

Salt Effects on Monolayers and Their Contribution to Surface Viscosity

A. K. Chattopadhyay,*

*ICI Explosives Group Technical Centre, McMasterville Site CD Complex, 801 Richelieu Boulevard,
McMasterville, Québec, J3G 1T9 Canada*

L. Ghaïcha,

*Centre de recherche en photobiophysique, Université du Québec à Trois-Rivières, 3351, boul. des Forges,
C.P. 500, Trois-Rivières, Québec, G9A 5H7 Canada*

S. G. Oh, and D. O. Shah

*Centre for Surface Science and Engineering, University of Florida, Gainesville, Florida 32611
(Received: January 9, 1992; In Final Form: March 11, 1992)*

The surface viscosities of monomolecular films of three homologous series of surfactants, viz. the diethanolamine derivatives of *n*-alkylsuccinic anhydride (alkyl = dodecyl, tetradecyl, and octadecyl), were measured by deep channel surface viscometry. The studies were carried out with concentrated salt solutions of NaCl and NH₄NO₃ (0–30 wt%) in the aqueous subphase. The viscosities of the surfactant monolayers increased as the NaCl concentration increased in the aqueous subphase, whereas a reverse trend was observed with NH₄NO₃ solutions. Such differences in viscosity behavior were mainly due to the changes in the environment of the polar group regions imposed by the nature of the salts.

Introduction

Water-in-oil type emulsions with highly concentrated aqueous salt solutions as an internal phase play a vital role in a number of industrial applications.^{1,2} The degree of stability of such emulsions toward breakdown or coalescence is imparted by the adsorption of surface-active agents at the interface. Few experimental studies have been conducted so far to understand the stability behavior of such emulsion systems. During the past two decades considerable research effort has been directed toward the understanding of the basic mechanisms of emulsion stability primarily on the basis of interfacial phenomena.^{3–6} It has also been recognized that interfacial rheological properties^{6–9} play key roles in determining the stability of foams and emulsions.

In an attempt to predict stability behavior in dispersed systems, several investigators studied model systems which involved the coalescence of individual droplets at liquid/liquid and gas/liquid interfaces.^{10–13} Fluid/fluid interfaces containing surface-active molecules often show rheological properties which differ from those exhibited by the bulk. The orientation of the adsorbed surfactant molecules, molecular interactions and packing, formation of complexes, or structural transformations at the interface can result in unusual rheological behavior.^{8,14} Interfacial viscosity provides valuable information about the nature of interactions, transport processes, and phase transitions in flowing monolayers.^{15–19} Interfacial viscosity can often strongly influence the velocity distribution in the proximity of an interface, suggesting its importance in a number of separation processes involving mass transfer across phase boundaries and also suggesting its importance in foam and emulsion stability.^{15–17}

Interfacial viscosity plays a significant role in altering the mass-transfer processes across interfaces.^{6,19–21} It has been recognized that surface viscosity is a primary factor and has been known to have a great effect on film transfer.^{22–25} Monolayer film viscosities for fatty acids have been investigated by many workers, who clarified the effect of alkyl chain length and metal ions added to a water phase.^{26–28} It has been found that the monolayer property is profoundly affected by their hydrophobic and hydrophilic interactions. Recent studies by Hühnerfuss^{29,30} delineate the optimum hydrophobic interaction between the hydrophobic alkyl chains that results in an increase in surface viscosity. The surface viscosity values measured by canal viscometry were

compared in a series of homologous compounds which exhibited optimum hydrophobic interactions.

The variations in monolayer properties as a function of ionic strength have not received much attention. In our recent studies on monolayers of strong electrolyte solution as a substrate, we described the effect of salt concentration on film compression and on the orientation of molecules at the air–aqueous salt solution interface.^{31,32}

The purpose of the present study has been to examine in more detail the effect of salt concentration as well as the nature of the salt on surface viscosity. The surface viscosities of the diethanolamine derivatives of *n*-alkylsuccinic anhydrides (alkyl = dodecyl, tetradecyl, and octadecyl) were measured at aqueous NaCl and aqueous NH₄NO₃ solution–air interfaces using a deep channel surface viscometer. The deep channel viscometer is the most commonly used device for measuring surface shear viscosity.^{33–35} It was found that the nature of the salt has a strong influence on the surface viscosity which probably originates from the differences in intermolecular interactions resulting from salt–ion binding and subsequent changes in the environment of the polar head groups of the surfactant molecules.

