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# Factors Affecting the Surface-Chemical Displacement of Bulk Water From Solid Surfaces

H. R. BAKER, C. R. SINGLETERRY, AND W. A. ZISMAN

*Surface Chemistry Branch  
Chemistry Division*

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## Factors Affecting the Surface-Chemical Displacement of Bulk Water from Solid Surfaces\*

H. R. BAKER, C. R. SINGLETERRY, AND W. A. ZISMAN

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Bulk water films can be displaced from a solid surface by a spreading organic liquid which creates and maintains a surface tension gradient in the air/liquid interface. Such a gradient can be maintained if the spreading agent escapes from the air/water interface by solution or evaporation after a few centimeters of travel away from the point of application. The resulting movement of the surface film sweeps along the water beneath by viscous entrainment (Marangoni effect). Displacement is effective and lasting only when the displacing agent (or a surface-active material dissolved in it) is strongly adsorbed to form an insoluble hydrophobic film on the solid surface. Effective water-displacing agents at 20°C should have the following properties: a spreading pressure above 25 dynes/cm on water, a boiling point above 90°C, and a solubility in water of between 2 and 25 percent by weight. The equilibrium spreading pressures for members of a given class of polar organic compounds decrease with rising boiling point. (These principles are well exemplified by a solution in normal butanol of 3 percent of basic barium dinonylnaphthalene sulfonate.) Such water-displacing agents have been found suitable in numerous applications.

### INTRODUCTION

The displacement of one kind of adsorbed molecule from a solid surface as a result of the competitive adsorption of another molecular species has been studied extensively. On the other hand, the displacement of bulk liquid films from a solid surface by the application of relatively small amounts of surface-active agents has been investigated very little, and in spite of its technical importance the process has been imperfectly understood. Close examination of the phenomena of water displacement shows that more than one mechanism is operative in the effective displacement of bulk water films. The present report describes the roles of surface activity, spreading pressure, surface tension gradients, solubility, boiling point, and the hydrophobic properties of the resulting adsorbed monolayer of displacing agent. Finally, we have also investigated the comparative water-displacing properties of a variety of surface-active liquid compounds and solutions.

### DESCRIPTION OF BULK WATER DISPLACEMENT BY A SURFACE-ACTIVE AGENT

Observations of bulk water displacement from a solid surface and measurements of the area of water displaced can be made readily by using the trough of a Langmuir hydrophilic film balance from which the torsion head and mica float have been removed (1). The wax-coated trough is filled to overflowing with distilled water, and a 4 × 4 × 1/8-cu in. sheet of polished and degreased 18/8 stainless steel is supported horizontally on clean glass disks so that the upper surface of the steel plate is within precisely 1 or 2 mm of the free surface of the water. The usual waxed metal or glass barriers are employed to scrape the free surface of the water clean of organic contamination. If the liquid, organic, surface-active compound being investigated is an effective water-displacing agent, a drop (usually 0.025 ml) of the compound placed gently on the surface of the water will cause a circular hole to form in the water immediately beneath, thus exposing the dry surface of the steel plate. The area of the hole will increase in a few seconds to attain a maximum value ( $\Sigma_{max}$ ) which varies from approximately 1 to 38 cm<sup>2</sup>, depending on the compound used. The hole later decreases in area, at a rate dependent

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on the volatility and solubility of the compound, until eventually the steel surface is once more completely covered by bulk water. For example, contraction of the hole is complete in 5 sec with 1-butanol, but it takes several hours with 2-ethylbutanol. If there has been dissolved in the alcohol a small concentration of any one of many types of high-boiling surface-active agents able to adsorb on the solid as a water-insoluble hydrophobic film (for example, glyceryl monooleate), the hole does not contract after reaching its maximum diameter, *i.e.*, the water in that area has been irreversibly displaced from the solid.

Because of the sensitivity of this water-displacement test to variations in water film thickness and to the random departures of displaced areas from true circular shape, the reproducibility of successive measurements was only  $\pm 10$  percent. The averages of several determinations of water displacement properties, as given in Tables 1 and 2, thus provided the most reliable guide about the ability of an organic liquid to displace thick films of water.

