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C_i	equilibrium concentration of the i th component	a_i^a	activity of component i in the condensed phase
Q_i	total number of moles adsorbed	a_i^l	activity of component i in the liquid phase
X_i^a	molar fraction of the i th component in the condensed phase	γ_i^a	activity coefficient of component i in the condensed phase
X_i	molar fraction of the i th component in the liquid phase	γ_i	activity coefficient of component i in the liquid phase
μ_i^a	chemical potential of component i in the condensed phase		
μ_i^l	chemical potential of component i in the liquid phase		

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Marangoni Effects in the Spreading of Liquid Mixtures on a Solid

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The spreading of binary liquid mixtures on Pyrex glass was experimentally studied, qualitatively and quantitatively, for a large number of liquids. The mixtures were classified according to the spreading behavior of the individual components and according to the expected direction of the Marangoni flow, which may be induced by the differences in volatilities and surface tensions between the components. The general trends of the results agree with previously reported data for other solid surfaces. The quantitative measurements led to novel conclusions regarding the rates of spreading of mixtures. Binary mixtures of completely spreading components spread faster than the individual components when the Marangoni flow is expected to coincide with the spreading direction. Spreading of such mixtures is delayed or arrested when the Marangoni flow is expected to oppose spreading, until a sufficient amount of the volatile component evaporates. The spreading rate of mixtures of only one completely spreading component may be insensitive to concentration when the Marangoni flow compensates for a decreased tendency for spreading. Many mixtures of two incompletely spreading components exhibit complete spreading when the Marangoni flow is expected to be in the direction of spreading. The effect of the component concentration is unsymmetric. Small concentrations of the less volatile component induce complete spreading of the mixture, while relatively high concentrations of the volatile liquid are required for the same purpose.

Introduction

Spreading of liquids on solids is a frequently encountered process, which is of great interest scientifically as well as industrially.¹⁻³ Applications based on wetting of solids by liquids include detergency, lubrication, adhesion, coating, and gas-liquid separation in packed columns. Spreading may be spontaneous or forced. The latter applies to situations where the contact angle is not zero and where the liquid is forced by external means to spread on the solid to a contact angle lower than the thermodynamic one. Of interest in the present paper is the case of complete spontaneous spreading, which is associated with a zero contact angle.

It is interesting to note that while most practical applications employ mixtures of liquids, the majority of hitherto published studies have been devoted to the spreading of single liquids.¹⁻³ However, some very interesting observations have been made regarding the spreading of aqueous surfactant solutions^{4,5} and liquid mixtures.⁶⁻⁹ The observed phenomena can be classified into four categories: enhancement of spreading, prevention of spreading, retraction, and "catastrophic" spreading. The latter refers to situations where irregular patterns are formed, some of which resemble dendritic growth. Satu-

rating water with some alcohols or ether appreciably enhanced the rate of spreading,⁶ as did the addition of low molecular weight hydrocarbons to distilled squalane.⁹ Moreover, some mixtures were reported to completely spread on freshly split mica, whereas the individual components did not.⁶ The opposite effect, namely, the prevention of spreading, was noticed when water was added to acetic acid,⁶ when solutes were added to oil, forming an adsorbed layer on the solid with a low critical surface tension,⁷ or when squalane was distilled.⁹ Retraction as well as catastrophic spreading was observed with oils containing additives or surfactants⁸ and with aqueous surfactant solutions.⁵

The above-mentioned phenomena are yet incompletely understood, but some of them have been explained in terms of flows induced by local surface tension gradients,⁷⁻⁹

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a phenomenon known as the Marangoni effect. This phenomenon has been studied from various perspectives, bearing different practical problems in mind [e.g., ref 10–12]. Recently, the Marangoni effect has been theoretically studied in relationship to the spreading of liquids on solid surfaces.¹³ A main conclusion of this study¹³ is that although surface tension gradients play an important role in the motion of liquid films, they are unable to overcome adverse wettability. This conclusion contradicts earlier experimental evidence,⁶ a point which deserves further study.

