Radial oscillations of gas bubbles covered with a monolayer of surface-active substances in the near-surface sea layer

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Abstract

Radial oscillations of gas bubbles in aqueous solutions of surface-active agents depend on the elasticity modulus of the adsorbed monolayer and the rate of diffusive molecule exchange within the layer resulting from its deformation. Relaxation time of the diffusion process was calculated for several surface-active substances present in the surface microlayer of natural waters. An estimate was made of a resonance frequency shift and an increase in the damping constant of radial oscillations of a gas bubble covered with a condensed monolayer of Extra 15 engine oil as compared with a bubble having a clean surface in the frequency range of the acoustic field $10^1 - 10^4$ s$^{-1}$ and the bubble radii of $3 - 50$ µm.

1. Introduction

Surface-active substances found in sea water are products of a very active biological life and a result of increasing pollution of the near-surface water layer, especially in the near-shore zone. Ocean chemists tend to agree that the composition of the near-surface layer is mainly determined by adsorption of these substances described by Gibbs' equation (Berger et al., 1974; Detwiler, 1979; Garret, 1967; Gershey, 1983; Jarvis et al., 1967; Johnson, Cooke, 1981). Physical properties of many hydrodynamic systems having interfacial surfaces with an adsorbed layer (emulsions, foams, capillary waves ...) to the greatest extent depend on the surface elasticity modulus of the monolayer (Davies, Vose, 1965; Lucassen-Reynders, Reynders, 1969; Robb, 1980). Unfortunately, the composition and the share of individual surface-active substances in sea water of selected areas is not yet known and the latest attempts to determine viscoelastic properties of organic surface films are of a
limited scope (Gershey, 1983). Considerations presented in this paper, dealing with radial oscillations of a gas bubble in the acoustic wave field, are based on studies of Glazman (1983, 1984) and limited to the case of a bubble covered with a monolayer of Extra 15 engine oil. The aim of the paper is to determine the effect of the presence of the oil layer on the resonance frequency and attenuation constant of the bubble, ie parameters directly affecting the scattering and damping of an acoustic wave propagating in a medium with bubbles. An estimate was made of the effect of increasing the frequency of the gas bubble free oscillations (visible especially in case of microbubbles placed directly near the water surface—Glazman, 1983) as well as of an increase in the damping constant of radial oscillations as compared with a bubble with a clean surface. Earlier papers dealing with this problem took no account of the important role of the adsorbed monolayer which resulted in incorrect estimations of, for instance, the frequency of the bubble free oscillations (Avenesov, Avetisyan 1976; Levitskii, 1979). Surface-active substances of natural origin in a proper concentration allow for the dissolution of oil substances in sea water in the process of micellar solubilization (Lindman, 1980). The process itself depends on the type of surface-active agent, kind of oil substance, presence of electrolytes, pH of the solution, and temperature (Mittal, 1977). Quaternary systems of the type water-oil-surface-active agent-electrolyte have recently become an object of great interest (Bais et al, 1984; Fakrul et al, 1986; Kalhweit et al, 1984). Crude oil derivatives dispersed in sea water may be accumulated on the surface of gas bubbles appearing as a result of intense undulation. Langmuir’s circulation and surface currents enable them to freely penetrate down and across the sea at considerable distances (Thorpe, Hall, 1983; Thorpe 1984a, b). The results of theoretical considerations presented here may in the future serve to formulate a method of estimation of sea pollution based on bubble spectrometry (Medwin, 1980).

2. Frequency of the bubble free oscillations and damping constant of radial oscillations of a gas bubble with an adsorbed layer

The classical Rayleigh's equation for the bubble oscillations was augmented by Glazman (1983) with an additional term taking into account viscoelastic properties of the adsorbed monolayer. The presence of a surface film results in a decrease of the average radius of the oscillating bubble as compared with a clean surface bubble and, as a consequence, leads to an increase in its free oscillations. The relation between the bubble free oscillations with and without an adsorbed layer is presented in the following
formula (Glazman, 1983):
\[ \omega_0/\omega_p = h^3k^3w(h + 3\beta h^3)/(3k - W)^{1/2}, \]  
where:
\[ h = R_0/R, \]
\( R_0 \) — equilibrium radius and \( R \) — average radius of the bubble (see equation 30 in Glazman, 1983),
\( k \) — polytropic exponent of gas in the bubble,
\[ W = 2\sigma/P_{i,eq} R_0, \]  
\( P_{i,eq} \) — gas pressure inside the bubble equal \[ 2\sigma R_0 + 1.013 \times 10^5 (1 + 0.1 H), \]
\( H \) — depth of the bubble in the liquid,
\[ \beta = \chi/\sigma, \]
\( \sigma \) — gas-liquid interfacial tension.
Elasticity modulus of the monolayer
\[ \chi = -\frac{d\sigma}{d\ln \Gamma}, \]  
is discussed in detail in the following section (see also Davies, Vose, 1965; Lucassen-Rynders, Lucassen, 1969; Robb, 1980).

