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WETTABILITY/SPREADING OF ALKANES AT THE WATER-GAS INTERFACE AT ELEVATED TEMPERATURES AND PRESSURES

by

Daniel Thanh-Khac Pham

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE Master of Science

APPROVED, THESIS COMMITTEE:

Dr. G. J. Hirasaki
Professor of Chemical Engineering

Dr. W. G. Chapman
Associate Professor of Chemical Engineering

Dr. C. A. Miller
Professor of Chemical Engineering

Dr. G. F. Teletzke
Exxon Production & Research Company, Houston

Houston, Texas
June, 1996
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Abstract

The spreading or non-spreading of oil at the water-gas interface is an important factor in residual oil saturation, capillary pressure and relative permeability in three phases system. This understanding is important for oil recovery and remediation of hydrocarbon contaminated soil above the water table. The Hamaker-Lifshitz theory of van der Waals interaction of two continuum phases separated by a thin continuum film phase and the structural interactions due to submonolayer adsorption of discrete molecules are used to calculate conditions for the spreading of alkanes at the water-gas interface. In the current work, the theory is extended to include effects of the temperature and pressure. The gas phase is considered as a mixture of saturated alkane and water vapor. The substrate is considered as pure water; however, the effect of NaCl dissolved into substrate water is also studied. The Peng-Robinson equation of state with volume translation for alkanes and the density translation for water is used to estimate the density as a function of pressure and temperature. The dielectric polarizability of the vapor and liquid phases at elevated temperature and pressure are estimated as a function of density through the Clausius-Mosotti equation. The retardation effect is also taken into
account in the disjoining pressure isotherm calculation. The results confirm that with pentane, hexane, and heptane it is possible to form a thick, metastable, spreading film when retardation is taken into account. The wetting transition temperature occurs for alkanes when the Hamaker constant of the water/alkane/vapor system changes sign. At saturated pressure, the wetting transition temperature of alkane at the water-gas interface is determined to be 43°C for pentane and increases with increasing of carbon number up to 233°C for decane. The low wetting temperature of pentane confirms that the behavior of pentane is marginal between spreading and nonspreading. The theory is validated by an experiment using the interference microscope to measure the contact angle of alkane at the water-gas interface at room temperature. The contact angle is used to determine the spreading coefficient of alkane at water-gas interface, and the results agree with the calculated values. The spreading behavior of alkane is also dependent on the NaCl concentration in the water phase. As the concentration of NaCl in the water substrate increases, octane and decane will spread as predicted by the Hamaker constant calculation, measured contact angle, and measured spreading coefficient. The theory of this study is also used to predict the flow of sulfur containing sour natural gas in a reservoir, and the calculations support the experimental results.
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I. INTRODUCTION:

Wetting phenomena are important for many practical processes such as dyeing, painting, coating and lubrication. In oil recovery and remediation, the spreading or non-spreading of oil at the water-gas interface is an important factor in residual oil saturation, capillary pressure and relative permeability in three phase systems. It determines the effectiveness of displacement and the amount of oil recovered.