Complete spreading has been known for a long time to be associated with the existence of a primary film spreading ahead of the bulk of the liquid.¹⁴ The thickness of this film seems to be less than 100 Å in the few case where it was measured.⁹ It is believed that selective evaporation from the primary film is enhanced compared with evaporation from the bulk of the drop, leading to surface tension gradients between them.⁹ Thus, the Marangoni effect, as related to the spreading of mixtures, seems to take place at the junction between the primary film and the drop.

Most of the experimental observations mentioned above are of qualitative nature and somewhat limited in scope, although quantitative studies were performed on very slowly spreading oils⁹ and on aqueous surfactant solutions.^{4,5} The purpose of the present paper is to present a systematic, qualitative, and quantitative study of the various possible effects of composition on the spreading behavior of binary mixtures, emphasizing the possible role of the Marangoni phenomenon. For this purpose, the liquid mixtures were classified according to the spreading properties of the individual components, as well as the direction of the possible Marangoni flow relative to the main spreading flow. The solid chosen was Pyrex glass. This may be considered an example of a common high-energy surface, which is different from the solid surfaces previously used for spreading studies. This fact and the large number of mixtures which were tested greatly assure the general validity of the present results, as well as those previously reported.

Experimental Section

Cleaning of the Solid Surface. Pyrex glass plates (5 × 5 cm) were cleaned according to the following procedure: (1) dipping in distilled water in an ultrasonic bath for 5 min; (2) heating in sulfochromic acid at 80 °C for 30 min; (3) rinsing with boiling distilled water; (4) dipping in distilled water in an ultrasonic bath for 5 min; (5) drying in an oven at 80 °C for 30 min. The glass plates were freshly prepared prior to each set of experiments. They were kept in a desiccator following the drying stage, until used. The sulfochromic acid was prepared according to the following recipe: 40 g of K₂Cr₂O₇/60 mL of H₂O/1000 mL of H₂SO₄.

Liquids. The liquids used were all chemically pure of analytical reagent grade.

Experimental System. Observations of the spreading behavior were qualitative as well as quantitative. The former applied when only the distinction between complete spreading (zero contact angle) and incomplete spreading (nonzero contact angle) was desired. This distinction is easily made by visual inspection, since both the basal area of the drop and the duration of spreading are markedly increased in complete spreading. Quantitative

Table I. Mixtures Tested (Each Component Completely Spreads)

acetone-ethanol	ethanol-heptane
acetone-heptane	ethanol-isopropyl alcohol
acetone-isopropyl alcohol	heptane-hexane
acetone-octane	heptane-octane
decane-heptane	hexane-octane
decane-octane	hexane-decane

measurements were performed by taking photographs of the spreading drop from below and measuring the liquid-solid contact area as a function of time. The details of the system were previously described.¹⁵ Measurements were performed at room temperature.

Results and Discussion

The questions to be answered by the present discussion are how does the spreading behavior of the mixture depend on the spreading characteristics of the individual components and what is the influence of the Marangoni effect on the spreading process? In order to answer these questions in a systematic way, the liquids were classified according to their individual spreading behavior on the same solid surface and according to the expected direction of the Marangoni flow. As for the former classification, three combinations can be identified regarding the individual behavior of components of binary mixtures: (a) each of the components completely spreads; (b) only one component completely spreads; (c) none of the components completely spreads.

With reference to the Marangoni effect, two possibilities exist. If $P_a < P_b$, where P_i is the vapor pressure of component i , and $\gamma_a > \gamma_b$, where γ_i is the surface tension of component i , then the relatively higher evaporation of component b tends to increase the surface tension. In this case, the Marangoni flow will be induced from regions of low evaporation rate (where the concentrations of a and b are close to nominal and so is the surface tension) to regions of high evaporation rate (where b is selectively depleted and the surface tension is increased). This behavior is demonstrated by the famous example of wine tears, where evaporation in the thin film region near the glass induces a climbing motion of the wine. Similarly, in the case of spreading of a drop, such a combination of volatilities and surface tensions leads to a Marangoni flow in the same direction as the spreading, i.e., away from the center of the drop. In the opposite situation, namely, $P_a < P_b$ and $\gamma_a < \gamma_b$, the Marangoni flow will oppose the spreading.

