Dynamic surface tension of foaming solutions and dispersions

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With 8 figures and 1 table

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Introduction

In the preceding papers the maximum bubble pressure method for the measurement of the dynamic surface tension ($\gamma_t$) of surfactant solutions was studied (1–3). The principal advantage of this method resides in the fact that it makes it possible to measure $\gamma_t$ practically from the zero age of the surface to the equilibrium surface tension, $\gamma_e$, also in solutions equilibrating very slowly, viz. by extrapolation. The disadvantage consists in a considerable scattering of the results. During measurements in some solutions serious difficulties may arise from the creeping of a liquid into the capillary at lower rates of bubbling which ultimately may cause a drop formation inside of the capillary and its clogging. By the creeping of the liquid the effective radius of the capillary decreases and, consequently, higher values of $\gamma_t$ are erroneously determined. The narrowing of the capillary may bring it about that after a certain prolongation of the interval between two consecutive bubbles the measured pressure does not drop respectively any more and, consequently, unreal values of $\gamma_e$ are obtained. Garner and Garfias (4) also mentioned the difficulties with the creeping of liquid into the capillary in the determination of surface tension from the dimensions of the bubble profile. Furthermore, the measurement may be affected or even made impossible by the hydrophobization of the capillary surface which may prevent an immediate restoring of the meniscus on the inside capillary edge after the bubble detachment, and thereby a continuous stream of bubbles arises (1). Last but not least, there are difficulties with measuring of foaming solutions when the foam fills the measuring cell.

For surface ages exceeding a few seconds the drop weighing method may be advantageously used. It is a lengthy method but yields very accurate results (5) even for solutions creating difficulties for the application of the maximum bubble pressure method.

In the two above methods the relationship between the measured interval of the bubble or drop formation and the effective surface age (i.e. period in which the static surface would reach $\gamma_t$) was studied (2, 5). The respective corrections enabling to measure $\gamma_t$ in dependency on the age of the static surface of the solution were suggested. For the thus evaluated results a good agreement of $\gamma_t$ of dodecyl sulfate solutions with the two above methods and with the static Wilhelmy plate method was found (5).

This paper deals with the results obtained in technical surfactant solutions and dispersions by the maximum bubble pressure and the drop weighing methods.

Experimental

Surface tension

Measurements by the maximum bubble pressure method were carried out on the apparatus described in a previous paper (1) and evaluated according to the empirical relationship, $\gamma = 3.758 \Delta p^*$ (dyn/cm) (cf. ref. (5)).

Measurements by means of the stalagmometer and the way of their evaluations were described in the preceding paper (5). The results represent values of the dynamic surface tension for a static surface of the age $t$ (sec) referred to.
Table 1. Characteristics of measured solutions and dispersions

<table>
<thead>
<tr>
<th>Text tag</th>
<th>Features*</th>
<th>Viscosity (cP)</th>
<th>Extrapolated $\gamma_s$ (dyn/cm)</th>
<th>Maximum pressure</th>
<th>Stalagmometer</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>s f</td>
<td>1.216</td>
<td>60.4–63.5</td>
<td>52.0–52.8</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>s n</td>
<td>2.114</td>
<td>45.0</td>
<td>52.8–55.6</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>d n</td>
<td>2.234</td>
<td>42.5–56.7</td>
<td>42.5</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>d f</td>
<td>1.009</td>
<td>53.6–60.9</td>
<td>43.7</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>d f</td>
<td>1.015</td>
<td>51.0–55.6</td>
<td>42.5</td>
<td></td>
</tr>
</tbody>
</table>

*) s = solution, d = dispersion, f = foaming, n = non-foaming

Solutions and dispersions

Characteristics of solutions and dispersions are given in Table 1. Distilled water and the following technical agents were used to their preparation:

A, dark red brown foaming solution of 0.2% sodium dinaphthylmethane disulfonate, 0.1% condensed phenol sulfonate, 0.2% polyvinylalcohol;
B, non-foaming solution after breaking of the dispersion C;
C, non-foaming unstable dispersion of 0.5% concentrated paraffin dispersion (paste), 0.2% carboxymethyl cellulose;
D, red brown foaming stable dispersion of 0.5% acrylate vinylacetate copolymer, 0.1% condensed product of formaldehyde, cresol and naphtholsulfonic acid;
E, light brown foaming stable dispersion of 0.5% acrylate vinylacetate copolymer, 0.25% dried sulfite waste liquor, 0.05% sodium dinaphthylmethane disulfonate.

Results and discussion

The determined $\gamma_s$ values in dependency on the surface age in a strongly foaming solution $A$ are presented in Fig. 1. When comparing the results obtained by the two methods, one should realize that in the maximum bubble pressure method all points lying on one curve resulted from one experiment during which the interval between two consecutive bubbles was gradually prolonged. Even if the points constitute a continuous curve, this does not attest to the reliability of results. The actual scattering of results is shown in Fig. 1 by the curves of three experiments demonstrating differences up to 5 dyn/cm. On the contrary, each point on the curve determined by drop weighing on the stalagmometer represents an independent measurement and the continuity of the curve plotted according to the points clearly attests to an excellent reproducibility of the results. The curves obtained by the maximum bubble pressure method show a relatively quick reaching of $\gamma_s$. If we consider the inferior reproducibility of experiments and relatively high $\gamma_s$ values, the presented results have small credibility, particularly because the solution contains a mixture of macromolecular compounds having diverse molecular weights. In such case a slow equilibration may be expected. Hence, it is obvious that the stalagmometer yields accurate results whereas in the maximum bubble pressure method the sources of errors mentioned in the introduction of this paper come to the fore.

In Fig. 2 there are the results obtained with solution $B$ prepared by the separation of the solid part after the breakdown of the little stable paraffin dispersion. The dispersion medium $B$ was slightly turbid and non-foaming. The dependency of $\gamma_s$ upon the age of the surface gives similar results by both methods; the maximum difference in the range measured amounts only to about 1 dyn/cm, the dependency course, however, is steeper in the maximum bubble pressure method. Fig. 3 displays the dependency $1/(\gamma_0 - \gamma_t)$ on $1/t$.