Separation of Multicomponent Hydrocarbon Mixtures Spreading on a Water Surface

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Abstract

The separation of multicomponent hydrocarbon mixtures spreading on a water surface is related to the spreading coefficients of the hydrocarbons, taking into account relative volatilities and solubilities. In both synthetic and crude oil systems, the separation can be explained by the differences in spreading coefficients.

INTRODUCTION

Berridge, Dean, Fallows, and Fish (*1*), in studies of the behavior of an oil slick at sea, noticed a peripheral flash of crude oil moving well ahead of the bulk of the oil. This flash occurs because some components of the oil spread very much faster than others. The present study was undertaken in order to examine the separation process embodied in the differential spreading of oil from a mixture of different hydrocarbons having different spreading coefficients, and from a blend of a synthetic mixture of hydrocarbons with crude oil.

When oil is spilled on a surface, inertial, gravity, and interfacial tension spreading regimes exist (*2*). During the surface flow of crude oil, two effects may be observed: the more volatile or more soluble fractions of the oil will be preferentially removed, and the stronger spreading fractions will

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separate from the remainder of the oil. Transport by spreading in the interfacial regime occurs at least an order of magnitude faster than evaporation or dissolution, which are limited by molecular diffusivities. Since evaporation, dissolution, and spreading all occur simultaneously in the environment, it was decided to allow the same to occur in the laboratory but to select a system of hydrocarbons in which it would be possible to separate the effect of spreading from that of evaporation and dissolution.

EXPERIMENTAL

A 35-cm diameter bowl containing a shallow pool of water was used for the experiments. A 2.5-cm diameter by 5 cm high open-ended glass cylinder was used to collect samples. The oil temperature was adjusted to that of the water in the spreading bowl (10°C) and the oil added by means of a burette to the center of the bowl. The volume of oil added was approximately 0.1 ml. At various times and at various radial positions from the

TABLE 1
Volatility of Toluene, n-Octane, and n-Decane (3)

	Vapor pressure (Torr)					
	760	1	5	10	20	40
Toluene (°C)	110.6	−26.7	− 4.4	6.4	18.4	3.8
n-Octane (°C)	125.7	−14	8.3	19.2	31.5	45.1
n-Decane (°C)	174.0	−16.5	−23	55.7	69.8	85.5

TABLE 2
Solubility of Toluene, n-Octane, and n-Decane (g/10^6 g at 20°C) (4)

Toluene	515
n-Octane	0.66
n-Decane	<0.66

TABLE 3
Interfacial Properties of Toluene, n-Octane, and n-Decane (20°C)

	Surface tension (dyn/cm)	Interfacial tension oil/water (dyn/cm)	Spreading coefficient (dyn/cm)
Toluene			+6.8 (5)
n-Octane			+0.22 (5)
n-Decane	23.9 (6)	51.2 (6)	−2.3[a]
Water	72.75 (5)		

[a]Calculated from given data and definition of spreading coefficient.

center, the sampling cylinder was lowered through the surface of the water and a small piece of tissue paper dipped into the captured ring. The tissue was removed and extracted with carbon disulfide, and the extract was analyzed with flame ionization gas chromatography.

The hydrocarbon mixture chosen was toluene, n-octane, and n-decane in approximately equimolar proportions. The three hydrocarbons were chosen because their ranking in terms of spreading coefficient is the same as their ranking in terms of volatility and water solubility. They rank for all three properties in the order toluene > n-octane > n-decane (Tables 1–3). The spreading coefficients range from positive through approximately zero to negative. The ranking order for volatility and water solubility means that that if separation is observed, it has occurred in spite of differences in these properties.

In addition to experiments with the synthetic mixtures, experiments were performed with one part of the synthetic mixture diluted with one part of Norman Wells crude oil. Norman Wells crude oil (Northwest Territories, Canada) was chosen for the present work because of its pertinence to the Mackenzie River.