Damping constant \( B \) of radial oscillations of the bubble may be calculated from the following expression (Glazman, 1984):
\[ B = \omega^{-1}(\text{Re} \tilde{\mu} - \frac{1}{2} \text{Im} \tilde{v})^2, \]  
where:
\( \omega \) — angular frequency of acoustic wave,
\( \tilde{\mu} \) and \( \tilde{v} \) — parameters defined in Glazman’s paper (Glazman, 1984) by expressions (38) and (37), respectively, and containing quantities \( \chi \) and \( \alpha \) characterizing monolayer.

The value \( \alpha \) is the angular frequency of relaxation processes of diffusion and reorientation of molecules of the surface-active agent in the monolayer under the influence of changes in its surface in the acoustic wave field.

3. Properties of adsorbed monolayers

A monolayer of a surface-active substance is formed as a result of surface adsorption described by Langmuir-Szyszkowski’s equations which show relations between surface pressure and adsorption (De Keyser, Joos, 1983):
\[ \Pi = \sigma_0 - \sigma = RT \tau \alpha (1 + c/a) \]  
(5)
\[ \Gamma = \Gamma_\infty \frac{c}{c + a}, \quad (6) \]

where:
- \( \sigma_0, \sigma \) — surface tension of solvent (water) and surface-active agent solution, respectively,
- \( \Pi \) — surface pressure \( (\Pi = \sigma_0 - \sigma) \),
- \( R \) — gas constant,
- \( T \) — absolute temperature,
- \( c \) — molar concentration of surface-active substance,
- \( \Gamma \) — adsorption,
- \( \Gamma_\infty \) — saturation adsorption (corresponds to above \( c \) for which \( \frac{d\sigma}{dc} = 0 \)),
- \( a \) — Szyszkowski’s surface activity coefficient.

Compression and expansion of the surface covered with the monolayer results in a change of surface adsorption. Adsorption and desorption of molecules between the monolayer and the near-surface area, as well as their reorientation within the monolayer, take place. Both processes are characterized by a certain, defined relaxation times. Viscoelastic properties may be expressed in the form of a complex modulus of expansional surface elasticity.

If we limit our discussion to diffusive relaxation, with an assumption that diffusion occurs according to Fick’s law (Joos, Bleys, 1983), then the above-mentioned modulus will take the form (Glazman, 1984):

\[ \chi = \chi_d + i\omega \eta_d, \quad (7) \]

where true and imaginary parts have the following form, respectively:

\[ \chi_d = -\frac{d\sigma}{d\ln \Gamma} \frac{1 + \tau}{1 + 2\tau + 2\tau^2}, \quad (8) \]

\[ \eta_d = -\frac{d\sigma}{d\ln \Gamma} \frac{\tau}{\omega(1 + 2\tau + 2\tau^2)}. \quad (9) \]

The diffusion parameter \( \tau \) has the form:

\[ \tau = \frac{dc}{d\Gamma} \frac{D}{\sqrt{2\omega}}, \quad (10) \]

where \( D \) is a diffusion coefficient.

The diffusional parameter for those monolayers whose pressure and adsorption are described by means of equations (5) and (6) may be expressed in the form:

\[ \tau = \frac{(c/a + 1)^2 a}{\Gamma_\infty} \frac{D}{\sqrt{2\omega}}. \quad (11) \]
Diffusional relaxation time is fully described by properties of the substance forming the monolayer and may be determined from the expression (Joos, Bleys, 1983):

$$t_r = \left[ \frac{a}{\Gamma_\infty \left( 1 + \frac{c}{a} \right)^2 \sqrt{D}} \right]^{-2}. \quad (12)$$

When there is no diffusion exchange ($t = 0$), the value of elasticity modulus is fully determined by the surface equation of the monolayer condition, which gives an equilibrium relation between $\sigma$ and $\Gamma$, assuming the form of equation (3).