#### COMPARATIVE WATER-DISPLACEMENT BEHAVIOR OF THE ALCOHOLS

It is usually helpful in revealing the mechanisms responsible for any surface-chemical process to compare the behavior of a homologous series of pure compounds. Accordingly, we studied the water-displacement properties of the family of fatty alcohols with the preceding technique. Subsequently, many branched and cyclic alcohols, as well as glycol monoethers and glycols, were examined in the same way. It was obvious very early that there was some relation between  $\Sigma_{max}$ , the maximum area of water displacement, and the volatility, the solubility in water, and the spreading pressure of the alcohol film on water. Hence, these properties were ascertained and are compared in Table 1. The data are organized by increasing molecular weight in the first column. Also,  $\Sigma_{max}$  was observed using a standard 0.025-ml drop of the alcohol on water layers 1- and 2-mm thick.

It was a troublesome question to decide how to relate  $\Sigma_{max}$  to the tendency of the alcohol drop to spread on the surface of water because water displacement is a dynamic process and one would not expect the mechanism to be fully described by

equilibrium film properties, such as the equilibrium spreading pressure  $F_e$  of Cary and Rideal (2). The initial spreading coefficient  $S_{b/a}$ , or the semi-initial coefficient  $S_{b'/a}$ , or the final spreading coefficient  $S_{b''/a'}$  of Harkins and coworkers (3-7) is not any more appropriate because  $S_{b/a}$  relates to an ideal initial state before spreading of the alcohol "b" over the water "a," or to an intermediate ( $S_{b'/a}$ ) or a final ( $S_{b''/a'}$ ) state, which has no fixed relation to the continuous succession of surface states occurring during the dynamic process. However, it seemed most promising to use as an approximation either  $F_e$  or  $S_{b/a}$ . We found, on the one hand, that  $F_e$  was speedily and accurately measured using less than 1 ml of the spreading agent by employing Washburn and Keim's (8-10) ingenious "piston monolayer" method with a piston monolayer of eicosyl alcohol. On the other hand,  $S_{b/a}$  can only be computed from knowledge of the two liquid surface tensions and the interfacial tension of the water/agent interface. As the latter value is laborious to obtain reliably when the two liquids are not mutually insoluble, we chose to use  $F_e$  as the constitutive surface-chemical variable to be corrected with the measurements of  $\Sigma_{max}$ .

It is pertinent to point out here that  $F_e$  is simply related to the semi-initial and final spreading coefficients because, as Harkins (6,7) has shown,

$$F_e = S_{b'/a} - S_{b''/a'} \quad (1)$$

Furthermore, as  $F_e$  becomes large, it approaches closer to the value of the initial spreading coefficient  $S_{b/a}$ . Now, the Washburn and Keim method of measuring  $F_e$  is more troublesome the higher the volatility and/or water solubility of the spreading compound becomes. For example, it is effective on all alcohols except methanol, ethanol, and propanol. However, the value of  $F_e$  for these three low homologues can be estimated readily as follows. As the number of carbon atoms per molecule of alcohol decreases toward three or less, the solubility in water becomes large and the interfacial tension against water approaches zero, which exemplifies Pound's well-known rule (11,12) relating interfacial tension to mutual solubility. Consider the Harkins expression for the initial spreading coefficient  $S_{b/a}$  given by

