylsulfoxide (DMSO)+water, diethylsulfoxide (DESO)+water, dipropylsulfoxide (DPSO)+water and diisopropylsulfoxide (DiPSO)+water have been recently determined at different temperatures [1]. Meanwhile the aqueous solutions of dibutylsulfoxide (DBSO), although its restricted solubility in water (up to 7 wt.%), have some practical application. A thermal ink jet printing composition contains DBSO which demonstrates rapid penetration properties that can be used for full color printing [2]. In addition, since inking processes operate under dynamic conditions, then surface tension measurements, determined within short time spans (milliseconds to seconds) are often more informative than equilibrium values.

The dynamic surface tension (DST or $\gamma(t)$) is the important property as it governs many important industrial and biological processes [3].

The maximum bubble pressure method (MBPM) is one of the most popular methods currently used to study the dynamic surface tension of surfactant solutions. This is shown by the number of published reviews [4–6] and original studies [7–10].

The surface composition depends on the surface mass transfer. One can then obtain estimates of the overall mass transfer across the interface and hence the surface composition. The diffusive mass transfer of small surfactant molecules from the liquid to the liquid–gas interface has been determined to be a dominant factor, because of the significant difference in diffusion coefficient between the liquid phase and the gas phase.

For relatively small surfactant molecules, diffusion from the bulk liquid to the interface is often the rate-determining step, and the mechanism underlying

dynamic surface tension is diffusion-controlled. A measurement of surface tension will allow us to evaluate the surface mass transfer and further to deduce the mechanism of the DBSO adsorption.

Materials and Methods. All solutions were prepared by weighing using bidistilled water. Dibutylsulfoxide was synthesized and purified according to the literature [11]. The concentration of DBSO was varied from 0,0004 to 0,24 mol/l (total 11 values). Surface tension measurements were performed using the SITA t60 tensiometer (SITA science line t60, Messtechnik, Germany), which employs the maximum bubble pressure method. From the measured maximum pressure (P) the surface tension can be calculated employing Young–Laplace equation: $\gamma = Pr/2$, where r is the radius of capillary. Detailed instrument design and experimental procedure have been described elsewhere [12].

DST measurements were conducted at temperature 25°C at bubble lifetimes in the range of 30 ms to 60 s per bubble (it gives corresponding surface ages for surfactant-like molecules to adsorb to the liquid-air interface). The instrument was calibrated using water, and a surface reading of 72,8±0,1 (mN/m) was regarded as accurately standardized. The temperature was controlled using MS LAUDA thermostat with the precision of ±0,1 (K).

For neutral molecules the surface tension decay $\gamma(t)$ for long times approximations have been given by Miller et al. [9] as

$$\gamma(t)_{t \rightarrow \infty} = \gamma_{eq} + \frac{RT\Gamma^2}{2c} \left(\frac{\pi}{Dt} \right)^{1/2}, \quad (1)$$

where γ_{eq} is the equilibrium surface tension. The parameters c , Γ and D represent the bulk concentration, equilibrium surface excess, and monomer diffusion coefficient of the surfactant.

The above mentioned equation has been used to describe our results with a correlation coefficient R equals to 0,9±0,05.

Results and Discussion. Example of $\gamma(t)$ decays is shown in Fig. 1 for solutions of DBSO. These data are representative for all solutions. As it follows from this Figure, only for the lowest concentration of DBSO (0,0004 mol/l) the initial surface tension does not significantly deviate from the surface tension of water: the decay of surface tension actually starts from the value γ_0 for pure solvent. Whereas for the other (intermediate and highest) concentrations at the shortest possible measuring lifetime of bubble (30 ms), the tensions were already lower than the solvent value γ_0 . Therefore, one can conclude that at 30 ms a significant amount of DBSO has already reached to surfaces. Obviously, these results are due to the higher diffusion rate of the DBSO molecule to the air/water interface.

For the investigated solutions the decrease of surface tension in time period 30–60000 ms is well described by the Eq. (1). Hence it is reasonable to assume that the $\gamma(t)$ decays are consistent with the diffusion controlled model.

Figure 1 shows the $\gamma(t)$ decay as predicted by Eq. (1). Similar agreements between the long time DST data and Eq. (1) were seen for all of the other concentrations. The equilibrium values of surface tension calculated in this way are shown in Fig. 2.