Binary Mixtures of Completely Spreading Components. Table I lists the liquid mixtures which were tested for their spreading behavior. Each component of these mixtures completely spreads on the Pyrex glass surface when employed by itself. The volume concentrations ranged from 10% to 90%, at 10% intervals (the volume percentages refer to the liquids prior to their mixing). All of these mixtures completely spread on the Pyrex glass surface, as intuitively expected. However, the quantitative study of the kinetics of spreading of these mixtures revealed interesting phenomena, heretofore not observed.

Figure 1 presents data for acetone, octane, and two of their mixtures: 10% and 50% acetone by volume. This figure demonstrates that the mixtures spread more slowly than the individual components. Figure 2 shows, that as the concentration of acetone in the mixture is increased, the spreading behavior deviates drastically from that of the pure components. For the mixture with 75% acetone,

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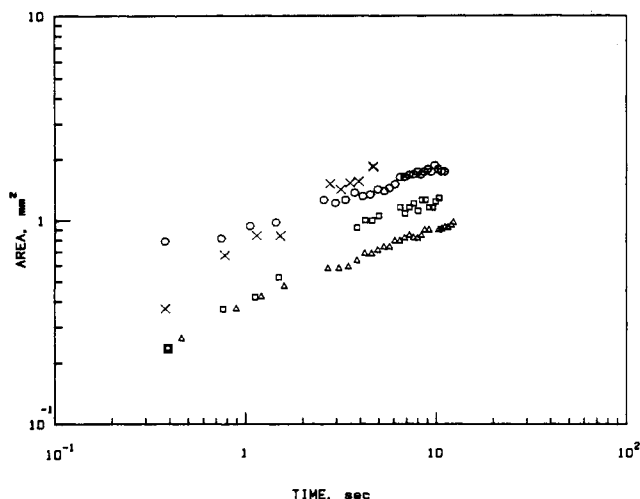


Figure 1. Spreading of acetone, octane, and their mixtures: (O) 0% acetone; (□) 10% acetone by volume; (Δ) 50% acetone; (X) 100% acetone.

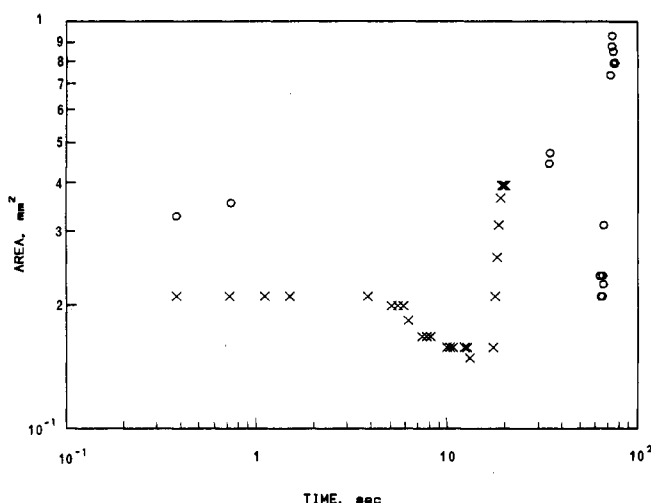


Figure 2. Spreading of acetone-octane mixtures at high acetone concentrations: (X) 75% acetone by volume; (O) 90% acetone by volume.

there is a decrease in the contact area of the drop for about 15 s, followed by rapid spreading. The same phenomena are evident for the mixture with 90% acetone; however, the decrease in the contact area is observed for a much longer period of about 65 s. These observations can be explained by considering the Marangoni effect. Acetone is more volatile than octane and its surface tension is higher than that of the latter. Therefore, the induced Marangoni flow is expected to be directed opposite to the spreading. This may explain the decrease in the rate of spreading relative to the pure components. As the concentration of acetone increases, the rate of spreading further decreases, until it is too low to overcome the decrease in the contact area due to evaporation. This is shown by the initial portions of the curves in Figure 2. Then, due to the continuing evaporation of acetone, its concentration in the mixture decreases to the point where spreading resumes, as demonstrated by the final portions of the curves in this figure.