$$S_{b/a} = \gamma_w - (\gamma_o + \gamma_{ow}) \quad (2)$$

TABLE I  
Water Displacement and Related Properties of the Alcohols

Alcohol	Boiling Point* (°C)	Percent Solubility of Fluid in Water*† (wt-% at 20°C)	Equil. Sprd. Press. at 20°C $F_c$ (dynes/cm)	Water Displacement $\Sigma_{max}$ (cm <sup>2</sup> )	
				1-mm Film	2-mm Film
<u>Aliphatic</u>					
Methanol	64.6	Complete	—	3	0
Ethanol	78.5	Complete	—	3	0
1-Propanol	97.2	Complete	—	5	0
2-Propanol	82.3	Complete	—	5	0
1-Butanol	117.7	7.9	48.5	20	12
2-Butanol	99.5	12.5	50.4	16	12
2-Methyl-1-propanol	108.4	9.5 at 18°	49.3	16	12
1-Pentanol	138.0	2.7 at 22°	39.5	16	1
2-Methyl-1-butanol	128.0	sl. sol.	43.3	16	1
3-Methyl-1-butanol	130.5	2.67 at 22°	44.9	16	1
2-Methyl-2-butanol	101.8	12.5	47.1	32	20
3-Pentanol	115.6	sl. sol.	44.0	20	5
1-Hexanol	157.2	0.59	36.9	16	0
2-Ethyl-1-butanol	149.5	0.63 at 24°	39.1	20	0
2-Methyl-1-pentanol	148	—	39.2	16	0
1-Heptanol	176.0	0.09 at 18°	37.3	12	0
2-Heptanol	160.4	0.35	40.3	12	0
2,4-Dimethyl-3-pentanol	140.0	v. sl. sol.	38.8	16	0
1-Octanol	195.0	i	35.5	5	0
2-Ethyl-1-hexanol	183.5	0.10	35.0	20	0
1-Nonanol	213.0	i	35.5	3	0
1-Decanol	231.0	i	34.5	—	—
5-Ethyl-2-nonanol	225.4‡	<0.02‡	29.7	—	—
1-Dodecanol	255.0	i	solid	—	—
2-Methyl-7-ethyl-4-undecanol	263.2‡	<0.02‡	22.0	1	0
2-Heptyl-1-nonanol	—	—	14.1 at 25°	0	0
3,9-Diethyl-6-tri-decanol	308.5‡	<0.02‡	19.6	0	0
<u>Cyclic</u>					
Benzyl alcohol	205.2	4.0 at 17°	27.4 at 25°	8	0
Cyclohexanol	161.5	5.67 at 15°	31.5	3	0
1-Ethyl cyclohexanol	—	—	32.0 at 25°	—	—
Furfuryl alcohol	171	Complete	—	32	3
Tetrahydrofurfuryl alcohol	177-178	Complete	—	8	1
<u>Ether Alcohols from Glycol</u>					
Monomethyl ether	124.5	Complete	41.2	5	0
Monoethyl ether	135.1	Complete	40.2	8	0
Monobutyl ether	171.2	Complete	39.6	16	3
2-Ethyl butyl ether	196.8	1.2	41.0	12	1
<u>Ether Alcohols from Diethylene Glycol</u>					
Monomethyl ether	194.2	Complete	41.6	5	0
Monoethyl ether	201.9	Complete	40.8	8	0
Monobutyl ether	230.4	Complete	40.1	8	0
<u>Glycols</u>					
Pentamethylene glycol	239.4	Complete	—	3	0
Ethylhexylene glycol	—	—	41.9	8	0

\*Unless otherwise indicated, the data in the first two columns was obtained from "The Handbook of Chemistry and Physics," 44th ed., Cleveland: Chemical Rubber Publ. Co., 1963.

†Definitions of symbols: i = insoluble; v. sl. sol. = very slightly soluble; and sl. sol. = slightly soluble.

‡Data from "Synthetic Organic Chemicals," 12th ed., Carbide and Carbon Chemicals Corp., 1946.

where  $\gamma_w$  and  $\gamma_o$  are the surface tensions of water and the organic agent, respectively, and  $\gamma_{ow}$  is their interfacial tension. We can consider  $\gamma_{ow}$  to be zero for methanol, ethanol, and propanol, and compute  $S_{b/a}$  from the surface tensions of the two pure phases. It is interesting that  $S_{b/a}$  for the lowest homologue, methanol, has the maximum (or limiting) value of 50.3 dynes/cm at 20°C because the lowest value of  $\gamma_o$  is 22.5 dynes/cm and  $\gamma_w - \gamma_o = 72.8 - 22.5 = 50.3$  dynes/cm. This maximum value can also be used as a good approximation of  $F_e$  for ethanol and the two propanols.

The alcohols and other polar liquids used for the measurements of equilibrium spreading pressures were the purest materials available from chemical supply houses or other commercial sources. Since minor amounts of other polar compounds had little effect on the spreading pressure, many compounds were used without further purification. When adequate purity was questionable, the compound was percolated slowly through a long adsorption column, packed with activated Florosil, alumina, and silica, until no further change in its spreading pressure occurred.

Using this series limit for the equilibrium spreading pressure of the lower alcohols and the

measured values for the higher alcohols in Table 1, one finds that  $F_e$  is not simply related to either the molecular weight or to the longest chain length of the aliphatic alcohols. If  $F_e$  is plotted against the atmospheric boiling points, the data can be correlated along two curves, one for the normal unbranched alcohols and another for the rest of the alcohols (Fig. 1). The divergence of the normal alcohols from the trend for all the others probably results from the unique ability of the higher members of this series to form close-packed monolayers exposing a dense array of methyl groups at the air/liquid interface.

