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Bubble rise in a liquid with a surfactant gas, in particular carbon dioxide

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When a gas bubble rises in a surfactant solution, the velocity field and the distribution of surfactant affect each other. This paper gives the theory for small Reynolds and internal Péclet numbers if the surfactant is gaseous or volatile, if its mass flux across the bubble and around its surface dominates its mass flux through the bulk liquid, and if slowness of both adsorption and convective diffusion must be allowed for.

The theory is tested on the experiments of Kelsall *et al.* (*J. Chem. Soc. Faraday Trans.*, vol. 92, 1996, p. 3879). Their bubbles rose as expected in a pure liquid until the apparatus was opened to the atmosphere. That significantly slowed the bubbles down. The effect is so sensitive to small concentrations of slowly adsorbing or reacting surfactants that atmospheric carbon dioxide could have caused it, even though it alters the equilibrium surface tension by less than four parts per million in pure air.

There are still unexplained discrepancies between experiment and theory. Additional experiments are suggested that would help to explain them.

1. Introduction

The purpose of this paper is to explain the experiments of Kelsall *et al.* (1996*a*) in which for the first time bubbles were observed rising at low Reynolds numbers in a dilute aqueous solution (surface tension and viscosity close to those of pure water) at the speed expected in a pure liquid, but after opening the apparatus to the air the bubbles slowed down to rates closer to those expected for contaminated surfaces. That effect was not constant, but varied both up and down over the next 30 hours. This paper explores the possibility of a surface-active soluble gas in the air significantly affecting the bubble rise.

To understand how a gas bubble rises in a surfactant solution, one must solve the coupled problems of fluid mechanics, adsorption kinetics, and convective diffusion. If the surfactant is only in the liquid and on the bubble surface, and the external Reynolds number is small, and either the external Péclet number is small or adsorption kinetics rather than convective diffusion is rate-limiting for surfactant transfer, then the surface speed u_θ is known to vary as $\sin\theta$ (Levich 1962, § 74–75), where we use spherical polar coordinates (r, θ) centred on the bubble, with $\theta = 0$ upwards. If the surfactant occurs both inside and outside a bubble, then its transport around the surface and in the liquid phase can be negligible in comparison to that across the bubble interior, and we still have $u_\theta \propto \sin\theta$. That appears to have been the case in the experiments of Kelsall *et al.* (1996*a*), but it is not covered by previous work.

Kelsall *et al.* (1996*a, b*) also worked on electrophoresis of bubbles, but their results raise issues beyond the scope of this work. In their experiments the Debye thickness parameter κ^{-1} of the electric double layers was in every case very much smaller than the bubble radius a ($a\kappa \approx 500$ for the smallest bubbles used), and the electrophoretic mobility was of the form $m_0 + m_1 a$, where m_0 and m_1 depended on the electric field strength, and m_0 and $m_1 a$ were of comparable magnitudes. In their theory, however, $m_0 = 0$, and the other available theory for very thin double layers on bubbles (Baygents & Saville 1991) gives $m_1 = 0$.

In this paper, § 2 describes the adsorption kinetics and § 3 the fluid mechanics for a slowly adsorbing single surfactant. For carbon dioxide, two chemical species, $CO_2(aq)$ and HCO_3^-, would both have been important in the experiments of Kelsall *et al.* (1996*a*), and the slow reaction is not adsorption but $CO_2(aq) \rightleftharpoons HCO_3^-$. Section 4 gives the theory of that case, § 5 summarizes the experiments, § 6 their implications in the light of the theory in § 4, and § 7 the conclusions.

2. Adsorption/desorption kinetics: one surfactant

As all aqueous solutions considered here are very dilute, we assume that they are ideal, and that the surface excess Γ (mol m^{-2}) of surfactant is far below its saturation value Γ_{sat}. Then the surface pressure Π (N m^{-1}), which is the reduction in surface tension due to the surfactant, obeys $\Pi = RT\Gamma$. If axial symmetry is assumed, the surfactant transfer around a spherical bubble of radius a obeys

$$\frac{\partial \Gamma}{\partial t} + \frac{1}{a \sin\theta}\frac{\partial}{\partial \theta}(\Gamma u_\theta \sin\theta) = \frac{D_s}{a^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial \Gamma}{\partial \theta}\right) + j + j_g, \tag{2.1}$$

where D_s is the surface diffusivity of surfactant, and j, j_g (mol m^{-2} s^{-1}) are the fluxes from the liquid and gas phases to the surface, given by