This study concentrates on the spreading of alkanes on water-gas interface at elevated temperature and pressure. Earlier investigators have shown that hexane and higher alkanes do not spread at equilibrium, but pentane, hexane, and heptane will initially spread on water (at room temperature and pressure) [13]. From the observation of Hauxwell and Ottewill [15] and the calculation of Richmond [16], pentane, hexane and heptane were found to spread. Del Cerro and Jameson [17] showed that hexane and heptane do not spread at equilibrium, and their calculation showed the same results if the appropriate dielectric data for water are used. The spreading behavior of pentane was marginal between spreading and non-spreading. Del Cerro and Jameson [17] also showed that pentane, hexane, and heptane are possible to form a thick, metastable, spreading film if retardation is taken into account. In the present study, the theoretical calculation will be extended to include effects of temperature and pressure. The system consists of three phases: water (substrate), alkanes (thin film and lens), and vapor (mixture of water and alkane
vapors at saturation). The conditions for the spreading of alkanes at the water-gas interface are calculated by the Hamaker-Lifshitz theory of van der Waals interaction of two continuum phases separated by a thin continuum film phase and the structural interactions due to submonolayer adsorption of discrete molecules. The submonolayer adsorption is modeled by the two dimensional van der Waals equation of state. The dielectric polarizability at elevated temperature and pressure for each phase is estimated as a function of density through the Clausius-Mosotti equation. The Peng-Robinson equation of state with volume translation for alkanes and the density translation for water is used to estimate the density as a function of pressure and temperature. The retardation effect is also taken into account in the disjoining pressure isotherm. The result of the disjoining pressure at high film thickness confirms the earlier results by Del Cerro and Jameson [17] about the retardation effect. The results of initial and equilibrium spreading coefficients calculated from the disjoining pressure isotherm curve confirm the experimental observation of Hauxwell and Ottewill [15] and Del Cerro and Jameson [17]. Experimental results obtained from measuring contact angle of alkane on water surface are used to calculate for the spreading coefficient of the system. Both calculated and experimental values of the equilibrium spreading coefficients agree with each other. The study of Hamaker constant calculated from the refractive index and dielectric constant is helpful to predict the spreading condition for other system which can not be calculated directly using Hamaker-Lifshitz theory. Hamaker constant for the
system of brine solution/alkane/vapor is estimated. The effect of NaCl in water to the spreading behavior of alkane shows that octane will spread on brine solution surface at the concentration of NaCl of 4.5M or higher from the result of Hamaker constant estimation. For other alkanes (decane and hexadecane), the Hamaker constant decreases (approaching zero) with increasing concentration of NaCl in water. Contact angles of alkanes at the brine-vapor interface are measured for decane and hexadecane, and the values decrease with increasing NaCl concentration in water. Wetting behavior of water/H₂S/sulfur is also studied, and the results support Coskumer's experiments [23].
II. Determination of wetting from spreading coefficient:

If a drop of liquid hydrocarbon is placed on water surface so that it is initially present in a layer of appreciable thickness, the drop of hydrocarbon will either spread or form a lens, as illustrated in Fig. II-1. The term best describing this behavior is called the spreading coefficient.

\[
S^\text{eq} = 0
\]

\[
S^\text{eq} < 0
\]

**Figure II-1:** What will happen to a drop of hydrocarbon on water surface at equilibrium.
The spreading coefficient of liquid hydrocarbon (o) over water surface (w) is called the spreading coefficient of (o) on (w). It is defined as

\[ S_{o/w}^l = \sigma_{sw} - \sigma_{vo} - \sigma_{ow} \]  \hspace{1cm} (II-1)

\[ S_{o/w}^{eq} = \sigma^{eq}_{vw} - \sigma_{vo} - \sigma_{ow} \]  \hspace{1cm} (II-2)

where: \(\sigma^{eq}_{vw}\) is the equilibrium surface tension of water (w) which the thin film tension of hydrocarbon has taken into account (v is the vapor phase). According to Adamson [24] and Dimitrov [30], \(\sigma_{sw}\) (surface tension of water with air) will change to \(\sigma^{eq}_{vw}\) (equilibrium surface tension of water with vapor phase saturated with alkane vapor) at saturation. At saturation, the water surface is in equilibrium with the alkane vapor. This results in a thin alkane film on the water surface. The thin alkane film will contribute to the equilibrium surface tension of water. \(\sigma_{vo}\) is the surface tension of liquid hydrocarbon (o), and \(\sigma_{ow}\) is the interfacial tension between hydrocarbon and water.

From the definition of work of adhesion and cohesion, the spreading coefficient is the difference between the work of adhesion of water (w) to alkane (o) and the work of cohesion of alkane (o), \(S_{o/w}^{eq} = \mathcal{W}_{ow} - \mathcal{W}_{oo}\), [1]. At equilibrium, the drop of liquid hydrocarbon will spread into the film if the equilibrium spreading coefficient is zero or into a lens with finite contact angle if the equilibrium spreading coefficient is negative.
The spreading coefficient can be determined from the disjoining pressure isotherm curve as illustrated in Fig. II-2 [1]. The disjoining pressure isotherm is modeled by using the two-dimensional van der Waals equation of state for submonolayer films and the Hamaker-Lifshitz theory for multilayer films. The plots of these two models are spliced together at the film thickness where they intersect (see next section for detail). The equilibrium spreading coefficient is equal to the area under the disjoining pressure isotherm from the equilibrium film thickness to infinity (negative). The initial spreading coefficient is equal to the net area under the disjoining pressure isotherm from zero to infinite thickness.