The effects of branching in the hydrocarbon portion of the alcohol are complex because branching affects the surface tension, the water solubility, and the geometry of the molecular aspect presented to the water at the interface. For the fourteen examples below octanol in molecular weight (Table 1) the net result of carbon chain branching in the alcohols is to increase the equilibrium spreading pressure above that of the isomeric normal alcohol. Secondary alcohols with unbranched carbon chains also have higher spreading pressure than the normal alcohol. These secondary alcohols, like the

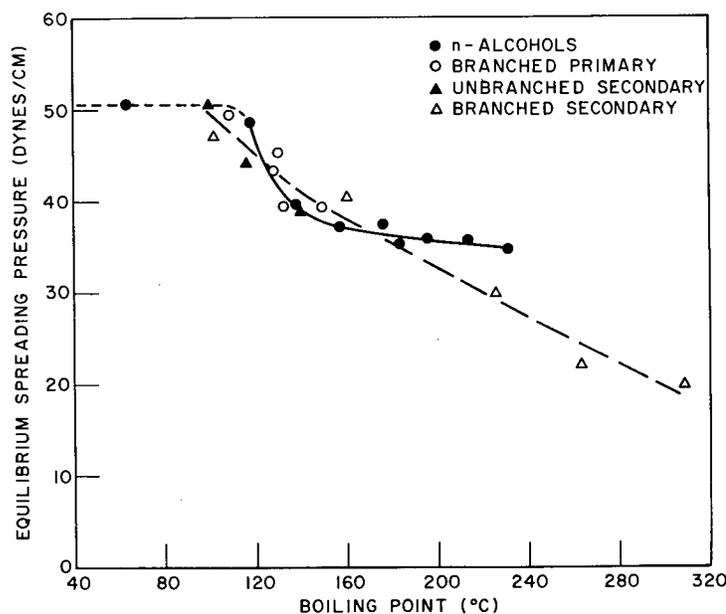


Fig. 1 — Equilibrium spreading pressures of monohydric aliphatic alcohols as a function of their atmospheric boiling points

branched primary alcohols, contain one more methyl group than the n-alkanols. It is instructive to consider the isomeric pentanols in Table 1. It will be noted that 2-methyl-2-butanol, which has three methyl groups, has the highest equilibrium spreading pressure of that group, whereas 1-pentanol, with one methyl group, has the lowest value.

If  $F_e$  for each alcohol is plotted against the maximum diameter of the circular area of water displaced, the points are found to be widely scattered (Fig. 2). Although strong water displacement is invariably associated with relatively high spreading pressure, there are also compounds with equally high spreading pressures which must be classified as poor water displacers. Hence, the spreading pressure is only one of several variables that influence water displacement.

One factor other than spreading pressure that affects the water-displacing ability of alcohols is revealed when attention is directed to the water solubilities of these compounds. From Table 1 it can be seen that the water-miscible lower alcohols, *i.e.*, methanol, ethanol, and propanol, though having the highest spreading pressures, are unable to displace a water layer 2 mm thick,

but can displace a small area of water 1 mm thick. The reason for this behavior is that the high volatility and solubility of these compounds causes them to be removed from the water surface before their high spreading pressures can result in large water-displacement areas. Therefore, it appears necessary to use displacing agents at 20°C whose atmospheric boiling points are above 90°C and which have a limited solubility in water.

The important effects of water solubility are further illustrated in Fig. 3 where  $F_e$  is plotted against the solubility in water (at 20°C) of each of the simple alcohols. The solubilities of the alcohols are found to be rather simply related to their water-displacing properties. (The latter are specified verbally on the figure.) On the right-hand section of the curve the vertical bars through the points are proportional to  $\Sigma_{max}$ , the area of water that one drop of the alcohol will displace in a 2-mm film. Displacement of a 2-mm film occurs only with the strongest displacing agents. The largest values of  $\Sigma_{max}$  are observed with alcohols whose solubilities in water are less than about 25 percent by weight, but greater than about 2 percent. Alcohols with solubilities between 2