The second type of relaxation caused by reorientation of molecules cannot be at present expressed in a simple way by macroscopically measurable parameters of the system.

In the surface microlayer of natural waters a great diversity of surface-active organic substances has been observed. Besides proteins and glycerides, characterized by small surface activity, there are also very active esters, fatty acids, and alcohols (Jarvis et al., 1967). The latter constitute main components of the surface layer as a result of competitive adsorption (Garret, 1967). They consist of molecules having between 11 and 22 carbon atoms in a hydrocarbon chain. The elasticity modulus of condensed monolayers of this type may reach a value of 200 mN·m⁻¹ (C₂₀H₄₁OH—see Joly, 1972). Table 1 presents the values of physical quantities characterizing several selected organic surface-active substances occurring on the surface of natural waters (Joly 1972). It includes relaxation times $t_r$ of particular monolayers at a state of maximum compression $c = 2a$ calculated from equation (12). The value of elasticity modulus (equation 3) obtained by means of equilibrium measurements from the expression $\sigma - \Gamma$ should be multiplied by the factor $A = (1 + \tau)/(1 + 2\tau + 2\tau^2)$ in order to take into account the process of diffusive molecular exchange. The values of $A$ in Table 1 are listed for selected deformation frequencies of the monolayer in the range $10^2 - 10^5$ s⁻¹. In the case of readily soluble substances ($a = 10^{-3} - 10^{-4}$ kmol·m⁻³) diffusion significantly reduces the value of the modulus and only above the frequency of $10^5$ s⁻¹ the monolayer may be considered ‘insoluble’. Substances having the activity coefficient $a = 10^{-6}$ kmol·m⁻³ and lower form insoluble monolayers within the whole range of deformation frequencies considered here and factor $A$ is close to 1. A serious experimental problem is encountered when determining the diffusion coefficient of slightly soluble surface-active substances occurring on the surface of natural waters and then calculating relaxation time of the diffusion process from relationship (12). De Keyser and Joos (1983) report a convenient method of measuring $D$, based on the analysis of relationship $\ln A/A_0$ of the monolayer as a function of time $t$, provided that the surface pressure is kept constant ($\text{d}c/\text{d}t = 0$). Diffusion coefficient is calculated from the relation (De Keyser, Joos, 1983):
Table 1. Effect of diffusive exchange of molecules accompanying the deformation of adsorption monolayers of various surface-active substances

<table>
<thead>
<tr>
<th>Substance</th>
<th>$t_r$ [s]</th>
<th>$\omega$ [s$^{-1}$]</th>
<th>$10^2$</th>
<th>$10^3$</th>
<th>$10^4$</th>
<th>$10^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_7H_{15}COOH$</td>
<td></td>
<td>0.00049</td>
<td>0.1514</td>
<td>0.3982</td>
<td>0.7171</td>
<td>0.9011</td>
</tr>
<tr>
<td>$a = 1.2 \cdot 10^{-3}$ kmol·m$^{-3}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>$\Gamma_x = 2 \cdot 10^{-9}$ kmol·m$^{-2}$</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>$D = 1.1 \cdot 10^{-10}$ m$^2$·s$^{-1}$</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{12}H_{25}SO_4Na$</td>
<td></td>
<td>0.00284</td>
<td>0.3241</td>
<td>0.6477</td>
<td>0.8708</td>
<td>0.9583</td>
</tr>
<tr>
<td>$a = 4.4 \cdot 10^{-4}$ kmol·m$^{-3}$</td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>$\Gamma_x = 5.7 \cdot 10^{-9}$ kmol·m$^{-2}$</td>
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<tr>
<td>$D = 7.3 \cdot 10^{-10}$ m$^2$·s$^{-1}$</td>
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<td></td>
</tr>
<tr>
<td>$C_{10}H_21OH$</td>
<td></td>
<td>10.3375</td>
<td>0.9782</td>
<td>0.9931</td>
<td>0.9973</td>
<td>0.9994</td>
</tr>
<tr>
<td>$a = 1.4 \cdot 10^{-5}$ kmol·m$^{-3}$</td>
<td></td>
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<tr>
<td>$\Gamma_x = 6.1 \cdot 10^{-9}$ kmol·m$^{-2}$</td>
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<tr>
<td>$D = 3.7 \cdot 10^{-10}$ m$^2$·s$^{-1}$</td>
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<td></td>
</tr>
<tr>
<td>$C_{12}H_{25}OH$</td>
<td></td>
<td>54.5291</td>
<td>0.9248</td>
<td>0.9968</td>
<td>0.9981</td>
<td>0.9999</td>
</tr>
<tr>
<td>$a = 4.3 \cdot 10^{-6}$ kmol·m$^{-3}$</td>
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<tr>
<td>$\Gamma_x = 7 \cdot 10^{-9}$ kmol·m$^{-2}$</td>
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<td></td>
</tr>
<tr>
<td>$D = 6.1 \cdot 10^{-10}$ m$^2$·s$^{-1}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{11}H_{23}COOH$</td>
<td></td>
<td>306.4293</td>
<td>0.9959</td>
<td>0.9987</td>
<td>0.9995</td>
<td>0.9999</td>
</tr>
<tr>
<td>$a = 1.4 \cdot 10^{-6}$ kmol·m$^{-3}$</td>
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<td></td>
</tr>
<tr>
<td>$\Gamma_x = 6 \cdot 10^{-9}$ kmol·m$^{-2}$</td>
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<td></td>
</tr>
<tr>
<td>$D = 7.4 \cdot 10^{-10}$ m$^2$·s$^{-1}$</td>
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</table>

