

De-Gassed Water Is a Better Cleaning Agent

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It is demonstrated that de-gassed water is more effective at dispersing hydrophobic “dirt”, such as liquid hydrocarbons or oils. This effect appears to be due to the reduction of natural cavitation, which would otherwise oppose the dispersion of hydrophobic liquid droplets into water. De-gassing of the oil enhances this effect still further, and this has led to a proposal for a novel cleaning process, based on using a combination of a de-gassed (hydrophobic) solvent followed by rinsing in de-gassed water. This method might be useful as an effective, detergent-free cleaning process. Also reported are some initial studies which suggest that the effect of “inert” dissolved gases on the electrical conductivity of water may need to be reconsidered.

Introduction

The fundamental reason oil molecules do not dissolve in water is because hydrocarbon (as well as fluorocarbon, chlorohydrocarbon, and silicone) molecules are nonpolar and so cannot replace the strong water–water bonds, broken to incorporate the solute molecule, with equally strong water–solute bonds. For hydrocarbon molecules to be dissolved in water, the water molecules have to be forced apart, and these (water) molecules then form icelike clusters around the hydrocarbon. The larger the hydrocarbon molecule the more water molecules disrupted and so the lower the solubility. For example, heptane is slightly soluble in water but the larger molecule dodecane is almost completely insoluble. Because of this unfavorable disruption of water, two (or more) hydrocarbon molecules will experience a short-range attractive force, caused by the favorable release of these affected water molecules back into their bulk state. Hydrocarbon molecules are, therefore, forced together and “bond” in water. This bond is called the hydrophobic bond.¹ The same factors explain why polar materials, such as sugars, alcohol, and salts, are readily soluble in water, because these solutes interact favorably with the surrounding water molecules. The presence in water of significant levels (millimolar) of dissolved nonpolar hydrophobic gas molecules, oxygen and nitrogen, from the atmosphere, is often ignored.

However, molecular solutions are not the only state for mixing phases. In nature many insoluble materials are “dispersed” in water in a finely divided form, as a colloidal solution, such as biological cells in blood, clay particles in river water, and oil/water emulsions. In each case, microscopic particles of one phase are stabilized in water, usually by repulsive electrostatic forces, which can overcome the ubiquitous attractive, van der Waals (vdw) force.² Over 20 years ago another important, long-range attractive force was discovered, acting between hydrophobic particles in water. This force was called the long-range hydrophobic interaction.³ The unexpected strength and range

of this force have made a proper theoretical explanation difficult, although it is well-accepted that this force is the major cause of instability of hydrophobic colloids in water.⁴ In the past few years many experimental studies have provided strong evidence in support of an explanation related to the presence of dissolved gas in water.^{4–6} Even in some of the early studies⁷ there was already strong experimental evidence for the formation of vapor- or gas-filled bridges created as two hydrophobic surfaces were separated in water. Further evidence for this effect was obtained recently in a study of the effect of complete de-gassing on the dispersion of oil droplets (and fine Teflon powder) in water.⁸ De-gassing appears to facilitate the dispersion of oils and finely divided hydrophobic solids, without the need for common dispersants, such as polymers and surfactants. However, gassing levels do not appear to affect the stability of the emulsions, once formed.^{8,9}

The relatively low level of dissolved gas present in water at room temperature, of about 1 mM (or 20 mL of atmospheric gas per liter) suggests that its influence should be limited to processes involving relatively low (hydrophobic) surface areas. Thus, for micellar¹⁰ solutions and microemulsions,¹¹ the number of dissolved gas molecules is small, relative to the interfacial area available per unit volume of mixture. It is not surprising, therefore, that de-gassing appears not to influence the properties of these systems.

By comparison, the breakaway of oil droplets from a macroscopic oil/water interface and the dispersion of finely divided hydrophobic particles offers a low surface area process which can be influenced by this level of dissolved gas. This is even more the case if dissolved gas molecules accumulate next to oil–water (and hydrophobic particle–water) interfaces, as is expected. Dissolved oxygen and nitrogen (dissolved carbon dioxide is at the much lower level of about 10 μ M) molecules, like hydrocarbons, will disrupt adjacent water molecules because of their nonpolar nature and weak, vdw interaction with water. The presence of macroscopic, hydrophobic surfaces ought to attract these dissolved gas molecules from the water phase, and this accumulation may also be aided by the increased gas solubility in hydrocarbon oils, typically 1 order of magnitude higher than water. The presence of this layer of dissolved gas,

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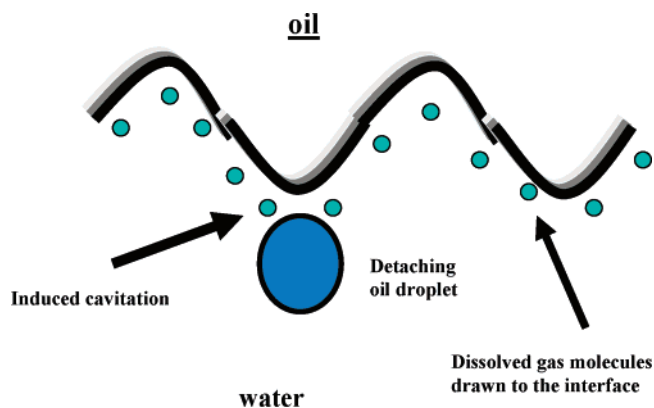


Figure 1. Schematic diagram of the detachment of an oil droplet from an oil/water interface. Dissolved atmospheric gas molecules will be drawn to the interface and assist the cavitation expected as two hydrophobic surfaces separate in water.

in a thin film, which is placed under a negative (suction) pressure during droplet/particle breakaway, apparently causes the nucleation of gas cavities, which will create a bridge between the surfaces and oppose droplet release. Vapor cavitation is expected for the separation of hydrophobic surfaces in water.¹² This situation is illustrated in Figure 1. The precise details of this process are not known, but cavity bridging between the surfaces and an enhanced vdW attraction between the surfaces will both act to hold the surfaces together (see later). Whatever the mechanism, recently reported force measurements between hydrophobic surfaces⁶ and experiments on dispersion^{8,9} clearly demonstrate the dramatic effect of de-gassing.