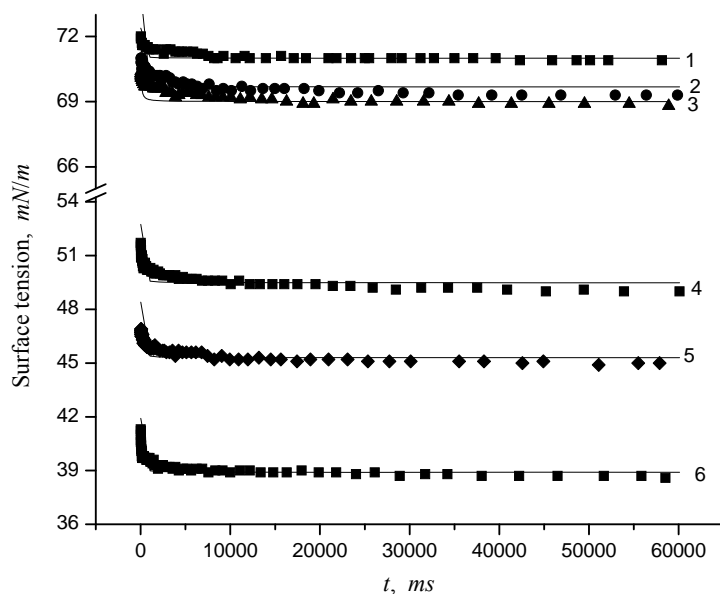


Fig. 1. Dependence of surface tension on time of DBSO solution at concentrations (mol/l): $4 \cdot 10^{-4}$ (1), $1 \cdot 10^{-3}$ (2), $2 \cdot 10^{-3}$ (3), $5 \cdot 10^{-2}$ (4), $1 \cdot 10^{-1}$ (5), $2,4 \cdot 10^{-1}$ (6).

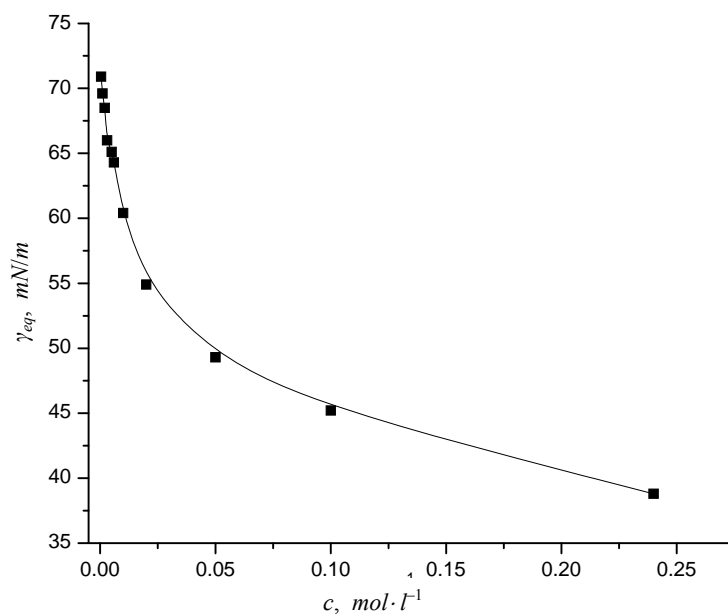


Fig. 2. Dependence of equilibrium surface tension on concentration, calculated by the Eq. (1).

An important feature of diffusion-controlled adsorption kinetics is that, for long lifetimes, the dynamic surface tension data from surfactant solutions linearize when plotted as $t^{-1/2}$ suggested by Eq. (1).

DST data for DBSO plotted vs $t^{-1/2}$ varies linearly, which additionally prove diffusion controlled mechanism of adsorption.

It is interesting to note that the same mechanism is valid for aqueous solutions of 1-octanol which has the same number of carbon atoms [13] as well as for nonanol and decanol [14].

As it follows from Fig. 1, the surface tension decay does not remarkably change with the increase of DBSO concentration. For DBSO, several seconds (2 s) are required for the molecules to saturate the surface and the equilibrium achieved within a shorter time scale.

Conclusions. The results of dynamic surface tension measurements of DBSO solutions show that a significant amount of surfactant is already adsorbed at the shortest possible measuring time (30 ms). The diffusion controlled adsorption model is well applied to describing the surface mass transfer at long surface lifetimes. These results indicate a fairly rapid initial reduction in surface tension.

