WATER SURFACE:
SURFACTANT MONOLAYERS AND EVAPORATION OF WATER

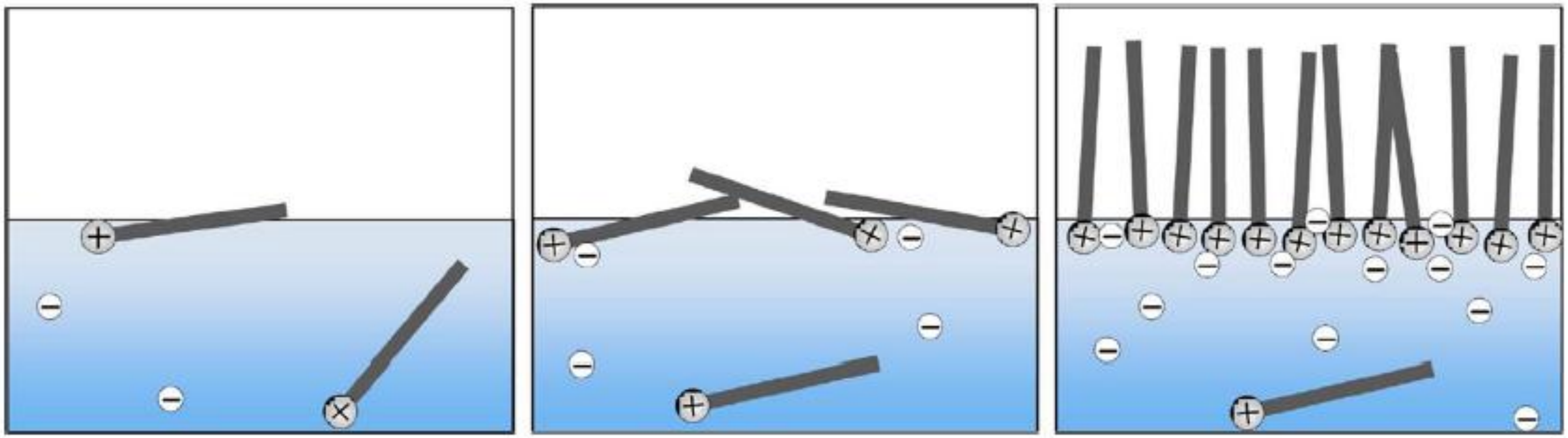
Water-soluble (**Gibbs**) or insoluble (**Langmuir**) layers

Ionic or non-ionic surfactants

Water/air or water/oil

With or without an indifferent electrolyte in water

Surfactant adsorption monolayers on water: Theory and experiment



The sketch of the adlayer of a cationic surfactant on water–air interface, from left to right: diluted solution; medium surfactant concentration; completely filled 2D layer

Soluble (Gibbs) monolayers

Here, a cationic surfactant is depicted. Of course, the same scheme is valid for an anionic surfactant.

Previously, the following equation was proposed:

$$\mathrm{d}\Pi = RT\Gamma_2^m \mathrm{d}\ln a_2 + RT\Gamma_3^m \mathrm{d}\ln a_2 + q_s \mathrm{d}\Psi$$

Surface pressure

As result, excluding the $\mathrm{d}\Psi$ value, we obtain:

$$\frac{\mathrm{d}\Pi}{RTd\ln a_2} = 2\Gamma_2 = \Gamma_2^m \left\{ 2 - (1-\beta)\frac{\mathrm{d}\ln\Gamma_2^m}{\mathrm{d}\ln a_2}\left[\frac{1}{[1-(\Gamma_2^m / \Gamma_2^{m\infty})]^{1+t}} - \frac{2b}{RT}\Gamma_2^m \right] \right\}$$

t = +1; – 1; and 0: Volmer; Henry; Langmuir adsorption isotherms for the surface-active ion.

Instead of the Gibbs excess **in the monolayer**, Γ_2^m

$$\frac{z_2F}{RT}\frac{d\Psi}{d\ln a_2} = 1 - \frac{d\ln\Gamma_2^m}{d\ln a_2}\times\frac{1}{[1-(\Gamma_2^m/\Gamma_2^{m\infty})]^2}$$

the corresponding areas $A = \frac{1}{\Gamma_2^{\mathrm{m}}N_{\mathrm{A}}}; \quad A_0 = \frac{1}{\Gamma_2^{\mathrm{m},\infty}N_{\mathrm{A}}}$

one obtains:

$$\frac{z_2e}{kT}\frac{\mathrm{d}\Psi}{\mathrm{d}\ln a_2} = 1 + \frac{A\mathrm{d}A}{(A-A_0)^2\mathrm{d}\ln a_2}$$

In these terms, the following equation may be obtained:

$$\boxed{\begin{aligned}\Pi + \Pi_c = -kT\int_{\infty}^{A}(1+\beta)\frac{\mathrm{d}A}{(A-A_0)^2} + \\ +\int_{0}^{\Psi}(1+\beta)\frac{z_2 e}{A}\mathrm{d}\Psi + \int_{0}^{\Psi}(1-\beta)\frac{z_2 e}{A}\mathrm{d}\Psi\end{aligned}}$$

Here, Π_c stands for the cohesive contribution to the surface pressure;

k is the Boltzmann constant; T is the absolute temperature;
e is the elemental electrical charge;
z_2 is the charge of the surface active ion;
β is the degree of the counter-ions binding;

Ψ is the electrical potential of the charged monolayer.

Different variations of the initial equation:

$$\Pi = \frac{kT}{A-A_0} - kT\int_{\infty}^{A} \frac{\beta \mathrm{d}A}{(A-A_0)^2} + \int_0^{\Psi} (1+\beta)\frac{z_2 e}{A}\,\mathrm{d}\Psi + \int_0^{\Psi} (1-\beta)\frac{z_2 e}{A}\,\mathrm{d}\Psi$$

$$\Pi + b\left(\frac{1}{A^2} - 2\int_{\infty}^{A} \frac{\beta dA}{A^3}\right) = \frac{kT}{A-A_0} - kT\int_{\infty}^{A} \frac{\beta dA}{(A-A_0)^2} + 2\int_0^{\Psi} \frac{z_2 e}{A}\,d\Psi$$

Using the last expression and neglecting the cohesive pressure, the following equation can be obtained:

$$\mathrm{d}\Pi = (1+\beta)\frac{kT}{A}\,\mathrm{d}\ln a_2 + (1-\beta)\frac{z_2 e}{A}\,\mathrm{d}\Psi$$

after excluding $\mathrm{d}\Psi$ may be represented as:

$$\mathrm{d}\Pi = \frac{2kT}{A}\,\mathrm{d}\ln a_2 + \frac{kT}{(A-A_0)^2}\,\mathrm{d}A$$

After integrating:

$$\boxed{\Pi = -\frac{kT}{A-A_0} + 2kT\int_0^{a_2}\frac{\mathrm{d}\ln a_2}{A}}$$

Accordingly, after excluding $\mathrm{d}\ln a_2$:

$$\mathrm{d}\Pi = -\frac{kT}{(A-A_0)^2}\,\mathrm{d}A + \frac{2z_2e}{A}\,\mathrm{d}\Psi$$

After integration:

$$\boxed{\Pi = \frac{kT}{A-A_0} + 2\int_0^{\Psi} \frac{z_2e}{A}\,\mathrm{d}\Psi}$$

Limiting cases

$$(1)\quad \boxed{\beta = 0;\ \ \Psi \to 0;\ \ d\Psi \to 0} \Longrightarrow \boxed{\Pi A = kT}$$

On the other hand:

$$\Pi = -\frac{kT}{A-A_0} + \boxed{2kT\int_0^{a_2}\frac{\mathrm{d}\ln a_2}{A}} \Longrightarrow \boxed{\frac{2kT}{A}}$$

(Henry equation valid)

$$\Pi = -\frac{kT}{A-A_0} + \frac{2kT}{A} \approx \frac{kT}{A};\qquad \boxed{\Pi A = kT}$$

$$\underline{\Gamma_2^m = 2\Gamma_2 = -2\Gamma_2^d.}$$

(2) $\boxed{\beta = 0;\ \Psi \neq 0;}$

$$\boxed{\sinh x = \frac{1}{2}[\exp x - \exp(-x)]}$$

$$\Pi = \frac{kT}{A - A_0} + 2\int_0^{\Psi} \frac{z_2 e}{A}\,\mathrm{d}\Psi$$

$$\Gamma_2^{\mathrm{m}} = const\, c_{\mathrm{surf}}^{1/2} \sinh\frac{z_2 e\Psi}{2kT};$$

$$\sinh\frac{z_2 e\Psi}{2kT} \approx \frac{1}{2}\exp\frac{z_2 e\Psi}{2kT}$$

$$d\ln\Gamma_2^{\mathrm{m}} = \frac{1}{2}d\ln c_{\mathrm{surf}} + \frac{z_2 e}{2kT}d\Psi$$

On the other hand (Henry equation):

$$\Gamma_2^{\mathrm{m}} = const'\, c_{\mathrm{surf}}\ \exp\frac{-z_2 e\Psi}{kT}$$

$$d\ln\Gamma_2^{\mathrm{m}} = d\ln c_{\mathrm{surf}} - \frac{z_2 e}{kT}d\Psi$$

$$d\Psi = \frac{kT}{2z_2 e}d\ln\Gamma_2^{\mathrm{m}}$$

$$\Pi = \frac{kT}{A - A_0} + 2\int_0^{\Gamma^{\mathrm{m}}} \frac{kT}{2z_2 e}\Gamma_2^{\mathrm{m}} N_{\mathrm{A}} z_2 e\, d\ln\Gamma_2^{\mathrm{m}} = \frac{kT}{A - A_0} + \frac{kT}{A} \approx \boxed{\frac{2kT}{A}}$$

Therefore:

$$2\int_0^{\Psi} \frac{z_2 e}{A}\, d\Psi \approx \boxed{\frac{kT}{A}}$$

(3) $\beta = 1$: **the double electrical layer is absent**; $\Gamma_2 = \Gamma_2^{\mathrm{m}}$

$$\Pi(A - A_0) = \boxed{2kT}$$

In the presence of a high concentration of a **foreign electrolyte**:

$$\Pi(A - A_0) = \boxed{kT}$$

Experimental study of the structure of monolayers: Direct determination of the surface excess

1. Radioactive tracers: beta-emitters ^{3}H, ^{14}C, ^{22}Na, ^{35}S
2. Ellipsometry
3. Neutron reflection

$$-d\sigma = d\Pi = \Gamma_2 RTd\ln a_2$$ ← non-ionic

$$-d\sigma = d\Pi = 2\Gamma_2 RTd\ln a_2$$ ← ionic surfactant

Direct determination

Measurement of the adsorption of surface-active agents at a solution/air interface by a radiotracer method