These recent observations and the mounting evidence that the long-range hydrophobic attraction is removed by de-gassing together act as a basis for the present study of a novel type of water-based cleaning system. Water-based cleaning is effective because hydrophilic, polar solutes, such as sugar and salt (i.e., "dirt") *dissolve* readily in water, which is a good general-purpose solvent. However, hydrophobic dirt, such as charcoal, grease, and oil, is not water-soluble at normal temperatures. To overcome this problem, these materials are *dispersed* in water via a combination of mechanical agitation (during conventional washing) and by the use of added surface-active solutes, such as soaps or detergents (surfactants), which coat hydrophobic materials in water. Surfactant molecules adsorb onto hydrophobic surfaces in water, making them hydrophilic, which enhances dispersion (not solubility) in water, so that they can be carried away in the aqueous phase during cleaning. It is important to realize that mechanical agitation is a vital component of conventional cleaning. Liquid hydrocarbon oils can also be absorbed into micelles formed by these surfactants, facilitating cleaning. The novel cleaning process studied here is analogous to some aspects of normal cleaning, in that the dispersion of hydrophobic dirt (e.g., oils and grease) is achieved by mechanical action, but in this study, de-gassed water is used rather than a detergent solution.

A second part of this work was focused on the issue of which other properties of water may be influenced by dissolved, nonpolar atmospheric gases, in the absence of dissolved carbon dioxide. The levels of these solutes (oxygen and nitrogen), typically at the level of 50 000 water molecules per dissolved gas molecule for water equilibrated with the atmosphere, are so low that for most properties we could expect little effect. However, some properties such as the electrical conductivity of water are extremely sensitive to solutes, especially ions. The natural conductance of "pure" water is based on the transport

of protons and hydroxyl ions largely by water molecule linkages and sequential bond cleavage.¹³ It is known that bulk water contains a network of hydrogen-bonded rings of water molecules and that nonpolar solutes also nucleate surrounding rings, which are not connected to the bulk structures.¹⁴ It is possible, therefore, that the presence of millimolar concentrations of these disrupting solutes might reduce the conductivity of water. Conversely, complete de-gassing might increase the conductivity of water.

It is interesting that, in the classic work of Kohlrausch and Heydweiller¹⁵ in 1894, the commonly accepted literature value¹⁶ for the conductivity of pure water was measured for clean, vacuum-distilled water, which was distilled under only a partial vacuum to facilitate distillation and not to remove dissolved oxygen and nitrogen. In the work reported here we have carried out some initial studies on determining the effect of complete de-gassing on the conductivity of distilled water.

Materials and Methods

Distilled water was produced from tap water via a sequential process of coarse filtration, activated charcoal filtration, reverse osmosis filtration, and finally, distillation into a Pyrex glass storage vessel housed in a laminar-flow, clean-air cabinet. All the chemicals used were of the purest grade commercially available and were used as purchased. Any surfactant contaminants present in the oil samples would actually reduce the differences between the gassed and the de-gassed conditions.

Samples of clean, distilled water were outgassed by a process of repeated freezing in liquid nitrogen, followed by pumping down to a pressure of typically about 0.01 mbar, or less, and then melting in a sealed Pyrex tube. The dissolved gas liberated on each melting cycle was removed on re-freezing. Although this process was carried out five times, typically no further de-gassing on melting was observed after three to four cycles. The vacuum pressure of 0.01 mbar corresponds to a de-gassing level of about 99.999%. This latter value is calculated on the assumption that the final pressure achieved on several cycles of freeze/thaw/pumping is given by the pressure in equilibrium with the final frozen liquid, which on being melted does not give any visible bubbling or outgassing. The de-gassed water was used within minutes after de-gassing. Nonaqueous liquids and mixtures with water were also de-gassed using this method.

This water was used in the cleaning experiments and was also used for the electrical conductivity measurements. Cleaning experiments were carried out on dodecane, squalene, hexamethyldisiloxane, and perfluorohexane in Pyrex glassware. Typically a small, known amount (~0.5 mL) of oil was poured into the bottom of a glass tube, ordinary distilled water and de-gassed water (27–28 mL) were introduced, the tube was sealed and vigorously shaken (typically for 10 s), and the resultant water phase turbidity was measured with time. In some experiments the oil was also de-gassed. Strips of standard filter paper, which had finely divided activated charcoal and carbon black rubbed into its surface to produce a uniform blackened region, were used for testing hydrophobic solid removal. The cleaning effects of distilled, gassed water and de-gassed water were compared by (a) simply pouring the same volume of water onto the dirty paper and (b) vigorously shaking by hand for 10 s with strips immersed in the water. All water transfers were carried out in laminar-flow, filtered-air cabinets.

Electrical conductivity measurements were carried out on ordinary distilled water equilibrated with the atmosphere, in distilled water following bubbling with clean nitrogen gas and in fully de-gassed water. All measurements were performed in

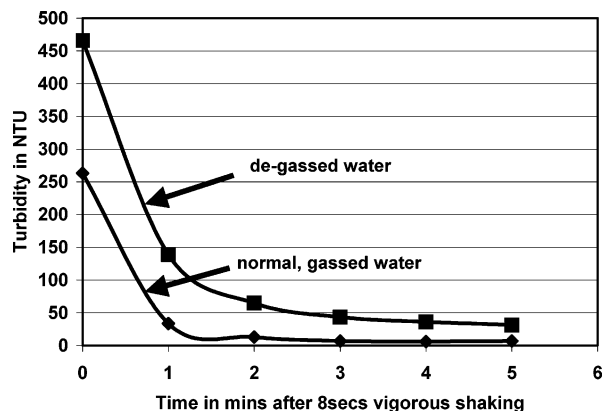


Figure 2. Difference in turbidity of the gassed and de-gassed cleaning water a few seconds after vigorous shaking with (gassed) dodecane "dirt" on glassware.

Pyrex vessels. The change in conductivity with time was also measured for de-gassed water and distilled water equilibrated with the atmosphere, when exposed to gentle bubbling of high-purity nitrogen gas. The temperature of the water was measured, and its pH was monitored. For distilled water, pH values were measured after the addition of a small amount of pure NaCl to stabilize the measuring current of the glass electrode.

Four different types of conductivity meters and cells were used in this study: a Radiometer CDM 80 conductivity meter was used with a three-electrode cell (platinum-black-coated) at a frequency of 50 Hz, and a Lovibond Con 200 conductivity meter and a manual Philips PR 9500 conductivity meter were also used (at 50 Hz) as well as a Radiometer CDM210 with CDC866T probe. The turbidity of the cleaning solutions was measured using an HF Scientific, Micro 100 turbidimeter.