The opposite mode of spreading behavior is demonstrated by a mixture of decane and hexane, as shown in Figure 3. Here, the mixtures at all concentrations spread faster than the individual components. In addition, it is worth noticing that the rate of spreading goes through a maximum. This is understandable, since there must be a continuous change of spreading rate from that of one

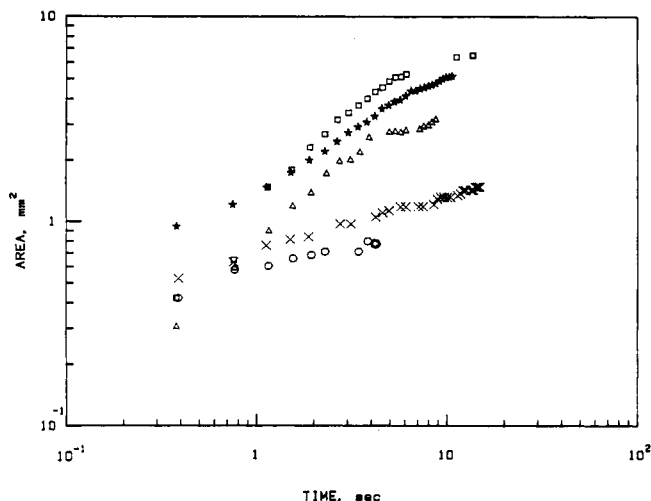


Figure 3. Spreading of hexane, decane, and their mixtures: (O) 0% decane; (Δ) 10% decane by volume; (□) 50% decane; (☆) 90% decane; (X) 100% decane.

Table II. Effect of Concentration on the Spreading of Mixtures of Ethanol with Nonspreading Components

component	ethanol, vol %								
	10	20	30	40	50	60	70	80	90
aniline	-	-	+	+	+	+	+	+	+
benzene	-	-	-	-	+	+	+	+	+
bromobenzene	-	-	-	-	+	+	+	+	+
<i>n</i> -buty alcohol	-	-	-	-	+	+	+	+	+
chlorobenzene	-	-	-	-	+	+	+	+	+
chloroform	-	-	-	+	+	+	+	+	+
cyclohexane	-	+	+	+	+	+	+	+	+
ethyl bromide	-	+	+	+	+	+	+	+	+
isopentane	+	+	+	+	+	+	+	+	+
phenetole	-	-	-	+	+	+	+	+	+
<i>n</i> -propyl alcohol	-	-	-	-	+	+	+	+	+
water	-	-	-	+	+	+	+	+	+

Table III. Effect of Concentration on the Spreading of Mixtures of Water with Spreading Components

component	water, vol %								
	10	20	30	40	50	60	70	80	90
acetic acid	+	+	+	+	-	-	-	-	-
acetone	+	+	+	+	+	+	-	-	-
acrylic acid	+	+	+	-	-	-	-	-	-
butylamine	+	+	+	+	+	-	-	-	-
isopropyl alcohol	+	+	+	+	+	+	-	-	-
ethanol	+	+	+	+	+	+	-	-	-

component to that of the other, both of which being smaller than the spreading rates of most of their mixtures. This type of behavior can also be explained by the Marangoni effect. Hexane is more volatile than decane but has a lower surface tension. The induced Marangoni flow is expected to coincide with the direction of spreading, thus enhancing the rate of spreading.

Binary Mixtures of Only One Completely Spreading Component. Two sets of mixtures were tested in this category: mixtures of ethanol, which completely spreads on the Pyrex glass, with other liquids, which incompletely spread, and mixtures of distilled water, which does not spread completely on the Pyrex glass, with other components which do. The former data are summarized in Table II and the latter in Table III. In these tables, a "+" sign indicates complete spreading, while a "-" sign indicates incomplete spreading. The general behavior is as can be intuitively expected: at some intermediate concentration there is a transition between incomplete and complete spreading. Again, however, some important features can