By D. J. Salley, A. J. Weith, Jr., Ann A. Argyle and J. K. Dixon

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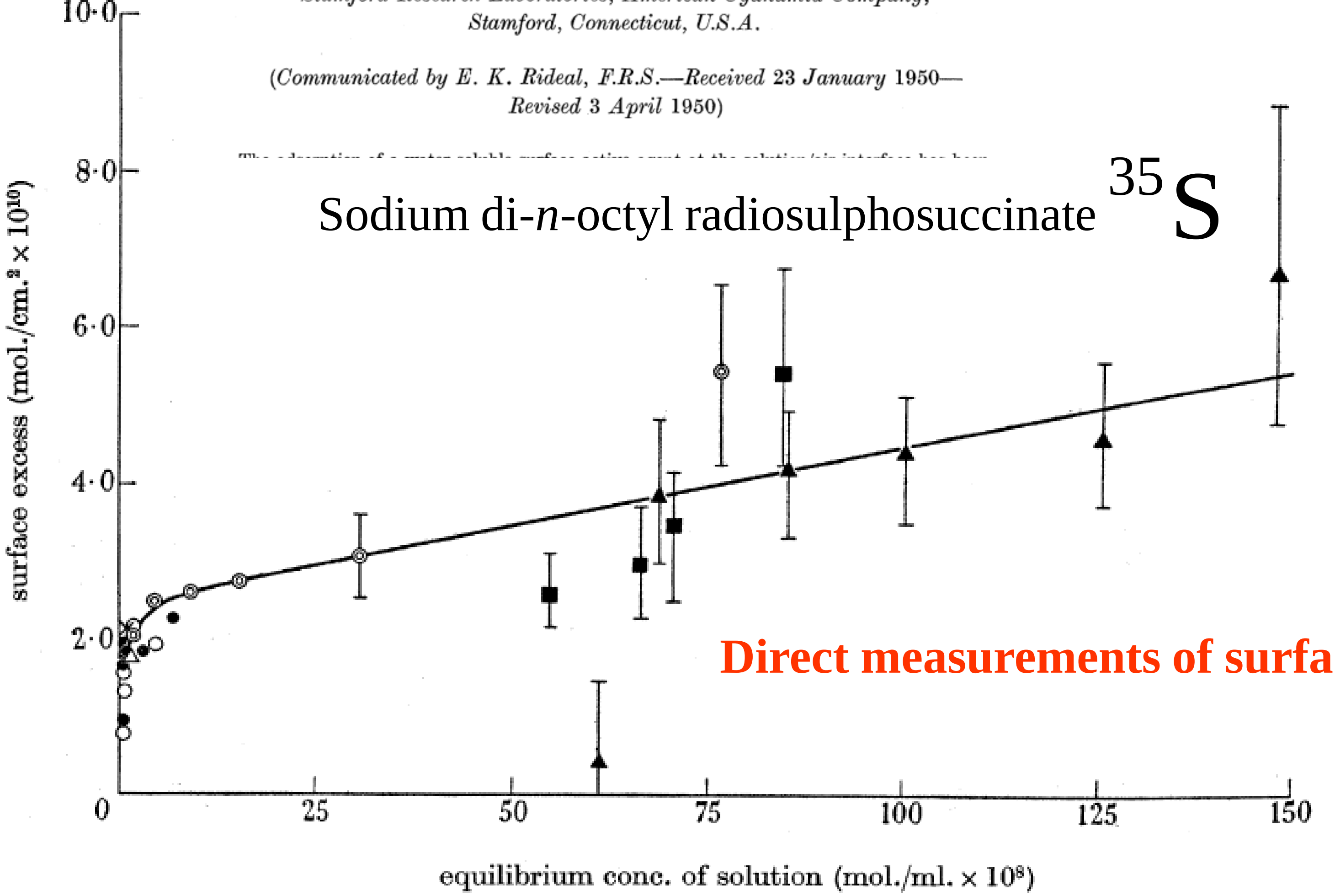
Stamford, Connecticut, U.S.A.

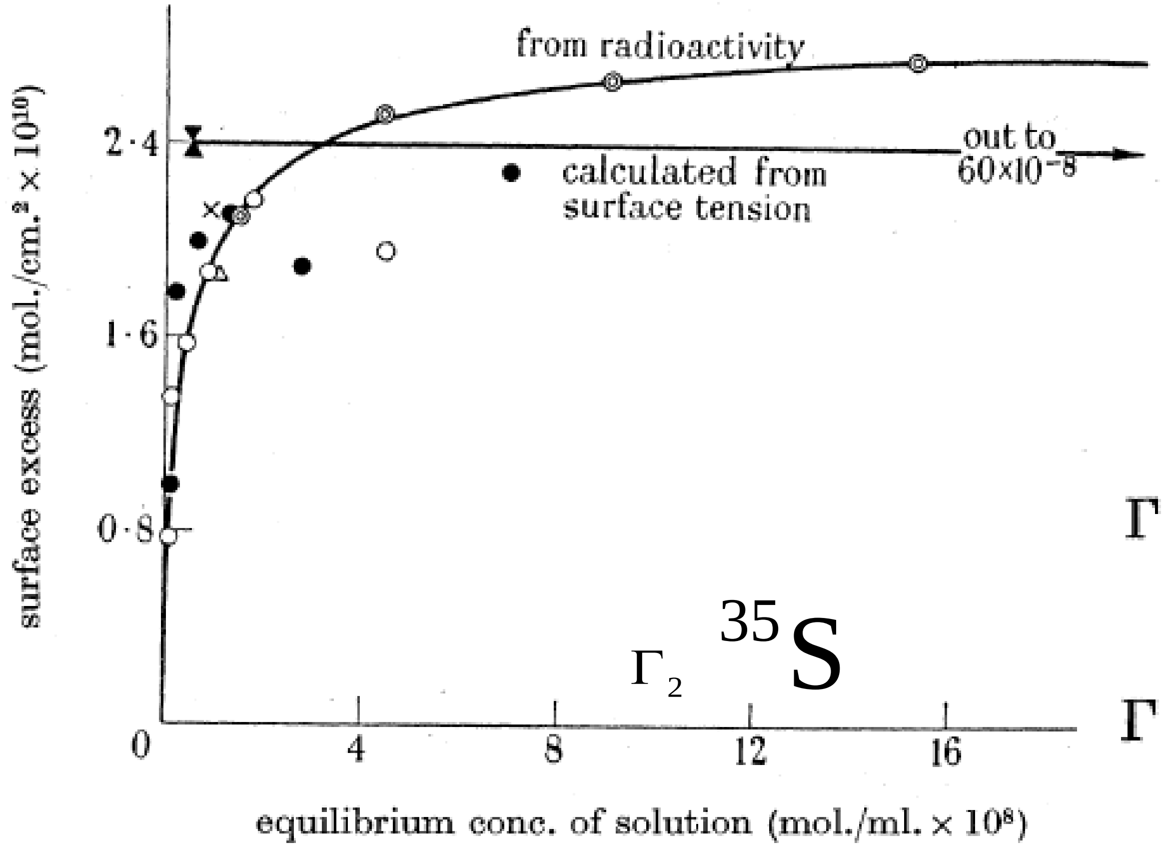
(*Communicated by E. K. Rideal, F.R.S.—Received* 23 *January* 1950—
Revised 3 *April* 1950)



Sodium di-*n*-octyl radiosulphosuccinate ^{35}S

Direct measurements of surface excess

Figure 1. Adsorption isotherm as determined from radioactivity. △ solution 38, ● series 48, × solution 70-1, ○ series 78, ◎ series 82, ■ series 183, ▲ series 187.



Γ_2 ^{35}S

FIGURE 2. Enlargement of radioactivity isotherm. △ solution 38, ● series 48, × solution 70-1, ○ series 78, ◎ series 82.

$$\Gamma = -\frac{1}{2RT}\frac{d\gamma}{d\ln c},$$

?

$$\Gamma = -\frac{1}{RT}\frac{d\gamma}{d\ln c}.$$

The deviation from *n* = 2 may be caused by experimental problems: In diluted solutions not Γ_2 but Γ_2^m

(see above, here: $\Gamma_2^m \rightarrow 2\Gamma_2$)

TABLE 1. ADSORBED AMOUNT AT GAS-SOLUTION INTERFACE OF SODIUM DODECYLSULFATE BY VARIOUS METHODS

Method	RI species	Saturated adsorption amounts, $\times 10^{-10}$ mol/cm^2	Temp. °C	Reference
RT	^3H	3.19	25	present paper
RT	^3H	5.0	25	3
RT	^3H	5.89	20	11
RT	^{35}S	3.7±1	28	4
RT	^{35}S	3.35		20
RT	^{35}S	7.5		21
RT	^{35}S	4.8±1		22
bubble		4.06	24—26	23
bubble		3.32	26	24
bubble		3.00	20	25
bubble		4.00	25	26
bubble		4.88	28	27
microtome		5.4	21—22	9*

$$\Gamma_2^{m,\infty} \sim \frac{1}{A_0}$$

* Sodium dodecylsulfonate

BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 1991—1998 (1970)

Radiotracer Studies on Adsorption of Surface Active Substance at Aqueous Surface. I. Accurate Measurement of Adsorption of Tritiated Sodium Dodecylsulfate

Kazuo TAJIMA, Mitsuo MURAMATSU and Tsunetaka SASAKI

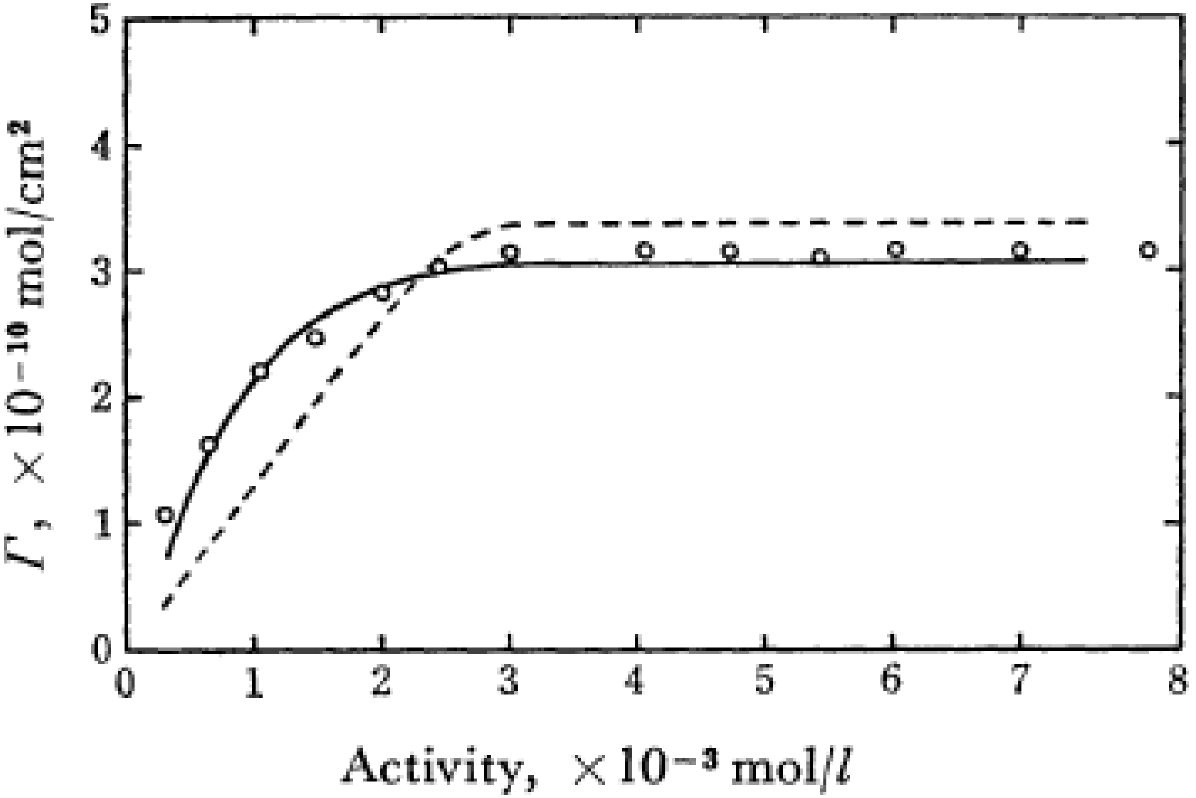
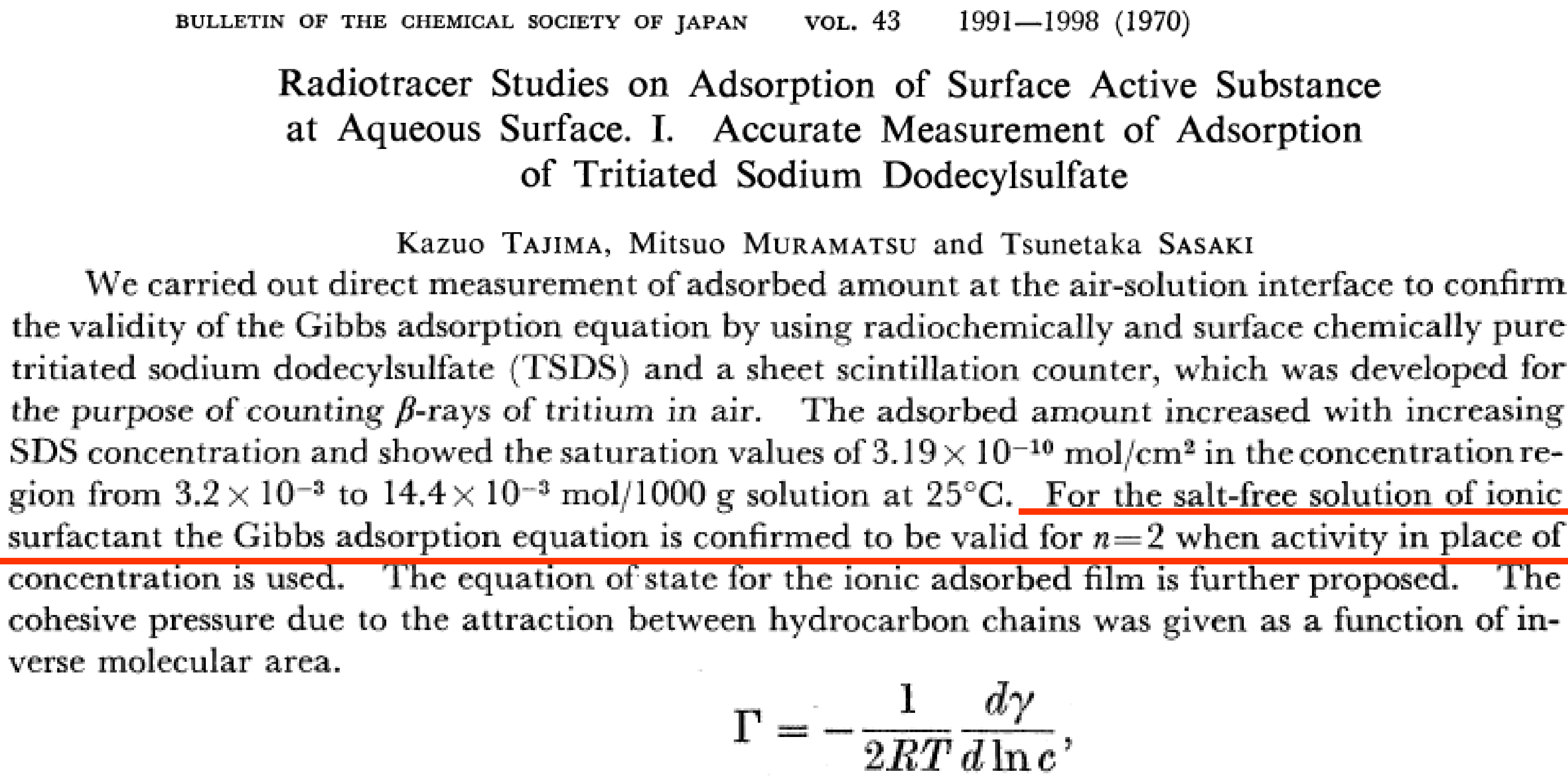


Fig. 7. Comparison of observed and calculated values of SDS adsorption using Eq. (3).