Figure II-2: Determination of spreading coefficients from the disjoining pressure isotherm
The spreading coefficient can be calculated directly from the exact integrals of the disjoining pressure isotherm without any numerical integration [1]. The equilibrium film thickness where the 2-D van der Waals disjoining pressure isotherm is equal to zero and the intercept of the 2-D van der Waals and Hamaker isotherms are obtained by numerical root finding methods.

The spreading coefficient can also obtained experimentally by the values of measured contact angle of the alkane lens, surface tension of alkane, and interfacial tension of alkane and water. Derivation of the equation is shown in the experimental section.

Plots of the calculated and experimental results for spreading coefficient of hydrocarbon on water are presented in the result section.

As mentioned above, at equilibrium the wetting transition occurs when the equilibrium spreading coefficient first becomes equal to zero, or the area between the disjoining pressure isotherm and the x axis from the equilibrium film thickness to infinite thickness first becomes non-negative (zero or positive). Another way to predict the wetting transition is when the Hamaker constant changes sign from positive to negative. Wetting transition temperature of the study system predicted by using Hamaker constant (calculated from Lifshitz theory and from the refractive index and dielectric constant) is discussed in the Hamaker constant section. From our Hamaker constant study, another method
for predicting the spreading behavior was derived by comparing the refractive index of each phase (see later for detail).
III. Determination of wetting behavior from disjoining pressure isotherm:

The equilibrium spreading coefficient determines whether a liquid drop of hydrocarbon will spread or form a lens at equilibrium. Both initial and equilibrium spreading coefficient can be determined from the value of the disjoining pressure isotherm. The disjoining pressure isotherm is estimated by combining the two-dimensional van der Waals equation of state which calculates the short-range interaction for submonolayer films and the Hamaker-Lifshitz theory which calculates the long-range interaction for multilayer films. These two models will be spliced together at the film thickness where the two models intersect assuming that each model is applied up to the intersection [1].

Following are assumptions used for calculating the disjoining pressure isotherm in the present study. Water and alkane film phases are assumed to be single component. Water is considered as a bulk phase. The alkane film phase is assumed to have the same density and dielectric properties as the bulk liquid alkane at its saturated condition. The vapor phase is assumed to be saturated vapor of the hydrocarbon and water.

1. Two-dimensional van der Waals equation of state - The short-range interaction for submonolayer films:
The equation of the disjoining pressure for the two-dimensional van der Waals equation of state is [1]:

$$\Pi = -\frac{A_{132}}{6\pi(h^*)^3} + \frac{2a_2}{\nu a} - \frac{kT}{\nu} \left[ \frac{a}{a-b_2} - \ln\left( \frac{a}{b_2} - 1 \right) \right]$$  \hspace{1cm} (III-1)

where

$A_{132}$ is the Hamaker constant for the substrate/liquid/vapor system.

$h^*$ is the interaction distance of a single molecule laying flat at the interface.

$a_2$ and $b_2$ are the 2-D van der Waals EOS parameters.

$a$ is the specific area (equals to the molecular volume, $\nu$, divided by the equivalent film thickness, $d$, $a = \frac{\nu}{d}$).

From equation (III-1) above, the temperature dependent terms in this equation are $T$, $A_{132}$ and $\nu$. $A_{132}$ is obtained from the result of calculating the long-range interaction for multilayer films (by the Hamaker-Lifshitz theory) as explained later in the Hamaker constant section. $\nu$ is the molecular volume which is obtained for each temperature by using modified Peng-Robinson EOS (see density estimation section).

The following table, Table III-1, presents the values of $a_2$, $b_2$ and $h^*$ for calculating the 2-D van der Waals EOS. The values of $a_2$ and $b_2$ are estimated from the critical temperature and pressure of the bulk fluid. The value of $h^*$ is
defined as the distance from the flat surface to the center of an n-alkane molecule lying on the surface.