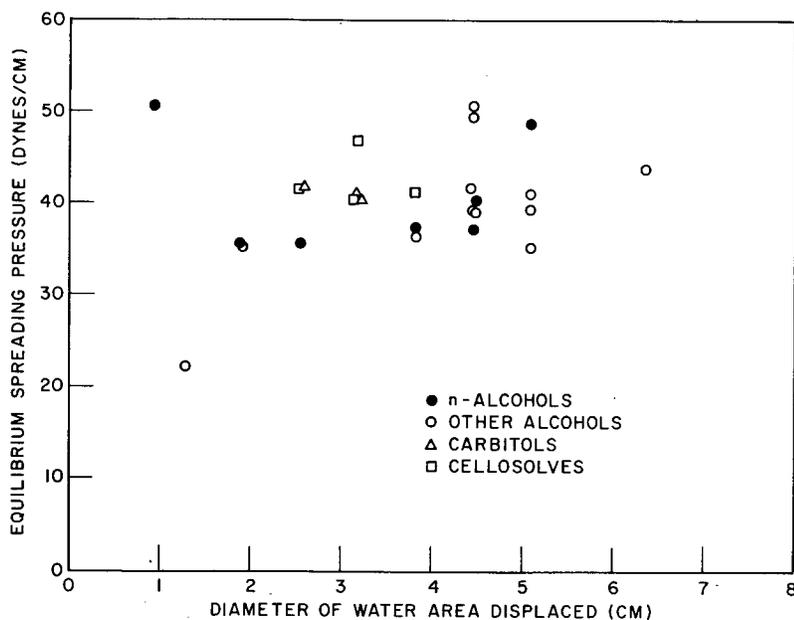


Fig. 2 — Equilibrium spreading pressures of aliphatic alcohols vs. the maximum diameter of a 1-mm-thick water film displaced by one drop of the alcohol

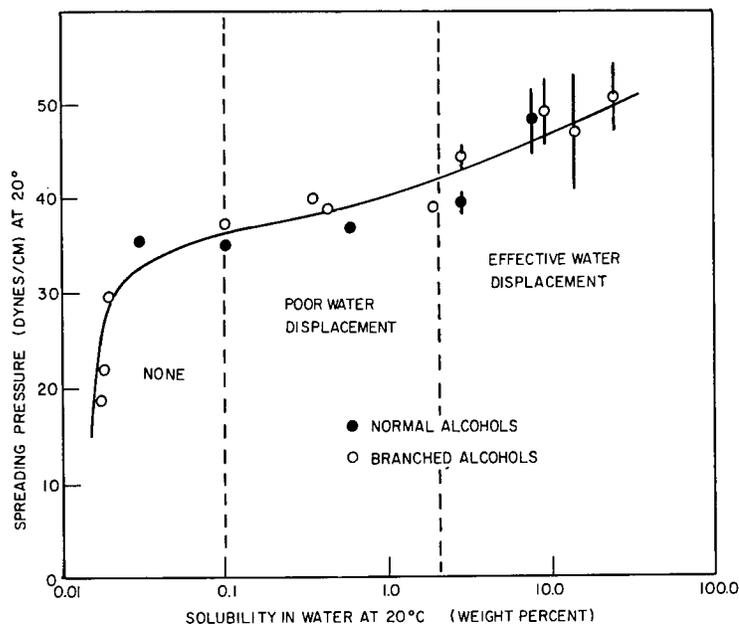


Fig. 3 — Relation of water solubility to equilibrium spreading pressure, showing water-displacing ability for simple monohydric alcohols. The vertical bars through points in the region of strong displacement are proportional in length to the areas of a 2-mm water film displaced by the respective alcohols.

and 0.1 percent have mild or weak displacing effects on the thinner films only 1-mm deep, and they cannot displace the 2-mm layer of water. Alcohols having solubilities below 0.1 percent will not displace even the 1-mm-thick film.

### THE MECHANISM OF WATER DISPLACEMENT

The observations of the relation of water solubility and spreading pressure to water displacement by alcohols, when coupled with the flow patterns observed in the film trough experiments, lead to a clear picture of the displacement mechanism. Water is transported away from the point of application of the alcohol by the viscous drag of the spreading alcohol film. Bressler, Talmud, and Talmud (13) and Schulman and Teorell (14) have observed and discussed the drag caused by a moving, insoluble, oriented monolayer on the bulk water beneath. The adsorbed hydrophilic groups are comprised of hydrogen bonded to adjacent water molecules and are thus effectively coupled to the extensively hydrogen-bonded system of water molecules

beneath. The viscous drag is greater the more rapid the lateral motion of the film, and this rate depends upon the spreading pressure of the alcohol. However, if the alcohol monolayer is completely insoluble in water, it will cover the entire surface of the water in the trough within a second, and spreading will stop before an appreciable amount of water has been displaced by viscous drag. Only if the spreading monolayer dissolves in the water after it has spread a few centimeters can the high film-spreading rate be maintained long enough to transport significant amounts of the substrate water away from the point of application of the drop. The process is illustrated for the case of *n*-butanol in Fig. 4. The transport of water by the spreading butanol drop is so rapid that water builds up as a visible ridge near the boundary of the spreading zone, accumulating more rapidly than it can flow away under gravity.