○ : observed values
··· : calculated values (drop volume method)
— : calculated values (Wilhelmy plate method)



BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 1991—1998 (1970)

Radiotracer Studies on Adsorption of Surface Active Substance at Aqueous Surface. I. Accurate Measurement of Adsorption of Tritiated Sodium Dodecylsulfate

Kazuo TAJIMA, Mitsuo MURAMATSU and Tsunetaka SASAKI

We carried out direct measurement of adsorbed amount at the air-solution interface to confirm the validity of the Gibbs adsorption equation by using radiochemically and surface chemically pure tritiated sodium dodecylsulfate (TSDS) and a sheet scintillation counter, which was developed for the purpose of counting β-rays of tritium in air. The adsorbed amount increased with increasing SDS concentration and showed the saturation values of 3.19×10^{-10} mol/cm^2 in the concentration region from 3.2×10^{-3} to 14.4×10^{-3} mol/1000 g solution at 25°C. For the salt-free solution of ionic surfactant the Gibbs adsorption equation is confirmed to be valid for $n=2$ when activity in place of concentration is used. The equation of state for the ionic adsorbed film is further proposed. The cohesive pressure due to the attraction between hydrocarbon chains was given as a function of inverse molecular area.

$$\Gamma = -\frac{1}{2RT}\frac{d\gamma}{d\ln c},$$

Hence, correct measurements result in coincidence of the Gibbs excess values as calculated from the surface tension isotherm and measured directly via radiotracers.

Neutron reflection

$C_{14}H_{29}N(CH_3)_3^+Br^-$

on water surface

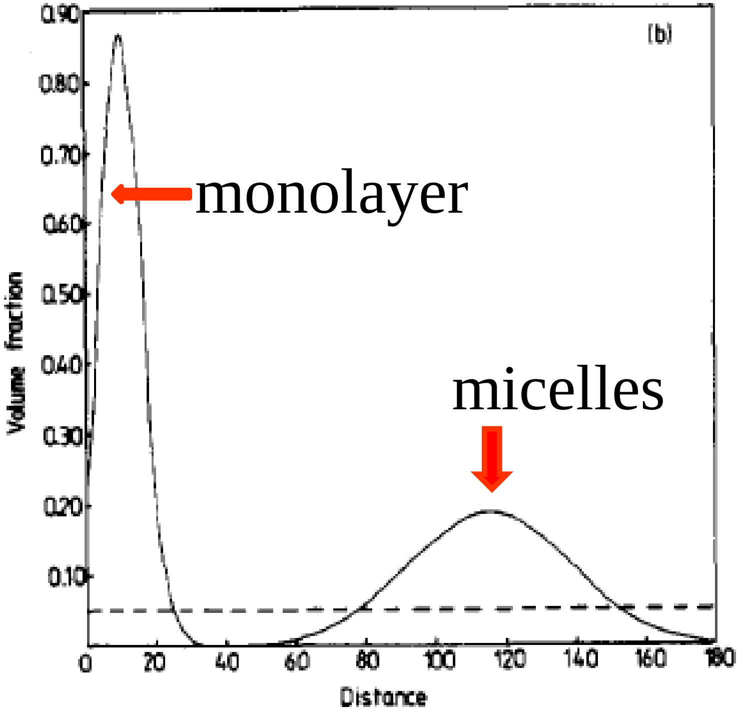


Figure 10. Volume fraction profile of $C_{14}TAB$ normal to the interface for (a) the best uniform layer model (see Table Ia for the width parameters in each layer) and (b) from direct fitting of the partial structure factors. The number density of the micellar layer is taken to be the average of the values fitted from the two contrasts as listed in Table Ib.

Structure of the Surface of a Surfactant Solution above the Critical Micelle Concentration

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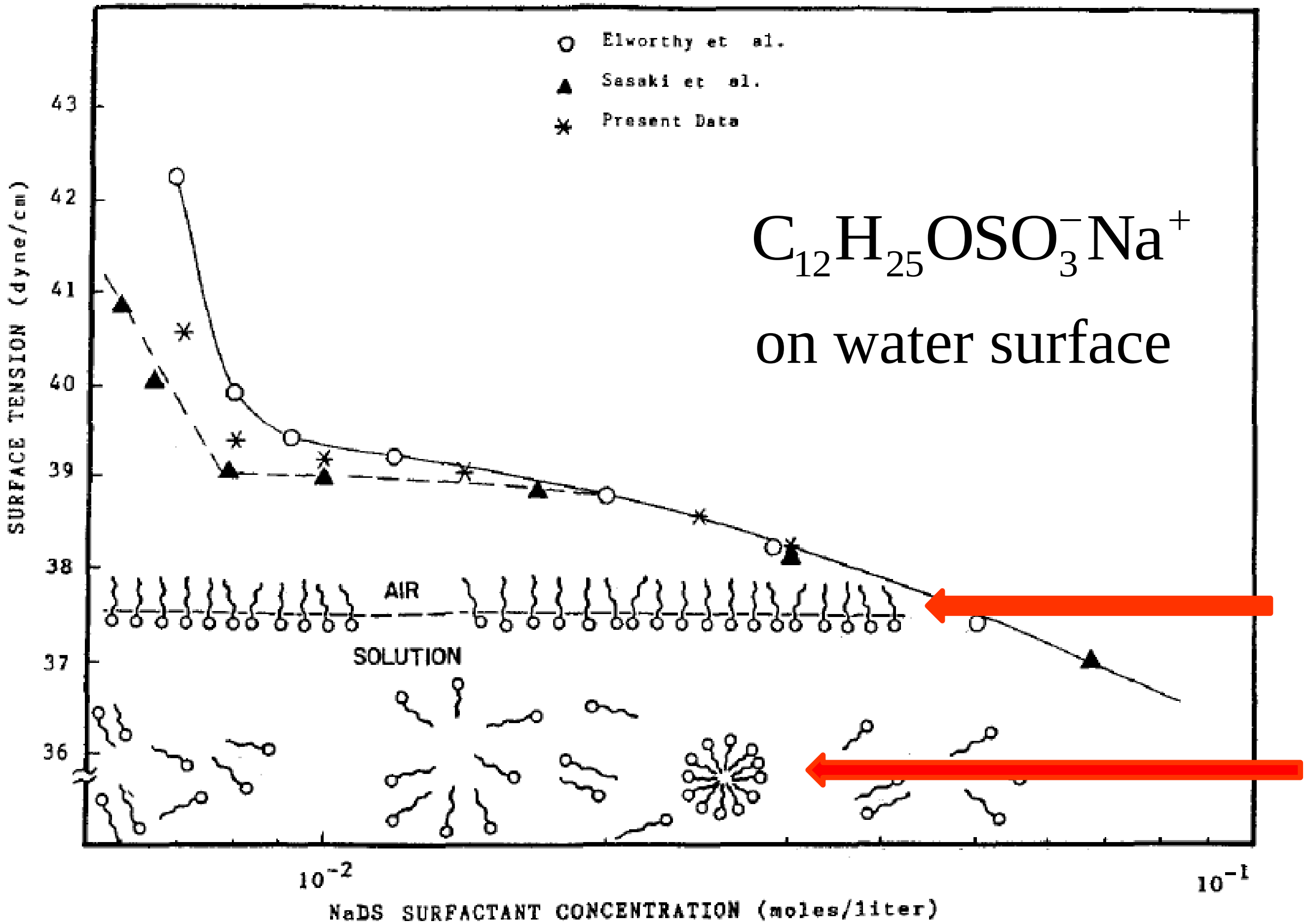


$C_{12}H_{25}OSO_3^-Na^+$

on water surface

monolayer

micelles

FIG. 1. Plot of the experimental data for the surface tension of a NaDS solution vs the surfactant concentration. The presence of surfactant monolayer at the surface and of the micelles in the bulk of the solution is illustrated schematically.

Ordered Micelle Structuring in Thin Films Formed from Anionic Surfactant Solutions

I. Experimental

A. D. NIKOLOV[1] AND D. T. WASAN[2]

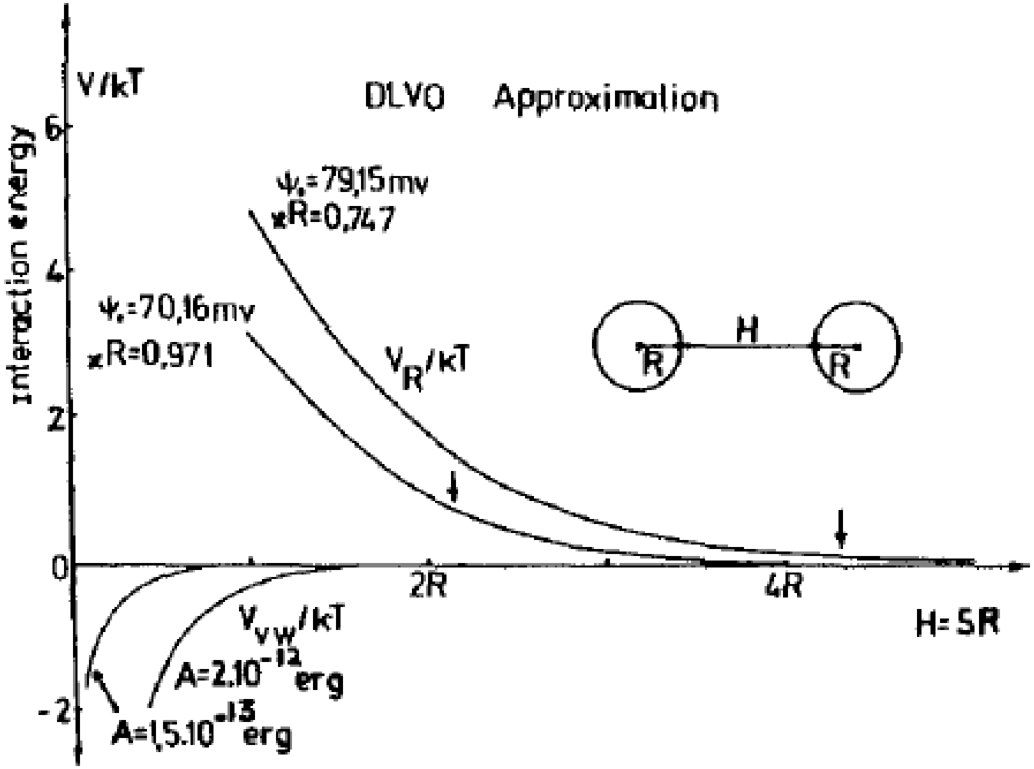


FIG. 5. Potential energies V^{el} and V^{vw} of the electrostatic repulsion between two micelles and of the van der Waals attraction between them. R is the radius of the micelles and H is the shorter distance between their surfaces.

RADIOTRACER STUDY OF SULFATE ION ADSORPTION AT THE AIR/SOLUTION INTERFACE IN SOLUTIONS OF SURFACE-ACTIVE AGENTS

By C. M. Judson, A. A. Lerew, J. K. Dixon and D. J. Salley

Stamford Research Laboratories, American Cyanamid Company, Stamford, Conn.

