

LIQUID DIFFUSION MEASUREMENT FOR SURFACTANTS AT LOW CONCENTRATIONS

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OP-10 surfactant has been used to show that the diffusion coefficient D of a surfactant in a liquid can be measured at low concentrations from the fall in the water level in a capillary. A simple formula is given for calculating D from the readings.

Optical methods are the best for measuring surfactant diffusion in liquids [1-6], but it is virtually impossible to use these at concentrations below 0.01% because the refractive-index change is very small. It is usual to determine D for very dilute solutions by extrapolating to zero the relation of D to concentration C found at higher concentrations, but this cannot be used for surfactants because micelles are formed, and the critical concentration C_{CR} for micelle formation usually lies below 0.01% [7], and these micelles alter the physical meaning of the diffusion coefficient. It is therefore necessary to measure D at low C , i.e., values that certainly do not exceed C_{CR} . We have used the reduction in the surface tension σ at the surface of a water column in a capillary, which can be done very simply with a light source, a thermostat, a capillary with a micrometer system, and a cathetometer.

Figure 1 shows the main part of the apparatus. The capillary 11 is fitted into the tube 6, which can be moved in a strictly perpendicular direction by the micrometer screw 4. The accuracy is governed mainly by the properties of the capillary. We used a circular glass capillary of constant cross section (internal diameter 2.00 mm). We checked that there was no capillary hysteresis [8]. The solution was placed in the small glass beaker 12.

The carefully washed capillary is filled with distilled water and inserted in tube 6. A piece of filter paper soaked in distilled water is placed at the bottom of the thermostat to produce a saturated atmosphere.

The set temperature is reached in 30-60 min, which is indicated to 0.02°C by the thermometer 3, and then screw 4 is operated to bring the capillary into contact with the surface of the solution.

The instant of contact is taken as the zero of time. One measures the initial height h_0 of the water column to 2 μ with the cathetometer. This is facilitated by glueing to the outside of the capillary a thin needle of length h equal to the calculated rise, and one measures from the top of the needle to the bottom of the meniscus, the difference giving the actual rise.

The bottom of the column in the capillary is kept at a constant surfactant concentration C_0 , and some molecules reach the surface in time t , which reduces the surface tension σ and hence the height h [9].

The relation of σ to C at low values is linear to a first approximation:

$$\sigma_0 - \sigma = kC. \quad (1)$$

The reduction in σ causes a reduction in h :

$$h_0 - h = (\sigma_0 - \sigma) \frac{2}{\rho g r}. \quad (2)$$

Then (1) and (2) give C for the free surface in the capillary as

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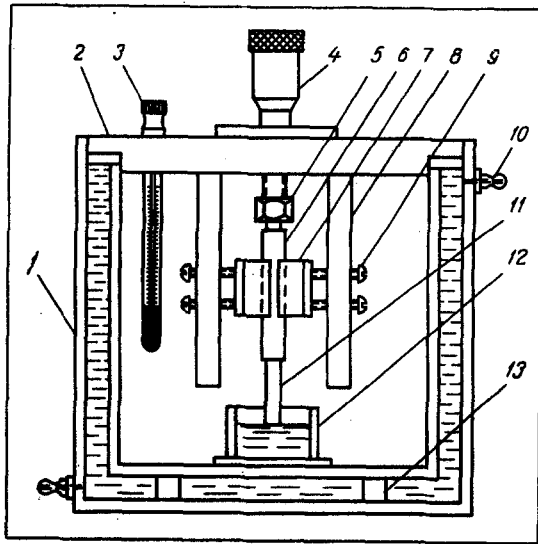


Fig. 1. System for measuring surfactant diffusion in liquids at low concentrations: 1) thermostat wall; 2) cover; 3) thermometer; 4) micrometer; 5) connecting sleeve; 6) tube; 7) guides; 8) supporting walls; 9) screws for setting tube vertical; 10) connecting pipe to ultrathermostat; 11) capillary; 12) beaker; 13) support.

$$C = (h_0 - h) \frac{\rho g r}{2k}. \quad (3)$$

Diffusion alters C at the surface. Fick's equation applies to a very dilute solution:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}. \quad (4)$$