While the bulk water near the surface is being displaced from an annulus about the drop of butanol, the rest of the disk of butanol is dissolving in the water beneath and is establishing a radial concentration gradient of butanol adsorbed

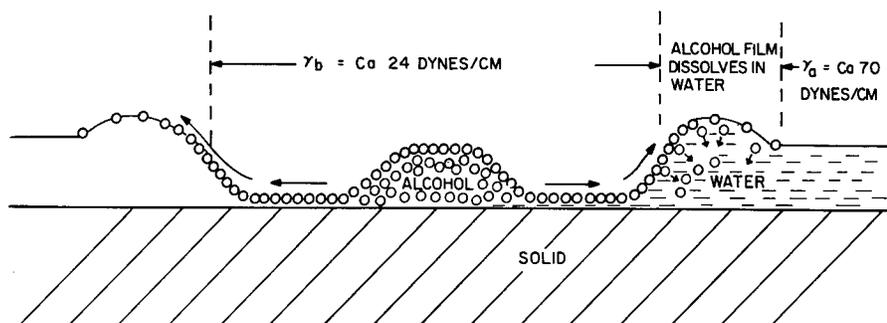


Fig. 4 - Schematic diagram for mechanism of water displacement by n-butanol

at the butanol/water interface, which causes an outward-directed film movement near the periphery of the disk. This movement under a surface tension gradient is an example of the so-called Marangoni effect (15-17), and it continues until all of the drop of butanol has spread and dissolved in the water or evaporated. Therefore, the radial flow continues until the central butanol disk disappears.

The butanol drop is rapidly consumed in the displacing action, and because any butanol left on the solid surface as an adsorbed film desorbs readily from the solid surface into the adjacent water, the latter finally respreads over the metal to completely cover it again. However, if the butanol drop contains a small concentration of an essentially insoluble, nonvolatile, surface-active agent which will quickly adsorb from the butanol solution to coat the bare solid surface with a hydrophobic monolayer, the resulting adsorbed film will prevent the water from spreading back. This action leaves the bulk water permanently displaced from the solid surface in that area and in a condition in which it can be separated easily and cleanly by gravity flow, air jet, or mechanical disturbance. An example of a suitable agent for the butanol is about 1 percent by weight of glyceryl monooleate. In the case of the water displacing action of the higher weight liquid alcohols, such as octanol or decanol, the displacing agent itself may adsorb on the solid to give an effective water-repellent film.

A wide variety of polar-nonpolar organic compounds are available which are soluble in the water-displacing liquids, are able to adsorb rapidly on common solid surfaces from solution in the liquid agent, and are not readily desorbed by contact with water. Among these compounds

are the high-molecular-weight carboxylic acids or their salts, the high-molecular-weight sulfonates, nonionic surface-active agents of lower percentage ethylene oxide (or propylene oxide) content having very low solubility in water, organic acids complexed with high-molecular-weight amines, and a great variety of high-molecular-weight amines, amides, and alcohols. However, it is necessary that the solute have some water solubility and be present in such a concentration that it will not poison the water transport mechanism by accumulating at the air/water interface beyond the transport boundary.

#### WATER DISPLACEMENT BY OTHER CLASSES OF SURFACE-ACTIVE COMPOUNDS

Analogous studies were undertaken of the comparative water-displacement properties of a variety of dialkyl ethers and ketones, as well as with esters of the appropriate boiling points, water solubilities, and equilibrium spreading pressures. The resulting data are grouped by chemical type and molecular weight in Table 2. The results were in every respect like those observed with the alcohols. Similar linear correlations were obtained between the values of  $F_e$ , as measured by us, and the atmospheric boiling points of the homologous compounds (Fig. 5). In each series a finite but limited water solubility was associated with effective water displacement. Evidently, a wide variety of organic liquid compounds are able to displace water effectively from solid surfaces, and many of these are familiar solvents in the low- or intermediate-boiling range.