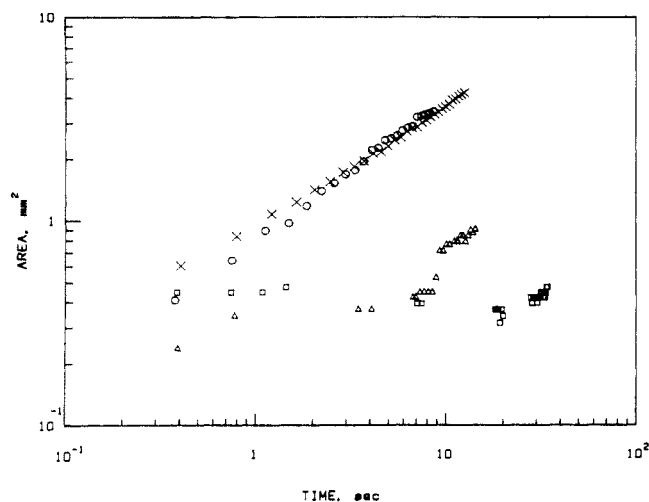


Figure 4. Spreading of ethanol and ethanol-chloroform mixtures: (O) 0% chloroform; (X) 10% chloroform by volume; (Δ) 40% chloroform; (\square) 60% chloroform.

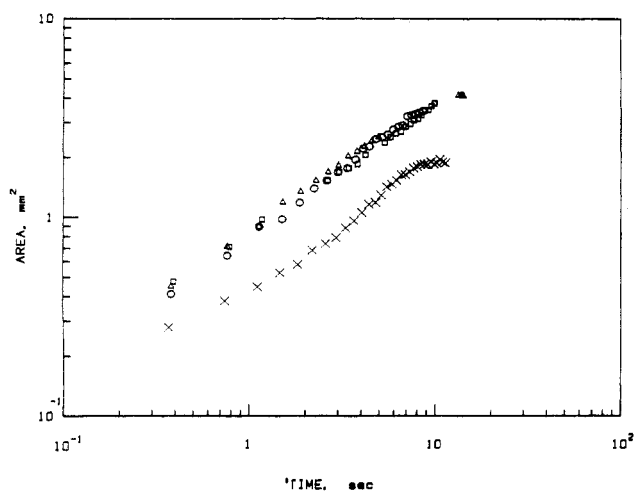


Figure 5. Spreading of ethanol and water-ethanol mixtures: (O) 0% water; (\square) 5% water by volume; (Δ) 30% water; (X) 60% water.

be elucidated by studying the quantitative results, which are shown for sample mixtures in Figures 4 and 5.

Figure 4 presents data for ethanol-chloroform mixtures and shows that as the concentration of chloroform increases, the rate of spreading decreases. At 40% and 60% chloroform, a delay in the spreading process is observed, which is similar to the behavior presented in Figure 2. This delay is caused by the fact that chloroform, which is more volatile than ethanol, has to evaporate in order to reduce its concentration to a level which is within the complete spreading range. The induced Marangoni flow should in this case oppose spreading. However, it is difficult to elucidate its contribution, because the transition concentration between incomplete and complete spreading cannot be determined independently of the Marangoni effect.

Figure 5 presents data for water-ethanol mixtures and shows a different type of behavior. The rate of spreading of these mixtures is shown to be hardly affected by the concentration of water, up to at least 30% water by volume. At 60% water, the spreading is visibly slowed down. The weak dependence of the spreading on the water concentration, up to 30% water, can be explained by considering two competing effects. As the water concentration increases, the interfacial tensions of the liquid-vapor and liquid-solid interfaces increase. This leads to a decrease in the thermodynamic driving force for spreading and

Table IV. Mixtures Tested (None of the Components Completely Spreads; Expected Marangoni Flow Is Inward)

component a	component b
<i>n</i> -butyl alcohol	benzene
<i>n</i> -butyl alcohol	chloroform
<i>n</i> -butyl alcohol	cyclohexane
cyclohexane	benzene
cyclohexane	chloroform
phenetole	bromobenzene
phenetole	chlorobenzene
<i>n</i> -propyl alcohol	benzene
<i>n</i> -propyl alcohol	chloroform
<i>n</i> -propyl alcohol	cyclohexane
<i>n</i> -propyl alcohol	ethyl bromide
<i>o</i> -xylene	benzene