We solve (4) subject to

$$\begin{aligned} C &= C_0 \quad \text{for all } t \text{ for } x = 0, \\ C &= C(x, t) \quad \text{for } t > 0 \text{ and } 0 < x < h, \\ \frac{\partial C}{\partial x} &= 0 \quad \text{for } x = h \text{ for all } t \end{aligned}$$

as an infinite series [11] (similar to a heated cylinder [10]):

$$C = C_0 \left\{ 1 - \frac{4}{\pi} \sum_{n=1}^{\infty} \frac{1}{2n-1} \exp \left[-\frac{D(2n-1)^2 \pi^2}{4h_0^2} t \right] \sin \frac{(2n-1) \pi x}{2h_0} \right\}. \quad (5)$$

As D appears in the exponent, it is difficult to derive it from (5) for $n \geq 2$, and so computer methods were used.

As the sine takes the values ± 1 as a function of n for $x = h_0$, we use (3) and the substitution

$$\exp \left[-\frac{D\pi^2}{4h_0^2} t \right] = y \quad (6)$$

to transform (5) to

$$\sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{2n-1} y^{(2n-1)^2} - \frac{\pi}{4} \left[1 - \frac{(h_0 - h) \rho g r}{2kC_0} \right] = 0. \quad (7)$$

If $n = 1$ we have the linear relation

$$y - \frac{\pi}{4} \left[1 - \frac{(h_0 - h) \rho g r}{2kC_0} \right] = 0; \quad (8)$$

if $n = 2$ we have an equation of ninth degree

$$-\frac{1}{3} y^9 + y - \frac{\pi}{4} \left[1 - \frac{(h_0 - h) \rho g r}{2kC_0} \right] = 0 \quad \text{etc.} \quad (10)$$

Then to find D we have to determine the real root of the equation to the required accuracy. To find k in (7) we need only determine Δh for $C = 0$ and $C_1 = 0.001\%$ (say), the result being multiplied by $|\rho g r / 2C_1|$.

TABLE 1. Diffusion Coefficients for OP-10 with $C_0 = 0.004\%$ at 293°K

t, sec	$h \cdot 10^2, \text{m}$	$\Delta h \cdot 10^2, \text{m}$	$C \cdot 10^3, \%$	$D \cdot 10^9 \text{ m}^2/\text{sec}$ $n=1$	$D \cdot 10^9 \text{ m}^2/\text{sec}$ $n=5$	$D \cdot 10^9 \text{ m}^2/\text{sec}$ $n=5$
1	2	3	4	5	6	7
0	1,4100					
75600	1,3598	0,0502	0,236	0,322	0,278	0,234
79200	1,3536	0,0564	0,265	0,316	0,277	0,232
82800	1,3464	0,0636	0,300	0,312	0,278	0,233
86400	1,3368	0,0732	0,344	0,309	0,281	0,234
90000	1,3290	0,0810	0,381	0,306	0,281	0,235
93600	1,3176	0,0924	0,434	0,308	0,287	0,238
97200	1,3086	0,1014	0,476	0,306	0,288	0,240
100800	1,2992	0,1108	0,521	0,306	0,290	0,242
104400	1,2901	0,1199	0,564	0,304	0,292	0,243
108000	1,2812	0,1288	0,605	0,303	0,292	0,243
111600	1,2736	0,1364	0,641	0,302	0,292	0,246
115200	1,2633	0,1467	0,689	0,302	0,294	0,247
162000	1,1680	0,2420	1,140	0,288	0,286	0,245
165000	1,1648	0,2452	1,150	0,285	0,282	0,241
169200	1,1560	0,2540	1,194	0,286	0,235	0,234
172800	1,1516	0,2584	1,214	0,282	0,280	0,241
176400	1,1458	0,2642	1,242	0,281	0,280	0,234
180000	1,1422	0,2678	1,257	0,279	0,278	0,241

This device thus enables one to measure D without having to use other equipment to measure σ as a function of C . We have used this method to determine D for OP-10 surfactant over a wide range in C . Capillary rise gave k for $C = 0.001\%$ for OP-10 as $10.3 \text{ N/m per } \%$. Table 1 gives C at the surface during diffusion of OP-10 from a 0.004% solution in distilled water. We calculated D from (6) after finding the roots of (7) for n of 1-5 via a program for defining and refining the roots of $f(y) = 0$.

The root was found by calculating $f(y)$ by steps of 10^{-3} in y in the direction of decreasing modulus until the sign changed. Then the root was refined by linear interpolation. The program was written in AK-2 autocode for an Ural-3 computer.