Results and Analysis

Cleaning Experiments. In these rudimentary cleaning experiments with hydrocarbon oils, it was immediately obvious from visual examination that the de-gassed water removed substantially greater amounts of the two oils dodecane and squalene. To quantify these observations turbidity measurements on the rinsing water were obtained for dodecane "cleaned" from Pyrex glassware. These results are given in Figures 2 and 3. The turbidity results indicate that de-gassed water is substantially more effective at dispersion of the (gassed) oil than ordinary water. Also, the difference is persistent; that is, the de-gassed oil droplet dispersions are more stable up to at least 1 h after shaking. The dramatic effects of de-gassing the solvent as well as the water are demonstrated by the results obtained with perfluorohexane cleaning from Pyrex glassware. The results of the comparison between gassed and de-gassed cleaning systems are shown in Figure 4. Clearly, the ability of rinsing water to disperse this oil and, hence, clean is significantly enhanced by de-gassing. Even within 1 min after shaking, the gassed liquids are almost completely phase-separated; that is, large droplets of residual oil are clearly visible on the walls of the glass vessel. By comparison, the de-gassed liquids form a uniform emulsion, as shown in the photograph in Figure 5, and the glass walls are visibly free of residual oil droplets.

Recent studies⁹ on de-gassed hydrocarbon dispersions have shown that the oil droplets are fairly monodisperse and of submicrometer size. The long-term stability of the perfluorohexane dispersion (see Figure 4) indicates that the dense droplets (of density 1.7 g/mL) must also be in this size range. There

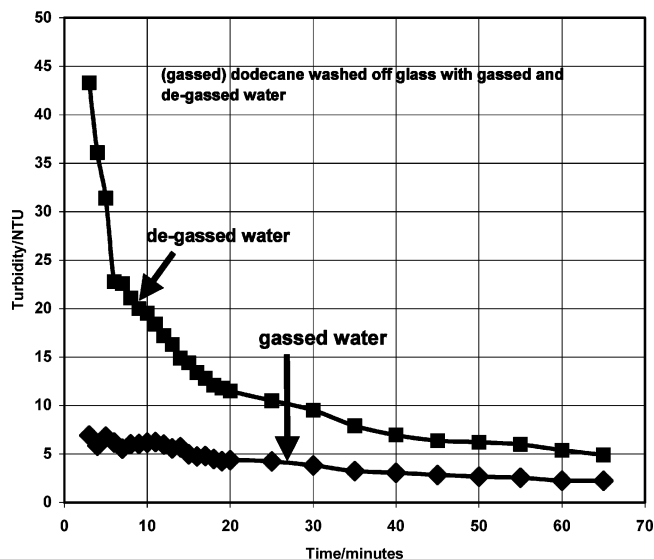


Figure 3. Difference in turbidity of gassed and de-gassed cleaning water minutes after vigorous shaking with (gassed) dodecane "dirt" on glassware.

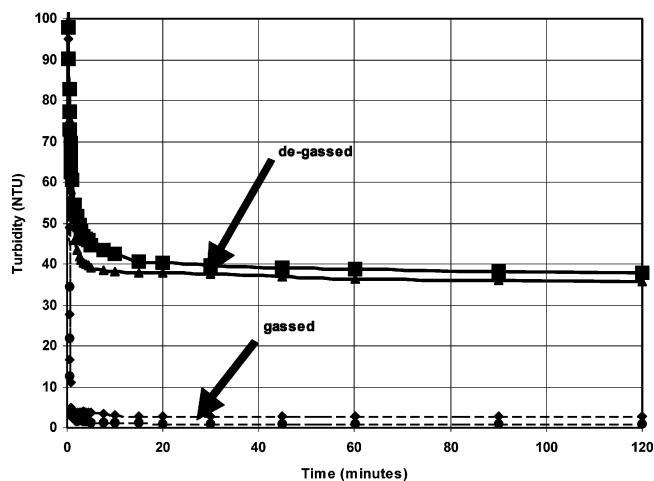


Figure 4. Difference in turbidity of gassed and de-gassed cleaning water minutes after vigorous shaking with de-gassed perfluorohexane "dirt" on glassware.

also must be little or no coalescence, as observed previously;⁹ otherwise, larger droplets would quickly settle and reduce the turbidity.

The dispersion cleaning of glassware using hexamethyldisiloxane was used to demonstrate the enhancement due to de-gassing both oil and water compared with the water de-gassed-only case and the nitrogen-gassed blank. The differences are shown in Figure 6. Although de-gassing the water does enhance removal of the gassed oil, the greatest effect is clearly obtained when the oil is also de-gassed. Once again, no oil droplets were visible on the glass walls when both liquids were de-gassed.

It was also found that de-gassing the aqueous cleaning solution was more effective even for a solution of 0.01 M of the cationic detergent cetyl trimethylammonium bromide (CTAB). This concentration is well above the critical micelle concentration for CTAB of 0.001 M, and the temperature was several degrees above the Krafft temperature of 20 °C. The results obtained using gassed dodecane oil are shown in Figure 7.

It will be argued later that de-gassing is expected to affect the dispersion or cleaning of any particulate materials, solid or liquid, if they are sufficiently hydrophobic. Clearly, the oils used in this study are strongly hydrophobic, but what about common

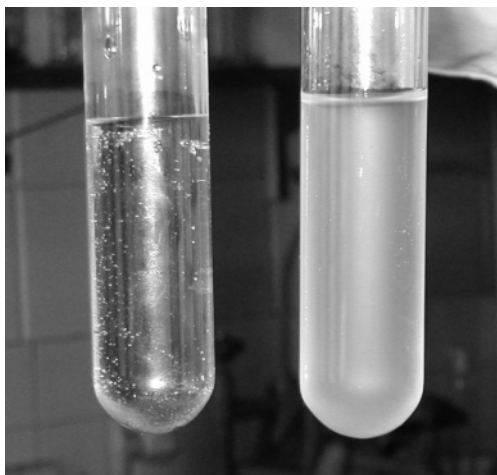


Figure 5. Photograph of the cleaning water 1 min after vigorous shaking with gassed (left-hand side) and de-gassed (right-hand side) cleaning water and perfluorohexane.