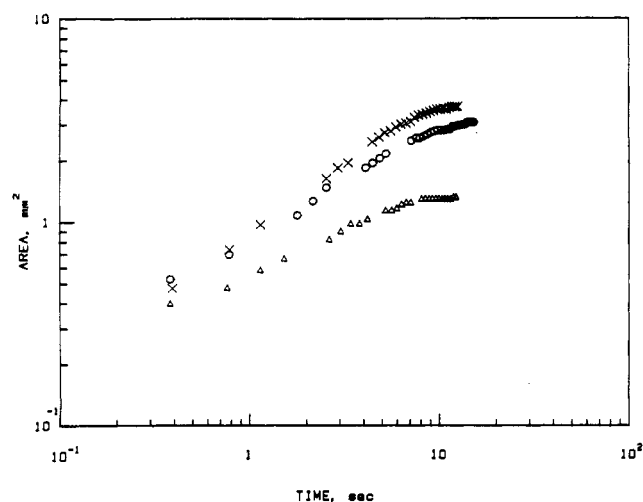


Figure 6. Spreading of benzene-phenetole mixtures: (Δ) 2% phenetole by volume; (X) 40% phenetole; (O) 80% phenetole.

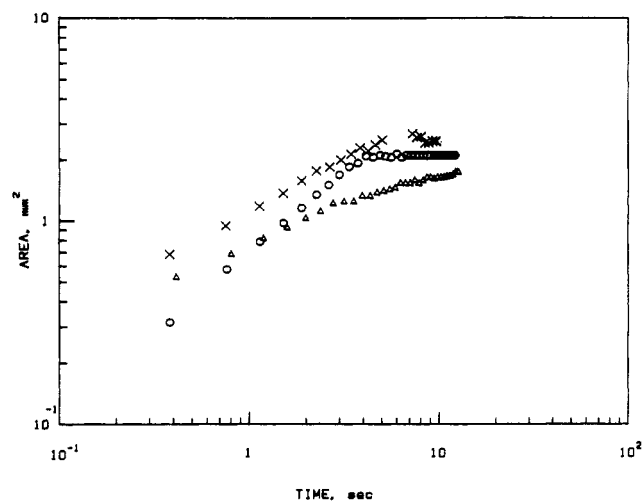


Figure 7. Spreading of benzene-aniline mixtures: (Δ) 1% aniline by volume; (X) 20% aniline; (O) 60% aniline.

should diminish the spreading rate. On the other hand, the direction of the Marangoni flow for this system coincides with the direction of spreading, i.e., against spreading, so the enhancement due to this effect may compensate for the reduced tendency to spread.

Binary Mixtures of Components None of Which Completely Spreads. Many liquid mixtures were tested in this category, to substantiate the results. Table IV lists those mixtures tested, the composition of which would be predicted to produce a Marangoni flow inward, i.e., against spreading. Indeed, none of these mixtures exhibited complete spreading at any of the following compositions (volumetric percentage) which were studied: 3, 10, 20, 30,

Table V. Mixtures Tested (None of the Components Completely Spreads; Expected Marangoni Flow is Outward)