**Table III-1**: Data for calculating disjoining pressure by two dimensional van der Waals EOS [1].

<table>
<thead>
<tr>
<th>Alkane</th>
<th>(a_1) (mJ m(^2) Å(^4))</th>
<th>(b_1) (Å(^2))</th>
<th>(h^*) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>40573</td>
<td>37</td>
<td>2.3</td>
</tr>
<tr>
<td>6</td>
<td>49147</td>
<td>42</td>
<td>2.3</td>
</tr>
<tr>
<td>7</td>
<td>59972</td>
<td>47</td>
<td>2.3</td>
</tr>
<tr>
<td>8</td>
<td>67798</td>
<td>51</td>
<td>2.3</td>
</tr>
<tr>
<td>10</td>
<td>82393</td>
<td>59</td>
<td>2.3</td>
</tr>
<tr>
<td>12</td>
<td>107198</td>
<td>70</td>
<td>2.3</td>
</tr>
</tbody>
</table>

2. The Hamaker-Lifshitz theory - The long-range interaction for multilayer films:

The disjoining pressure per unit area between two phases, 1 and 2, separated by a medium phase 3, from the Lifshitz theory [9], is calculated by

\[
\Pi_{132}(d) = -\left(\frac{\partial F_{132}(d)}{\partial d}\right)_T \approx -\frac{A_{132}}{6\pi d^3}
\] (III-2)

where:

\(\Pi_{132}(d)\) is the disjoining pressure with respect to film thickness \(d\)

\(d\) is film thickness

\(A_{132}\) is the Hamaker constant
\( F_{132}(d) \) is the interaction energy per unit area calculated by Lifshitz theory, expressed as an integral over a dummy variable \( x \)

\[
F_{132}(d) = \frac{kT}{8\pi d^2} \sum_{n=0}^{\infty} \int x \, dx \, \ln(1 - \Delta_{13}^{\prime} \Delta_{23} e^{-x}) \tag{III-3}
\]

the prime on the summation indicating that the \( n=0 \) term is given by half weight. 

where

\[
\Delta_{jk} = \frac{\varepsilon_j(i\xi_n)x_k - \varepsilon_k(i\xi_n)x_j}{\varepsilon_j(i\xi_n)x_k + \varepsilon_k(i\xi_n)x_j} \quad (j,k=1,2,3) \tag{III-3.a}
\]

\[
x_j^2 = x^2 + r_n^2 \left( \frac{\varepsilon_j(i\xi_n)}{\varepsilon_3(i\xi_n)} - 1 \right) \quad (j=1,2) \tag{III-3.b}
\]

\( \varepsilon_j(i\xi_n) \) is related to the dielectric response function of material \( j \) and evaluated at the discrete set of frequencies \( \xi_n \) which

\[
\xi_n = n \left( \frac{2\pi kT}{\hbar} \right) \quad (\hbar \text{ is Planck's constant}) \tag{III-3.c}
\]

\( r_n \) is the ratio of the time taken for an electromagnetic wave of frequency \( \xi_n \) to travel across the distance of separation \( d \) and back, to the period of the wave

\[
r_n = \frac{2d\xi_n(\varepsilon_3(i\xi_n))^{0.5}}{c} \quad (c \text{ is the speed of light in vacuum}) \tag{III-3.d}
\]

From equation (III-2), the disjoining pressure isotherm estimated by Hamaker-Lifshitz theory can be determined if the quantities \( \varepsilon_j(i\xi_n) \) are obtained for each phase. From Appendix C, the derivation of \( \varepsilon_j(i\xi_n) \) from the dielectric
susceptibility is discussed. Following are equations to estimate the value of \( \varepsilon_f(i\xi_n) \) for the hydrocarbon, vapor and water phases available from literature.