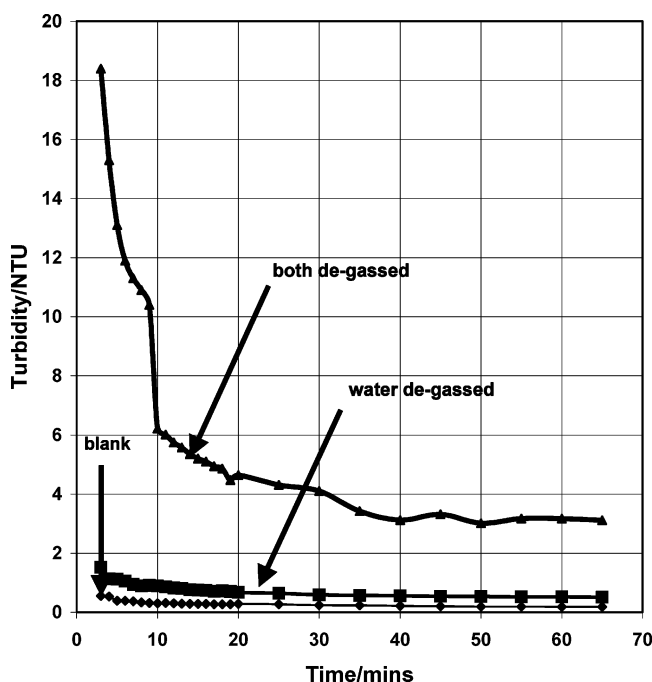


Figure 6. Turbidity of water used to clean hexamethyldisiloxane off glassware using gassed and de-gassed water. The cleaning effect was substantially enhanced by de-gassing the silicone oil as well as the water.

particulate solids? It will be demonstrated later that the important criterion is to have a material with a water contact angle greater than 90° . However, almost all common solid “dirt” particles are not so hydrophobic, as can be seen from Table 1. Cleaning studies were carried out using both de-gassed and gassed water for the removal/cleaning of carbon black, graphite, and activated charcoal from standard cellulose (hydrophilic) filter paper. The results were inconsistent and not very reproducible. It seems likely that the hydrophobicity of these materials is on the borderline and that surface heterogeneity might be important but leads to variable results. In addition, it seems likely that differences in buoyancy of porous fine particles in gassed and de-gassed water leads to some degree of flotation cleaning, which also produces variable results. Unfortunately, very hydrophobic, finely powdered materials were unavailable. For example, finely powdered polypropylene would have been

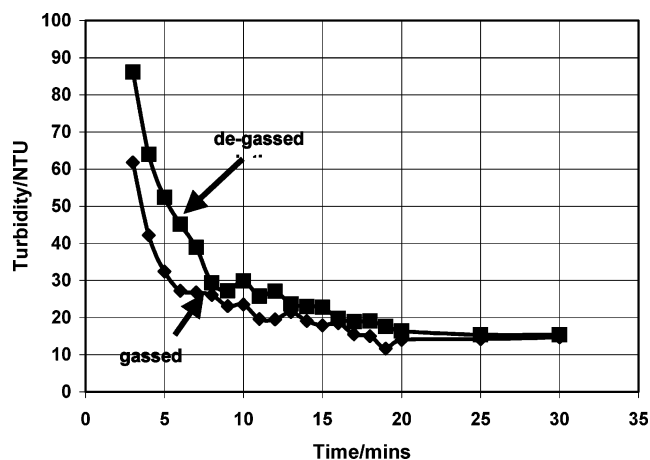


Figure 7. Turbidity of CTAB detergent cleaning solutions after cleaning (gassed) dodecane from glassware. Even with detergents present, de-gassing was found to enhance dispersion into the cleaning solution.

TABLE 1: Water Droplet Contact Angles (Advancing) on Some Common Hydrophobic Solids

Teflon	110°	graphite	86°
polypropylene	110°	activated charcoal	$\sim 80^\circ$
paraffin wax	110°	carbon black	$< 90^\circ$

TABLE 2: Summary of Values for the Electrical Conductivity of Water under Various Conditions^a

conditions	this study	literature values
equilibrated with air	0.9 (pH 5.7)	0.7 ⁽¹⁷⁾
nitrogen gassed	0.07 (22 °C, pH 7.0)	
de-gassed	1.2 (22 °C, pH 7.0)	
standard value—unknown conditions ^b		0.055 (25 °C)

^a Comparison with some literature values. All values are in $\mu\text{S cm}^{-1}$. The temperatures and pH values are given in parentheses. ^b Kohlrausch and Heydweiller¹⁵ (1894) and SI Data book.¹⁶

interesting to study because of its hydrophobicity but it is not readily available or easily produced.

Electrical Conductivity of Distilled Water. The results obtained for the electrical conductivity of water under a range of conditions are summarized in Table 2. These results are compared with standard literature values, with the appropriate conditions under which they were measured. These results clearly demonstrate that de-gassing has a substantial effect on increasing the electrical conductivity of water. Literature values from the SI data book¹⁶ are $0.042 \mu\text{S cm}^{-1}$ at 20°C ($24 \text{ M}\Omega\cdot\text{cm}$) and $0.055 \mu\text{S cm}^{-1}$ at 25°C ($18 \text{ M}\Omega\cdot\text{cm}$). These values are consistent with those measured in the classic work of Kohlrausch and Heydweiller¹⁵ in 1894 who measured a value of $0.06 \mu\text{S cm}^{-1}$ at 25°C . These values are typically obtained for commercial ultrapure water units such as those produced by Millipore. However, these values appear to correspond to the conductivity of water with CO_2 removed but not nonpolar dissolved gases, such as oxygen and nitrogen. Much higher values are obtained for atmospheric, carbon dioxide equilibrated pure water¹⁷ at about $0.75 \mu\text{S cm}^{-1}$. However, the results of 25 different experiments on the de-gassing of distilled water indicate that complete de-gassing causes an increase in conductivity to about $1.2 \pm 0.5 \mu\text{S cm}^{-1}$. The pH of the de-gassed water was found to be 7.0 ± 0.2 , as expected. By comparison, we have found that nitrogen bubbling through either single-distilled water or completely de-gassed water reduces its conductivity to around $0.07 \mu\text{S cm}^{-1}$ at pH 7.0 (see Figure 8). These results, summarized in Figure 9, indicate that nitrogen

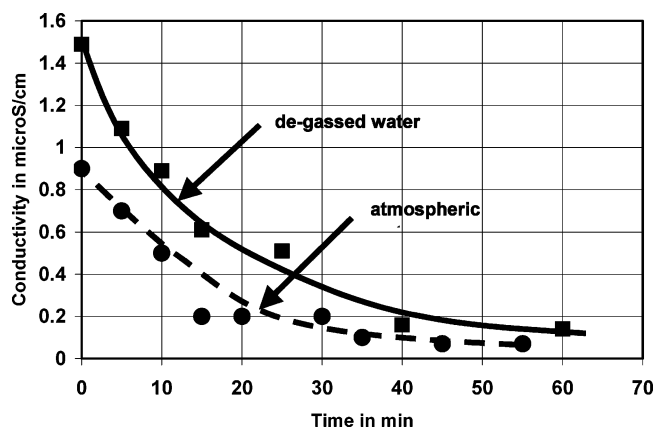


Figure 8. Effect of nitrogen gas purging on the electrical conductivity of de-gassed and ordinary distilled water.