Method

The deep channel surface viscometer (as shown in Figure 1) used for the present study is very similar to that used by various workers.^{33–35} The diameter of the inner channel wall is 9.21 cm, and the diameter of the outer channel wall is 11.35 cm. The ratio of depth to width of the liquid channel (*D*) was chosen such that *D* always remained greater than $2/\pi$. For all our experimental purposes, a constant volume of the liquid substrate was used and *D* was measured as 0.75 (channel width 0.87 cm).

In the deep channel surface viscometer, the channel walls are stationary concentric cylinders; the floor of the viscometer moves with a constant angular velocity. It is important to note that, in order to estimate the center-line velocity of the interface, the velocity of more than one particle carefully placed at the surface of the liquid in the annular channel needs to be measured.

The general assumptions in order to get an expression for surface viscosity at the air–liquid interface are^{34–36} (1) both the liquid and the gas phases may be described as incompressible, Newtonian fluids, (2) the interface is flat, (3) any surfactant present is uniformly distributed over the interface, and (4) there is no mass transfer across the interface.

* To whom correspondence should be addressed.

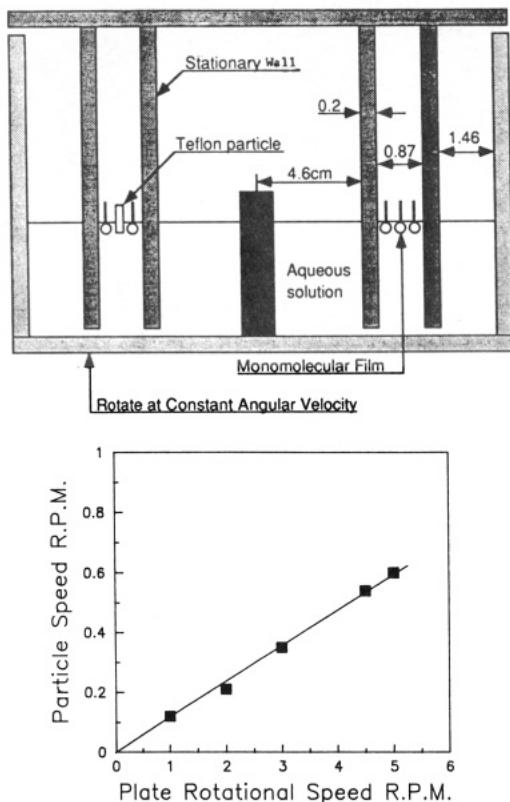


Figure 1. (top) The deep channel surface viscometer. (bottom) Particle speed as a function of dish rotational speed for the air–water interface.

With the above assumptions, for deep channels (i.e., $D > 2/\pi$), the fluid velocity at the fluid–fluid interface can be expressed as^{34,35}

$$V = \frac{8V_b / \pi e^{\pi D}}{1 + \pi \epsilon / \eta y_0 + \frac{\sin(\pi y / y_0)}{\eta^*(\tanh \pi D_1 + \epsilon^* \pi / \eta y_0)}} \quad (1)$$

where η is the bulk viscosity of the lower fluid, η^* the bulk viscosity of the upper fluid, y_0 the channel width, V_b the plate rotational speed, ϵ the interfacial viscosity for the lower liquid, and ϵ^* the interfacial viscosity for the upper liquid. Expression 1 can be further modified for liquid–air interface where η^* (the viscosity of the upper phase, i.e. air) can be considered as zero. By substituting $y = y_0/2$ for the center-line velocity and $\eta^* = 0$, eq 1 can be simplified as

$$V = \frac{8V_b}{\pi e^{\pi D}} \frac{1}{1 + \pi \epsilon / \eta y_0} \quad (2)$$

By rearranging eq 2, the final expression for the surface viscosity (ϵ) at a liquid/air interface can be described as

$$\epsilon = \frac{\eta y_0}{\pi} \left[\frac{8V_b}{\pi V e^{\pi D}} - 1 \right] \quad (3)$$

In order to determine the center-line velocity, a small Teflon particle was placed at the interface, and the time for that particle to make one complete revolution was recorded. Each experiment was repeated at least five times, and the average velocity of the particle was used for calculating surface viscosity. The problem often encountered while placing the particle at the interface was the shift in radial position of the particle during motion. This was mainly due to the difference in interfacial tension gradient developed in the immediate neighborhood of the particle due to surface contamination. In our case, the particles were spread on a large volume of distilled water and allowed to stand for several hours before depositing them on the surface. The small amount of water carried by the particles also causes shift in their position. This problem was greatly reduced by allowing the system to equilibrate over a long period of time (2–4 h) before taking any measurement.