For hydrocarbon or vapor phases, according to Ninham and Parsegian [3], \( \varepsilon_f(i\xi_n) \) is estimated by

\[
\varepsilon_f(i\xi_n) = 1 + \sum_{i=1}^{n} \frac{C_i}{1 + \left(\frac{i\xi_n}{\omega_i}\right)^2} \quad (\text{III-4})
\]

For transparent non-polar materials, the behavior of \( \varepsilon_f(i\xi_n) \) in the infra-red and the ultra-violet regions of the spectrum is important in the calculation of accurate interaction energy \( F_{132}(d) \). \( \varepsilon_f(i\xi_n) \) can be approximated by single adsorption frequency in the infrared and the ultraviolet as

\[
\varepsilon_f(i\xi_n) = 1 + \frac{C_{IR}}{1 + \left(\frac{i\xi_n}{\omega_{IR}}\right)^2} + \frac{C_{UV}}{1 + \left(\frac{i\xi_n}{\omega_{UV}}\right)^2} \quad (\text{III-5})
\]

where:

- \( C_{IR}, C_{UV} \) are oscillation strength constants for the infra-red and ultra-violet regions.
- \( \omega_{IR}, \omega_{UV} \) are absorption frequency in the infra-red and ultra-violet regions.

For water, \( \varepsilon_f(i\xi_n) \) is determined by using the Gingell-Parsegian representation [8]

\[
\varepsilon_{H_2O}(i\xi_n) = 1 + \sum \frac{C_i}{1 + \left(\frac{i\xi_n}{\omega_i}\right)^2 + \left(\frac{g_i\xi_n}{\omega_i^2}\right)^2} \quad (\text{III-6})
\]
where:

$g_i$ is the line widths of the absorption peaks

$C_i$ is oscillator strength constant for water which depends to its density

$C_i$ and $\omega_i$ can be estimated by using "Cauchy plot" or "Clausius-Mosotti plot" methods. In our calculation, we use "Cauchy plot" method for estimating $C_i$ and $\omega_i$.

For $\xi_n$ in the visible region, $\varepsilon(i\xi_n)$ is given by [11]

$$\varepsilon(i\xi_n) = 1 + \frac{C_{UV}}{1 + \left(\frac{\xi_n}{\omega_{UV}}\right)^2}$$

(III-7)

In the visible region, $\varepsilon(\omega) = \varepsilon'(\omega) = n^2(\omega)$ and $\omega = i\xi$ then

$$n^2(\omega) = 1 + \frac{C_{UV}}{1 - \left(\frac{\omega}{\omega_{UV}}\right)^2}$$

(III-8)

Equation (III-8) can be rearranged to

$$n^2(\omega) - 1 = \left[\frac{n^2(\omega) - 1}{\omega_{UV}^2}\right] \frac{\omega^2}{\omega_{UV}^2} + C_{UV}$$

(III-9)

The plot of $\left[n^2(\omega) - 1\right]$ versus $\left[n^2(\omega) - 1\right]\omega^2$ should yield a straight line of slope $\frac{1}{\omega_{UV}^2}$ and intercept $C_{UV}$. Therefore, by measuring the refractive index as a function of frequency in visible region, the values of $C_{UV}$ and $\omega_{UV}$ can be determined.
Once $C_{IR}$, $\omega_{IR}$, $C_{UV}$, $\omega_{UV}$, have been determined, $\varepsilon(i \xi_n)$ is estimated for each medium by the above equations. The interaction energy and disjoining pressure of the system are obtained by substitute $\varepsilon(i \xi_n)$ into equation (III-3) and (III-2).
IV. Extension of the theory to elevated temperature and pressure:

The theory can be extended to the reservoir temperature and pressure by estimating the dielectric function of materials at elevated temperature and pressure as a function of density through the Clausius-Mosotti equation. Since the vapor phase is a mixture of saturated alkane and water vapor, the dielectric function of the vapor phase will be estimated from a mixture of saturated alkane and water vapor.

1. Dielectric function of the liquid and film phases:

From equation (III-7), at zero frequency $C_{uv}$ relates to refractive index of the medium as

$$C_{uv} = n_o^2 - 1$$  \hspace{1cm} (IV-1)

where:

$n_o$ is the refractive index of the medium in the visible extrapolated to zero frequency

According to Clausius-Mosotti equation, the refractive index of a material is related to its density by [22]

$$\frac{3}{n^2 + 2} = N\alpha$$  \hspace{1cm} (IV-2)

where:

$N$ is number of atoms in a unit volume. $N$ depends on the density of the material.
\( \alpha \) is called the atomic polarizability. It is not a function of \( T \) but is a function of frequency.