component		vol % of component a															
a	b	1	2	5	10	20	30	40	50	60	70	80	90	95	98	99	
aniline	benzene	+	+	+	+	+	+	+	+	+	-	-	-	-	-	-	
aniline	bromobenzene	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
aniline	<i>n</i> -butyl alcohol	+	+	+	+	+	+	+	-	-	-	-	-	-	-	-	
aniline	chlorobenzene	+	+	+	+	+	+	+	-	-	-	-	-	-	-	-	
aniline	chloroform	+	+	+	+	+	+	+	+	+	+	-	-	-	-	-	
aniline	ethyl bromide	+	+	+	+	+	+	+	+	+	+	-	-	-	-	-	
aniline	phenetole	+	+	+	+	+	+	+	+	-	-	-	-	-	-	-	
aniline	<i>n</i> -propyl alcohol	+	+	+	+	+	+	+	+	-	-	-	-	-	-	-	
benzene	ethyl bromide	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
benzene	chloroform	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
benzene	isopentane	+	+	+	+	+	+	+	+	-	-	-	-	-	-	-	
bromobenzene	benzene	+	+	+	+	+	+	+	+	+	+	-	-	-	-	-	
bromobenzene	<i>n</i> -butyl alcohol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
bromobenzene	chlorobenzene	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
bromobenzene	chloroform	+	+	+	+	+	+	+	+	+	+	+	+	-	-	-	
bromobenzene	cyclohexane	+	+	+	+	+	+	+	+	+	+	+	+	-	-	-	
bromobenzene	ethyl bromide	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
bromobenzene	<i>n</i> -propyl alcohol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
chlorobenzene	benzene	+	+	+	+	+	+	+	+	+	+	-	-	-	-	-	
chlorobenzene	<i>n</i> -butyl alcohol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
chlorobenzene	chloroform	+	+	+	+	+	+	+	+	+	+	+	+	-	-	-	
chlorobenzene	cyclohexane	+	+	+	+	+	+	+	+	+	+	+	+	-	-	-	
chlorobenzene	ethyl bromide	+	+	+	+	+	+	+	+	+	+	+	+	-	-	-	
chlorobenzene	<i>n</i> -propyl alcohol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
cyclohexane	ethyl bromide	+	+	+	+	+	+	+	+	+	+	+	-	-	-	-	
cyclohexane	isopentane	+	+	+	+	+	+	+	+	+	+	+	+	-	-	-	
<i>o</i> -nitrobenzene	benzene	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	
<i>o</i> -nitrobenzene	cyclohexane	+	+	+	+	+	+	+	+	+	+	+	+	-	-	-	
phenetole	benzene	+	+	+	+	+	+	+	+	+	+	+	+	-	-	-	
phenetole	<i>n</i> -butyl alcohol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
phenetole	chloroform	+	+	+	+	+	+	+	+	+	+	+	+	+	-	-	
phenetole	cyclohexane	+	+	+	+	+	+	+	+	+	+	+	+	+	-	-	
phenetole	ethyl bromide	+	+	+	+	+	+	+	+	+	+	+	+	+	-	-	
phenetole	<i>n</i> -propyl alcohol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	

40, 50, 60, 70, 80, 90, 95, and 98.

In contrast, the experiments with mixtures which would be expected to induce a Marangoni flow coinciding with the spreading direction revealed interesting details. Figures 6 and 7 present sample quantitative data for the mixtures benzene-phenetole and benzene-aniline, respectively. It is clearly seen that these mixtures completely spread, although none of the components spreads by itself. It also is interesting to note the maximum in the rate and extent of spreading at intermediate concentrations. Once the complete spreading of these mixtures is recognized, this maximum is to be expected, since spreading is incomplete at the limits of single components.

Table V summarizes the experiments performed with all mixtures which are expected to induce a Marangoni flow in the direction of spreading. The "+" sign indicates complete spreading and the "-" sign stands for incomplete spreading. It is clear that many of these mixtures exhibit complete spreading, although none of the individual components does so. It is interesting to note that the effect of the concentration of the components, in the cases where complete spreading occurs, is unsymmetric. Very low concentrations of the less volatile component (shown in Table V as component a) are sufficient to induce complete spreading, while this is not true for the more volatile component. It should also be noticed that some mixtures did not completely spread at any of the concentrations studied.

The phenomenon of complete spreading of a mixture where the individual components incompletely spread, although noticed many years ago for a small number of mixtures,⁶ has not, to our knowledge, been explained. An explanation may be derived from the observation that in some cases an adsorbed film surrounds a drop of a pure liquid, even when complete spreading does not take

place.^{6-9,14} When a mixture of such liquids is employed, the static picture of a drop surrounded by an adsorbed film may change into a dynamic complete spreading situation, due to the Marangoni phenomenon at the junction between the film and the drop. Thus, while pure liquids may be rendered "autophobic" by the adsorbed film,¹⁶ i.e., their complete spreading may be prevented by lowering the surface energy of the solid, mixtures of "autophobic" liquids can be made completely spreading by the Marangoni effect which originates at the film. The liquids which were tested indeed seem "autophobic", because they do not spread on the high energy surface used, despite their low surface tensions. The possibility that these liquids did not completely spread because the Pyrex glass might have been contaminated seems unlikely, since some of the liquids tested here, benzene, chloroform, chlorobenzene, bromobenzene, aniline, *n*-propyl alcohol, and *n*-butyl alcohol, did not completely spread on the high-energy surface of freshly split mica, even when exposure to air was avoided.⁶ The contradiction between the present experimental data and previous theory,¹³ which was mentioned in the introduction, may be due to the neglect of the effect of the adsorbed film in the latter.