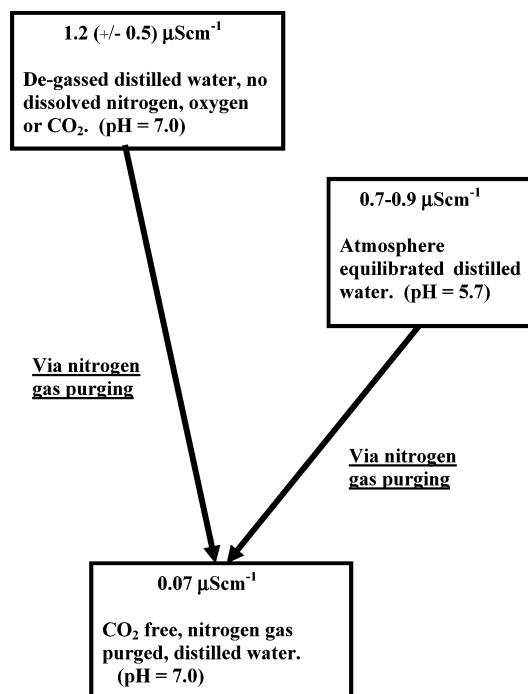


Figure 9. Schematic diagram to illustrate the observed electrical conductivity values for distilled water under various conditions.

purging can reduce the conductivity of even single-distilled water to values close to those accepted in the literature for ultrapure water. Complete de-gassing actually increases the electrical conductivity above the value for atmosphere equilibrated water, which contains dissolved CO_2 . The results in Figure 8 also indicate that the high conductivity values observed for de-gassed water cannot be due to ionic contamination produced during the de-gassing process because lower values are easily generated simply by purging this water with nitrogen gas.

It is interesting that the theoretical conductivity of pure water is often calculated from the equilibrium 10^{-7} M concentration (at 25 °C) and the conductivities at infinite dilution of H_3O^+ and OH^- ions. The ion conductivities of the corresponding electrolyte solutions (NaCl, NaOH, and HCl) would, presumably, have been measured under CO_2 -free nitrogen (i.e., rather than in completely de-gassed solutions) for convenience. Extrapolation to infinite dilution for the hydroxyl ion and hydronium ion in water of $\Lambda_{\text{OH}}(\text{infinite dilution}) = 199.2 \text{ S cm}^2 \text{ mol}^{-1}$ and $\Lambda_{\text{H}}(\text{infinite dilution}) = 350.1 \text{ S cm}^2 \text{ mol}^{-1}$, gives $\Lambda(\text{total}) = (199.2 + 350.1) \times 10^{-10} \text{ S cm}^{-1} = 0.055 \text{ μS cm}^{-1}$

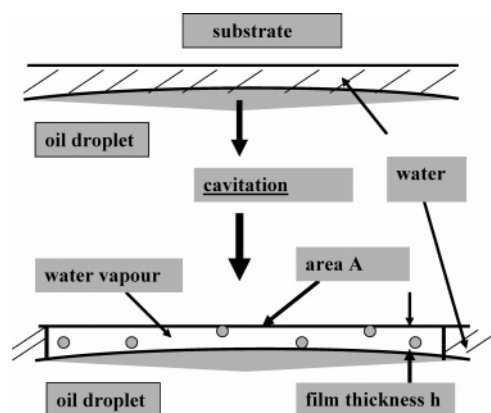


Figure 10. Diagram illustrating the cavitation process expected as two hydrophobic surfaces separate in water.

at 25 °C. This value is the same as that accepted as “standard” (see, for example, the SI data Book)¹⁶ and agrees closely with the best measured value of Kohlrausch and Heydweiller¹⁵ of 0.058 μS cm^{-1} . This standard calculation, once again, appears to correspond to CO_2 -free but not de-gassed water. The standard values for the water conductivity with temperature¹⁶ also agree closely with the values obtained by Kohlrausch and Heydweiller.

A simple analysis of the thermodynamics of cavitation is considered in the following section.

Simple Thermodynamic Model of the Cleaning/Dispersion of Hydrophobic Materials in Water. The removal of hydrophobic dirt or oil from a substrate can be simply modeled at close separation distances (nanometers), as illustrated in Figure 10. Analysis of this process predicts that cavitation will occur for hydrophobic surfaces pulled apart in water (this was first observed in ref 7, but see also refs 12 and 18), even if only one of the surfaces is hydrophobic. As a first approximation, the thermodynamics of the cavitation process can be considered simply in terms of the surface free energy driving force, that is, where $\gamma_{\text{SL}} > \gamma_{\text{SV}}$, balanced against the free energy cost of vaporizing this volume (i.e., Ah) of water vapor at room temperature and atmospheric conditions (i.e., under standard conditions). Hence, the total free energy of cavitation is approximately given by

$$\Delta G(h) = 2A(\gamma_{\text{SV}} - \gamma_{\text{SL}}) + Ah\Delta G_{\text{H}_2\text{O}}^{\text{vap}} \left(\frac{P_{\text{water}}}{P_{\text{atm}}} \right) \frac{1}{0.0224}$$

where the standard free energy of vaporization of water, $\Delta G_{\text{H}_2\text{O}}^{\text{vap}}$, is 8 kJ mol^{-1} and 1 mol of gas at standard temperature and pressure occupies 0.0224 m^3 . The relative vapor pressure of water is given by $P_{\text{water}}/P_{\text{atm}}$, which is equal to $17.5/760$ at 20 °C. Also, if it is assumed that $A^{0.5} \gg h$, we can safely ignore the border or perimeter surface energy term. That is at the air/water border. Rearranging this equation gives

$$\frac{\Delta G(h)}{A} = 2\gamma_{\text{LV}} \cos \theta + h \times 8.22 \times 10^3 \quad (\text{in J m}^{-2})$$

Typical calculated values are shown in Figure 11. The slope of the curve, $[\partial \Delta G(h)/A]/\partial h = 8220 \text{ N m}^{-2}$, corresponds to an attractive pressure between the particle and the substrate of 0.082 atm. It should be noted from this analysis that if only one surface is hydrophobic, the free energy per unit area depends on the reduced contact angle at the other surface. For example, if the other surface has a contact angle of 90° the surface term is halved.