$$j = +D\frac{\partial c}{\partial r} = k\,(hc - \Gamma), \tag{2.2}$$

$$j_g = -D_g\frac{\partial c_g}{\partial r} = k_g(h_g c_g - \Gamma), \tag{2.3}$$

where the subscript g indicates the gas phase, D, D_g are the bulk-phase diffusivities, k, k_g are the desorption rate constants (s^{-1}) of the surfactant, c, c_g are the surfactant concentrations (mol m^{-3}), h and h_g are the adsorption depths (m) defined by the equilibrium values of $\lim_{c\to 0}(\Gamma/c)$ and $\lim_{c_g \to 0}(\Gamma/c_g)$, R is the gas constant, and T is the absolute temperature. Ignoring slowness of adsorption is equivalent to replacing (2.2) and (2.3) by $j = D\partial c/\partial r$, $j_g = -D_g \partial c_g/\partial r$, $\Gamma = hc = h_g c_g$, and $k = k_g = \infty$.

We also use the chemists' notation pH $= -\log_{10}([H^+]/\text{mol L}^{-1})$, and [X] for the concentration of X. In an aqueous solution [X] is $c/1000$, in a gas it is p_g/p_a, where p_g is the partial pressure; p_a is 101.325 kPa in Bard, Parsons & Jordan (1985), 100 kPa in Lide (2006).

Various authors use various notation for our adsorption parameters. Many use Γ_∞ for Γ_{sat}, but we use the subscript ∞ for equilibrium conditions in the liquid far from the bubble or in the external air; our $\Gamma_\infty = hc_\infty = h_g c_{g\infty}$. The present k, h and the adsorption speed V of Harper (2004) are given in terms of k^a, k^d of Chang & Franses (1995), or k_a, β of Cuenot, Magnaudet & Spennato (1997), or k_{ad}, k_{des}, K_H of Dukhin, Miller & Loglio (1998), by

$$k = k^d = \beta k_a = k_{des}, \tag{2.4}$$

$$h = k^a/k^d = \Gamma_{sat}/\beta = k_{ad}/k_{des} = K_H, \tag{2.5}$$

$$V = kh = k^a = k_a \Gamma_{sat} = k_{ad} = k_{des}K_H. \tag{2.6}$$

	h_g	h	Abundance	Π_∞
Units	nm	nm	% by volume	$\mu\mathrm{N\,m}^{-1}$
Gas				
O_2	0.769	25	20.9	16
N_2	0.824	51	78.1	65
Ar	0.829	36	0.934	0.78
CO_2	7.69	8.53	0.0376	0.29

TABLE 1. Data for gases in air at water surfaces at 25 °C. For CO_2 the table gives $h_g = \Pi/RTc_g$, $h = \Pi/RTc_{CO_2}$, where all four of adsorbed CO_2, H_2CO_3, HCO_3^- and CO_3^{2-}contribute to Π, but only $CO_2(g)$ to c_g, and only dissolved $CO_2(aq)$ to c_{CO_2}.

Table 1 gives data for some common gases in air, from Bard *et al.* (1985), Lide (2006), and Turkevich & Mann (1990) whose τ is our $-h_g$. Values of k and k_g appear not to be known for any of the gases, but are probably very large except for CO_2; see below.

3. Low internal Péclet number: one surfactant

3.1. *Mass transfer*

Levich (1962) dealt with slow adsorption in § 74, and with surfactant transport outside and on the surface but not inside in § 75, and Harper (1972) considered a surfactant both inside and outside, but ignored slowness of adsorption. If the Péclet numbers $Pe_g = 2Ua/D_g \ll 1$ and $Pe = 2Ua/D \ll 1$, he showed that external surfactant transport is much less than internal if $D_g/h_g \gg D/h$. For bubbles with $Pe_g \ll 1$ but $Pe \gg 1$, external transport is still negligible if $D_g/h_g \gg Pe^{1/2}D/h$. That still holds for a bubble in water if $h_g < 100h$ because D_g is of order $10^4 D$, so $Pe_g \ll 1$ implies that $Pe^{1/2} \ll 100$. Because D_s is of the same order as D, we may also ignore surface diffusion for bubbles with $a > h$.

