

Spreading kinetics for low viscosity n-alkanes on a water surface as recorded by the high-speed video system

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The spreading of small hydrocarbon droplets (pentane, heptane, dodecane, hexadecane) on the water surface was recorded using a Kodak high-speed video system with a speed of 1000 frames per second. The results showed that the spreading of low-viscosity hydrocarbons on a water surface is a very spontaneous process and is usually completed in 10-15 ms for drops with a diameter of 3-4 mm. It was found from the recorded images that the kinetics of a hydrocarbon droplet spreading on the deionized water surface follow a time n -power law: $D \sim t^n$, where D is the lens diameter, t is the time, and $n=0.4-0.5$. The kinetics of spreading for hexadecane droplets were slowed down and the n value was reduced to $n=0.36-0.39$ when deionized water was replaced by sodium dodecyl sulfate solutions. These results suggest that the kinetics of hydrocarbon spreading can be controlled through molecular arrangements at the water-fluid interfaces.

1. INTRODUCTION

Recovery of oil from oil sands, remediation of oily soil, and purification of oily water, are usually accomplished with flotation separation techniques. In these processes, the oil phase, which is dispersed in the aqueous phase as droplets or exists as oil lenses at solid particle surfaces, is collected by gas bubbles, intentionally dispersed or nucleated in the aqueous phase. Fundamental aspects of the oil flotation process include: 1) maintaining an affinity of the oil phase for the gas phase (this thermodynamic condition is satisfied for most systems due to the nonpolar nature of oil and air); 2) providing sufficient time for attachment between gas bubbles and oil (this kinetic condition includes the time

required to destabilize the aqueous film separating the gas-water and oil-water interfaces, as well as the time required for the oil to spread at the “bubble surface”); and 3) stabilizing the oil lens and/or film on the gas bubble surface under the prevailing flow (hydrodynamic condition). Although all of these criteria are important to ensure the success of oil separation by flotation, the hydrodynamic condition is usually ignored in laboratory activities of interfacial chemistry researchers. On the other hand, oil attachment to a gas bubble can be promoted and stimulated by appropriately-selected solution chemistry, and both the kinetic and thermodynamic conditions can be controlled by this approach. In this communication, we focus our discussion on the kinetics of oil spreading on the water surface as this aspect of oil flotation has received relatively little experimental attention.

Fraaije and Cazabat [1] reported their experimental results on the spreading of small drops of polydimethylsiloxane (PDMS) on about a 4 mm thick layer of a mixture of glycerol with water. The kinetics of spreading was recorded with a camera through observations of interference fringes of white light reflected from the spreading PDMS. The researchers [1] found that the spreading of PDMS follows a power law relation: $R_i \sim t^{n_i}$ where R_i is the radius of an interference fringe related to the dimensions of the PDMS drop and precursor film(s) of this drop, i is the order of the interference (related to the thickness of the spreading PDMS film), and n is the power that varies from about 0.46 (black film - precursor film) to 0.2 (innermost interference fringe - bulk of the PDMS drop). Fraaije and Cazabat [1] also found that the spreading rate is independent of the PDMS viscosity. The same system, the PDMS drop on a mixture of glycerol with water, was also recently used in the examination of liquid-on-liquid spreading kinetics by Bacri et al. [2]. Recording the kinetics of PDMS spreading with a CCD camera, their results supported the power law relation describing the spreading phenomenon. Additionally, they found that the PDMS drops spread with different velocities in capillary-driven and gravity-driven spreading regimes. For those regimes, the power was determined to be $n=0.26 \pm 0.02$ and $n=0.51 \pm 0.02$, respectively.

In this communication, the spreading kinetics of aliphatic hydrocarbons at the water surface are reported. The measurements were done using an advanced video technique with a resolution of 1 ms, as only such a fast-motion technique is able to record the kinetics of spreading for low-viscosity alkanes. To our knowledge, spreading experiments involving short-chain n-alkanes have not been previously reported in the literature.