Received April 8, 1953

Radioactive tracer methods have been used to measure the adsorption of sulfate at the air/solution interface in solutions containing sulfate with various cationic, anionic and non-ionic agents. Measurements of sulfate adsorption with solutions of Aerosol[1] SE Cationic Agent indicate that there is a surface hydrolysis which can be explained in terms of competition between sulfate and hydroxyl gegenions. It also has been shown that sulfate gegenions replace chloride gegenions with the replacement substantially complete in the presence of a moderate excess of sulfate. At high concentrations it was found that multilayers of gegenion were adsorbed. Multilayer adsorption of sulfate, up to an equivalent of about 200 monolayers, was also found in solutions containing sodium sulfate with anionic and non-ionic agents. It appears that when a layer of surface-active agent is present at the surface, electrolyte which may be present in the solution tends to accumulate in the region adjacent to the surface in an amount which is proportional to the concentration of the electrolyte. Multilayers of surface-active electrolyte apparently form in the same way as multilayers of any other electrolyte, in spite of the fact that long chain ion micelles may be involved as well as small ions.

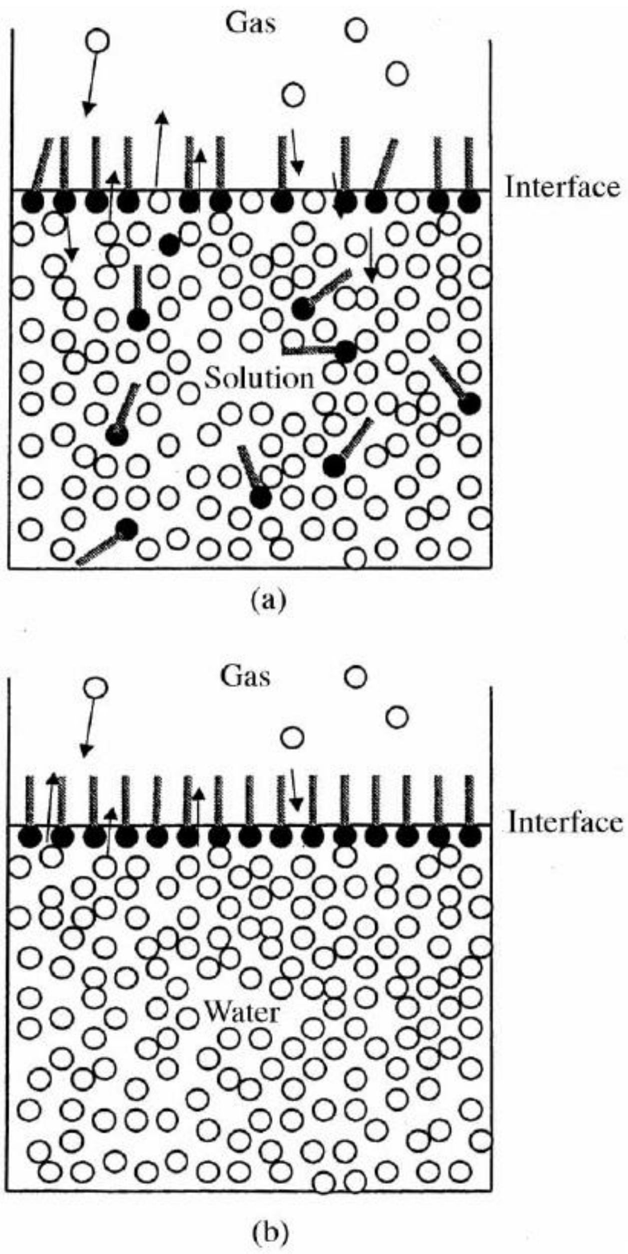
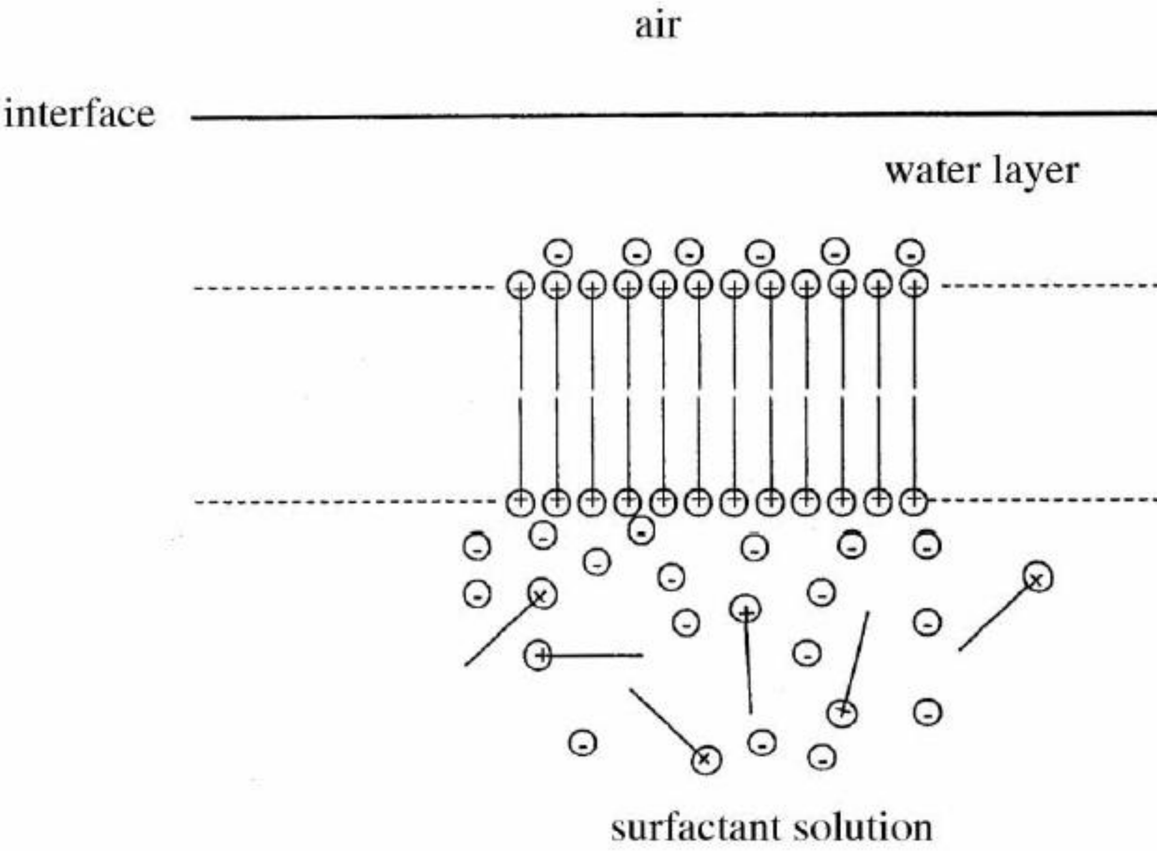


Figure 11. Conventional model of surfactant solution (a) and insoluble monolayer model (b).



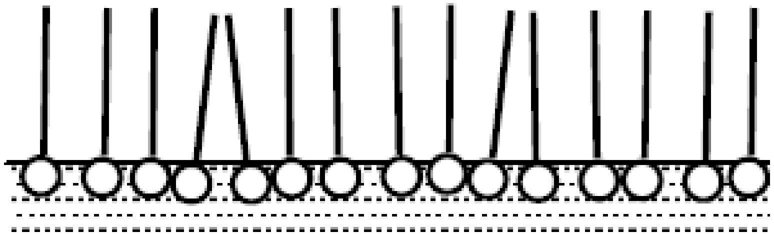
Air/Solution Interface and Adsorption – Solution for the Gibbs Paradox*

Yoshikiyo Moroi

Benjamin Franklin

Mount Pond (Clapham Common) (heute)

$l \approx 2.5\,\mathrm{nm}$



Insoluble surfactant layers on water surface: Evaporation suppression from water surfaces.

Diffusion resistance of evaporation

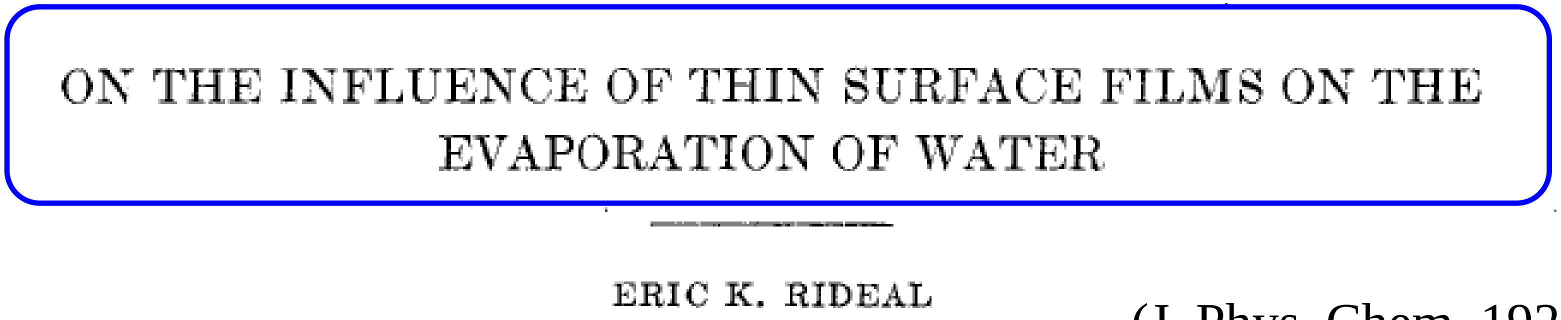
$$R = R_0 + R_{\text{film}}$$

$$\frac{m}{tA} = \frac{C_w - C_d}{R} \quad \left(\frac{g}{s\,cm^2}\right)$$

C – equilibrium concentration of water vapors

$$r = A(C_w - C_d)\left[\left(\frac{t}{m}\right)_f - \left(\frac{t}{m}\right)_w\right]$$

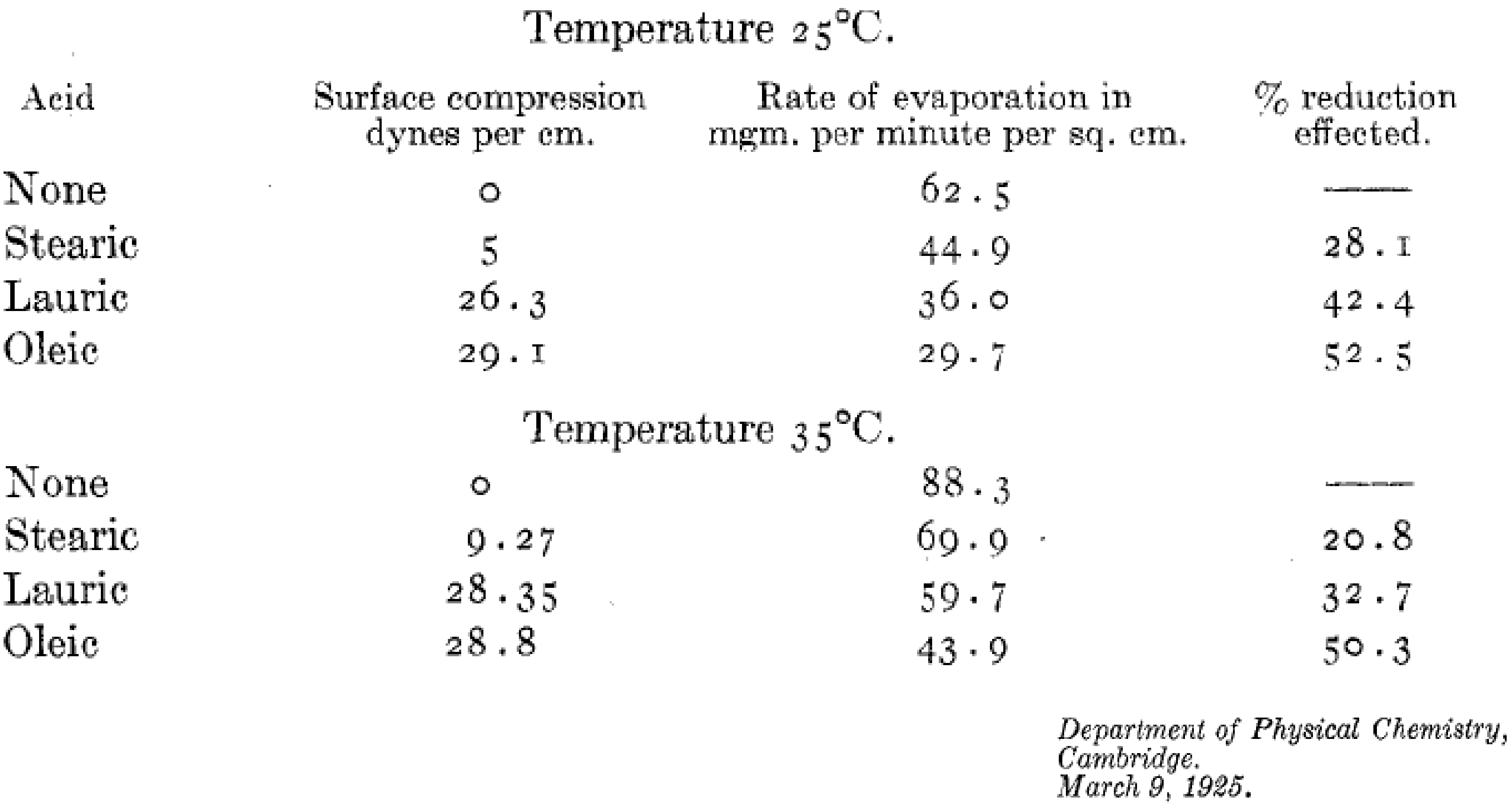
Specific resistance to evaporation



ON THE INFLUENCE OF THIN SURFACE FILMS ON THE EVAPORATION OF WATER

ERIC K. RIDEAL

(J. Phys. Chem. 1925)



Temperature 25°C.