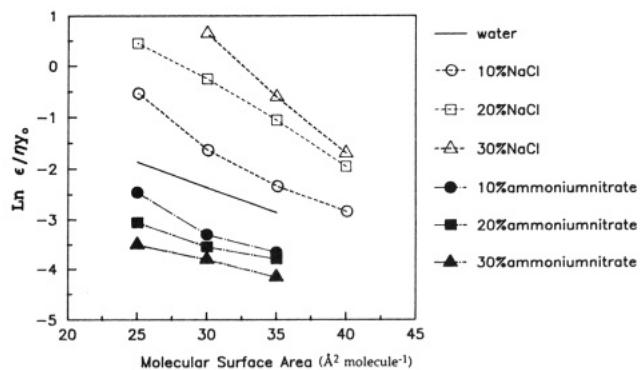


Figure 2. Plot of $\ln \epsilon / \eta Y_0$ versus molecular surface area of dodecylsuccinic anhydride derivative at 20°C with different concentration of NaCl and NH_4NO_3 .

In this manner the center-line velocity was measured on the monolayer of three different surfactants, viz. diethanolamine derivatives of *n*-alkylsuccinic anhydride (*n*, alkyl = C_{12} , C_{14} , and C_{18}) deposited on aqueous salt solution substrates where the salt concentrations were varied between 0 and 30 wt %. Each surfactant system was investigated in the presence of aqueous NaCl and aqueous ammonium nitrate solution substrates.

Experimental Section

The dodecyl-, tetradecyl-, and octadecylsuccinic anhydrides (Humfry Chemicals, USA) were derivatized with diethanolamine (Aldrich Chemicals) by reacting 1:1 molar quantities of each alkylsuccinic anhydride and diethanolamine at 80°C .

Pure recrystallized sodium chloride and ammonium nitrate salts from BDH were used without any further purification. The surface pressure as a function of area was obtained with an automated Langmuir trough by using a compression speed of $5 \text{ \AA}^2/(\text{molecule min})$. A Teflon-coated movable barrier was used for film compression. The details of the experimental procedure are mentioned elsewhere.³⁷ All quartz doubly distilled (Brinkman Instruments, Canada) water used for the experiment was first drawn through a Millipore filtering system (Millipore Co., Canada). The quality of aqueous subphase was tested prior to each run by compressing the surface without any surfactant present while noting any rise in surface pressure.

The “deep channel surface viscometer” was used for measuring surface viscosity. The surface viscosity was measured at a constant plate rotational speed of 4.6 rpm. Prior to selecting the rotational speed of 4.6 rpm, the linearity of plate rpm versus particle rpm was checked at an air/water interface. The linearity of the result shown in Figure 1b represented laminar flow of liquid at 4.6 rpm.

Both for the surface pressure-area and surface viscosity-area measurements, the surfactants were spread at the air–aqueous solution interface using high-purity distilled chloroform (Fluka). A period in excess of 15 min was allowed for the solvent to evaporate. Solutions of ammonium nitrate and sodium chloride were prepared immediately before use. The surface viscosities were measured at various concentrations of each surfactant which correspond to the range of molecular surface area for a certain surface pressure. All experiments were done at $20 \pm 1^\circ\text{C}$.

Results and Discussion

The surface viscosity data for each surfactant system were expressed as the dimensionless Boussinesq number $\epsilon / \eta y_0$, and the plots of $\ln \epsilon / \eta y_0$ versus molecular surface area of the surfactants are shown in Figures 2–4. In all our experiments surface viscosities were measured below the film collapse pressures of the monomolecular films of the surfactants.

The surface viscosity of each surfactant monolayer at an air–aqueous NaCl solution interface was found to increase with the salt concentration. However, in the presence of the NH_4NO_3 solution substrate the surface viscosity was found to decrease with increased NH_4NO_3 concentration. The surface viscosity as a function of molecular surface area was also found to increase at a much faster rate at the NaCl solution–air interfaces compared