TABLE 2  
Results of Water Displacement Experiments on Various Ethers, Ketones, and Esters

Compound	Boiling Point* (°C)	Percent Solubility of Fluid in Water*† (wt-% at 20°C)	Equil. Sprd. Press. at 20°C $F_e$ (dynes/cm)	Water Displacement $\Sigma_{max}$ (cm <sup>2</sup> )	
				1-mm Film	2-mm Film
<u>Ethers</u>					
Isopropyl ether	67.5	0.2	31.2	—	—
n-Butyl ether	142	sl. sol.	24.7	—	—
n-Amyl ether	190	i	18.1	—	—
Isoamyl ether	172.5	i	18.7	—	—
n-Hexyl ether	226.2	0.01	17.2	—	—
1,4-Dioxane	101.5	Complete	35.7	—	—
Diethylene glycol diethyl ether	188.9	Complete	39.6	8	0
Glycol diethyl ether	121.4	21.0	46.7	8	1
Tetrahydrofuran	64-66	Complete	—	12	0.3
<u>Ketones</u>					
Acetone	56.5	Complete	—	12	0
Methyl ethyl ketone	79.6	35.3 at 10°	46.2	5	0
Methyl butyl ketone	127.2	v. sl. sol.	37.6(b)	—	—
Ethyl propyl ketone	124	v. sl. sol.	33.8(b)	—	—
Methyl n-amyl ketone	150	v. sl. sol.	35.8	38	1
Methyl hexyl ketone	173.5	i	31.9(b)	—	—
Diisobutyl ketone	168	i	26.8	32	0
Acetyl acetone	139.0	12.5	31.9	1	0
Acetonyl acetone	192	Complete	—	5	0.3
Diacetone alcohol (4-Hydroxy-4-methyl-pentanone-2)	164-166	Complete	—	8	1
Methyl phenyl ketone	202.3	i	21.6 at 25°(c)	—	—
<u>Esters</u>					
Ethyl acetate	77.15	8.6	41.9	—	—
Butyl acetate	126.5	0.5 at 25°	34.1	—	—
Amyl acetate	148	0.18	31.1	—	—
"Cellosolve" Acetate (Ethylene glycol monoethyl ether acetate)	156.0	22.9	43.2	8	1
Ethyl lactate	154	Complete	—	20	1
Butyl lactate	160-190	sl. sol.	43.5	32	1
Dimethyl carbonate	90-91	i	40.1	8	0
Diethyl carbonate	125.8	i	33.1	32	0
Diethyl oxalate	185.4	sl. sol.	29.3	25	0
Ethyl acetoacetate	180.0	14.3 at 16.5°	35.2	—	—
Butyl acetoacetate	213.9(a)	0.40(a)	30.2	—	—
Methyl amyl acetoacetate	—	—	31.5	—	—

\*Unless otherwise indicated, the data in the first two columns was obtained from "The Handbook of Chemistry and Physics," 44th ed., Cleveland: Chemical Rubber Publ. Co., 1963.

†Definitions of symbols: i = insoluble; v. sl. sol. = very slightly soluble; and sl. sol. = slightly soluble.

NOTES: (a) Data from "Synthetic Organic Chemicals," 12th ed., Carbide and Carbon Chemicals Corp., 1946; (b) Data from W.D. Harkins and A. Feldman (Ref. 5); and (c) Data from L.F. Transue, E.R. Washburn, and F.H. Kahler (Ref. 10).

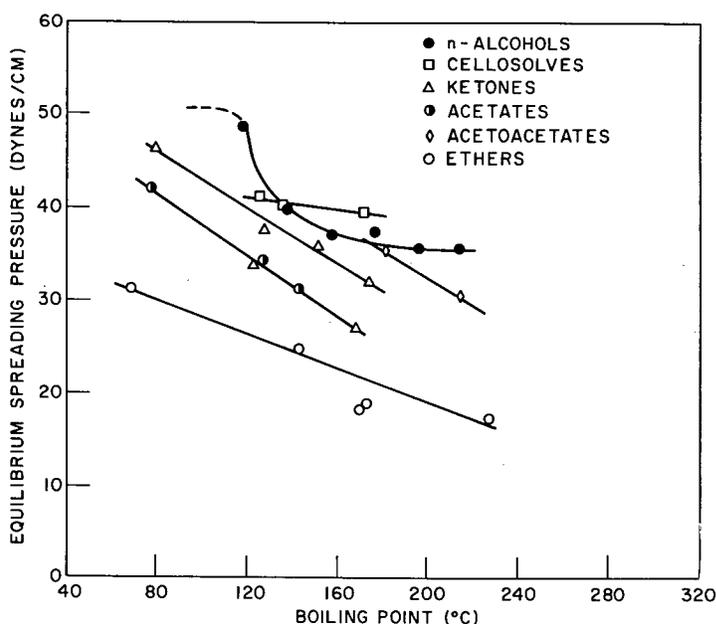


Fig. 5 - Equilibrium spreading pressures vs. atmospheric boiling point for various aliphatic water displacing compounds