Apply \( n_0 \), which is known at 20°C, into equation (IV-2), the value of \( N\alpha \) can be calculated at 20°C. At temperature \( T \), \( N\alpha \) can be estimated by

\[
N\alpha_{atT} = N\alpha_{at20C} \times \frac{\rho_{atT}}{\rho_{at20C}} \tag{IV-3}
\]

where:

\( \rho_{atT} \) is the density of the material at temperature \( T \) estimated by using modified Peng-Robinson equation of state (see later)

Then, the refractive index at zero frequency, \( n_{e\alpha T} \), at temperature \( T \) can be calculated as

\[
n_{e\alpha T}^2 = 1 + \frac{N\alpha_{atT}}{1 - \frac{N\alpha_{atT}}{3}} \tag{IV-4}
\]

Substituting equation (IV-4) into (IV-1), we have

\[
C_{uv} = \frac{N\alpha_{atT}}{1 - \frac{N\alpha_{atT}}{3}} \tag{IV-5}
\]

If equation (IV-5) is substituted into equation (III-7), \( \varepsilon(\text{i}\xi_\alpha) \) can be estimated at temperature \( T \). Once \( \varepsilon(\text{i}\xi_\alpha) \) is determined, the interaction energy and disjoining pressure of the system can be calculated by substituting \( \varepsilon(\text{i}\xi_\alpha) \) into equation (III-3) and (III-2).
Appendix B compares the dielectric property estimation for material by using above approach and the approach assuming $C_{uv}$ depending directly proportional to the density of material.

2. Dielectric function of the vapor phase:

The vapor phase consists of water and alkane vapor at saturation. Assuming total pressure equals to the sum of saturated vapor pressure of water and alkane, $P = P_{sat}^{H_2O} + P_{sat}^{alkane}$.


$$3\left(\frac{n^2 - 1}{n^2 + 2}\right) = \sum_i N_i \alpha_i$$  \hspace{1cm} (IV-6)

where:

$\alpha_i$ is the polarizability of each component

$N_i$ is the number of atoms of each component per unit volume

$n$ is the refractive index of the mixture

Using the same approach as equation (IV-3), we have

$$N_{j,\text{vap. at } T}\alpha_j = N_{j,\text{liq, at } 20^\circ C}\alpha_j \times \frac{P_{\text{vap. at } T}}{P_{\text{liq, at } 20^\circ C}}$$ \hspace{1cm} (IV-7)

Where $N_{j,\text{liq, at } 20^\circ C}$ can be calculated by equation (IV-2) for each component using its refractive index at 20°C. Then equation (IV-6) at temperature $T$ becomes
\[ 3\left(\frac{n^2 - 1}{n^2 + 2}\right)_{\text{vap, at } T} = \sum_j (N_j \alpha_j)_{\text{vap, at } T} \quad \text{(IV-8)} \]

After rearrange, we have

\[ n_{\text{vap, at } T}^2 = 1 + \frac{\sum_j (N_j \alpha_j)_{\text{vap, at } T}}{1 - \frac{3}{\sum_j (N_j \alpha_j)_{\text{vap, at } T}}} \quad \text{(IV-9)} \]

Substituting equation (IV-9) into (IV-1) for a mixture of vapor phase, we have

\[ C_{uv_{\text{vap, at } T}} = \frac{\sum_j (N_j \alpha_j)_{\text{vap, at } T}}{1 - \frac{3}{\sum_j (N_j \alpha_j)_{\text{vap, at } T}}} \quad \text{(IV-10)} \]

3. Dielectric constant:

Dielectric constant of the film and vapor phases can be determined by using equation (III-7) at zero frequency since the adsorption in the IR and microwave range is small compared to that in the UV range.

For water phase, the static dielectric constant \( \varepsilon_0 \) is calculated by using the Stankov representation [6 & 7].

\[ \varepsilon_0 = \exp\left( \frac{U_{in} + 0.0067 \times 10^{-13}(T - 273.15)^{0.0752}}{kT} \right) \quad \text{(IV-11)} \]

where
\( \bar{u}_w \) (heat of vaporization of water at 20\(^{\circ}\)C) = 1.688013E-13 erg.