TABLE I: Comparison of Monolayer Film Collapse Pressures and Areas at Different Salt Concentrations in the Aqueous Subphase

surfactants		% NaCl				% NH ₄ NO ₃			
		0	10	20	30	0	10	20	30
diethanolamine derivative of dodecylsuccinic anhydride	collapse pressure (mN/m)	45	48.4	52.8	56.2	45	47.4	48.4	50
	area/molecule at collapse (\AA^2)	12.5	19.3	26.13	30.11	12.5	18.18	21.02	22.72
diethanolamine derivative of tetradecylsuccinic anhydride	area/molecule at the condensed state (\AA^2)	22.5	42.22	52.22	53.33	22.5	40.0	46.66	48.33
	collapse pressure (mN/m)	45.0	48.4	52.5	54.0	45.0	45.0	45.8	48.4
diethanolamine derivative of octadecylsuccinic anhydride	area/molecule at collapse (\AA^2)	20.0	26.13	27.27	28.4	20.0	27.27	27.80	27.80
	area/molecule at the condensed state (\AA^2)	39.44	45.55	47.22	48.33	39.44	42.77	43.88	43.88
	collapse pressure (mN/m)	63.4	66.8	69.7	71.0	63.4	66.8	68.7	72.3
	area/molecule at collapse (\AA^2)	22.4	22.4	22.4	22.4	22.4	16.52	17.08	18.5
	area/molecule at the condensed state (\AA^2)	31.11	32.77	36.66	36.66	31.11	38.88	38.88	40.55

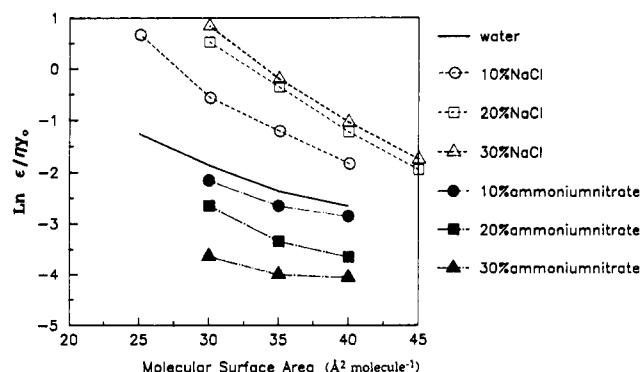


Figure 3. Plot of $\ln \epsilon / \eta Y_0$ versus molecular surface area of tetradecylsuccinic anhydride derivative at 20 °C with different concentration of NaCl and NH₄NO₃.

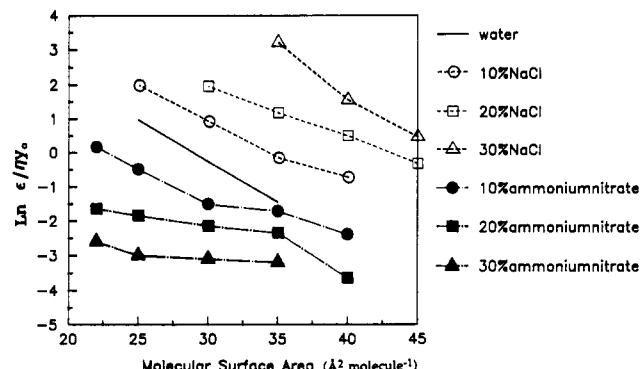


Figure 4. Plot of $\ln \epsilon / \eta Y_0$ versus molecular surface area of octadecylsuccinic anhydride derivative at 20 °C with different concentration of NaCl and NH₄NO₃.

to NH₄NO₃ solution-air interfaces.

The reasons for such behavior of surface viscosity is not very clear. However, some differences in the pressure-area isotherms (shown in Figures 5-7) of these surfactants are quite apparent. The main distinguishable features are the following: (1) At low surface pressure, the monolayer of the surfactants is more expanded at the NaCl solution substrate. (2) Increases in film collapse pressure as well as molecular surface area at collapse are less pronounced in the presence of NH₄NO₃ rather than NaCl. (3) The slopes of the pressure-area ($P-A$) isotherms near the collapse pressure are higher in the presence of NaCl than in the case of NH₄NO₃, indicating less fluidity of the surface films in the presence of NaCl. Such evidence is even clearer with the surfactant comprising octadecyl hydrocarbon chains. A "solid-type" surfactant monolayer was observed at the NaCl solution-air interfaces.

In Table I the values of film collapse pressure and molecular surface area at collapse are given for comparison.