We may then ignore j and the term in D_s in (2.1), and in a steady state we may also put $\partial\Gamma/\partial t = 0$. If $Pe_g \ll 1$ and $Re = 2Ua\rho/\eta \ll 1$, where ρ, η are the liquid density and dynamic viscosity, Levich (1962, § 74–75) showed that c_g and Γ both remain close to their mean values, and the difference is proportional to $\cos\theta$, while the surface velocity u_θ is proportional to $\sin\theta$. Hence there are constants Π_0, Π_1, c_1, u_1 such that

$$\Pi = \Pi_0 + \Pi_1 \cos\theta = RT\Gamma, \tag{3.1}$$

$$c_g = c_0 + c_1(r/a)\cos\theta, \tag{3.2}$$

$$u_\theta = u_1 \sin\theta. \tag{3.3}$$

Terms independent of θ in (2.1) give $\Pi_0 = RTh_g c_0$, so $\Pi_0 = \Pi_\infty$ if the mean surfactant concentration inside the bubble is the same as in the ambient air. It is not obvious whether it is; the point is taken up later. Terms in $\cos\theta$ give

$$2u_1\Pi_0 = -D_g RT c_1. \tag{3.4}$$

Terms involving higher powers of $\cos\theta$ are negligible.

3.2. *Fluid mechanics*

At a Reynolds number $Re \ll 1$ we may write the stream function ψ of the flow relative to the bubble as

$$\psi = \begin{cases} \dfrac{Ua^2}{2}\left[\left(\dfrac{r^2}{a^2} - \dfrac{a}{r}\right) - \alpha\left(\dfrac{r}{a} - \dfrac{a}{r}\right)\right]\sin^2\theta & \text{if } r \geqslant a, \\ \dfrac{Ua^2\alpha_g}{2}\left(\dfrac{r^4}{a^4} - \dfrac{r^2}{a^2}\right)\sin^2\theta & \text{if } r \leqslant a, \end{cases} \tag{3.5}$$

for some dimensionless constants α, α_g. If the tangential velocity u_θ and the shear stress τ are given on the surface $r = a$ in the liquid phase by u_s, τ_s, and in the gas phase by u_{gs}, τ_{gs}, and η_g is the internal dynamic viscosity, then

$$u_{gs} = \alpha_g U \sin\theta, \tag{3.6a}$$

$$u_s = \left(\tfrac{3}{2} - \alpha\right)U \sin\theta = u_{gs}, \tag{3.6b}$$

$$\tau_{gs} = 3\eta_g\alpha_g(U/a)\sin\theta, \tag{3.6c}$$

$$\tau_s = 3\eta(\alpha - 1)(U/a)\sin\theta = \tau_{gs} + (1/a)(\partial\Pi/\partial\theta). \tag{3.6d}$$

The Stokeslet contribution to ψ, i.e. the term in $r\sin^2\theta$ for $r \geqslant a$ in (3.5), comes from the resultant force on the bubble. Hence, if ρ_g is the internal density,

$$\alpha = \frac{(\rho - \rho_g)ga^2}{3U\eta}. \tag{3.7}$$

3.3. *Consequences*

If the mass-transfer slowness $S\,(\mathrm{s\,m^{-1}})$ and effective interior viscosity $\eta_S\,(\mathrm{Pa\,s})$ are defined by

$$S = \frac{2}{3}\left\{\frac{h_g}{D_g} + \frac{1}{ak_g}\right\}, \tag{3.8}$$

$$\eta_S = \eta_g + S\Pi_0, \tag{3.9}$$

then equations (2.1), (2.3), (3.6) and (3.7) lead to

$$u_1 = \frac{U\eta}{2(\eta + \eta_S)}, \tag{3.10}$$

$$\Pi_1 = -3u_1 S\Pi_0, \tag{3.11}$$

$$U = \frac{2(\rho - \rho_g)ga^2(\eta + \eta_S)}{3\eta(2\eta + 3\eta_S)}. \tag{3.12}$$

Equations (3.8), (3.9) and (3.12) show that at low internal Péclet number, U may be quite sensitive to the adsorption speed, unlike the stagnant-cap case (Harper 2004). In a pure liquid, $\eta_S = \eta_g$, and U is the classical Rybczyński–Hadamard result, but when a surfactant is present, (3.12) extends various known special cases (Dukhin *et al.* 1998) to allow for slow adsorption/desorption and interior convective diffusion.

For the atmospheric gases Ar, N_2 and O_2, the values of Π_∞ and h_g are so small and of k_g are so large that $\eta_S \approx \eta_g$, i.e. these gases are ineffective as surfactants. The same is true of CO_2 if the surface pressure is mainly due to the gas CO_2(g) and its unreacted solution CO_2(aq), but not if the surface pressure of HCO_3^- is important, because of the slowness of reactions between it and CO_2(aq). This matter is taken up in the next section.