Acid	Surface compression dynes per cm.	Rate of evaporation in mgm. per minute per sq. cm.	% reduction effected.
None	0	62.5	—
Stearic	5	44.9	28.1
Lauric	26.3	36.0	42.4
Oleic	29.1	29.7	52.5

Temperature 35°C.

Acid	Surface compression dynes per cm.	Rate of evaporation in mgm. per minute per sq. cm.	% reduction effected.
None	0	88.3	—
Stearic	9.27	69.9	20.8
Lauric	28.35	59.7	32.7
Oleic	28.8	43.9	50.3

Department of Physical Chemistry,
Cambridge.
March 9, 1925.

Vol. 38, No. 5 Transactions, American Geophysical Union October 1957

Evaporation Suppression from Water Surfaces

W. J. Roberts

Abstract—Techniques used for measuring the effect of monomolecular films to suppress evaporation from water surfaces are reviewed. A brief history of chemical studies and field testing of organic compounds is presented. Research in Illinois by the State Water Survey indicates that normal evaporation may be reduced by as much as one-third by efficient use of monolayers.

Introduction—Hydrologic phenomena are extremely variable in their intensity, quantity, and time of occurrence. The more apparent factors such as rainfall and runoff have received much study, while equally important phenomena such as evaporation have been accorded comparatively little attention. Evaporation is an important factor from the water supply standpoint and in recent years many scientists all over the world have been experimenting on means to reduce this direct water loss. Since 1952 the Australian Commonwealth Scientific and Industrial Research Organization (CSIRO) has been testing an insoluble chemical to 24 pct on the African lake. The Australians report that their method of saving water is presently effective only in reservoirs up to two acres in area.

Properties required in a suppressant—An effective evaporation suppression agent must possess several characteristics. From the standpoint of the water for domestic use, it must be non-toxic and easily handled. It should be in a form that is readily applied to the reservoir surface and the cost should be reasonable. It must be sufficiently pure so as not to cause any taste problems in the finished water nor should it prevent proper treatment of the water.

pressure. *Langmuir* and *Schaefer* [1943] devised a technique for measuring evaporation resistance. They suspended a solid desiccant above the water surface and measured the amount of water evaporated by a stream of dry air blown over the surface film. The resistance to evaporation is represented as an energy barrier related to the film pressure. *Rosano* and *La Mer* [1956] carried on studies of evaporation rates through monolayers of esters, acids, and alcohols.

Field research in the United States—In the United States, research in evaporation suppression has been carried on by federal, state, and private organizations in addition to the studies by physical chemists. The United States Bureau of Reclamation and the United States Geological Survey have both made fundamental studies on energy balance and film spreading techniques and several laboratory studies of evaporation savings. A team of North Texas State College students in collaboration with six government agencies has conducted studies on physical and biological effects of hexadecanol in a five-acre lake near Oklahoma City. The Southwest Research Institute has a program of research on control of evaporation from reservoirs in Texas.

The Illinois program—The work of the Illinois State Water Survey in this field has been concentrated on the measurement of differences in evaporation rates from pairs of identical water containers where one surface is unprotected and the second surface has a coating of hexadecanol. These studies have also been applied to a 100,000-gallon capacity tank.

The Survey operates three evaporation stations, in northern, central, and southern Illinois. These

FIG. 1 – Evaporimeters at Urbana, Illinois, evaporation station

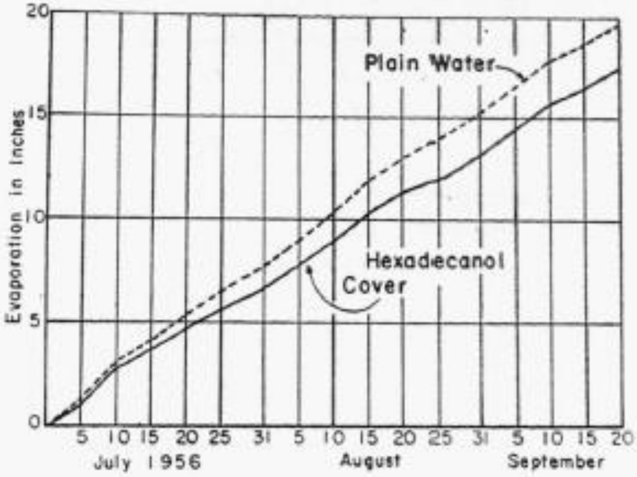
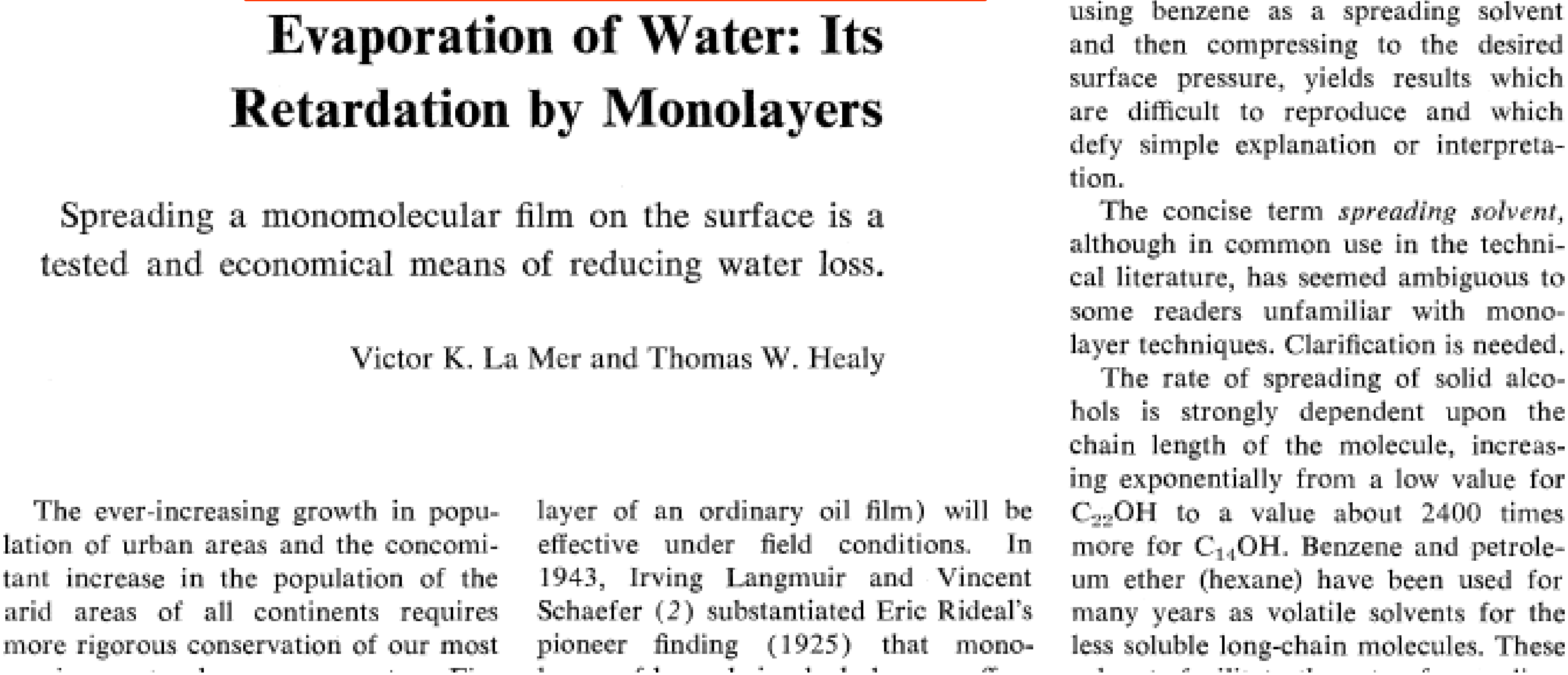


FIG. 2 – Cumulative evaporation from evaporimeter pans at Urbana, Illinois

Evaporation of Water: Its Retardation by Monolayers
Author(s): Victor K. La Mer and Thomas W. Healy
Source: *Science*, New Series, Vol. 148, No. 3666 (Apr. 2, 1965), pp. 36-42
Published by: American Association for the Advancement of Science

In the USA: $2\times10^{10}\ \mathrm{m}^3$ / year



Evaporation of Water: Its Retardation by Monolayers

Spreading a monomolecular film on the surface is a tested and economical means of reducing water loss.

Victor K. La Mer and Thomas W. Healy

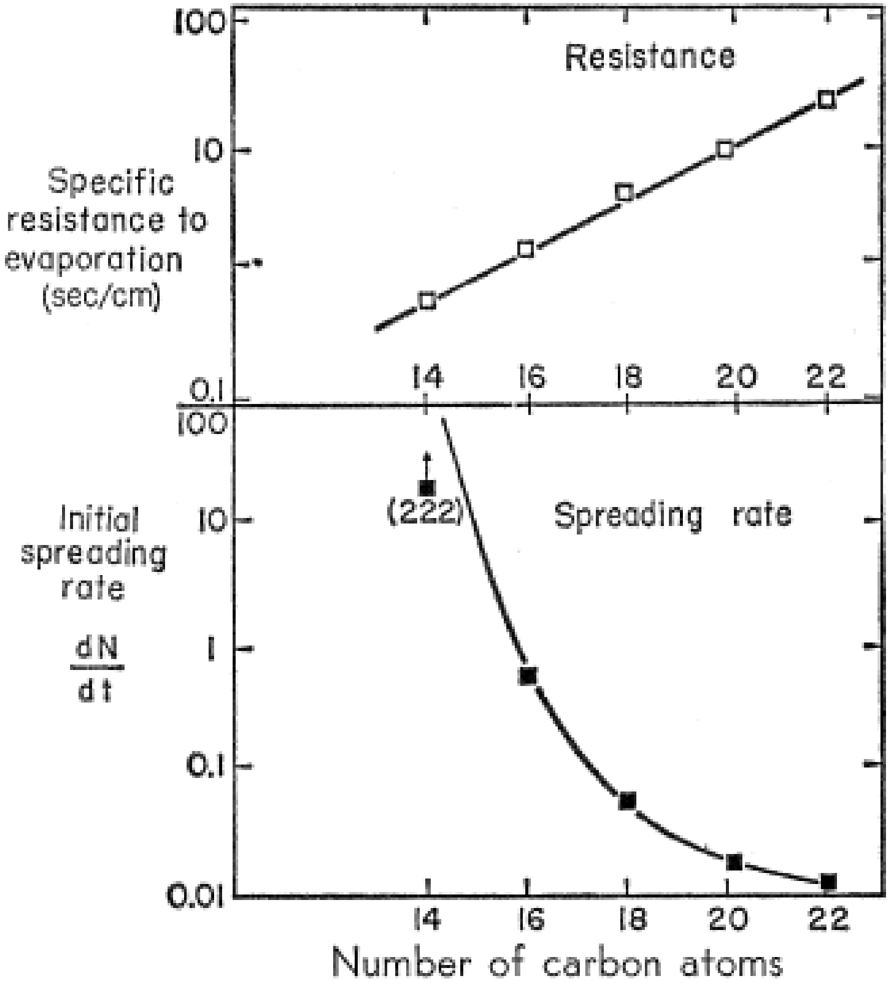
The ever-increasing growth in population of urban areas and the concomitant increase in the population of the arid areas of all continents requires more rigorous conservation of our most

layer of an ordinary oil film) will be effective under field conditions. In 1943, Irving Langmuir and Vincent Schaefer (2) substantiated Eric Rideal's pioneer finding (1925) that mono-

Archer and La Mer (*6*, *7*) that Langmuir's method of spreading the film, by using benzene as a spreading solvent and then compressing to the desired surface pressure, yields results which are difficult to reproduce and which defy simple explanation or interpretation.