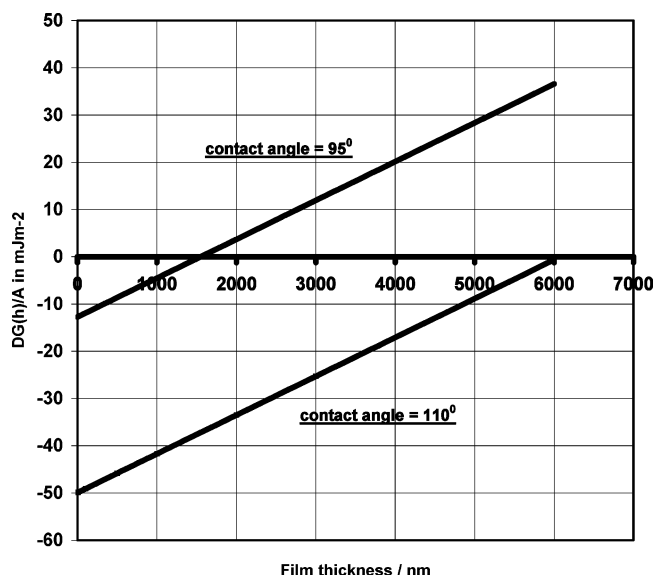


Figure 11. Estimated change in free energy (ΔG) per unit area as two hydrophobic surfaces separate in water. Two cases are shown with different water contact angles.

One other term to consider is the vdw energy associated with changing the intervening fluid from water to vacuum (or vapor), in the narrow gap formed during separation. This can be estimated at close separations (where the effect is strongest), say at 1 nm, using the equation for the vdw interaction between parallel flat surfaces² separated by the distance L :

$$V_{123}^F(L) = -\frac{A_{123}}{12\pi L^2}$$

The Hamaker constants (A) for hydrocarbon/vacuum/hydrocarbon and hydrocarbon/water/hydrocarbon are 6×10^{-20} J and 0.5×10^{-20} J, respectively. With the use of these values the vdw change in energy on cavitation is about -0.00145 J m⁻². As can be seen from Figure 11, this contribution is small relative to the surface energy term and becomes even less important as the film thickens. However, the vdw attraction is important at very small separations, that is, when the surfaces are just starting to pull apart (<0.5 nm). In fact, it has been demonstrated that materials are at least 1 order of magnitude more cohesive in a vacuum than in water.¹⁹ Thus, the removal of dissolved gases, which act to prevent cavitation, will also remove this effect and so, once again, enhance the release of attached dirt.

In summary, at very close separation distances, cavitation yields the surface tension free energy release for little cost, in terms of the work required to vaporize the water in a thin film. However, as the surfaces pull further apart, more water must be vaporized, for little or no surface energy gain, and this leads to an attractive force between the droplet/particle and the substrate. In addition, cavitation strongly enhances the vdw attraction between dirt and the substrate. As a hydrophobic particle or droplet detaches from a hydrophilic or hydrophobic interface, the presence of dissolved gas will aid cavitation, presumably by providing nucleation sites, which is driven by the interfacial energy balance and the negative suction pressure generated in the water film. The dispersion of hydrophobic dirt will, therefore, be sensitive to the presence of dissolved gas. Thus, hydrophobic dirt with a water contact angle greater than 90° will be easier to remove in de-gassed water. In general, cavitation is expected for materials which have a significantly higher interfacial tension with water than with air. Liquids with

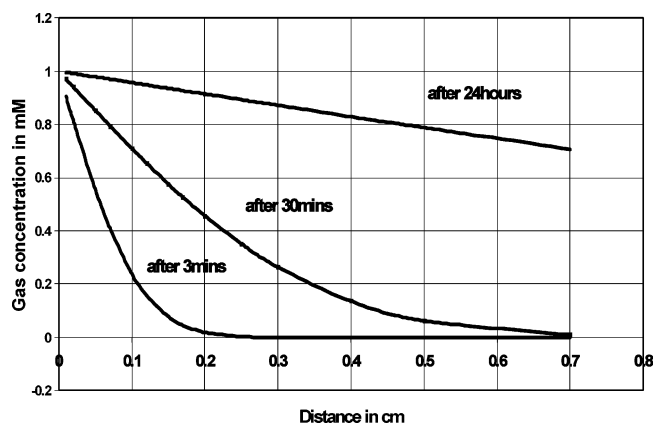


Figure 12. Calculated rate of diffusion of dissolved atmospheric gases (oxygen and nitrogen) into de-gassed water.

this property include hydrocarbons, fluorocarbons, silicones, and some chlorohydrocarbons.

Because the practical use of de-gassed water for cleaning is limited by the rate of diffusion of oxygen and nitrogen into water, this is considered in detail in the following section.

Diffusion of Air (Oxygen and Nitrogen) into Water at Room Temperature. For the diffusion of gas in one direction (x), the appropriate equation is Fick's second law in the form

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

where C is the solute concentration and D is the diffusion coefficient. At the initial condition, when completely de-gassed water is exposed to air at atmospheric pressure, there must be a very thin layer at the surface of the water which will be at the saturated dissolved concentration (1 mM). This layer will form rapidly and will maintain its saturated concentration from then onward (in equilibrium with the atmosphere), and the dissolved gas will diffuse into the water.

Thus, Fick's law must be solved for the boundary conditions $C = C_0$, when $x = 0$ for any value of t and $C_x = 0$ for $x > 0$ when $t = 0$. Also, $C_x = C_0$ for any value of x , as t becomes very large. The solution to Fick's law under these conditions²⁰ is

$$C = C_0 \left[1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right]$$

where the error function can be calculated using either tables or, as for the present calculation, using the series

$$\operatorname{erf} x = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt = \frac{2x}{\sqrt{\pi}} \left[1 - \frac{x^2}{1.3} + \frac{x^4}{2.1.5} - \frac{x^6}{3.2.1.7} + \dots \right]$$

For oxygen and nitrogen the value of the diffusion coefficient D in water at 20°C is 2×10^{-5} cm²/s and the saturated gas concentration C_0 is 1 mM. Using these values, we obtain the results in Figure 12. These calculated results show that, for quiescent water, re-gassing to the 3% solubility level will occur only to a depth of about 2 mm after several minutes of exposure to atmospheric pressure. The 3% level is relevant because earlier work⁵ indicated that 97% removal of dissolved gas only caused a very minor change in the oil dispersion (even after vigorous shaking). The time taken to reach full saturation is surprisingly

long, although surface vibrations and convection will speed the diffusion process in water. These values must, therefore, represent an upper limit to the time taken to re-gas. However, the rate of diffusion of air into de-gassed water is remarkably slow and so should not present a problem for cleaning processes, where the de-gassed water might be exposed to air for only a brief length of time.