4. Carbon dioxide: two surfactants, only one in the gas phase

Carbon dioxide exists in aqueous solution in four forms, $CO_2(aq)$, HCO_3^-, H_2CO_3 and CO_3^{2-}, but the weakly acidic solutions of Kelsall *et al.* (1996*a*) would have contained such small concentrations of the latter two that we may ignore them, even though H_2CO_3 is an intermediate product in the reversible reactions between $CO_2(aq)$ and HCO_3^-. Pocker & Bjorkquist (1977) studied these reactions; the two main ones and their rate constants at 25 °C are

$$CO_2(aq) + H_2O \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} HCO_3^- + H^+, \tag{4.1}$$

$$CO_2(aq) + OH^- \underset{k_{-2}}{\overset{k_{+2}}{\rightleftharpoons}} HCO_3^-; \tag{4.2}$$

$$k_{+1} = 1.8 \times 10^{-2}\ \mathrm{s^{-1}}, \tag{4.3}$$

$$k_{-1} = k_{H^+}[H^+], \tag{4.4}$$

$$k_{H^+} = 4.1 \times 10^{4}\ \mathrm{L\ mol^{-1}\ s^{-1}}, \tag{4.5}$$

$$k_{+2} = k_{OH^-}[OH^-], \tag{4.6}$$

$$k_{OH^-} = 6.0 \times 10^{3}\ \mathrm{L\ mol^{-1}\ s^{-1}}, \tag{4.7}$$

$$k_{-2} = 1.4 \times 10^{-4}\ \mathrm{s^{-1}}, \tag{4.8}$$

where k_{H^+}, k_{OH^-} are from Pocker & Bjorkquist (1977), and k_{+1}, k_{-2} were calculated from the equilibrium constants K_1, K_2 of reactions (4.1), (4.2), which were themselves deduced (personal communication, G. H. Kelsall) from Bard *et al.* (1985):

$$K_1 = \frac{k_{+1}}{k_{H^+}} = \frac{[HCO_3^-][H^+]}{[CO_2(aq)]} = 4.33 \times 10^{-7}\ \mathrm{mol\,L^{-1}}, \tag{4.9}$$

$$K_2 = \frac{k_{OH^-}}{k_{-2}} = \frac{[HCO_3^-]}{[OH^-][CO_2(aq)]} = 4.29 \times 10^{7}\ \mathrm{L\,mol^{-1}}, \tag{4.10}$$

$$K_1/K_2 = [H^+][OH^-] = 1.01 \times 10^{-14}\ \mathrm{mol^2\ L^{-2}}. \tag{4.11}$$

From (4.1)–(4.8), the overall rate constants k_+ for $CO_2(aq) \rightarrow HCO_3^-$ and k_- for $HCO_3^- \rightarrow CO_2(aq)$ are $k_+ = k_{+1} + k_{+2}$ and $k_- = k_{-1} + k_{-2}$.

We now modify the analysis of § 3 to include the effects of finite k_- and k_+ and account for adsorbed CO_2 and HCO_3^- but with only $CO_2(g)$ inside the bubble. Let the surface concentrations of CO_2 and HCO_3^- be Γ_{CO_2} and $\Gamma_{HCO_3^-}$. As CO_2 is the only volatile species, and its partial pressure p_g is very small, we use $c_g = p_g/RT$ for its concentration in the gas phase, and c_{CO_2} in the liquid phase. We assume equilibrium at the surface between dissolved and adsorbed CO_2 and HCO_3^- separately, i.e. $\Gamma_{CO_2} = h_{CO_2}c_{CO_2}$, $\Gamma_{HCO_3^-} = h_{HCO_3^-}c_{HCO_3^-}$, and a reversible reaction between adsorbed CO_2 and HCO_3^- with rate constants k_{s+}, k_{s-} not necessarily equal to the bulk-solution values k_+, k_-. We also assume for simplicity that variations with time may be ignored, and that the reaction $CO_2(g) \rightleftharpoons CO_2(aq)$ is instantaneous. (In § 3 the slow reaction was assumed to be at the bubble surface; now slow reactions are considered both there and in the bulk liquid.) As c_{CO_2} and c_g are both measured in $\mathrm{mol\,m^{-3}}$, the equilibrium constant deduced from the Gibbs energies of formation of $CO_2(g)$ and $CO_2(aq)$ (Bard *et al.* 1985) is the dimensionless partition coefficient

$$K = c_{CO_2}/c_g = 0.90. \tag{4.12}$$

In the absence of added acid or alkali, electroneutrality implies

$$[\mathrm{H}^+] = [\mathrm{OH}^-] + [\mathrm{HCO}_3^-], \tag{4.13}$$

so that pH < 7, and in equilibrium, (4.9), (4.10) and (4.13) lead to

$$p_g = \frac{1000RT}{K}\left(\frac{[\mathrm{H}^+]^2}{K_1} - \frac{1}{K_2}\right). \tag{4.14}$$