\[
\ln \frac{A}{A_c} = -\frac{2c}{\Gamma} \left(\frac{Dt}{\pi}\right)^{1/2},
\]

(13)

where:

$A_0$ — initial surface of monolayer,
$A$ — surface after time $t$ (after compression).

Values of $c$ and $\Gamma$ are taken from equilibrium measurements and $\pi$ equals 3.14...

Diffusive relaxation times assume very diverse values which depend on the molecular structure of a surface-active substance (length of hydrocarbon chain, type, number, and position of polar groups in the molecule).

Experimental data and theoretical estimations presented by Davies and Vose (1965) concerning the effect of length of the hydrocarbon chain in a molecule of anionic surface-active agent ($C_8H_{17}SO_4 - C_{14}H_{29}SO_4$) provide the values of $\alpha (\alpha = 2\pi/t_r)$ 20 – 500 s$^{-1}$, respectively. However, theoretical considerations are very limited and cannot be applied to all kinds of surface-active agents (cationic or nonionic).

An important result of the above-mentioned study is the method of experimental determination of the characteristic time of a relaxation process.
on the basis of the dependence of attenuation coefficient of surface capillary wave propagating on a surface covered with a monolayer as a function of the wave frequency. The inflection point on the curve points to the occurrence of this process. Investigating a similar dependence for a water surface covered with a monolayer of various oil derivatives by means of a method of reflected ultrasonic beam (Pogorzelski et al, 1984), in the 20–60 Hz frequency range of the surface wave, the author also observed an inflection point on the curve. For a monolayer of *Extra 15* light engine oil in the state of compression $H = 25 \text{ mN} \cdot \text{m}^{-1}$, it appears at a frequency $f = 28.5 \text{ Hz}$ ($\alpha = 179.1 \text{ s}^{-1}$), which is illustrated in Figure 1. The acoustic method may be useful for determining parameter $\alpha$ which is of great importance alongside $a$, $D$, and $I_\infty$ when dealing with the problems of dynamic changes of adsorption monolayers. At the same time, it gives an opportunity for *in situ* investigations of surface films occurring naturally.

![Graph](image)

*Fig. 1. Attenuation coefficient of a capillary surface wave propagating on a water surface covered with a monolayer of *Extra 15* oil as a function of wave frequency, determined by the acoustic method.*

The arrow shows the inflection point of the curve which appears at a frequency of $\omega = \alpha = 179.1 \text{ s}^{-1}$

### 4. Examples and calculations

The object of the author's study were monolayers of oil derivatives with very diversified physical properties, formed on the surface of water (Pogorzelski, 1985). Substances which represent certain classes of oil products, occurring most often on the surface of natural waters in the form of oil pollutants, were selected for the study. Light oil fractions: 78 ethyl gasoline, kerosene,
Diesel oil are characterized by low surface activity, and the elasticity modulus of their monolayers in a state of maximum compression ($\Pi \approx 20 \text{ mN} \cdot \text{m}^{-1}$) does not exceed $20 \text{ mN} \cdot \text{m}^{-1}$.