The monomolecular films with high viscosity in the presence of NaCl solution substrate indicated solidlike domains, and the films with low viscosity in the presence of NH₄NO₃ indicated fluid domains.³⁸

However, the reverse trend in surface viscosity profiles observed in the presence of NH₄NO₃, i.e. a drop in surface viscosity with

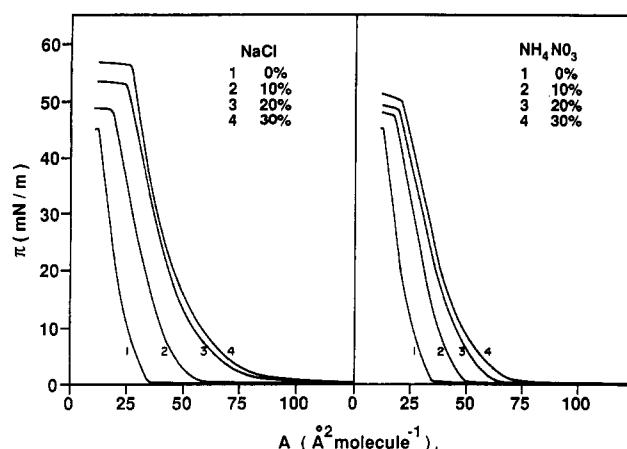


Figure 5. Dodecylsuccinic anhydride derivative isotherms at 20 °C with different concentration of NaCl and NH₄NO₃ in the subphase.

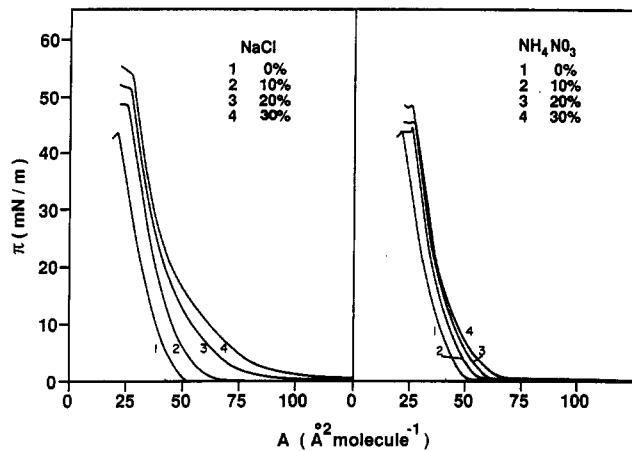


Figure 6. Tetradecylsuccinic anhydride derivative isotherms at 20 °C with different concentrations of NaCl and NH₄NO₃ in the subphase.

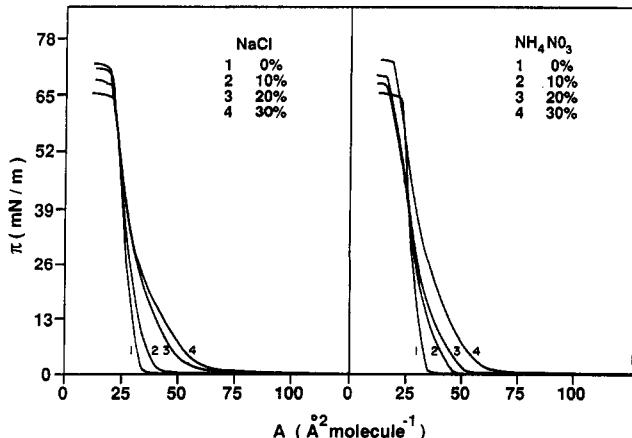


Figure 7. Octadecylsuccinic anhydride derivative isotherms at 20 °C with different concentration of NaCl and NH₄NO₃ in the subphase.

TABLE II: Rate of Water Evaporation through the Monolayer of Diethanolamine Derivative of Octadecylsuccinic Anhydride Measured at 13 mN/m

substrate	surf. area/ molecule at 13 mN/M	surf. viscosity ϵ/η_0	rate of evaporation (g/cm ² /min) $\times 10^4$
20% NaCl solution	39.75	1.85	4.1
20% NH ₄ NO ₃ solution	37.5	0.053	5.8

an increase in NH₄NO₃ concentration in the aqueous subphase, is difficult to explain.

A strong hydrophobic cohesion can generate a high-viscosity value and a hard "solidlike" domain.³⁸ For example, viscosity measurement with the octadecylsuccinic anhydride derivative at a 30% NaCl solution-air interface became virtually impossible above the surface pressure 26 mN/m (i.e., below 35 Å² in molecular surface area), the region where a sharp change from liquid to solid state occurred. Contrary to the NH₄NO₃ solution substrate, a sharp rise in surface viscosity was noticed near the film collapse pressure for all surfactants in the presence of NaCl solution substrates.

The anomalous viscosity behavior of the surfactants observed with NH₄NO₃ appears to be caused by the weaker cohesions as opposed to the potential hydrophobic cohesion observed with NaCl.

The deviations in surface viscosity profiles may be explained from the effect of ionic interactions with the hydrophilic groups.