2. EXPERIMENTAL PROCEDURE

The experimental set-up and experimental procedure were similar to those used by Bacri et al. [2] and thus, are not described in detail in this paper. A high-speed video camera of 1000 frames per second and 10 μ s exposure time

(Kodak EktraPro 1000 High-Speed Video System) was coupled with a photographic lens. A plastic dish was filled with water that formed a 6-7 mm deep layer. In selected experiments 0.05 mM and 1 mM aqueous solutions of sodium dodecyl sulfate (SDS; 95% purity from Sigma Chemical Co.) (pH 9.5) with a surface tension of $\gamma_{LV}=67.5$ mN/m and $\gamma_{LV}=37.0$ mN/m at 25 °C, respectively, were used. Next, a small hydrocarbon droplet (~3-4 mm diameter) was made at the tip of a needle using a microsyringe and was then released from the needle tip onto the surface of deionized water (surface tension of $\gamma_{LV}=72$ mN/m at 25 °C, pH 6.0). The distance between the tip of the needle and the water surface was adjusted to such a position that the hydrocarbon droplet attached to the water surface before complete detachment from the needle. This was done in order to minimize the energy generated during the transfer of the drop to the water surface. However, this distance was great enough to insure fast detachment of the drop from the needle tip, almost instantaneously (1-3 ms) after contact of the droplet with the water surface. The spreading of the hydrocarbon was observed from a 20-25° angle, above the water surface, which allowed observation of both the real image of the hydrocarbon lens and its reflection on the water surface.

Table 1. Hydrocarbons used in the study of spreading kinetics (20 °C; or otherwise stated)^{*)}

Hydrocarbon	Density [kg/m ³]	Viscosity [mPa]	Surface Tension [mN/m]	Water-Oil Interfacial Tension	Spreading Coefficient	
					Initial [mN/m]	Equilibrium [mN/m]
Pentane ($\geq 99.9\%$; EM Science)	626	0.24	16.1	49.0	8.0 6.1(24.5°C)	1.3 -0.5(24.5°C)
Heptane ($\geq 99\%$; Mallinckrodt)	684	0.42	20.1	50.2	2.2 1.2 (24.5°C)	0.4 -0.07(24.5°C)
Dodecane ($\geq 99\%$; Sigma)	750	1.35 (25°C)	25.4	52.8 (24.5°C)	-5.8 (24.5°C)	-6.1(24.5°C)
Hexadecane ($\geq 99\%$; Sigma)	773	3.34	27.5	53.3 (24.5°C)	-8.5 (24.5°C)	? (~-8.5)

^{*)} Density and viscosity of hydrocarbons are from Ref.[3] (20 °C; or other stated); surface tensions from Ref.[4]; interfacial tensions and spreading coefficients are from Ref.[5]. Spreading coefficient (S) is defined as: $S = \gamma_w - (\gamma_o + \gamma_{ow})$, where $\gamma_w, \gamma_o, \gamma_{ow}$ are the interfacial tensions for water-air, oil-air, and oil-water interfaces, respectively. Initial spreading coefficient is that which exists between two phases in an early stage of contact between pure phases, whereas an equilibrium spreading coefficient is that which is established after a mutual saturation of phases (see Refs [6,7] for details).

The entire event, starting with the release of the hydrocarbon droplet from the needle, to the attachment of the droplet at the water surface, and then the hydrocarbon spreading, were recorded with a video camera. The spreading process was viewed in slow motion and the kinetics of spreading were determined with an accuracy of 1 ms. Between 4 and 6 measurements were performed for each system. The entire event of the spreading of dodecane and hexadecane lenses could be distinguished from recorded images. In the case of pentane and heptane, about 10 ms of the spreading phenomenon could be observed due to the relatively clear image of the spreading lens. After about 10 ms, the lenses of pentane and heptane could not be observed as these hydrocarbons formed thin films during the final stage of the spreading process. The hydrocarbons used in the experiments and their properties are listed in Table 1.