**Note:** Equation (IV-11) is derived by extrapolation. According to Stankov [6 & 7], equation (IV-11) can be applied for temperatures from 0\(^{\circ}\)C to 100\(^{\circ}\)C. At 0\(^{\circ}\)C, the equation will give \( \varepsilon_0 \) value at 0\(^{\circ}\)C temperature even though \( \bar{u}_w \) is heat of vaporization at 20\(^{\circ}\)C.
V. Density estimation:

From above, the theory has been extended to calculate the disjoining pressure isotherm at elevated temperature and pressure. However, the density of each phase at elevated temperature and pressure is required for such a calculation. From equations (IV-3) and (IV-7), \( N \), number of atoms in a unit volume, is estimated by using the ratio of density of material at temperature \( T \) and at 20°C. This estimation required the density at 20°C be the same as the experimental data (not discontinuous at 20°C) since the refractive index of material is measured at room temperature, 20°C. Peng-Robinson (PR) and Redlich-Kwong-Soave (RKS) EOS can be used to estimate the equilibrium density of the vapor and liquid. However, both EOS estimate the molar volume of decane at 20°C with approximate 8 and 9 percent error, respectively (see Appendix C for the standard forms of PR and RKS-EOS).

Pe'neloux et al. [4] proposed a method to improve the molar volume estimation by introducing a third parameter into the RKS-EOS. This third parameter does not change the vapor/liquid equilibrium conditions (saturated pressure at temperature \( T \)), but it modifies the phase volumes by effecting certain translations along the volume axis. By applying Pe'neloux-Rauzy-Fre'ze (PRF) method for PR and RKS-EOS to match the molar volume at 20°C with experimental data, the PR and the RKS-EOS then become

Modified PR-EOS
\[ P = \frac{RT}{V^{\text{corr}} - b^{\text{corr}}} - \frac{a}{V^{\text{corr}} + 2V^{\text{corr}}(b^{\text{corr}} + s) + 2s^2 - b^{\text{corr}^2}} \]  
(V-1)

Modified RKS-EOS [4]

\[ P = \frac{RT}{V^{\text{corr}} - b^{\text{corr}}} - \frac{a}{(V^{\text{corr}} + s)(V^{\text{corr}} + b^{\text{corr}} + 2s)} \]  
(V-2)

with

\[ V^{\text{corr}} = V - s \]  
(V-3)

\[ b^{\text{corr}} = b - s \]  
(V-4)

where:

- \( V^{\text{corr}} \) is the corrected volume after applied the volume shift parameter
- \( V \) is the molar volume which is calculated by the original EOS's
- \( s \) is the third parameter (volume shift parameter) used to match the molar volume estimate at 20°C with the experimental value, which is determined by

\[ s = V - V_{\text{experimental value at 20°C}} \]  
(V-5)

Figure V-1 to V-5 are plots of estimated density by PR and RKS-EOS using PRF method and experimental data at various temperature of n-butane, n-hexane, benzene, n-decane, and n-tetradecane. (Experimental data are obtained from Texas A&M University. American Petroleum Institute research Project 44). Table V-1 contains values for calculating the density of those components.
Table V-1: Critical values and molar volumes.

<table>
<thead>
<tr>
<th>Component</th>
<th>Tc (K)</th>
<th>Pc (bar)</th>
<th>ω</th>
<th>V at 20°C (cm³ mol⁻¹)</th>
<th>s (cm³ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Butane</td>
<td>425.2</td>
<td>38.0</td>
<td>0.193</td>
<td>100.44  a</td>
<td>-4.668</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>507.4</td>
<td>29.7</td>
<td>0.296</td>
<td>130.451</td>
<td>1.055</td>
</tr>
<tr>
<td>Benzene</td>
<td>562.1</td>
<td>48.9</td>
<td>0.212</td>
<td>90.6192  b</td>
<td>-2.135</td>
</tr>
<tr>
<td>n-Decane</td>
<td>617.7</td>
<td>21.2</td>
<td>0.489</td>
<td>194.4885</td>
<td>15.118</td>
</tr>
<tr>
<td>n-Tetradecane</td>
<td>693.0</td>
<td>14.4</td>
<td>0.581</td>
<td>208.3472</td>
<td>28.743</td>
</tr>
</tbody>
</table>

a value at 70°F, b value at 100°F

(Sources from Smith and Van Ness, Introduction to Chemical Engineering Thermodynamics; Texas A&M University, American Petroleum Institute research Project 44; Reid, Prausnitz, and Poling, The Properties of Gases and Liquids)
Figure V3: Density vs. Temperature for Benzene