In our earlier studies we found that the polar head groups of stearic acid molecules have a tendency to form an association with ammonium nitrate through a hydrogen-bonded network.³¹ Such tendencies were found to be even stronger with the poly(isobutylene)succinic anhydride derivatives (polar head groups are similar to the polar head groups of the present study).³² The influence of ammonium nitrate on the large structural changes of polar head groups when determined from the IR spectra of Langmuir-Blodgett films suggested that the electrostatic interactions between the head groups affect the packing of acyl chains by increasing the spacing and corresponding van der Waals interactions between the chains.³² The increased volume of hydrophilic groups due to the association with NH₄NO₃ can prevent their hydrocarbon chains from approaching each other easily. Such steric hindrance will lower the molecular cohesion. The observed effect with the two different kind of salts (NaCl, NH₄NO₃) on the stability of monomolecular films of surfactants is probably the sum of several differing and perhaps competing interactions, such as polar head group-solvent, polar head group-electrolyte, and electrolyte-solvent interactions.^{39,40} The effects can be arbitrarily divided into two major classes: the first is due to "direct interactions" of the ions with the polar head groups of the surfactant; the second class of effect arises primarily from an indirect process whereby the ions affect the orientation to the polar head groups through their modification of the solvent environment.³² The two effects outlined may be regarded as extremes of behavior because one is unlikely to achieve either type of interaction in isolation; it should be permissible, however, to discuss an observed effect on surface viscosity as being a combination with one or other of the types of interaction predominating.

The manner in which the electrolyte ions modify the aqueous environment of the polar head groups is markedly dependent upon the structure and constituents of the ions; for example, salts such as NaCl modify the environment mainly by polar forces, monopole-monopole and monopole-dipole. Salts such as NH₄NO₃ can modify solvent by polar forces, but they also interact with the polar head groups by direct hydrogen bonding.^{31,32}

It is pertinent at this point to draw attention to studies on the effect of concentrated salt solutions of different types. The present studies indicate that probably two other important effects are also operative in the anomalous behavior of surface viscosity; the first is "salting out" which is attributed to changes in the internal pressure of the solvent, and the second is "salting in". The properties of monolayers at the salt solution-air interface can be markedly altered by the nature of ions, because depending upon the nature of salts ("salting-in" type or "salting-out" type) the distributions of cations and anions at the interface can be com-

pletely different. The inorganic cations (Na⁺ or NH₄⁺), because of their hydration requirement, are all excluded equally from the air-water interface, whereas the anions because of their smaller degree of hydration show wide variations in the extent of their exclusion. The exclusion of anions from the interface, however, is in decreasing order of exclusion, e.g. F⁻ > OH⁻ > Cl⁻ > BrO₃⁻ > Br⁻ > NO₃⁻.⁴⁰⁻⁴³ This formalism has the advantage of being able to account for the insensitivity of various processes to the nature of the cation and for the large but graded effectiveness of anions. The interpretation of our results shows some agreement on the basis of "salting-out" and "salting-in" phenomena. In the presence of NaCl the polar head groups of the surfactant molecules are forced out of the aqueous phase due to the "salting-out" phenomenon which results in the formation of "solidlike" domains at the interface. Such tendencies will increase with increased NaCl concentration in the aqueous substrate. Contrary to the above the surfactant molecules are drawn more into the aqueous phase with increased concentration of NH₄NO₃, resulting in the formation of "liquid-type" domains at the interface.

The conclusions were further supported by the experimental evidence of the rate of evaporation of water from the monomolecular film of the diethanolamine derivative of octadecylsuccinic anhydride in the presence of 20% NaCl and NH₄NO₃, respectively, in the aqueous substrate.

The surfactant was spread on the aqueous substrate in a Langmuir trough and compressed to a certain molecular area. A known amount of predried CaCl₂ was kept above the monolayer. The weight gained by CaCl₂ due to the absorption of water from evaporation was measured after 5 min.⁴⁴

The results showed (see Table II) that the rate of water evaporation in the presence of NH₄NO₃ is significantly higher compared to the rate of evaporation measured in the presence of NaCl solution. This indicates that the surfactant molecules in the presence of NaCl are well oriented and exert stronger cohesive interactions between the hydrocarbon chains which results in the formation of solid-type films. This particular behavior is responsible for the lower rate of water evaporation through the surfactant monolayer in the presence of NaCl, whereas a liquid type film formed in the presence of NH₄NO₃ allows the water molecules to escape more readily through the surfactant monolayer.