3. RESULTS AND DISCUSSION

Four different hydrocarbons were used in the experiments; pentane, heptane, dodecane, and hexadecane. Both pentane and heptane spread spontaneously at the water surface due to the initial positive spreading coefficient (Table 1). Although thin films of both pentane and heptane may break to lenses when an equilibrium state is approached, i.e., the water becomes saturated with hydrocarbon, and the temperature is raised to more than about 24 °C (Table 1). The spreading of dodecane and hexadecane is different as both hydrocarbons never form a thin film on the surface of the water at room temperature. Instead these hydrocarbons remain as lenses at any stage of the spreading process, due to a negative spreading coefficient (Table 1). Thus, the systems selected are significantly different regarding their macroscopic appearance at the water surface. Such a selection of systems allowed for observation whether any difference in the kinetics of hydrocarbon spreading exists between two systems having completely different initial spreading coefficients. It must be added here that our experimental set-up allowed for observations of spreading lenses but no precursor film, moving in front of the spreading lens [1], could be recorded. This is an important limitation of these experiments because precursor film(s) is probably present in some of the systems studied, especially for pentane and heptane - both having positive initial spreading coefficients.

The experimental results of hydrocarbon spreading on the surface of deionized water are shown in Figures 1 and 2. In general, good reproducibility of the spreading kinetics was observed for all of the systems examined, particularly for the systems in their advanced stage of spreading, i.e., the experimental error was larger in the first 2-3 ms of the process than beyond this period. It is interesting to note that the spreading of hexadecane was slower than dodecane, heptane, and pentane, which "correlates" with the difference in viscosity of hydrocarbons. On the other hand, no similar "relationship" was observed for the lower

molecular weight hydrocarbons, pentane and heptane. Heptane spread faster than pentane, in spite of the fact that it has a greater viscosity and a smaller initial spreading coefficient (Table 1). We do not have a clear explanation for this behavior of heptane and pentane.

Experimental data for the entire spreading process, from the moment when the hydrocarbon drop was placed on the water surface to the final moment of observation (final stage of the spreading for dodecane and hexadecane was when a “stable lens” formed; and the last moment for the spreading of pentane and heptane was just prior to the formation of a “continuum film”), can be described by an n -power law relation as follows: $D \sim t^n$, where: D is the diameter of spreading hydrocarbon droplet/lens; and t is the time of spreading; and n is constant and is listed in Table 2.

Table 2. The values of n calculated from experimental data of hydrocarbon spreading on deionized water (pH 6) and sodium dodecyl sulfate solutions (pH 9.5) using linear regression analysis and assuming that the kinetics of spreading are described by $D \sim t^n$; average values, standard errors, and the correlation coefficients are given

Spreading Hydrocarbon	Substrate	n	R^2
Pentane	Water	0.47±0.02	0.95
Heptane	Water	0.49±0.01	0.97
Dodecane	Water	0.42±0.02	0.91
Hexadecane	Water	0.41±0.01	0.95
	0.05 mM SDS	0.39±0.02	0.99
	1 mM SDS	0.36±0.02	0.98

As shown in Figure 2, the experimental data fit well to a linear relationship in a log-log plot. A small deviation from this linearity could sometimes be distinguished, as marked by the broken line in Figure 2A. Whether this deviation is due to experimental errors or a systematic tendency, could not be resolved based on these experimental results. It must be mentioned, however, that such a transition from one slope to another for the $\log D$ vs $\log t$ relationship has already been observed by other authors [2,8], and was attributed to the existence of different regimes in the liquid expansion process.

As shown in Table 2, the value of n is 0.45 to 0.50 for pentane and heptane, and decreases to 0.41 for dodecane and hexadecane. When we used sodium dodecyl sulfate (SDS) solutions (0.05 mM to 1 mM) instead of pure water, the spreading of hexadecane droplets was slowed down (Figure 3). The value of n dropped to about 0.39 (0.05 mM SDS) and 0.36 (1 mM SDS). These results suggest that the kinetics of spreading for low-viscosity hydrocarbons can be controlled, to a certain extent, by molecular arrangements at water-fluid interfaces, which might be worth exploration in future research activities.