The dimensionless total solubility s is

$$s = \{c_{\mathrm{CO}_2} + c_{\mathrm{HCO}_3^-}\}/c_g = K(k_- + k_+)/k_- > K. \tag{4.15}$$

Lide (2006) implies $s = 0.83 < K$, but the true value will turn out to be unimportant for our purposes, especially as $k_+ < 0.2k_-$ in the experiments. In equilibrium,

$$k_{s+}\Gamma_{\mathrm{CO}_2} = k_{s-}\Gamma_{\mathrm{HCO}_3^-}, \tag{4.16}$$

$$k_+ c_{\mathrm{CO}_2} = k_- c_{\mathrm{HCO}_3^-}, \tag{4.17}$$

$$\therefore\ h_{\mathrm{CO}_2}k_{s+}/k_+ = h_{\mathrm{HCO}_3^-}k_{s-}/k_-; \tag{4.18}$$

$$\Gamma_{\mathrm{CO}_2} + \Gamma_{\mathrm{HCO}_3^-} = \Gamma = h_g c_g = h_{\mathrm{CO}_2}c_{\mathrm{CO}_2} + h_{\mathrm{HCO}_3^-}c_{\mathrm{HCO}_3^-} \tag{4.19}$$

$$= (h_{\mathrm{CO}_2} + h_{\mathrm{HCO}_3^-}k_+/k_-)c_{\mathrm{CO}_2}, \tag{4.20}$$

$$h_g = \frac{s(h_{\mathrm{CO}_2}k_- + h_{\mathrm{HCO}_3^-}k_+)}{k_- + k_+}. \tag{4.21}$$

Note that (4.18) implies that if $k_{s+} = k_+$ and $k_{s-} = k_-$ then $h_{\mathrm{CO}_2} = h_{\mathrm{HCO}_3^-}$; the values of k_{s+}, k_{s-}, h_{CO_2} and $h_{\mathrm{HCO}_3^-}$ are, however, generally unknown. The surface transport equations become

$$\frac{1}{a\sin\theta}\frac{\partial}{\partial\theta}\left\{\Gamma_{\mathrm{CO}_2}u_\theta\sin\theta\right\} = +k_{s-}\Gamma_{\mathrm{HCO}_3^-} - k_{s+}\Gamma_{\mathrm{CO}_2} - D_g\frac{\partial c_g}{\partial r}, \tag{4.22}$$

$$\frac{1}{a\sin\theta}\frac{\partial}{\partial\theta}\left\{\Gamma_{\mathrm{HCO}_3^-}u_\theta\sin\theta\right\} = -k_{s-}\Gamma_{\mathrm{HCO}_3^-} + k_{s+}\Gamma_{\mathrm{CO}_2}, \tag{4.23}$$

$$\therefore\ \frac{1}{a\sin\theta}\frac{\partial}{\partial\theta}\left\{\Pi u_\theta\sin\theta\right\} = -D_g RT\frac{\partial c_g}{\partial r}. \tag{4.24}$$

The analogue of (3.1) is the set of equations

$$2\Pi_{\mathrm{CO}_2} = RT\Gamma_{\mathrm{CO}_2} = \Pi_{\mathrm{CO}_2,0} + \Pi_{\mathrm{CO}_2,1}\cos\theta, \tag{4.25}$$

$$\Pi_{\mathrm{HCO}_3^-} = RT\Gamma_{\mathrm{HCO}_3^-} = \Pi_{\mathrm{HCO}_3^-,0} + \Pi_{\mathrm{HCO}_3^-,1}\cos\theta, \tag{4.26}$$

$$\Pi = RT\Gamma = \Pi_0 + \Pi_1\cos\theta = \Pi_{\mathrm{CO}_2} + \Pi_{\mathrm{HCO}_3^-}. \tag{4.27}$$

Equations (3.2) and (3.3) remain unchanged. Terms independent of θ now give

$$k_{s+}\Pi_{\mathrm{CO}_2,0} = k_{s-}\Pi_{\mathrm{HCO}_3^-,0}, \tag{4.28}$$

while terms in $\cos\theta$ give the mass-transfer slowness S as

$$S = \frac{2}{3}\left\{\frac{h_g(k_{s-} + k_{s+})}{D_g k_{s-}} + \frac{k_{s+}}{k_+}\left(\frac{k_-}{k_{s-}}\right)^2\frac{k'}{a}\right\}, \tag{4.29}$$

where

$$k' = \frac{k_+}{k_-(k_- + k_+)}. \tag{4.30}$$

Equations (3.9)–(3.12) remain unchanged if one uses the value of S given by (4.29), which is the two-surfactant analogue of (3.8).