### WATER DISPLACEMENT BY ORGANIC SOLUTIONS

In a liquid of low or moderate polarity the addition of an organic, strongly polar, hydrophilic solute lowers the interfacial tension between the liquid and water, producing a higher equilibrium spreading pressure. This higher spreading pressure, combined with the deposition on the solid of an adsorbed hydrophobic film from which water spontaneously recedes, tends to improve the water-displacing effectiveness over that of the corresponding pure liquid. In this way one can even confer mild water-displacing properties on liquid hydrocarbons which are nonspreading when pure. For example, in Fig. 6 shows the effect of a modest proportion of butanol in increasing the equilibrium spreading pressure and water-displacing ability of a hydrocarbon (Stoddard solvent, 104°F high-flash naptha) which is nonspreading if free of polar impurities.

We will report elsewhere (18) the evolution from these principles of new methods and compositions of water-displacing agents leading to many successful applications of water displacement by

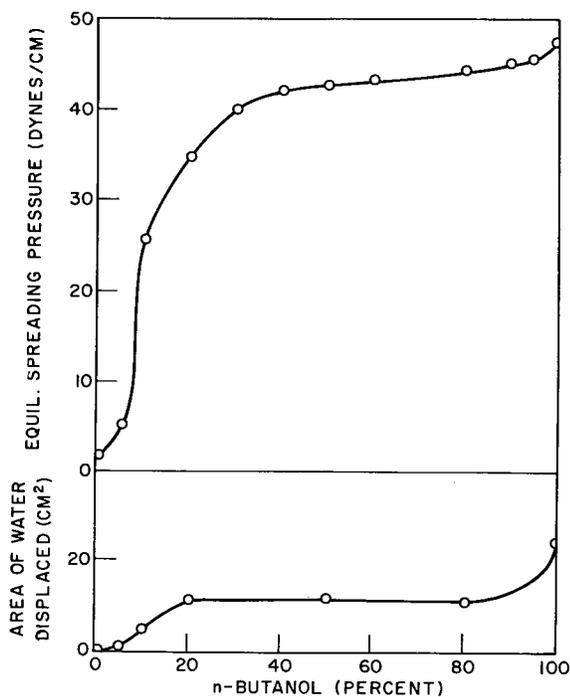


Fig. 6 - Effect of n-butanol, added to 104°F flash naptha, on the equilibrium spreading pressure and the displacement of a 1-mm water film as a function of butanol content

surface-chemical methods. The composition of one very effective water-displacing solution is given here to exemplify the principles already presented. Such a composition consists of 1-butanol (93.75 wt-%), basic barium dinonylnaphthalene sulfonate (3%), volatile hydrocarbon solvent for the sulfonate (3%), and 2,6-ditert-butyl-4-methyl phenol (0.25%). The selection of 1-butanol from the many vigorous water-displacing polar liquids reported in Tables 1 and 2 reflects such considerations as flash point, solvent power for the sulfonate hydrophobic film-forming solute and rust inhibitor, rate of evaporation, compatibility with plastics, and commercial availability. The oxidation inhibitor imparts storage stability to the organic formulation, but it does not significantly alter water-displacement properties.

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13. ABSTRACT <p>Bulk water films can be displaced from a solid surface by a spreading organic liquid which creates and maintains a surface tension gradient in the air/liquid interface. Such a gradient can be maintained if the spreading agent escapes from the air/water interface by solution or evaporation after a few centimeters of travel away from the point of application. The resulting movement of the surface film sweeps along the water beneath by viscous entrainment (Marangoni effect). Displacement is effective and lasting only when the displacing agent (or a surface-active material dissolved in it) is strongly adsorbed to form an insoluble hydrophobic film on the solid surface. Effective water-displacing agents at 20°C should have the following properties: a spreading pressure above 25 dynes/cm on water, a boiling point above 90°C, and a solubility in water of between 2 and 25 percent by weight. The equilibrium spreading pressures for members of a given class of polar organic compounds decrease with rising boiling point. (These principles are well exemplified by a solution in normal butanol of 3 percent of basic barium dinonylnaphthalene sulfonate.) Such water-displacing agents have been found suitable in numerous applications.</p>		

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