The power law for the liquid-on-liquid spreading, as obtained based on the experimental results, is consistent, in general, with theoretical predictions [1,2,9]. However, the value of power determined in this study ($n=0.45$ - 0.50 for pentane and heptane on water, $n=0.41$ for dodecane and hexadecane on water, and $n=0.36$ - 0.39 for hexadecane on SDS solutions) indicates that the spreading of these low-viscosity hydrocarbons could not be described by one of the simple theoretical equations proposed in the literature [1,2,9] for the capillary-driven or gravity-driven flow of droplets on a liquid substrate. Nevertheless, van Kats and Egberts [9] predicted, based on simulations of the capillary-driven spreading phenomenon, that the value of n should be equal to $n=0.42\pm 0.03$ in the first spreading period. This theoretical value is very close to our experimental results, particularly for dodecane and hexadecane (Table 2). However, it must be recognized that our video-recording covered almost the entire process of droplet spreading, not just the first phase. Additionally, our experiments involved the spreading of small droplets over a large water surface. Both phases, hydrocarbon and water, were not saturated with each other before the experiments. This means that spreading took place in conditions that were far from equilibrium. Unfortunately, we could not quantify the dynamic state of our systems and its effect on the kinetics of spreading.

Also, van Kats and Egberts [9] noted only a small effect of spreading coefficient on the value of exponent, n . This theoretically predicted effect is roughly consistent with our experimental findings, as we noted a slight and positive effect of increasing the initial spreading coefficient on the kinetics of hydrocarbon spreading (Tables 1 and 2). However, no clear correlation between the kinetics of hydrocarbon spreading and spreading coefficient values, that are listed in Table 1, could be found in this study. Also, we could not find a clear relationship between kinetics of spreading and spreading coefficient for SDS solutions (not shown here). For example, the kinetics of spreading for heptane was superior to pentane in spite of a larger initial spreading coefficient for pentane (Figure 1). On the other hand, the standard error of n values (Table 2) indicates that there was no distinguishable difference in this value between systems with pentane and heptane, as can be deduced based on statistics. If any n vs. S correlation should be expected, the contamination of hydrocarbons selected for this study might be one of the reasons for the scatter of data. We used commercial hydrocarbons with a purity of about 99% without further purification. Different contaminants could be dissolved in each of the hydrocarbon products and thus, they would have different effects on hydrocarbon spreading. Also, the spreading of hydrocarbon drops was very fast, such that even recording with our video system was difficult and the exact size of the spreading lens was sometimes difficult to determine precisely, particularly for pentane and heptane. These difficulties certainly reduced the precision of our measurements of the kinetics of spreading for low-viscosity hydrocarbons on water.