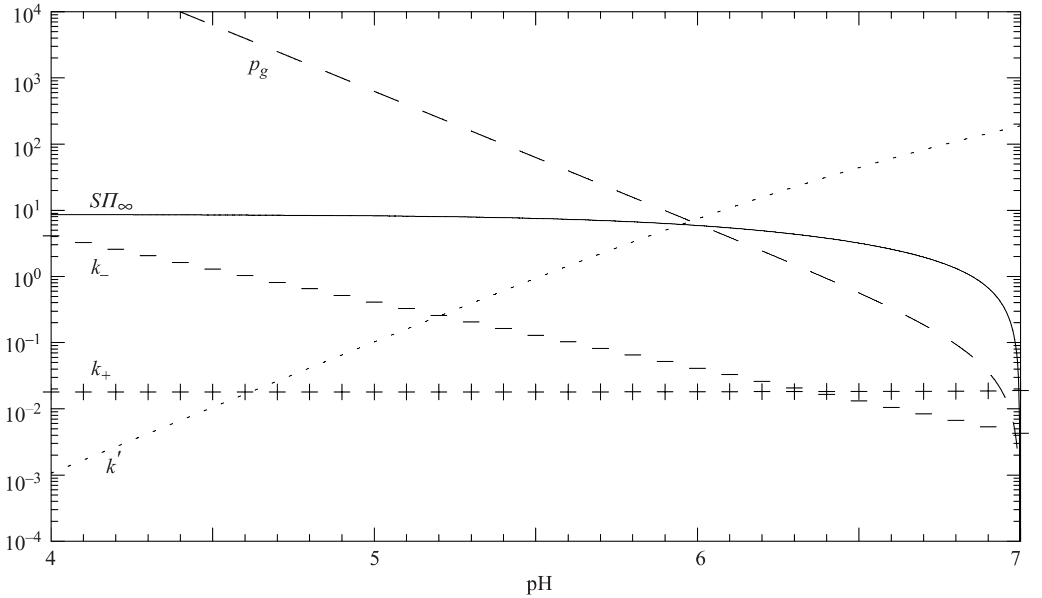

FIGURE 1. Rate constants, $S\Pi_\infty$ and p_g for acidic CO_2 solutions if $k_{s+} = k_+$, $k_{s-} = k_-$, $a = 40\ \mu\text{m}$, in terms of pH. $+$, k_+/s^{-1}; $-$, k_-/s^{-1}; solid curve, $S\Pi_\infty/(\text{m Pa s})$; dashed curve, $p_g/\text{Pa} \approx 10^5 p_g/p_a$; dotted curve, k'/s.

The term involving h_g in (4.29) is negligible if the bubbles are small enough for our low-*Re* theory to apply and if k_{s-}, k_{s+} are of magnitudes similar to k_-, k_+, so S then depends only on a and the rate constants. Figure 1 plots these variables against pH: $S\Pi_\infty$ (for $a = 40\ \mu\text{m}$), p_g, k_+, k_-, and k', which is close to $\frac{3}{2}Sa$ if $k_{s+} = k_+$, $k_{s-} = k_-$.

5. Experiments

If bubbles in water are small enough for low-*Re* theory to apply, they will rise as if they were rigid spheres unless the value of Π_∞ is extraordinarily low, so the system purity must be very high. Kelsall *et al.* (1996*a*,*b*) achieved that with oxygen bubbles ($T = 298$ K, $\eta_g = 20.6\ \mu\text{Pa s}$), rising between plane electrodes 7 to 9 mm apart that were perforated to let the bubbles pass through, in a cell about 30 mm in diameter filled with a $10^{-4}\ \text{mol L}^{-1}$ solution of $NaClO_4$ ($\eta = 895\ \mu\text{Pa s}$).