References and Notes

- (1) Chattopadhyay, A. K. Water-in-oil emulsion explosives. Patent US4919179, 1990. (b) Chattopadhyay, A. K.; Shah, D. O.; Ghaicha, L. *Langmuir* 1992, 8, 27.
- (2) Bamfield, H. A.; Cooper, J. *Encyclopedia of Emulsions Technology*; Marcel Dekker: New York, 1988; Vol. 3, p 281.
- (3) Becher, P. *Emulsion: Theory and Practice*, 2nd ed.; Krieger: New York, 1966.
- (4) Jeffreys, G. V.; Davies, G. A. In *Recent Advances in Liquid-Liquid Extraction*; Hanson, C., Ed.; Pergamon: New York, 1971.
- (5) Lissant, K. J. *Emulsions and Emulsion Technology*; Marcel Dekker: New York, 1974; Part 1.
- (6) Wasan, D. T.; Gupta, L. In *Improved Oil Recovery by Surfactant and Polymer Flooding*; Shah, D. O., Schechter, R. S., Eds.; Academic Press: New York, 1977; p 161.
- (7) Shah, D. O.; Djabbarab, N. F.; Wasan, D. T. *Colloid Polym. Sci.* 1978, 258, 1002.
- (8) Maru, H. C.; Mohan, V.; Wassan, D. T. *Chem. Eng. Sci.* 1979, 34, 1283.
- (9) Pintar, A. J.; Israel, A. B.; Wasan, D. T. *J. Colloid Interface Sci.* 1971, 37, 52.
- (10) Aronson, M. P.; Petko, M. F.; Princen, H. M. *J. Colloid Interface Sci.* 1978, 65, 296.
- (11) Jain, R. K.; Ivanov, I. B.; Maldarelli, C.; Ruckenstein, E. *Lecture Notes in Physics: Dynamics and Instability of Fluid Interfaces*; Sorensen, T. S., Ed.; Springer-Verlag: New York, 1979; p 140.
- (12) de Feijter, J. A.; Rijnbout, J. B.; Vrig, A. J. *J. Colloid Interface Sci.* 1978, 64, 258.
- (13) Mackay, G. D.; Mason, S. G. *Can. J. Chem. Eng.* 1963, 41, 203.
- (14) Goodrich, F. C. In *Solution Chemistry of Surfactants*; Mittal, K. L. Ed.; Academic Press: New York, 1979; Vol. 2, p 733.
- (15) Vold, R. D.; Mittal, K. L. *J. Colloid Interface Sci.* 1972, 38, 451.
- (16) Callahan, I. C.; Neustader, E. L. *Chem. Ind.* 1981 (Jan 17), 53.
- (17) Dimitrov, D. S.; Ivanov, I. B. *J. Colloid Interface Sci.* 1978, 64, 97.
- (18) Chesters, A. K.; Hofman, G. *Appl. Sci. Res.* 1962, 38, 353.
- (19) Choi, S. J.; Schowalter, W. R. *Phys. Fluids* 1975, 18, 420.
- (20) Slattery, J. C. *AIChE J.* 1974, 20, 1145.

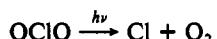
- (21) Cairns, R. J. R.; Grist, D. M.; Neustadter, E. L. In *Theory and Practice of Emulsion Technology*; Smith, A. L., Ed.; Academic Press: New York, 1976; p 125.
- (22) Buhaenko, M. R.; Goodwin, J. W.; Richardson, R. M. *Thin Solid Films* **1988**, *159*, 171.
- (23) Malcolm, B. R. *Thin Solid Films* **1985**, *134*, 201.
- (24) Daniel, M. F.; Hast, J. T. *J. Mol. Electron.* **1985**, *1*, 97.
- (25) Egusa, S.; Nakayama, T.; Gemma, N.; Miura, A.; Azhme, M. *Thin Solid Films* **1989**, *178*, 165.
- (26) Joly, M. J. *Colloid Sci.* **1956**, *11*, 519.
- (27) Jarvis, N. L. *J. Phys. Chem.* **1965**, *69*, 1789.
- (28) Earnshaw, J. C.; Winch, P. J. *Thin Solid Films* **1988**, *159*, 159.
- (29) Hünnerfuss, H. J. *Colloid Interface Sci.* **1987**, *120*, 281.
- (30) Hünnerfuss, H. J. *Colloid Interface Sci.* **1988**, *126*, 384.
- (31) Ghaicha, L.; Chattopadhyay, A. K.; Tajmir-Riahi, H. A. *Langmuir* **1991**, *7*, 2007.
- (32) Ghaicha, L.; Chattopadhyay, A. K.; Leblanc, R. M. *Langmuir*, in press.
- (33) Mannheimer, R. J.; Schechter, R. S. *J. Colloid Interface Sci.* **1970**, *32*, 225.
- (34) Wasan, D. T.; Gupta, L.; Vora, M. K. *AIChE J.* **1971**, *17*, 1287.
- (35) Wasan, D. T.; Pintar, A. J.; Vora, M. K. Paper presented at AIChE, Washington, D. C., meeting, Nov. 16–20, 1969.
- (36) Jiang, T.; Chen, J.; Slattery, J. C. *J. Colloid Interface Sci.* **1983**, *96*, 7.
- (37) Dijkmans, H.; Munger, G.; Aghion, J.; Leblanc, R. M. *Can. J. Biochem.* **1981**, *59*, 328.
- (38) Naito, K.; Iwakiri, T.; Miura, A.; Azuma, M. *Langmuir* **1990**, *6*, 1309.
- (39) Treiner, C.; Chattopadhyay, A. K. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 2915.
- (40) Klotz, I. M.; Shikama, K. *Arch. Biochem. Biophys.* **1968**, *123*, 551.
- (41) Robinson, D. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1965**, *87*, 2470.
- (42) Long, F. A.; McDevit, W. F. *Chem. Rev.* **1952**, *51*, 119.
- (43) Diamond, R. M. *J. Phys. Chem.* **1963**, *67*, 2513.
- (44) Rao, Y. K.; Shah, D. O. *J. Colloid Interface Sci.* **1990**, *137*, 25.