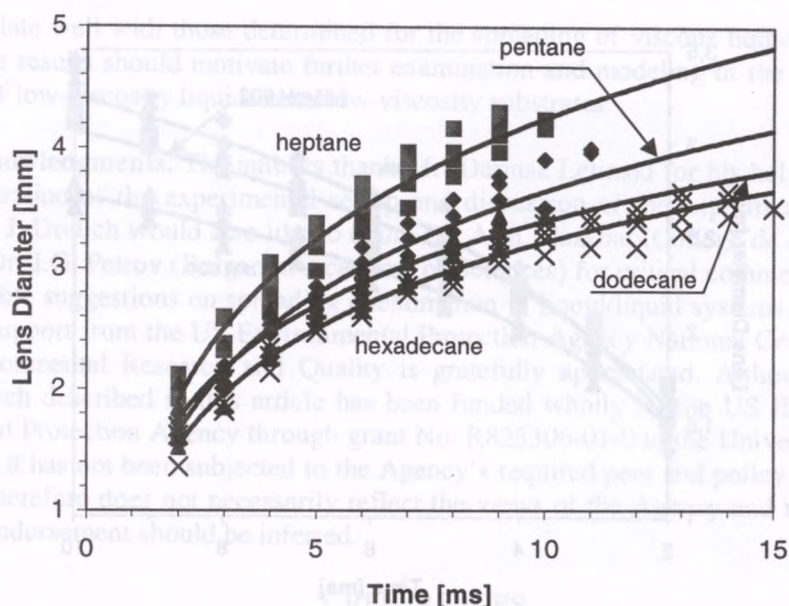


Figure 1. Spreading diameter versus spreading time for hydrocarbon droplets placed on the water surface. The experiments were repeated 4-6 times for each of the systems examined. Note that some of the markers overlap

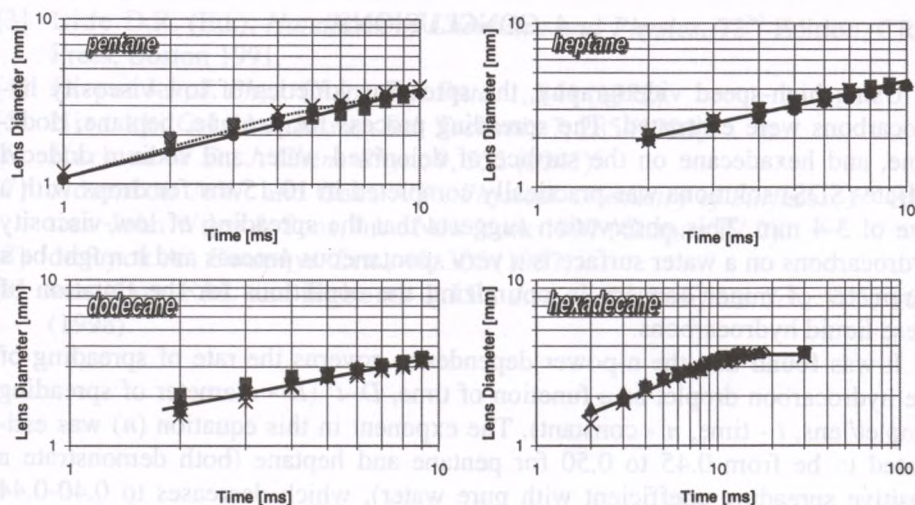


Figure 2. Spreading diameter versus spreading time for hydrocarbon droplets placed on the water surface. The results are the same as in Figure 1 but presented in log-log plot

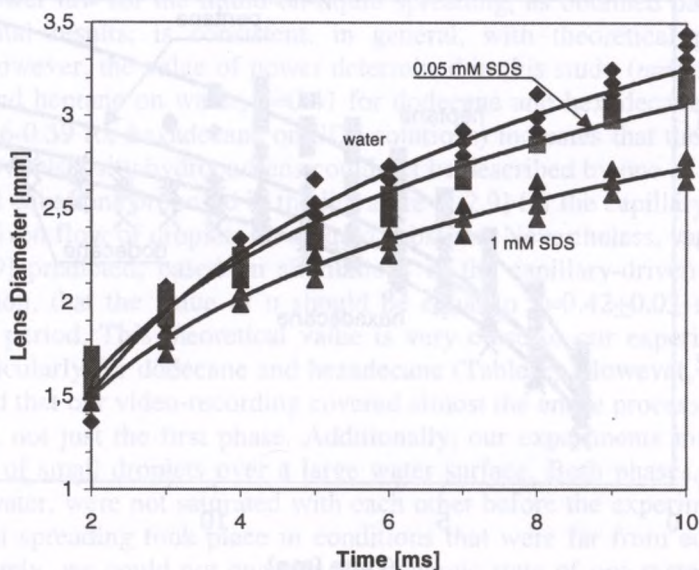


Figure 3. Spreading diameter versus spreading time for hexadecane droplets placed on the surface of water (pH 6), and 0.05 mM and 1 mM sodium dodecyl solutions (pH 9.5). The experiments were repeated four times for each of the systems. Note that some of the markers overlap