To purify the system they purged it for 3 hours with a swarm of microbubbles (Scott 1975). When the cell was sealed from the laboratory atmosphere, all bubbles with diameters from 30 to 110 μm were reported to rise at the speed U_p expected in a pure liquid if $Re \ll 1$, e.g. for $d = 80\ \mu\text{m}$, $U = U_p = 5.16\ \text{mm s}^{-1}$, so that $Re = 0.46$. Nobody else seems to have reported experiments with bubbles that rose at low Reynolds numbers in water or dilute aqueous solutions as if the liquid was pure.

For the present purpose, the particularly interesting part of Kelsall *et al.*'s work is what happened when they opened their cell to the atmosphere after purging. Over the next 19 hours, U for bubbles with $a = 40\ \mu\text{m}$ reduced, rapidly at first then gradually, from $5.16\ \text{mm s}^{-1}$ to $4.02\ \text{mm s}^{-1}$. Then U increased over the following 7 hours to $4.19\ \text{mm s}^{-1}$. That suggests that the concentration of airborne surfactant varied during the day, but does not show what it was.

6. Implications

One cannot just assume Stokes flow with $\eta_g = 0$ and $\rho_g = 0$ when applying the foregoing theory: that would give $U_p = 5.83$ mm s^{-1}. The actual values of η_g, ρ_g and Re would give 5.30 mm s^{-1} in an infinite liquid, which removes much of the discrepancy with the experimental 5.16 mm s^{-1}. The remaining 3% is understandable because the precision attained in the measurement of U was ± 1% and the bubble diameter was about 2% of the distance to the nearest solid boundary. We therefore use $U_p = 5.16$ mm s^{-1}.

When U reduced to 4.02 mm s^{-1}, (3.12) implies that $\eta_S = 1.475\eta = 1.32$ mPa s. In Kelsall's laboratory, CO$_2$ was 0.0376% of the air (personal communication, G. H. Kelsall). From table 1, $\Pi_\infty = 0.29$ μN m^{-1}, and (4.14) gives pH = 5.61 when the apparatus was opened. The theory leading to (4.29) then gives $S = 2.48 \times 10^4$ s m^{-1} if $k_{s+} = k_+$ and $k_{s-} = k_-$, but (3.9) and the experimental values of η_S and η_g imply that $S = 4.55 \times 10^3$ s m^{-1} if $\Pi_\infty = \Pi_0$: 18% of the theoretical result. When U rose again to 4.19 mm s^{-1}, the experimental η_S decreased to 0.86 mPa s and S to 2.97×10^3 s m^{-1}: 12% of the theoretical result.

Because $S\Pi_\infty$ varies little with pH and hence c_g if pH < 5.7 (8.57 mPa s at pH 4 to 7.04 mPa s at pH 5.7) the explanation cannot be simply a poor estimate of the CO$_2$ abundance. One might imagine that c_g inside the bubbles was only about 18% of its value in the ambient air, so $\Pi_0 = 0.18\Pi_\infty$ because the bubbles were still absorbing CO$_2$ from solution. If so, bubbles would be gradually slowing down as they rose. Kelsall *et al.* (1996*a*) would have detected that because they measured the speed of each bubble twice, at different heights. Also, that does not explain why after several more hours c_g had reduced even more, to 12% of its value in the ambient air, instead of rising to a value nearer 100%.

A more likely possibility is another gas as well as CO$_2$ dissolving in water to form an acid, HX say. Even if HX is not surface-active and ionises instantaneously, (4.13) would still need to change, to $[\mathrm{H}^+] = [\mathrm{OH}^-] + [\mathrm{HCO}_3^-] + [\mathrm{X}^-]$, and (4.14) would become

$$p_g = \frac{1000RT}{K}\left(\frac{[\mathrm{H}^+]^2}{K_1} - \frac{1}{K_2} - \frac{[\mathrm{H}^+][\mathrm{X}^-]}{K_1}\right). \tag{6.1}$$

That would increase [H$^+$] and reduce pH at any given value of the partial pressure p_g of CO$_2$, which would reduce k' and hence reduce the effect of CO$_2$ on the speed of bubble rise. The observed time dependence of the speed U would then suggest a diffusivity of HX or X$^-$ lower than that of CO$_2$(aq) or HCO$_3^-$.

Surface-active dust settling on the water seems an unlikely cause of the variations in bubble speed, as its effect would be monotonic in time. Temperature variation is also an unlikely cause: Kelsall *et al.* (1996*a*) kept the temperature constant in their apparatus, and heat is a very ineffective surfactant (Harper *et al.* 1967).