The concise term *spreading solvent*, although in common use in the technical literature, has seemed ambiguous to some readers unfamiliar with monolayer techniques. Clarification is needed.

The rate of spreading of solid alcohols is strongly dependent upon the chain length of the molecule, increasing exponentially from a low value for $C_{22}OH$ to a value about 2400 times more for $C_{14}OH$. Benzene and petroleum ether (hexane) have been used for many years as volatile solvents for the less soluble long-chain molecules. These



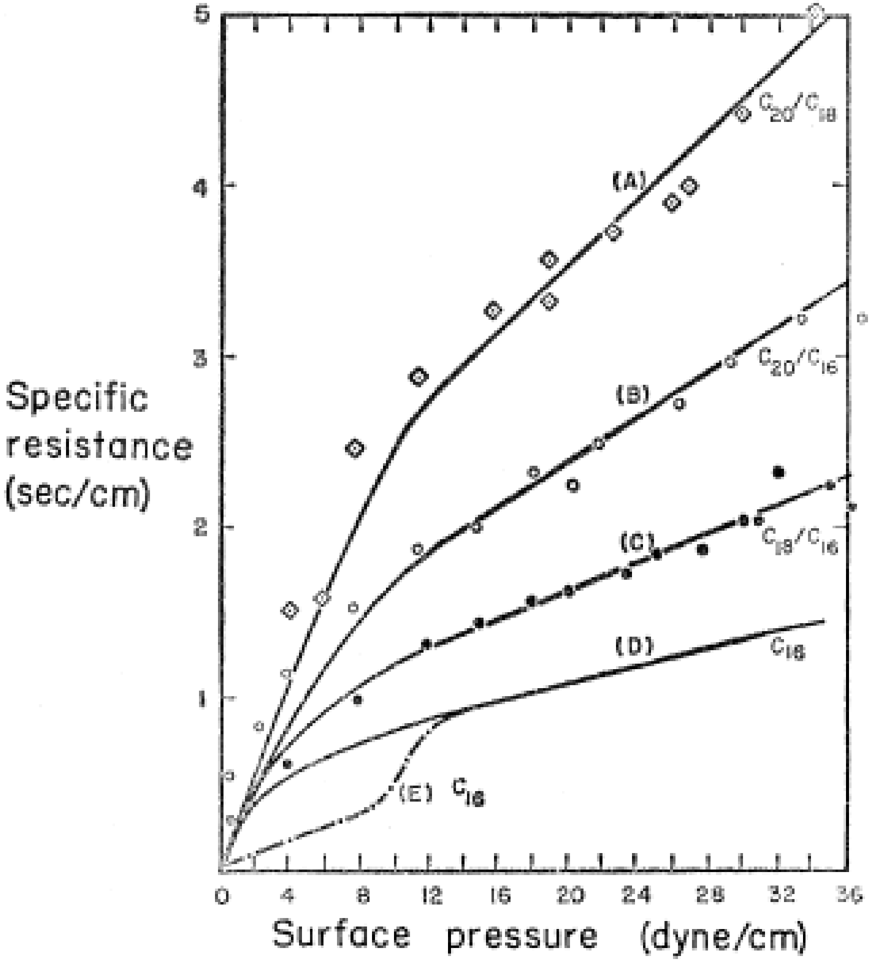


Fig. 1 (left). (Top) Effect of chain length (number of carbon atoms in the chain of the paraffinic alcohol molecule) on resistance to evaporation (*r*, expressed in centimeters per second) [From data of Aylmore (*23*)]. (Bottom) Plot of chain length (abscissa) against initial rate of spreading (ordinate) [Data for rate of spreading from Deo (*22*)]. Fig. 2 (right). Plot of specific resistance against surface pressure, at constant temperature, for mixtures of paraffinic alcohols (from experimental data. (*A* to *C*) Curves for 1:1 mixtures of *n*-alcohols calculated on the basis of the values for free energy in Eq. 5. (*D*) Curve for pure $C_{16}OH$. (*E*) Curve (kinked) for $C_{16}OH$ containing a small amount of impurity, which is squeezed out at pressures above 12 dyne/cm [Based on data of Barnes and La Mer (see *1*)].

Review of Literature on Evaporation Suppression

By GEORGE B. MAGIN, Jr., and LOIS E. RANDALL

STUDIES OF EVAPORATION

GEOLOGICAL SURVEY PROFESSIONAL PAPER 272-C

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON : 1960

RESERVOIR EVAPORATION IN THE WESTERN UNITED STATES

Current Science, Challenges, and Future Needs

Katja Friedrich, Robert L. Grossman, Justin Huntington, Peter D. Blanken, John Lenters,
Kathleen D. Holman, David Gochis, Ben Livneh, James Prairie, Erik Skeie, Nathan C. Healey,
Katharine Dahm, Christopher Pearson, Taryn Finnessey, Simon J. Hook, and Ted Kowalski

Reservoir evaporation represents a substantial loss of available water. Improved understanding, estimation, and forecasting of evaporation rates will help to manage this water loss more efficiently, particularly when water is scarce.

Water scarcity has become—and will remain—the greatest threat to food security, human health, and natural ecosystems during the twenty-first century (Seckler et al. 1999). More than one billion people living in arid regions are expected to face water scarcity by 2025, forcing reductions in per capita water use across multiple sectors, including food production (Seckler et al. 1999; Oki and Kanae 2006). Worldwide, but especially in arid regions, the effects of climate change and rising temperatures threaten to reduce available surface water through enhanced evaporation, especially in surface storage reservoirs. Recently, reservoirs across the southwestern United States have been experiencing extremely low water levels, with water demands increasing and supplies decreasing (Figs. 1, 2; Fulp 2005; Barnett and Pierce 2008). The effective capacity of water stored by the mountain snowpack has been reduced by recent intense droughts, as well as from earlier snowmelt and runoff as a result of rising temperatures, rain-on-snow events, and enhanced dust on snow (Christensen et al. 2004; Seager et al. 2007; Barnett and Pierce 2008;

Fig. 1. Low water levels at Lake Mead (Nevada), shown as white bathtub rings and highlighting the importance of quantifying reservoir evaporation (credit: Kyle Simourd, CC 21). Between the high water mark in 1942 (33,000,000,000 m^3) and the present photo (2015), the lake has lost about 66% (21,000,000,000 m^3) of its water, based on stage and storage data at Hoover Dam (http://goo.gl/fktcft). According to the U.S. Bureau of Reclamation, Lake Mead's water level reached an all-time low in May 2016 (Jacobo 2016).

Overpeck and Udall 2010; Rasmussen et al. 2014).

Currently, freshwater demands in arid and semiarid regions of the western United States exceed the available supply in a given year (Fig. 2), increasing the dependence on reservoirs and water-harvesting techniques (see sidebar "The cost of water in the southwestern United States" for more information; WWAP 2015). Water consumption in the western United States has been reduced in recent years through programs such as "conservation at the spigot" (e.g., Southern Nevada Water Authority 2014; Addink 2005; *Las Vegas Sun*, 27 April 2015), but additional conservation is still needed in order to meet current and future water demands. One mitigation strategy for water scarcity

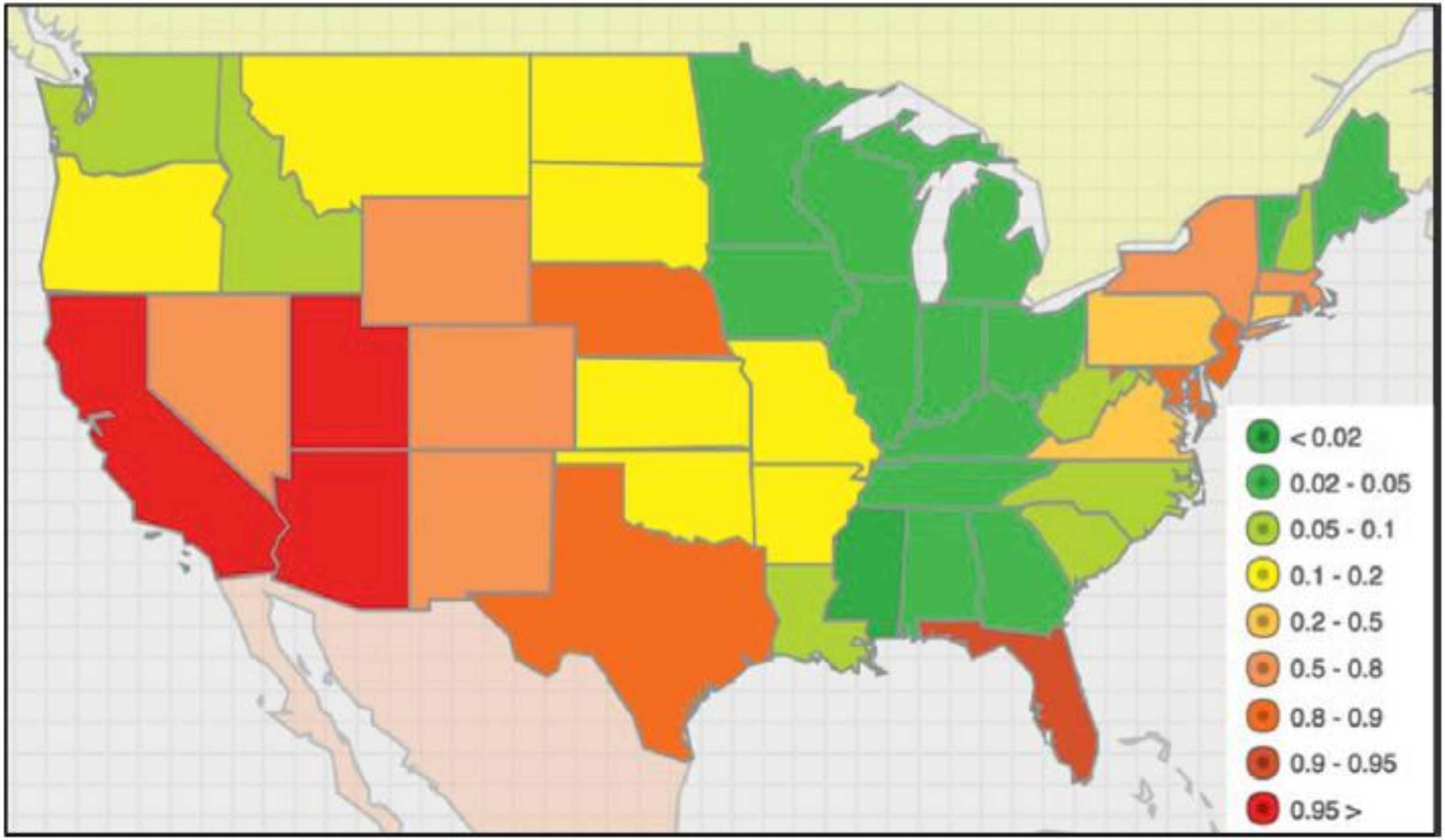


Fig. 2. Water stress level as defined by Pfister et al. (2009) for the United States. Levels for each state indicate the ratio of water withdrawal to hydrologic availability, along with a variation factor to account for the variability in precipitation.

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Article

Reduction of Evaporation of Natural Water Samples by Monomolecular Films

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A capacidade de filmes monomoleculares de álcoois graxos em reduzir a evaporação de amostras naturais de água, coletadas em dois reservatórios de São Paulo (Guarapiranga e Billings), foi estudada em laboratório. As reduções da evaporação foram determinadas diretamente, medindo-se o volume de água evaporado dos recipientes de teste após certo tempo. Filmes mistos de hexadecanol e octadecanol apresentaram alto potencial de redução da evaporação (até 57%) e persistência na superfície da água, por cerca de 48 horas. Uma breve discussão sobre a melhor eficiência desses filmes mistos na redução da evaporação de água é também apresentada.

The ability of monomolecular films of fatty alcohols in reducing evaporation of natural water samples collected from two reservoirs in São Paulo (Guarapiranga and Billings) was studied in the laboratory. Evaporation reductions were determined directly by measuring the volume of water evaporated from the test recipients after a certain period of time. Mixed films of hexadecanol and octadecanol showed high potential of evaporation reduction (up to 57%) and persistence on the water surface of *ca*. 48 hours. A brief discussion on the better efficiency of these mixed films in reducing water evaporation is also presented.