4. CONCLUSIONS

Using high-speed videography, the spreading kinetics of low-viscosity hydrocarbons were estimated. The spreading process for pentane, heptane, dodecane, and hexadecane on the surface of deionized water and sodium dodecyl sulfate (SDS) solutions was practically completed in 10-15 ms for drops with a size of 3-4 mm. This observation suggests that the spreading of low-viscosity hydrocarbons on a water surface is a very spontaneous process and it might be a parameter of minor concern in optimizing the conditions for the flotation of these liquid hydrocarbons.

It was found that the n -power dependence governs the rate of spreading of the hydrocarbon droplet as a function of time, $D \sim t^n$ (D - diameter of spreading droplet/lens, t - time, n - constant). The exponent in this equation (n) was estimated to be from 0.45 to 0.50 for pentane and heptane (both demonstrate a positive spreading coefficient with pure water), which decreases to 0.40-0.44 for systems with a negative spreading coefficient (dodecane and hexadecane on the water surface). Further, substituting pure water with sodium dodecyl sulfate solutions reduced the n value to 0.39 (0.05 mM SDS) and 0.36 (1 mM SDS) for the spreading of hexadecane droplets. Surprisingly, all of these n values do not

correlate well with those determined for the spreading of viscous liquids [1,2]. These results should motivate further examination and modeling of the spreading of low-viscosity liquids over low-viscosity substrates.

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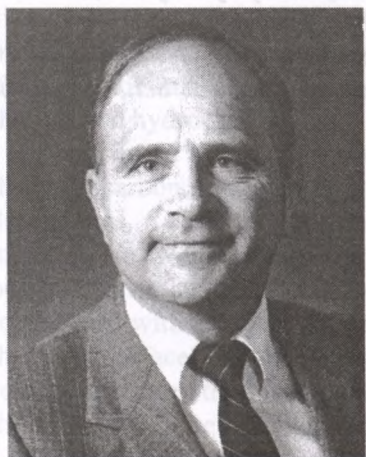
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CURRICULA VITAE



Jaroslaw Drelich. Born in Kolbudy (near Gdańsk) in Poland in 1957. He graduated from the Technical University of Gdańsk (Poland) in 1983 and received his M.S. degree in chemical technology. In 1993, Drelich received his Ph.D. degree in metallurgical engineering from the University of Utah in Salt Lake City (USA). Next, he worked at the University of Utah for over four years as a postdoctoral fellow and research assistant professor. From 1997, Dr. Drelich works at Michigan Technological University, Department of Metallurgical and Materials Engineering, in Houghton (USA), as an Assistant Professor. His main interest is in fundamental

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J.D. Miller. Graduated from State College High School in 1960 and received his B.S. degree, graduating with Distinction, from the Pennsylvania State University in 1964. His graduate degrees (M.S. and Ph.D.) in Metallurgical Engineering were earned at the Colorado School of Mines. Dr. Miller joined the Metallurgy and Metallurgical Engineering faculty at the University of Utah in 1968 and currently holds the rank of Professor. He has received the Departmental Teaching Excellence Award on three occasions and is well known for his numerous technical contributions in the areas of surface chemistry, coal

tions in the areas of surface chemistry, coal preparation, mineral processing, hydrometallurgy, and environmental technology, with more than 300 publications. His recent research activities involve both fundamental and applied aspects of surface and colloid chemistry, the use of X-ray computed tomography in the 3-D analysis of multiphase particles, and the development of air-sparged hydrocyclone technology.

In 1993 Miller was honored with the A.M. Gaudin Award by the Society for Mining, Metallurgy and Exploration and was further distinguished in the same year by being elected to the U.S. National Academy of Engineering. More recently, in 1997, he was recognized with the AIME Mineral Industry Education Award.