The unsymmetric dependence on the concentration of the components may be due to the fact that the more volatile component quickly evaporates from the film and therefore higher concentrations of it are required to sustain the spreading. The incomplete spreading of some of the mixtures listed in Table V may be explained by one of two possible reasons: either one of the components does not become involved in the adsorbed film or the difference in surface tensions between the components is insufficient

to induce an appreciable Marangoni flow. The latter case may be true, for example, for bromobenzene, which did not spread as expected when mixed with aniline, since it has the closest surface tension to that of aniline among the various liquids tested. Clearly, this point should be further tested in the future.

Some final comments, which pertain to all of the experiments presented above, seem appropriate. The solid surface which was chosen, Pyrex glass, is not as well defined as freshly split mica or freshly deposited metals that were previously used.^{6,9} The cleaning with sulfochromic acid is very efficient for removal of organic contamination, but may modify the surface to some extent, by adsorption of inorganics. The surface still remains a high energy one, and the results presented above were always repeated at least twice and were always reproducible. Moreover, the fact that they are similar in nature to those previously reported for very well-defined surfaces like freshly split mica is helpful in assuring that these results may be generally applicable to commonly used high-energy surfaces in daily life applications, which are most often not very well defined.

Another effect, which should be considered in attempting to explain the observations of this study, is evaporative cooling. Enhanced evaporation at the edge of the drop, in the primary film region, can lead to a local decrease in temperature, which in turn can increase the surface tension and cause a Marangoni flow in the spreading direction. However, this effect always acts in the same direction. Therefore, although its contribution cannot be denied, it certainly cannot explain the differences between enhanced and diminished spreading.

As for the kinetics of spreading, it was previously realized^{2,15} that a simple logarithmic relationship, $A = kt^n$, holds for pure liquids, where A is the contact area, t is the time, and k and n are empirical constants. The value of n is usually between 0.2 and 0.25, but values as low as 0.066 and as high as 0.6 have been reported. The value of k may vary over a few orders of magnitude. Inspection of the present data shows that the more complex nature of spreading of mixtures is also reflected in the fact that the

above simple relationship holds only for part of the time. However, for those segments of the curves for which a straight line can be fitted on a log-log scale, the values of n and k fall within the range reported for pure liquids.

Summary and Conclusions

A large number of liquid mixtures were systematically tested for their spreading behavior on Pyrex glass, in order to extend the validity of previously reported data on other solid surfaces. These previous studies were limited in the variety of liquids used and were mostly qualitative. The quantitative results of the present study enabled the elucidation of important features, which have been so far unknown. The following conclusions can be drawn from the present data:

1. The qualitative behavior on Pyrex glass of the liquid mixtures studied is similar to that previously reported for spreading on other solid surfaces.⁶⁻⁹ The scope of liquids studied here and their systematic combinations is much larger than in previous studies, thus adding support to the generality of the phenomena observed.

2. For binary mixtures of completely spreading components it was shown that the rate of spreading of a mixture is higher than that of the components when the Marangoni flow is expected in the direction of spreading and vice versa. In the latter situation, spreading may be delayed or arrested until sufficient amounts of the more volatile component are evaporated.

3. For binary mixtures of only one completely spreading component, it was demonstrated that the rate of spreading may be weakly dependent upon the concentration of the incompletely spreading component, when the Marangoni flow is expected in the direction of spreading.

4. Many binary mixtures of incompletely spreading components show complete spreading when the Marangoni flow is expected to be in the direction of spreading. The effect of the concentration of the components on this phenomenon is unsymmetric, in the sense that very small concentrations of the less volatile component are sufficient to induce spreading. This is not the case for the more volatile component.