Discussion

The results presented here clearly demonstrate that de-gassed water is more effective at removing residual oil "dirt" from glass surfaces. These results are particularly interesting and important because, unlike in the original study,⁸ the oil was not de-gassed but was completely equilibrated with the atmosphere prior to cleaning and, hence, contained dissolved gas at a significantly higher level than even gassed water. Removal of dissolved gas from the oil phase enhances this dispersion still further. These results can be understood from the fact that cavitation is expected when hydrophobic surfaces are separated in water and this cavitation will oppose the separation of, say, two hydrophobic particles or droplets in water. The role of de-gassing appears to be simply to increase the activation barrier for cavitation, and, hence, de-gassing enhances the dispersion of hydrophobic particles in water. It also seems clear that the higher level of dissolved gas in the oil phase acts as a reservoir, so its removal has a strong effect on dispersion.

Recently, some attention²¹ has been given to the freeze-thaw method used to de-gas oil-and-water mixtures, in the earlier studies.^{8,9} This is a little surprising because it has been known for some considerable time that freezing is a standard method for de-gassing liquids. However, in the current experiments even when only the water is de-gassed there is a clear enhancement of the dispersion of even gassed hydrocarbon oils, once again demonstrating that de-gassing is the cause of the enhanced dispersion. It is also interesting that even with detergents present de-gassing still enhances dispersion. Further studies would be required to evaluate the practical value of detergent/de-gassed water cleaning systems and de-gassed solvent/de-gassed water sequential cleaning systems. However, the results presented here do indicate that there may be some useful applications in cleaning where detergent residues need to be avoided, for example, in silicon wafer manufacture and surgical equipment cleaning. The slow re-gassing rate in water should enable cleaning applications where there is little time of exposure to the atmosphere prior to dispersion. A suggested cleaning system is illustrated in Figure 13. In such cleaning methods it will be important to both reduce exposure time and also supply mechanical action to aid dispersion. In the case illustrated this is supplied as liquid spray pressure and momentum. Because it appears that de-gassed oil is more effectively dispersed by de-gassed water than gassed oil, sequential spray cleaning based on de-gassed oil rapidly followed by de-gassed water may offer an effective detergent-free cleaning solution. The de-gassed oil could be a hydrocarbon, fluorocarbon, chlorohydrocarbon, or silicone liquid. This type of system offers effective detergent-free cleaning which should disperse and remove all hydrophobic and hydrophilic forms of dirt. In the current study de-gassing was achieved by the freeze/thaw/pump system, but industrially other methods may be more appropriate. For example, water can be de-gassed using a hydrophobic porous membrane.²²

Mechanical action combined with the dispersive power of de-gassed water will disperse hydrophobic dirt (oils and grease) and hydrophilic, polar dirt (e.g., salts, sugars) will be dissolved in the normal manner. Long-term stability of the dispersion of

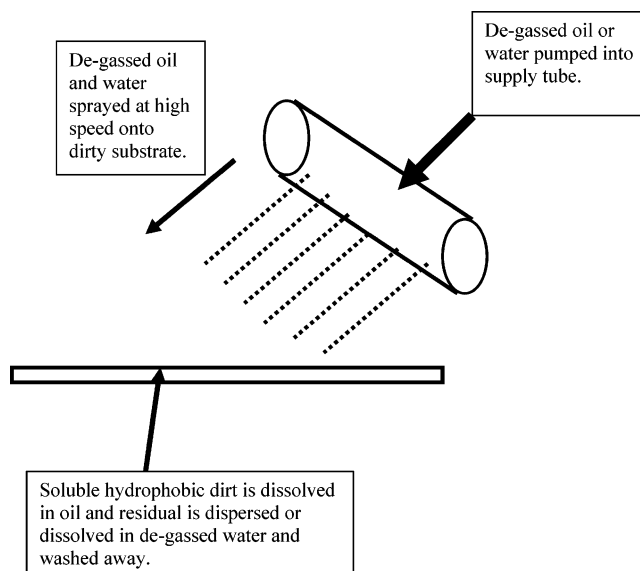


Figure 13. Diagram of a system designed to clean by the sequential application of de-gassed solvent and de-gassed rinsing water.

dirt in water is not required in cleaning, and subsequent de-stabilization could actually be useful. Using de-gassed water to aid in the dispersive removal of hydrophobic (solid or liquid) dirt represents an entirely different approach compared to cleaning with detergents. The main detergent action is to coat hydrophobic surfaces to make them hydrophilic and, hence, readily dispersible in water. However, in both cases the crucial step will involve the separation of two surfaces from intimate molecular contact and the exposure of at least one hydrophobic surface to water. This crucial step will occur even in the presence of detergent, just prior to its adsorption.

In detergent cleaning, hydrophobic materials usually become charged as a result of detergent adsorption, and this helps to stabilize them. However, it has recently been demonstrated that hydrophobic colloids naturally develop a significant charge in water which also helps stabilize them in water.²³ In detergent cleaning, the surfactant-coated hydrophobic dirt is thermodynamically more stable in water than hydrophobic dirt dispersed under de-gassed conditions. However, it has been demonstrated that, although not thermodynamically stable in water, hydrocarbon oil droplets, dispersed using de-gassed conditions, do not coalesce⁹ and remain in a meta-stable state of more than sufficient duration to be effective in cleaning.

In principle, enhanced dispersion in de-gassed water should occur for any oil or solid dirt with an interfacial tension with water higher than the surface tension in air. However, as with conventional cleaning, the addition of hydrophilic, polymeric stabilizers, such as sodium carboxymethylcellulose, might also be useful to enhance the longer term dispersive power of de-gassed water, preventing dirt re-disposition.