Keywords: water, evaporation, fatty alcohols, monomolecular films, surface tension

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WATER RESOURCES DEVELOPMENT: ECONOMIC AND LEGAL ASPECTS

Evaporation Reduction from Water Reservoirs in Arid Lands Using Monolayers: Algerian Experience[1]

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Abstract—The extremely high rate of evaporation from water surfaces in arid and semi-arid areas greatly reduces optimal utilization of water reservoirs. In Algeria, which is at 80% an arid country, water resources are scarce and renewable due to low annual precipitation. Considering the importance of optimal utilization of renewable water resources, about 70 dams with capacity of 7.4 billion m^3 were constructed. One of the biggest problems of water in dams in Algeria is the huge amount of water loss through evaporation due to high evaporation rate. Therefore, applying techniques to reduce evaporation are greatly needed. One of the most recommended techniques for reducing evaporation is the application of a thin chemical film on the surface of the water. The present study aims to investigate the effect of this technique under arid conditions. Experiment was conducted for 20 weeks in Touggourt with three Colorado-type evaporation pans. Fatty alcohol with various doses were used in different pans. First pan was filled with water without adding fatty alcohol while in second pan, fatty alcohols was added with recommended concentration (0.3 kg/10^4 m^2/day) and similarly in third pan fatty alcohol was added with concentration (0.5 kg/10^4 m^2/day). The preliminary results of the study indicated that evaporation rate from surface water was reduced overall up to 16 and 22% in the second pan and the third one, respectively as compared to the non covered pan.

Keywords: water plans, evaporation reduction, Hexadecanol, arid area, Touggourt

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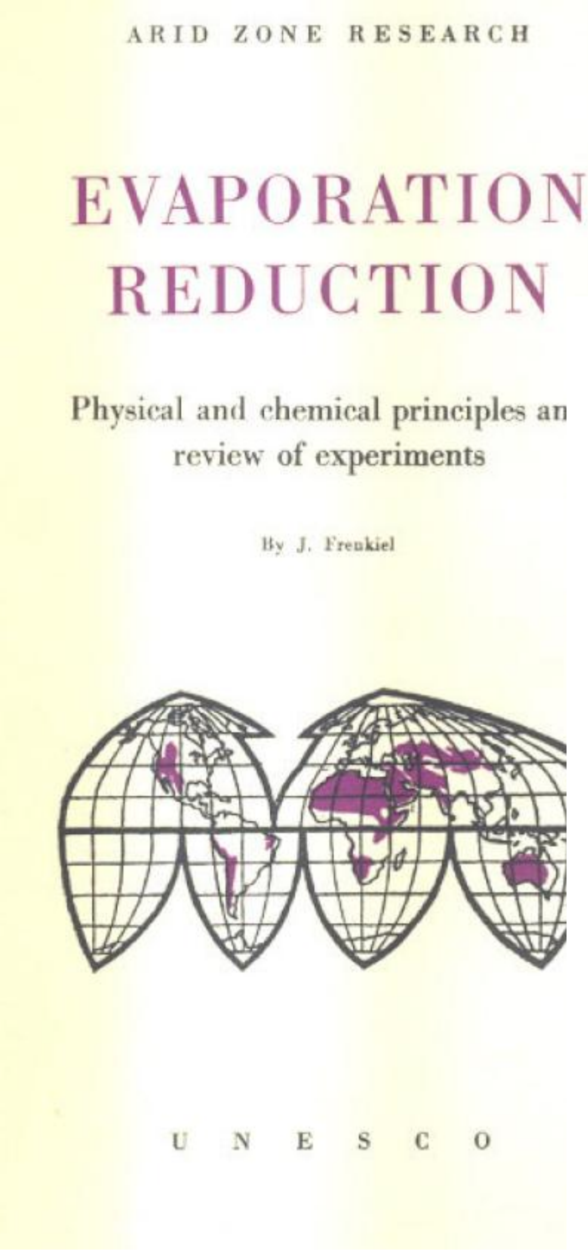

ARID ZONE RESEARCH

EVAPORATION REDUCTION

Physical and chemical principles an
review of experiments

By J. Frenkiel

UNESCO

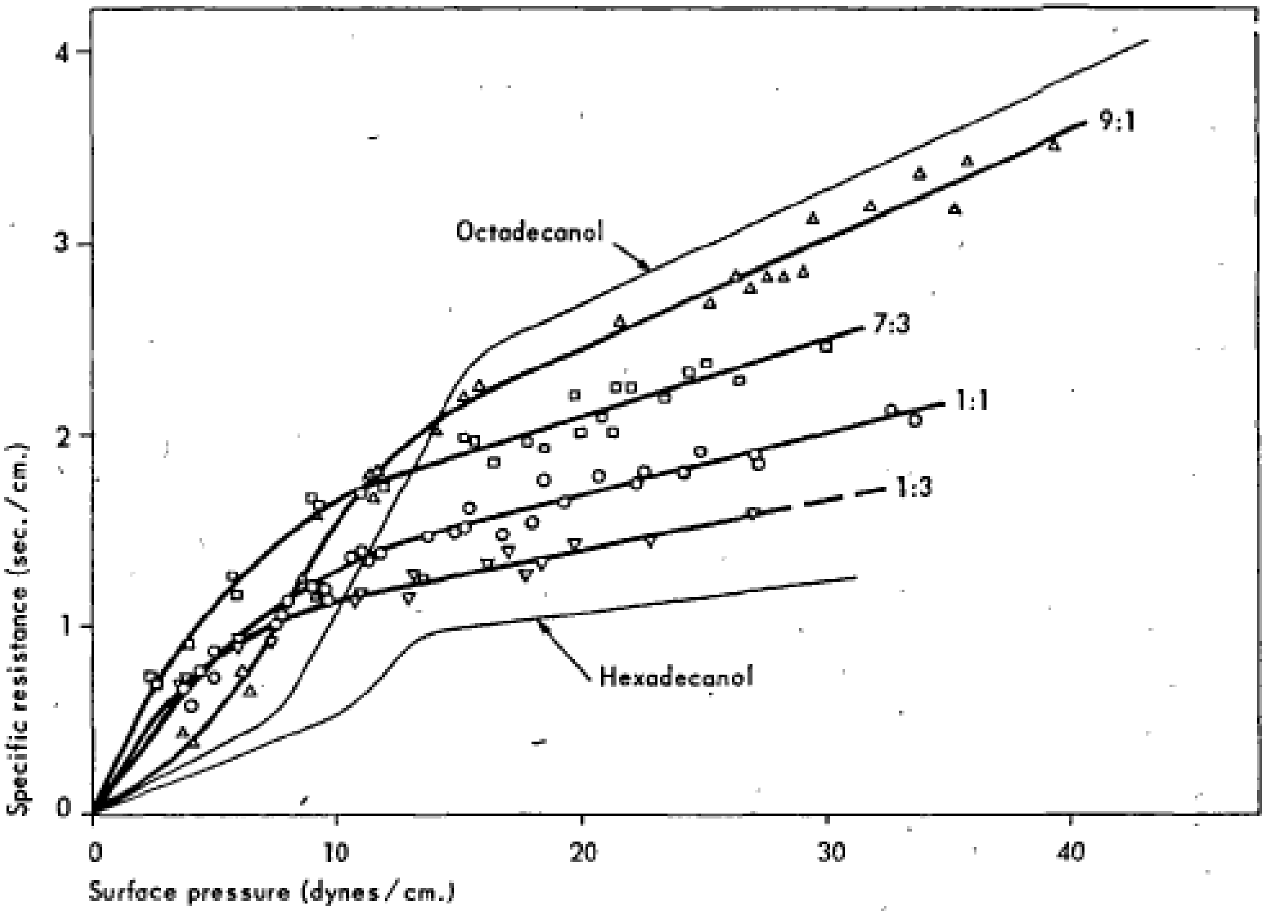

Fig. 2. Evaporation resistance as a function of surface pressure for mixed monolayers of octadecanol and hexadecanol at 25° C. The ratios of octadecanol to hexadecanol are shown in the figure. From Barnes and La Mer (1962*a*).

Colloids and Surfaces A: Physicochem. Eng. Aspects 415 (2012) 47–58

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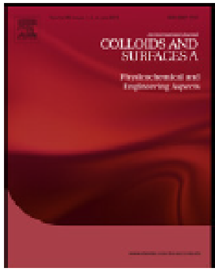
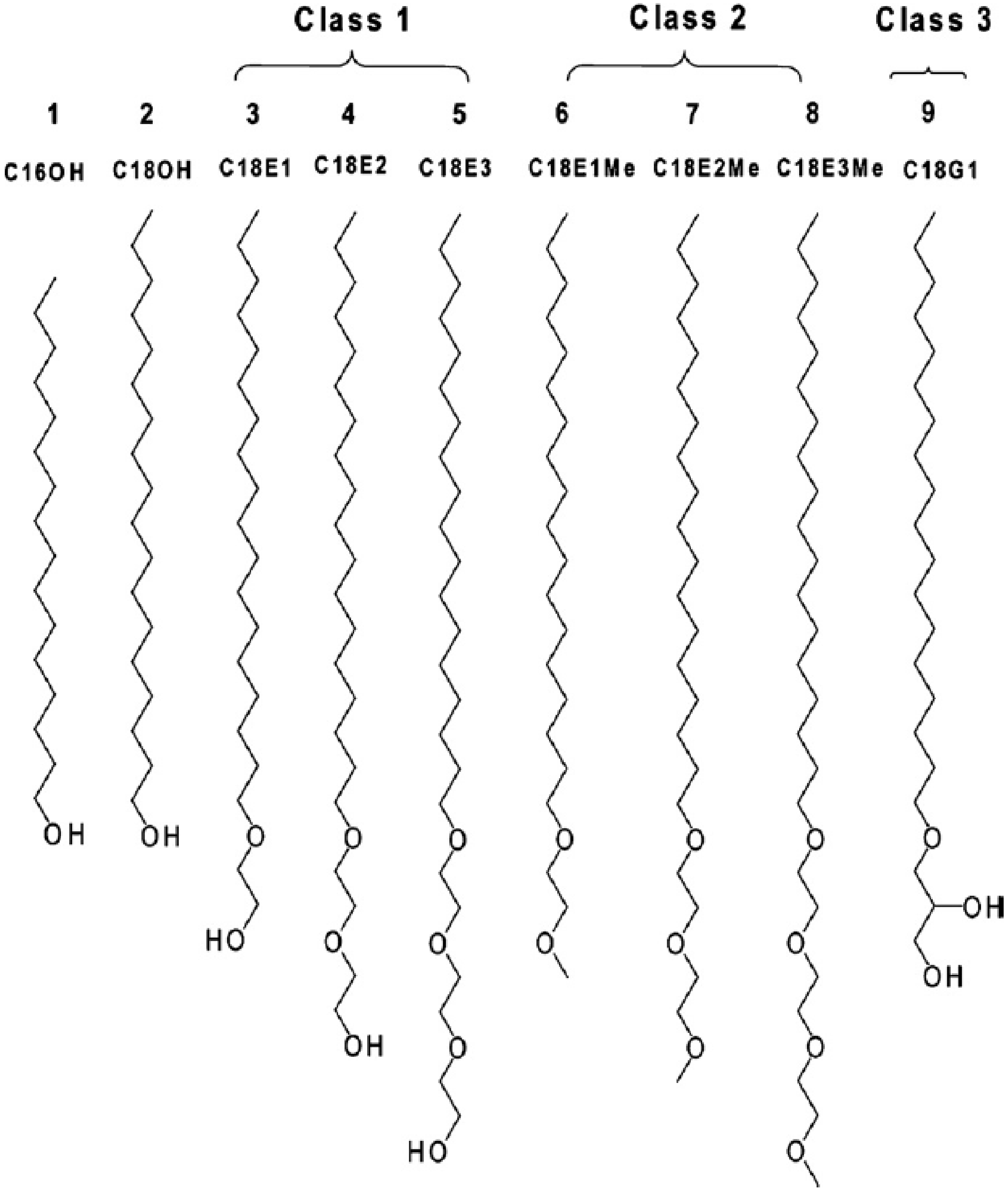


Rational design of monolayers for improved water evaporation mitigation

Emma L. Prime[a], Diana N.H. Tran[a], Michael Plazzer[b], Devi Sunartio[a], Andy H.M. Leung[a], George Yiapanis[b], Svetlana Baoukina[b,1], Irene Yarovsky[b,**], Greg G. Qiao[a,*], David H. Solomon[a,*]