ADDITIONS AND CORRECTIONS

1991, Volume 95

Elizabeth Bishenden, Jennifer Haddock, and D. J. Donaldson*: Resonance-Enhanced Multiphoton Ionization Measurement of Cl($^2P_{3/2}$ and $^2P_{1/2}$) Produced in the Photolysis of OCIO from 355 to 370 nm.

Page 2113. We¹ have studied the near-UV single-photon reaction



by photolyzing room temperature OCIO in the wavelength region 355–370 nm and detecting the chlorine atom product in both the spin-orbit ground and excited states by (2 + 1) resonance-enhanced multiphoton ionization (REMPI). The previous report stated that the peak yield of chlorine atoms was found at 362 nm. More recent experiments have shown that the dye laser used for OCIO photolysis was miscalibrated; wavelengths given in that report were too high by about 2 nm. The corrected chlorine atom

action spectrum appears here as Figure 1, which shows the relative Cl($^2P_{3/2}$) REMPI signal divided by the photolysis laser pulse energy. In the corrected spectrum the photolysis of OCIO that gives maximum Cl atom yield is approximately 360 nm, in accord with the absorption spectrum of OCIO.² Because our original quantum yield experiments were performed at the signal maximum, we believe that the value of 0.15 ± 0.1 still holds.

The corrected spectrum in Figure 1 shows that there is a significant yield of chlorine atoms from photolysis of OCIO at wavelengths longer than 364 nm. This result differs from our previous report. We are undertaking a thorough study of the wavelength dependence of chlorine atom yield, both at room temperature and in a free jet expansion.

- (1) Bishenden, E.; Haddock, J.; Donaldson, D. J. *J. Phys. Chem.* **1991**, *95*, 2113.

- (2) Richard, E. C.; Vaida, V. *J. Chem. Phys.* **1990**, *94*, 153.

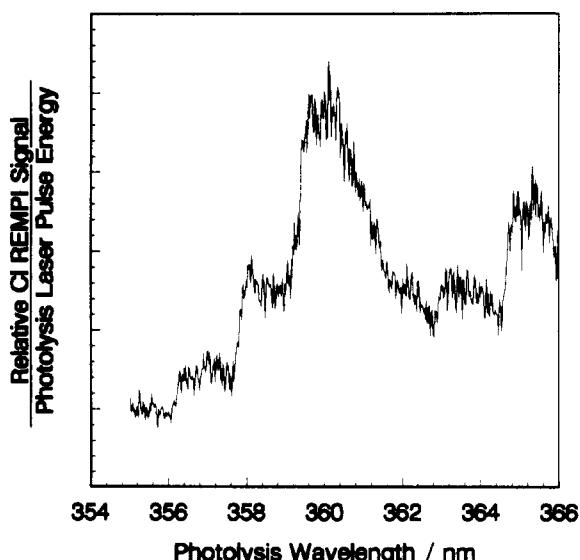


Figure 1. REMPI action spectrum of ground-state Cl($^2P_{3/2}$) formed in the photodissociation of OCIO. The probe laser is fixed at 235.4 nm, and the pump laser is scanned from 355 to 366 nm. The spectrum is normalized for the pump laser energy.