RESULTS AND DISCUSSION

Figures 1 to 4 show the mole fraction as a function of distance from the center. Although replicated experiments show some scatter, the following conclusions can be drawn. The mole fraction of toluene, the component with a positive spreading coefficient, increases from the center of the slick toward the periphery. The mole fraction of n-octane, which has a spreading coefficient of about zero, slightly increases then decreases from the center, and the mole fraction of n-decane, which has a negative spreading coefficient, decreases from the center. The maximum mole fraction of toluene occurs somewhere near the edge of the slick and that of n-decane near the center. The overall trend for the synthetic system of Figs. 1 and 2 is preserved in the crude oil system of Figs. 3 and 4.

It is important to note that the observed separation has occurred in spite of the opposing tendency of evaporation and dissolution, and that it is consistent with a spreading coefficient mechanism. It should be pointed out, however, that the spreading coefficient, as defined, represents the spreading force for a liquid spreading on pure water, and does not take account of the modification of the surface tension of the water by the presence of the various hydrocarbons.

The rate of separation can be related to the drag force. Since viscous drag is proportional to velocity, at the steady state defined by spreading
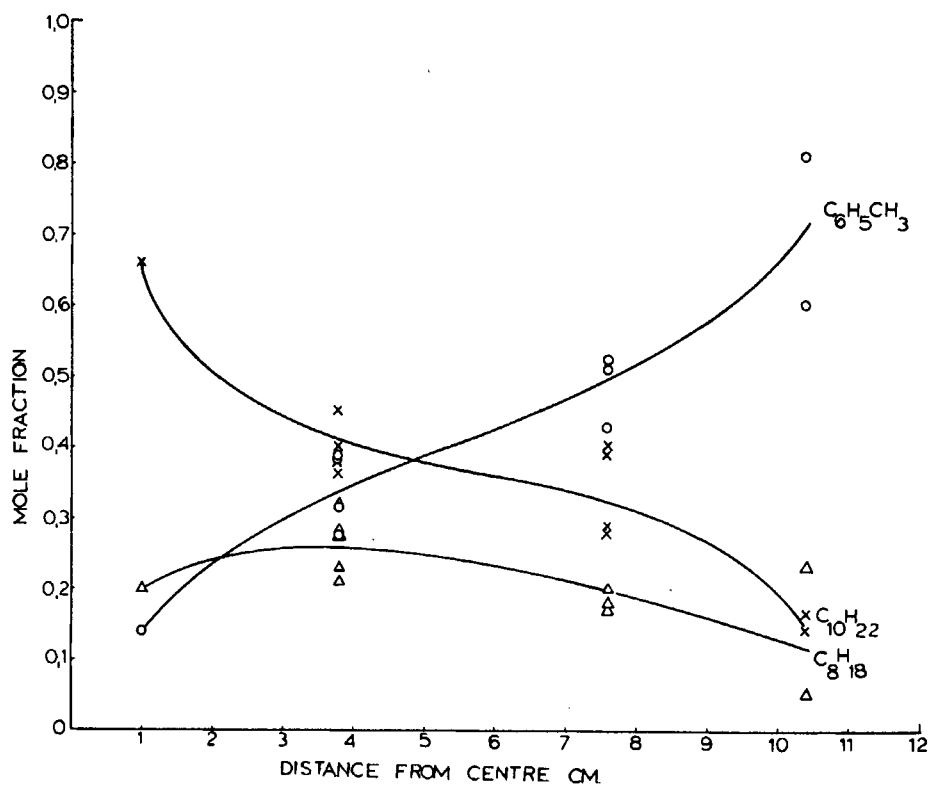
FIG. 1. Mole fraction vs distance for synthetic mixture equimolar in toluene, *n*-octane, and *n*-decane spreading on water, 5 sec after commencement of spreading.
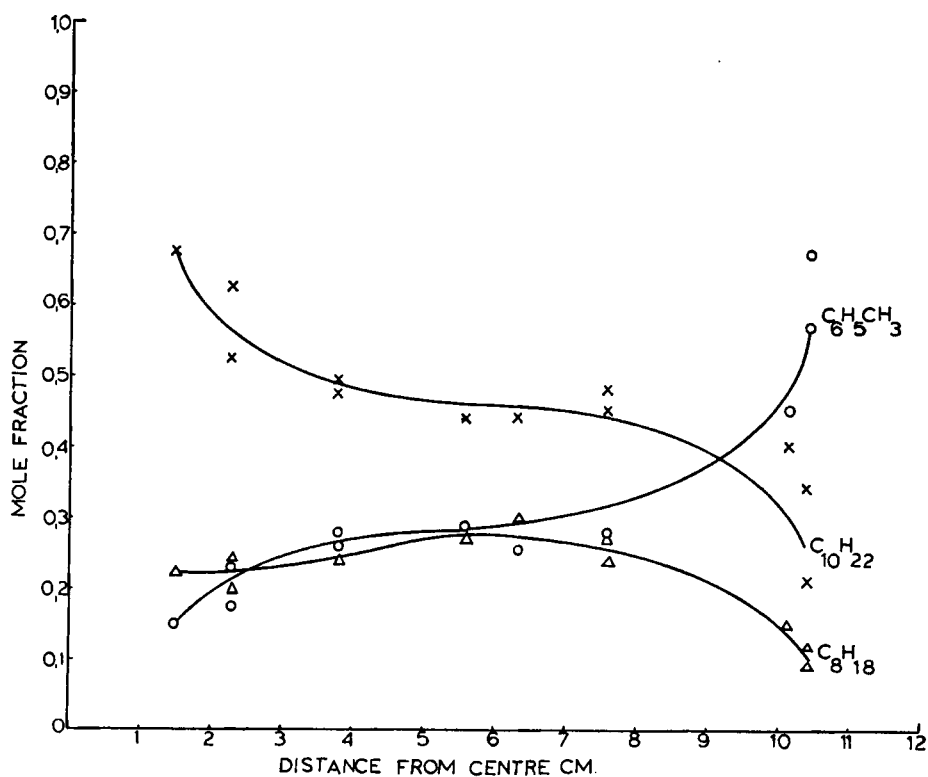
FIG. 2. Mole fraction vs distance for synthetic mixture equimolar in toluene, *n*-octane, and *n*-decane spreading on water, 15 sec after commencement of spreading.
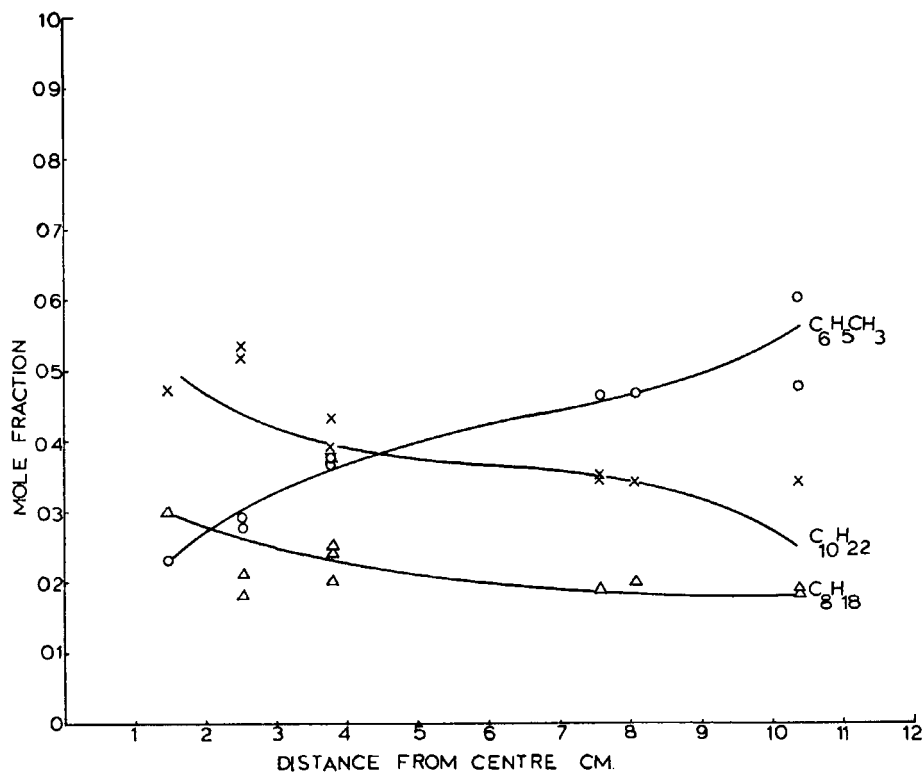
FIG. 3. Mole fraction vs distance for spreading on water of blend of synthetic mixture equimolar in toluene, n-octane, and n-decane with Norman Wells crude oil in 1:1 volume ratio. Samples were taken 5 sec after commencement of spreading.
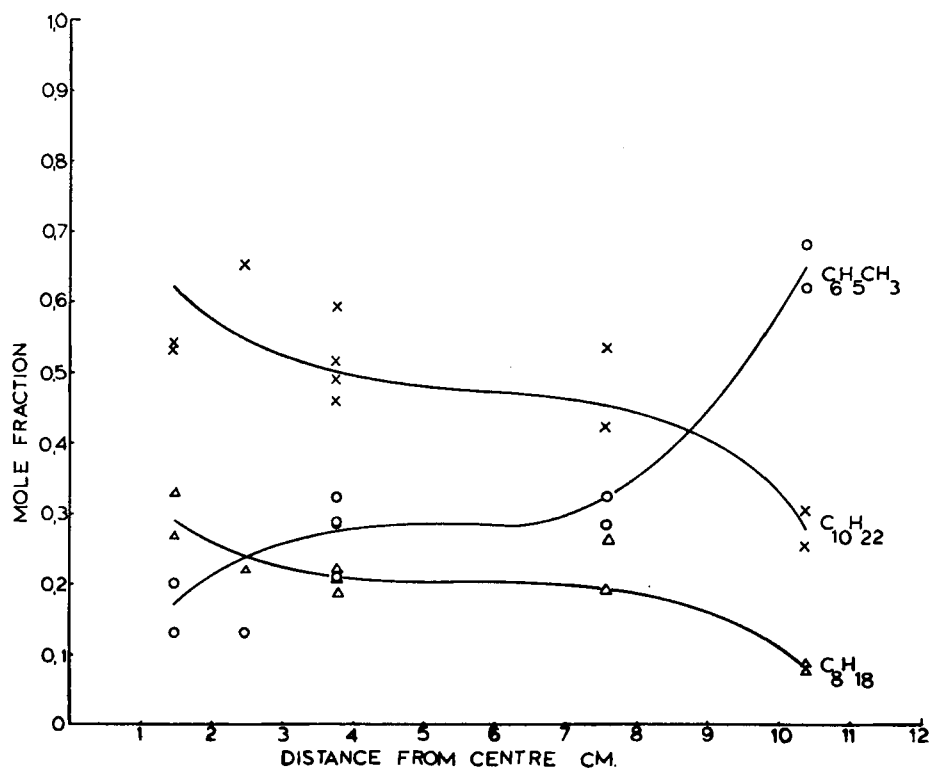
FIG. 4. Mole fraction vs distance for spreading on water of blend of synthetic mixture equimolar in toluene, *n*-octane, and *n*-decane with Norman Wells crude oil in 1:1 volume ratio. Samples were taken 15 sec after commencement of spreading.

force = viscous drag, the velocity of spreading of each component should be proportional to its spreading coefficient in the oil mixture. This spreading coefficient, as noted earlier, may not be the same as that for a single hydrocarbon on water. The data here do not allow a test of this possible relation. A further difficulty is the large inertial effect which is present at the beginning of the flow of the slick. In the environment, a wind would usually be superimposed on any differential velocity of oil on water, and, in addition, lateral diffusion would occur.

CONCLUSIONS

Separation of individual hydrocarbons from a multicomponent oil film on water occurs due to differences in the spreading coefficients. This conclusion is independent of the effect of relative volatility and solubility. The differential spreading mechanism is therefore operating during the dispersal of oil slicks on water.

Acknowledgments

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