Columns 5 and 6 of Table 1 give D . The value for $n = 1$ differs from that for $n = 5$ on average by about 5% , while the values from $n = 3$ to $n = 5$ are virtually identical. There is then only a negligible error in replacing the sum of the series in (5) by the partial sum for $n \geq 3$.

Although the actual diffusion corresponded closely to the mathematical model, the D calculated from (5) may be somewhat too high, for the following reasons. Surfactant that has reached the meniscus is adsorbed on the surface, so the process for a long while remains analogous to free diffusion, which will facilitate the accumulation of surfactant at the surface in excess of that for a solute without surface selectivity but having the same D . The fall in σ is governed by the rate of accumulation at the surface, so the observed C can give over-estimates for D . However, we cannot estimate the error arising from this cause exactly, although the result from (5) can be compared with that from Fick's equation for an unbounded cylinder to get a rough value.

We solve (4) with $C = 0$ at $t = 0$ for all x and with $x = 0, C = C_0$ for all t to get

$$\frac{C_1}{C_2} = \exp \left[- \frac{x_1^2 - x_2^2}{4Dt} \right]. \quad (11)$$

This result is acceptable also for a capillary of finite length over a time interval not greatly exceeding the time for a molecule to diffuse to the surface.

The fall is very slow, so we assume that the height distribution of C is unvarying, i.e., there is parallel upward transport of the surfactant molecules along with the medium. This means that all molecules passing through $x = 0$ travel the same distance to the meniscus before the latter starts to fall.

This assumption ($x = h_0$) is used with C_0 and with the origin placed at the contact of the capillary with the surface of the solution ($x_0 = 0$) to get from (11) a simpler expression for D :

$$C = C_0 \exp \left[-\frac{h_0^2}{4Dt} \right]. \quad (12)$$

The last column of Table 1 gives the results for D. The result from (5) is 20% larger than that from (12).

Only 0.5% error is involved in measuring t , h_0 , and Δh , so one expects about 2% error from this source in D in any given run. The main sources of error in D are C_0 and k , which contribute 6%.

For this reason, two parallel runs with different solutions having the same C_0 give 10% discrepancy in D.

From (12) we get the concentration ratio at two given times as

$$\frac{C_i}{C_j} = \exp \left[-\frac{h_0^2}{4D} \left(\frac{1}{t_i} - \frac{1}{t_j} \right) \right]. \quad (13)$$

From (3) we find that (13) is equivalent to

$$\frac{\Delta h_i}{\Delta h_j} = \exp \left[-\frac{h_0^2}{4D} \left(\frac{1}{t_i} - \frac{1}{t_j} \right) \right]. \quad (14)$$

Taking logarithms in (14) gives us a straight line with a slope of $h_0^2/4D$ from which we get D without determining k . The results of Table 1 then give D as $0.21 \cdot 10^{-9}$ m²/sec. The result from (14) is independent of k and also of the contact angle θ , which has been omitted from (2), which results in an overestimate of Δh because of the assumption $\cos \theta = 1$. It is therefore logical to find a D somewhat smaller than that given by (12).

It is therefore best for practical purposes to use the solution to (4) in the form of (12) to calculate D.

The following are values of D for OP-10 in distilled water at 293°K.

C, %	0.001	0.004	0.006	0.008	0.01	0.8	1.0	2.0
D · 10 ⁹ , m ² /sec	0.19	0.24	0.20	0.19	0.19	0.17	0.16	0.15

The critical concentration for OP-10 lies [7] between 0.006 and 0.01%; D falls appreciably for C above 0.01%. From this we conclude that concentrations less than this should be used in surfactant applications [12] where the rate is limited by the surfactant diffusion rate [13].

NOTATION

σ_0	is the surface tension of water;
σ	is the surface tension of solution;
C	is the concentration of surfactant;
k	is the constant of proportionality;
C_0	is the concentration of solution under study;
h_0	is the initial height of water column in capillary;
h	is the height of water column corresponding to surface tension σ ;
ρ	is the density of water;
g	is the acceleration due to gravity;
r	is the radius of capillary;
D	is the coefficient of diffusion;
t	is the time;
$\Delta h_i, \Delta h_j$	are the decreases in column heights in times t_i and t_j .

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