The limited study, presented here, of the electrical conductivity of single-distilled, nitrogen-gassed and de-gassed water indicates that the precise value for "pure" water needs to be reexamined. It seems that the presence of significant levels of nonpolar atmospheric gases can suppress the conductivity of water and that complete or partial de-gassing can increase it substantially. It is possible that some earlier studies on de-gassed water obtained higher values than the accepted literature values and dismissed their results as due to suspected ionic contamination (for example, see ref 24). Conversely, artificially low conductivity values can be obtained by nitrogen gassing. It is interesting that the major water purification company Millipore²⁵

recently stated that “It is clear that $18.2 \text{ M}\Omega\cdot\text{cm}$ is no longer a ‘quality certification’ value.” This was because latest developments in inductively coupled plasma mass spectrometry ultra-trace analysis were pushing back the definition of “pure water”. The water used in the present study was prepared as standard laboratory “single-distilled” water and stored in Pyrex vessels in a laminar-flow cabinet. It is surprising that the values obtained here, simply by thoroughly purging with high-purity nitrogen gas, should give water with conductivity values reasonably close to the best values published in the literature.

The extrapolated conductivity value of $0.055 \mu\text{S cm}^{-1}$, calculated from the infinite dilution conductivities of hydroxyl and hydronium ions (at 25°C), and the classical measured value¹⁵ of $0.058 \mu\text{S cm}^{-1}$ both appear to be derived from solutions which were not completely free from dissolved, nonpolar gases. The results presented here indicate that complete de-gassing actually leads to significantly higher conductivity values, which may well be mistaken, in practice, for ionic contamination.

The conductivity of pure water is a very sensitive measure of the structure of water and the presence of solutes, both ionic and nonpolar. It is interesting to speculate on other properties of water that might also depend on the presence of dissolved oxygen and nitrogen. For example, the dielectric constant of water at static and low frequencies might be affected by the presence of hydrogen-bonded rings around nonpolar solutes at the millimolar level. The presence of dissolved gas is known to affect the cavitation or bubbling pressure of water under suction, and it may even affect its boiling point, although any such effect would be difficult to study.

Conclusions

This study has demonstrated that almost complete de-gassing of water improves its ability to disperse and, hence, remove hydrophobic dirt. If the dirt is a hydrophobic liquid, this dispersion is further enhanced by de-gassing of the liquid, as well as the water. This has led to the suggestion that detergent-free cleaning is possible using a sequential combination of de-gassed (hydrophobic) solvent followed by rinsing with de-gassed water. Use of different de-gassed, hydrophobic solvents could enhance the application of this cleaning process to a wide range of systems. An initial study of the electrical conductivity of single-distilled water has led to the conclusion that although

nitrogen-purged distilled water has a conductivity close to the literature value, completely de-gassed water has a significantly higher electrical conductivity. These results suggest that dissolved, nonpolar gases, even at relatively low levels, perturb the water structure and reduce its electrical conductivity.

References and Notes

- (1) Tanford, C. *The Hydrophobic Effect*; J. Wiley: New York, 1980.
- (2) Israelachvili, J. N. *Intermolecular and Surface Forces*; Academic Press: New York, 1992.
- (3) Israelachvili, J. N.; Pashley, R. M. *Nature* **1982**, *300*, 341–343.
- (4) Christenson, H. K.; Claesson, P. M. *Adv. Colloid Interface Sci.* **2001**, *91* (3), 391–436.
- (5) Karaman, M. E.; Ninham, B. W.; Pashley, R. M. *J. Phys. Chem.* **1996**, *100*, 15503–15507.
- (6) Ishida, N.; Sakamoto, M.; Miyahara, M.; Higashitani, K. *Langmuir* **2000**, *16* (13), 5681–5687.
- (7) Pashley, R. M.; McGuiggan, P. M.; Ninham, B. W.; Evans, D. F. *Science* **1985**, *229*, 1088–1089.
- (8) Pashley, R. M. *J. Phys. Chem. B* **2003**, *107* (7), 1714–1720.
- (9) Maeda, N.; Rosenberg, K. J.; Israelachvili, J. N.; Pashley, R. M. *Langmuir* **2004**, *20* (8), 3129–3137.
- (10) Alargova, R. G.; Kochijashky, I. I.; Zana, R. *Langmuir* **1998**, *14* (7), 1575–1579.
- (11) Sierra, M. L.; Zana, R. *J. Colloid Interface Sci.* **1999**, *212* (1), 162–166.
- (12) Yaminsky, V. V.; Yushchenko, V. S.; Amelina, E. A.; Shchukin, E. D. *J. Colloid Interface Sci.* **1983**, *96* (2), 301–306.
- (13) Eisenberg, D.; Kauzmann, W. *The Structure and Properties of Water*; Oxford University Press: Oxford, U.K., 1969.
- (14) Head-Gordon, T. *Proc. Natl. Acad. Sci. U.S.A.* **1995**, *92*, 8308–8312.
- (15) Kohlrausch, F.; Heydweiller, A. Z. *Phys. Chem.* **1894**, *14*, 317.
- (16) Aylward, G.; Findlay, T.; *SI Chemical Data*, 3rd ed.; J. Wiley: New York, 1994.
- (17) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed.; Butterworths: London, 1959.
- (18) Wennerstrom, H. *J. Phys. Chem. B* **2003**, *107* (50), 13772–13773.
- (19) Bailey, A. I.; Kay, S. M. *Proc. R. Soc. London, Ser. A* **1967**, *301*, 47.
- (20) Crank, J. *The Mathematics of Diffusion*, 2nd ed.; Clarendon Press: Oxford, U.K., 1975; pp 20–21.
- (21) Burnett, G. R.; Atkin, R.; Hicks, S.; Eastoe, J. *Langmuir* **2004**, *20*, 5673–5678.
- (22) Tai, M. S. L.; Chua, I.; Li, K.; Ng, W. J.; Teo, W. K. *J. Membr. Sci.* **1994**, *87* (1–2), 99–105. Wiesler, F. *Ultrapure Water* **2003**, 38–42.
- (23) Marinova, K. G.; Alargova, R. G.; Denkov, N. D.; Velev, O. D.; Petsev, D. N.; Ivanov, I. B.; Borwankar, R. P. *Langmuir* **1996**, *12* (8), 2045–2051.
- (24) Bunkin, A. F.; Bunkin, N. F.; Lobeyev, A. V.; Nurmatov, A. A. *Phys. Lett. A* **1996**, *225*, 344–355.
- (25) Millipore – Technical Publications – Ultrapure Water for Elemental Analysis down to ppt levels. www.millipore.com/publications.nsf/docs/rd002 (accessed Jul 2004).