*Marinoll 111* and *Extra 15* engine oils form condensed monolayers of a 'solid' type (Joly, 1972) and the highest observed values of the modulus equal to $93.6$ and $136.8 \text{ mN} \cdot \text{m}^{-1}$, respectively (Pogorzelski, 1985). It was determined by separate measurements from the relationship $\sigma - \Gamma$ with Wilhelmy's method (Joly, 1972). Figure 2 presents the ratio of gas bubble free oscillations frequency for a gas bubble covered with a monolayer of *Extra 15* oil to the clean bubble free frequency for the entire range of surface pressures of the monolayer calculated using formula (1). Calculations were performed for two kinds of gas bubbles: $R_0 = 3 \mu\text{m}$; $k = 1$ (solid line) and $R_0 = 30 \mu\text{m}$; $k = 7/5$ (dashed line), placed at a depth $H = 0.2 \text{ m}$ under the water surface. The effect of increase of the bubble free oscillations is considerable for a microbubble within the range of high surface pressures (elasticity modulus reaches then a value of the order of $10^2 \text{ mN} \cdot \text{m}^{-1}$) and is partly a result of the fact that relative share of capillary component $W$ (equation 2) in the total pressure inside the microbubble is quite large, having a value of the order of $0.4$ at a depth $H = 0.5 \text{ m}$. Using expression (4) for damping constant $B$ of radial oscillations of the bubble with an adsorbed layer, values $\chi = 136.8 \text{ mN} \cdot \text{m}^{-1}$, $\sigma = 47.5 \text{ mN} \cdot \text{m}^{-1}$, $\alpha = 179.1 \text{ s}^{-1}$ were introduced into it; they characterize an *Extra 15* oil monolayer on the water surface at a surface pressure $\Pi = 25 \text{ mN} \cdot \text{m}^{-1}$. Calculations were carried out for bubbles with radii of $5 \mu\text{m}$ and $50 \mu\text{m}$ (dashed line in Fig. 3). For comparison a solid line was used to denote values of $B$ for the system with a clean bubble in water close to the surface ($P_{i,eq} = 101325 \text{ Pa}$) at a temperature of $293\text{K}$. The
Fig. 3. Damping constant of radial oscillations of the gas bubble as a function of angular frequency of acoustic wave.

An adsorbed layer of *Extra 15* oil (*H = 25 mN·m⁻¹, *χ = 136.8 mN·m⁻¹, *α = 179.1 s⁻¹*) — dashed line, a clean surface — solid line. The radii of gas bubbles are 5 and 50 μm.

5. Conclusions

(i). Radial oscillations of gas bubbles in aqueous solutions of surface-active agents depend to a decisive degree on the value of elasticity modulus of a surface adsorption monolayer and the rate of diffusive molecular exchange in the layer under the influence of its deformation. The values...
assumed by these quantities are closely related to the molecular structure of the surface-active substance (length of hydrocarbon chain, number, type, and distribution of polar groups within the molecule).

(ii). The presence of a condensed monolayer of a surface-active oil substance on the surface of a microbubble (with a radius of $10^{-6}$ m and smaller) may lead to a considerable increase in the frequency of its free oscillations as compared with a clean surface, especially close to the water surface.

(iii). The damping constant of radial oscillations of a microbubble with an adsorption layer of oil is larger by several orders of magnitude than that of a bubble with a clean surface within a frequency range of acoustic wave comparable and smaller than the characteristic frequency of relaxation process taking place in the monolayer under the influence of its deformation.

(iv). Mean radius, resonance frequency, and damping constant of oscillations of a gas bubble are parameters which influence scattering and extinction cross-sections of the acoustic wave in a medium with bubbles. Therefore, the measurements of dissipation and attenuation of an acoustic wave on a bubble cloud in the near-surface natural water layer, supplemented with data on the kind of surface-active substances occurring there, may lead to creation of an effective method of evaluation of pollution of sea waters with surface-active agents including crude oil derivatives. Moreover, parameters whose changes were calculated also occur in equations describing the phenomena of a threshold of generation of the bubble surface waves (Francescutto, Nabergoj, 1978) as well as the generation and development of cavitation (Lauterborn, Cramer, 1981), which points to the necessity of revising earlier estimates related to these problems, in which the important role of the adsorbed monolayer had been neglected.

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Gas-bubbles oscillations covered with a surface-active substances


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