If the rate constants k_{s+}, k_{s-} for adsorbed CO$_2$ $\rightleftharpoons$ HCO$_3^-$ had values different from their bulk-solution values, S in (4.29) would be multiplied by $(k_{s+}/k_+)(k_-/k_{s-})^2$. That might explain one of the experimental S values, but not both.

There must have been a vertical gradient of surfactant concentration in the liquid when the apparatus was first opened, making the surface tension then lowest at the top. That would speed the bubbles up (Young, Goldstein & Block 1959), but after some hours the concentration would become uniform and the vertical gradient would disappear. This was probably the case when U reached 4.02 mm s^{-1}, and if a re-established vertical gradient was the reason for the subsequent rise to 4.19 mm s^{-1}, it must have been because the air was then less polluted than it was initially.

7. Conclusions

Although atmospheric carbon dioxide causes very small changes in surface tension, this is more than enough to affect the behaviour of bubbles because of the slowness of the reaction between CO_2 and HCO_3^-. Our theory suggests that the effect of CO_2 should have been larger than was observed. A possible cause is an acid air pollutant in addition to the carbon dioxide. Kelsall *et al.* (1996*a*, *b*) did two experiments in sealed apparatus, which if repeated in apparatus opened to the air (or with known CO_2 concentrations) would help elucidate the problems: measuring pH in the liquid, and using bubbles of various diameters less than 80 μm, which is near the upper limit for Stokes flow to be a good approximation.

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REFERENCES

Bard, A. J., Parsons, R. & Jordan, J. (Ed.) 1985 *Standard Potentials in Aqueous Solution*. Marcel Dekker.

Baygents, J. C. & Saville, D. A. 1991 Electrophoresis of drops and bubbles. *J. Chem. Soc. Faraday Trans.* **87**, 1883–1898.

Chang, C.-H. & Franses, E. I. 1995 Adsorption dynamics of surfactants at the air/water interface: a critical review of mathematical models, data, and mechanisms. *Colloids Surfaces* A **100**, 1–45.

Cuenot, B., Magnaudet, J. & Spennato, B. 1997 The effects of slightly soluble surfactants on the flow around a spherical bubble. *J. Fluid Mech.* **339**, 25–53.

Dukhin, S. S., Miller, R. & Loglio, G. 1998 Physico-chemical hydrodynamics of rising bubble. In *Drops and Bubbles in Interfacial Research* (ed. D. Möbius & R. Miller), pp. 367–432. Elsevier.

Harper, J. F. 1972 The motion of bubbles and drops through liquids. *Adv. Appl. Mech.* **12**, 59–129.

Harper, J. F. 2004 Stagnant-cap bubbles with both diffusion and adsorption rate-determining. *J. Fluid Mech.* **521**, 115–123.

Harper, J. F., Moore, D. W. & Pearson, J. R. A. 1967 The effect of the variation of surface tension with temperature on the motion of bubbles and drops. *J. Fluid Mech.* **27**, 361–366.

Kelsall, G. H., Tang, S. Y., Smith, A. L. & Yurdakul, S. 1996*a* Measurement of rise and electrophoretic velocities of gas bubbles. *J. Chem. Soc. Faraday Trans.* **92**, 3879–3885.

Kelsall, G. H., Tang, S. Y., Yurdakul, S. & Smith, A. L. 1996*b* Electrophoretic behaviour of bubbles in aqueous electrolytes. *J. Chem. Soc. Faraday Trans.* **92**, 3887–3893.

Levich, V. G. 1962 *Physicochemical Hydrodynamics*. Prentice-Hall.

Lide, D. R. (Ed.) 2006 *CRC Handbook of Chemistry and Physics*, 87th edn. CRC Press.

Pocker, Y. & Bjorkquist, D. W. 1977 Stopped-flow studies of carbon dioxide hydration and bicarbonate dehydration in H_2O and D_2O. Acid-base and metal ion catalysis. *J. Am. Chem. Soc.* **99**, 6537–6543.

Scott, J. C. 1975 The preparation of water for surface-clean fluid mechanics. *J. Fluid Mech.* **69**, 339–351.

Turkevich, L. A. & Mann, J. A. 1990 Pressure dependence of the interfacial tension between fluid phases. 2. Application to liquid-vapor interfaces and to interfaces of amphiphilic solutions. *Langmuir* **6**, 457–470.

Young, N. O., Goldstein, J. S. & Block, M. J. 1959 The motion of bubbles in a vertical temperature gradient. *J. Fluid Mech.* **6**, 350–356.