Class 1
Class 2
Class 3
1
C16OH
2
C18OH
3
C18E1
4
C18E2
5
C18E3
6
C18E1Me
7
C18E2Me
8
C18E3Me
9
C18G1
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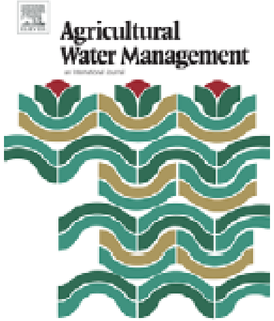

Review

The potential for monolayers to reduce the evaporation of water from large water storages

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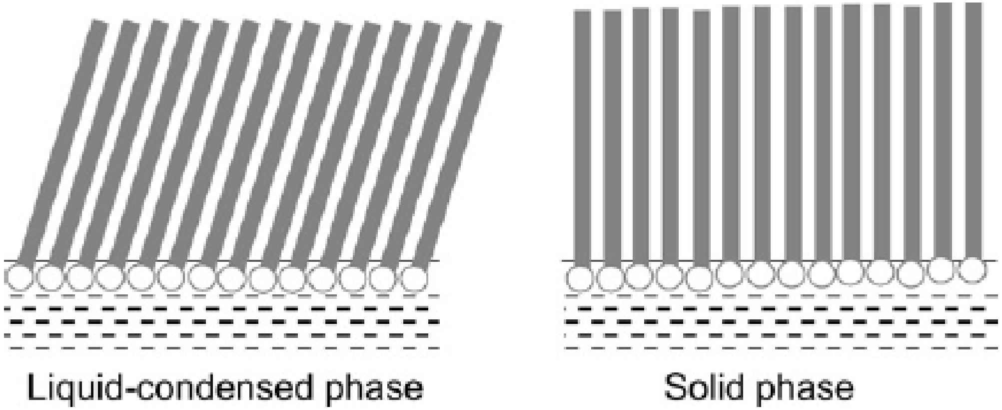

Fig. 1 – Schematic diagram showing the structures of the liquid-condensed and solid monolayer phases. The hydrophilic groups are shown as open circles, and the hydrocarbon (alkyl) chains as grey lines.

Table 1 – Equilibrium spreading pressures, Π^{eq}, for some amphiphiles

Monolayer	Π^{eq} at 20 °C (mN m^{-1})	Π^{eq} at 40 °C (mN m^{-1})	Reference
Hexadecanol	39	47	Brooks and Alexander (1962)
Octadecanol	35	44	Brooks and Alexander (1962)
Hexadecanoic acid	8	20	Cary and Rideal (1925)
Octadecanoic acid	2	13	Cary and Rideal (1925)
Hexadecoxy ethanol	51	–	Deo et al. (1962, 1964a)
Octadecoxy ethanol	48	–	Deo et al. (1962, 1964a)

Table 2 – Evaporation resistance data for various monolayers

Monolayer	Useful range (mN m^{-1})	Resistance (s cm^{-1})	Reference
$C_{16}H_{33}COOH$	13–25	1.4	Archer and La Mer (1955)
$C_{17}H_{33}COOH$	13–25	2.3	Archer and La Mer (1955)
$C_{18}H_{33}COOH$	13–25	4.0	Archer and La Mer (1955)
$C_{19}H_{33}COOH$	13–25	6.5	Archer and La Mer (1955)
$C_{14}H_{29}OH$	None	< 0.5	La Mer et al. (1964)
$C_{16}H_{33}OH$	15+	≤ 1.8	La Mer et al. (1964)
$C_{18}H_{37}OH$	5+	≤ 3.5	La Mer et al. (1964)
$C_{20}H_{41}OH$	5+	1.9–8.2	La Mer et al. (1964)
$C_{22}H_{45}OH$	5+	2.2–19.5	La Mer et al. (1964)
$C_{17}H_{35}COOCH_3$	6–12	≤ 2.4	Barnes and La Mer (1962a)
$C_{15}H_{31}COOC_2H_5$	None	<0.2	Rosano and La Mer (1956)
$C_{17}H_{35}COOC_2H_5$	8–30	≤ 4.2	Rosano and La Mer (1956)
$C_{16}H_{33}OC_2H_4OH$	42+	≤ 6	Deo et al. (1961, 1965)
$C_{18}H_{37}OC_2H_4OH$	20+	≤ 7	Deo et al. (1961, 1965)
$C_{20}H_{41}OC_2H_4OH$	18+	≤ 14	Deo et al. (1961, 1965)
$C_{22}H_{45}OC_2H_4OH$	18+	≤ 19	Deo et al. (1961, 1965)
Sodium docosyl sulfate	None	≤ 0.8	Costin and Barnes (1975)
Poly(vinyl stearate)	None	c. 0.3	Fukuda et al. (1979)
Poly(octadecyl acrylate)	None	0.15	Machida et al. (1998)
Poly(octadecyl methacrylate)	None	<0.3	Drummond et al. (1992a)

"Useful range" is the range of surface pressures for which the evaporation resistance is greater than 1.0 s cm^{-1}.

6.1. *Australia*

By carefully scaling up his experiments Mansfield was able to develop a technique for spreading cetyl alcohol monolayers on farm dams. The alcohol was in pellet form and held in floating gauze rafts. Appreciable reductions in evaporation were reported (Mansfield, 1955), but the procedure was not practicable because of factors such as deterioration of the cetyl alcohol pellets, destruction of mooring lines by yabbies, attacks on polythene floats by cockatoos, and the growth of algae blocking the gauzes (Vines, 1960a).

Spreading of a mixture of cetyl and stearyl alcohols over large areas as a dust was successfully trialed by Vines (1960a,b, 1962). He found that micronised powder could be spread by an agricultural duster, but storage was difficult as the particles tended to fuse. This was not a problem with globular "spray-dried" powder. However the best procedure was to use solid blocks of the alcohol which were shredded by a rotating wire brush and blown out behind a boat. Substantial reductions in evaporation rates were reported, but the material was applied daily.

However Fitzgerald and Vines (1963) reported that after a period of high wind that caused retraction of the monolayer, material that was washed up onto a gently sloping sandy shore was essentially lost, but if the shore was steep and rocky the material blown ashore would respread when the wind eased and full cover of the reservoir would be restored. For up to 2 months after treatment had ceased, monolayers would form spontaneously in calm conditions providing good cover with significant evaporation reduction on a steadily diminishing basis.

There is now renewed interest in using monolayers to reduce evaporation, generated partly by the introduction and promotion of new commercial products. A Canadian product, based on cetyl alcohol, is being tested on a large storage used for cotton growing (Knights, 2005) and on several dams in Australia (www.flexiblesolutions.com). It is being applied as a freshly prepared slurry. Published results indicate savings of about 20%, but ranging from 0% to 40% depending on environmental conditions.

A silicone-based oil, Aquatain, has been developed by Ultimate Agri-Products (2006). It is claimed to have a high resistance to evaporation, to spread readily, and be environmentally benign. At the recommended application rate the film is about 600 nm thick, much thicker than a monolayer.

A survey of methods for reducing evaporation losses from water storages has been prepared by Brown (1984). This includes some references additional to those in this report.

6.2. *Brazil*

There has been some research at the University of Brazil with evaporimeter pans and using long-chain alcohols (Lemos, 2004).

Lótus Química Ambiental have developed a monolayer product based on fatty alcohols and limestone and have carried out small-scale tests (Gugliotti, 2006).

6.3. *Canada*

In recent years O'Brien (2006 and earlier) has developed and commercialised a product (Water$avr™) for applying cetyl alcohol to water surfaces. This material consists of hexadecanol mixed with substantial quantities of calcium hydroxide and a little silica. There have been several trials on large water storages described on the Flexible Solutions web site (www.flexiblesolutions.com) and there is a published report of Australian tests (Knights, 2005). Useful reductions in evaporation loss are reported. There do not appear to be any comparisons of spreading rates.

6.4. *India*

Researchers at the National Chemical Laboratory have done extensive laboratory studies on the evaporation resistances and other monolayer properties of long-chain alcohols and alkoxy ethanols, propanols and butanols (Deo et al., 1964a,b, 1965; Katti et al., 1962, 1968a,b,c). The alkoxy ethanols had the highest evaporation resistances and also the fastest spreading rates (Katti and Sansare, 1970). However there do not appear to have been any field trials other than open pans.

More recently an emulsion based on fatty alcohols (mostly cetyl and stearyl alcohols) obtained from vegetable oils (Acilol TA 1618 WER) was tested near Jaipur. The material was applied by a drip-feed arrangement mounted on floating rafts anchored at different places on the lake. With daily application of about 50 $\mathrm{mg\,m^{-2}}$ evaporation losses were reduced by about 30% (Desai et al., 1990; Asian Institute of Technology, 1982).

6.5. *Israel*

Tahal, Water Planning for Israel, has published two reports on evaporation reduction by Frenkiel (1963, 1965). These are essentially reviews of the relevant information at those dates.

While reducing evaporation losses from the Sea of Galilee was the ultimate goal of the Israeli program most experiments were performed on smaller lakes where the effects could be more accurately monitored. In these tests an alcohol suspension was pumped continuously onto the surface. The amphiphiles in the suspension were hexadecanol and eicosanol with 5–10% ethoxylate to improve spreading rates (Deo et al., 1964b). Using such data Reiser (1969a) calculated that savings of up to 40% were possible for the Sea of Galilee.

The suspension process was again used in trials by Dressler and Guinat (1973). The amphiphile was a hexadecanol + octadecanol mix. Wind speeds above which it was not possible to maintain monolayer cover were 25 km h^{-1} for a lake of 3 km^2.

Bursztyn (1966) spread powdered solid paraffin with various white reflective pigments on the water surface in Class A pans and obtained significant reductions in evaporation. The particles were easily removed by light winds but liquid paraffin gave more stable films and greatly reduced the water evaporation rates.

6.6. *Kenya*

Experiments with cetyl alcohol on reservoirs in East Africa tested a variety of application methods. The most satisfactory method was discharge of a solution from jets spaced around the windward side of the storage (Grundy, 1962). It was reported that the fan-shaped areas of smooth water surface trailing from the jets did not necessarily represent satisfactory monolayer coverage as measurements using indicator oils showed low surface pressures at the edges of these trails.

6.7. *South Africa*

The results of Class A pan experiments found the best evaporation results with a 1:1 mixture of cetyl and stearyl alcohols and essentially confirmed the observations about particle size and daily dosing of other workers (Roberts, 1962).

6.8. USA

After screening tests with evaporimeter pans, the US Bureau of Reclamation selected high purity hexadecanol for use in large-scale field trials (Timblin et al., 1962). They determined that such a monolayer would not have any adverse effects on human or aquatic life. Problems with the caking of dry hexadecanol powder led them to try aqueous slurries, but they found that previously wetted particles sit very low in the water with a substantially reduced line of contact with the surface. Despite this, aqueous slurries, freshly prepared, were used in some of the large-scale field tests with moderately satisfactory results. Better results were obtained when the hexadecanol was distributed as dry powder or by spraying the molten alcohol.

Crow and associates (Manges and Crow, 1966) found that continuous application of a mixture of long-chain alcohols gave good evaporation reduction and also improved the performance of wind barriers and shade cloth.

Tests of Mansfield's floating mesh rafts found deterioration of the cetyl alcohol pellets over a few days (Roberts, 1962). There were fewer problems when a cetyl alcohol slurry was continuously fed onto the water surface, and a saving of 43% was reported.

Aerial distribution of evaporation retardants as a liquid and as a powder were tried on lakes in Utah and New Mexico. Both materials gave satisfactory films at high surface pressures but the spreading from powder was faster (Israelsen and Hansen, 1963; Newkirk, 1963).

Many of these reports mention decomposition of the monolayer material by microbial action and Chang et al. (1962) have investigated this point in more detail. Laboratory studies showed that of the many bacteria commonly found in large water storages only *Pseudomonas* and *Flavobacterium* sp. were able to grow on inorganic agar containing hexadecanol.

Magin and Randall (1960) have reviewed the literature on evaporation suppression to 1959.

Table 3 – Loss of monolayer material from monolayers spread on water

Monolayer	Surface pressure, Π (mN m^{-1})	Half-life at 20 °C, $t_{1/2}$ (h)	Half-life at 40 °C, $t_{1/2}$ (h)
Cetyl alcohol	35	48	1.3
Stearyl alcohol	35	>200	9.6
Cetyl/stearyl mix, 33/67	35	–	3.2
Cetyl/stearyl mix, 67/33	35	–	1.9

Area changes at constant surface pressure (Brooks and Alexander, 1960) converted to half-lives.