This work was partially supported by the project ANSEF # 1534.

Chair of Physical Chemistry

Received 04.07.2008

REFERENCES

1. **Markarian S.A., Terzyan A.M.** J. Chem. Eng. Data., 2007, v. 52, p. 1704.
2. US Patent Issued on July 30, 1996, "Thermal ink jet composition".
3. **Kazakov V.N., Sinyachenko O.V., Trukhin D.V., Pison U.** Colloids Surf. A, 1998, № 143, p. 441.
4. **Eastoe J., Dalton J.S.** Adv. Colloid Interf. Sci., 2000, v. 85, p. 103.
5. **Kovalchuk V.I., Dukhin S.S.** Colloids Surf. A, 2001, v. 192, p. 131.
6. **Chang C.H., Franses E.I.** Colloid. Surf. A, 1995, v. 100, p. 1.
7. **Fainerman V.B., Miller R.** Adv. Colloid Interf. Sci., 2004, v. 108–109, p. 287.
8. **Fainerman V.B., Kazakov V.N., Lylyk S.V., Makievski A.V., Miller R.** Colloids Surf. A, 2004, v. 250, p. 97.
9. **Fainerman V.B., Makievski A.V., Miller R.** Colloids Surf. A, 1994, v. 87, p. 61.
10. **Christov N.C., Danov K.D., Kralchevsky P.A., Ananthapadmanabhan K.P., Lips A.** Langmuir., 2006, v. 22, p. 7528.
11. **Markarian S.A., Tadevosyan N.** Method of purification of diethylsulfoxide. Patent of Republic of Armenia № 1196A2, P 20010041, 2002.
12. **Fainerman V.B., Makievski A.V., Miller R.** Rev. Sci. Instr., 2004, v. 75, p. 213.
13. **Bleys G., Joos P.** J. Phys. Chem., 1985, v. 89, p. 1027.
14. **Fainerman V.B., Miller R.** J. Colloid Interf. Sci., 1996, v. 178, p. 168.

Ա. Մ. ԹԵՐԶՅԱՆ, Շ. Ա. ՄԱՐԿԱՐՅԱՆ

ԳԻՔՈՒԹԻԼՍՈՒԼՖՕԲՍԻԳԻ ՋՐԱՅԻՆ ԼՈՒԾՈՒՅԹՆԵՐԻ ԳԻՆԱՄԻԿ
ՄԱԿԵՐԵՎՈՒԹԱՅԻՆ ԼԱՐՎԱԾՈՒԹՅԱՆ ՉԱՓՈՒՄՆԵՐԸ

Ա մ փ ո փ ո մ

Գիրութիլսուլֆօբսիդի (ԳԲՍՕ) 0,0004–0,24 մոլ/լ կոնցենտրացիոն տիրույթում ջրային լուծույթների դինամիկ մակերևութային լարվածությունների $\gamma(t)$ ուսումնասիրության համար օգտագործվել է պոպջակի մաքսիմալ ճնշման մեթոդը: $\gamma(t)$ -ի նվազումները չափվել են 30 մկ-ից մինչև 60 մկ ժամանակային

տիրույթում և նկարագրվել են Վարդի և Տորդեյի հավասարման ասիմպտոտիկ լուծումներով: Գինամիկ մակերևութային լարվածությունները կանխորոշելու և մակերևույթ նյութի տեղափոխման պրոցեսը նկարագրելու համար կիրառվել է դիֆուզիայով պայմանավորված ադսորբցիայի մոդելը:

А. М. ТЕРЗЯН, Ш. А. МАРКАРЯН

ИЗМЕРЕНИЕ ДИНАМИЧЕСКОГО ПОВЕРХНОСТНОГО НАТЯЖЕНИЯ ВОДНЫХ РАСТВОРОВ ДИБУТИЛСУЛЬФОКСИДА

Резюме

Метод максимального давления в газовом пузырьке был использован для изучения динамического поверхностного натяжения $\gamma(t)$ водных растворов дибутилсульфоксида в концентрационном интервале от 0,0004 до 0,24 моль/л.

Спад $\gamma(t)$ был измерен в диапазоне от 30 мс до 60 с и проанализирован с помощью уравнений Варда и Тордея. Для описания кинетики адсорбции и предсказания поверхностного натяжения была использована адсорбционно-диффузионная модель.