Figure V4: Density vs. Temperature for n-Decane
For water, after applying PRF method, the liquid density error pattern rises with temperature (see Fig. V-6). However, by observing the density vs. temperature curve of water, I propose a density shift parameter for water. This parameter will translate the density curve calculated by unmodified PR-EOS along the density axis.

$$\rho^{orr} = \rho - sd \quad \text{(V-6)}$$

where \(sd\) is density shift parameter

The density shift parameter, \(sd\), can be determined to match the density of water at 20°C by

$$sd = \rho - \rho_{at \; 20°C} \quad \text{(V-7)}$$

The density shift can be related to corrected volume shift as
\[ V_{\text{corr}} = \frac{1}{\rho_{\text{corr}}} = \frac{1}{\rho - sd} \]  

(V-8)

compare to \( s \) from PRF method, \( sd \) relates to \( s \) as

\[ s = \frac{1}{sd} \]  

(V-9)

then the corrected volume is related to volume shift parameter as

\[ V_{\text{corr}} = \frac{1}{\frac{1}{V} - \frac{1}{s}} \]  

(V-10)

or

\[ V_{\text{corr}} = \frac{Vs}{s-V} \]  

(V-11)

Figure V-7 is plot of experimental data and estimated density by PR-EOS using density shift parameter method at various temperature of water. Table V-2 contains values for calculating the density of water.
Figure V-7: Density vs. Temperature for Water
(Density shift parameter is applied)

Table V-2: Critical data and specific volume for water.

<table>
<thead>
<tr>
<th>Component</th>
<th>Tc (K)</th>
<th>Pc (bar)</th>
<th>ω</th>
<th>V at 20°C (cm³ g⁻¹)</th>
<th>sd (cm³ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>647.3</td>
<td>220.5</td>
<td>0.344</td>
<td>1.002</td>
<td>0.15756</td>
</tr>
</tbody>
</table>

(Sources from Smith and Van Ness, Introduction to Chemical Engineering Thermodynamics)

Both modified PR-EOS and RKS-EOS can be used to estimate the vapor phase density for n-butane, n-hexane, and benzene, (experimental data for vapor phase density of n-decane, n-dodecane, and n-tetradecane are not available). At near critical temperature, modified PR-EOS give a better
estimation for liquid density than RKS-EOS compared to experimental data. For that reason, modified PR-EOS is using to calculate liquid density for this work.

The Pe'neloux-Rauzy-Fre'ze (PRF) method (volume shift) gives a better density estimation for liquid alkanes. The proposed density shift method gives a better density estimation for liquid water.
VI. Hamaker constant:

As shown in the calculation of the short-range interaction for submonolayer films, the Hamaker constant for the substrate/liquid/vapor system appears in the equation for calculation of the disjoining pressure isotherm. This constant is calculated from the polarizability of the materials using the refractive index as a function of the wavelength (non-zero frequencies) and the static dielectric constant data (zero frequency). In this section, the Hamaker constant will be studied to see the relationship of the zero and non-zero frequency terms in the Hamaker constant and the spreading behavior of the system. We will derive the Israelachvili expression for the Hamaker constant as a function of the refractive index extrapolated to zero frequency and the static dielectric constant. The Israelachvili approximation shows that the non-zero frequency term in Hamaker constant disappears when the film has the same refractive index as the substrate. The wetting transition occurs when the Hamaker constant passes through zero.

From the Hamaker-Lifshitz theory, the Hamaker constant is defined as

$$A_{13} = \lim_{d \to 0} 12 \pi d^2 F_{13}(d) = \lim_{d \to 0} 6 \pi d^3 \Pi(d)$$  \hspace{1cm} (VI-1)

The interaction free energy per unit area, $F_{13}(d)$ between two phases, 1 and 2, separated by a film phase 3 in a non-retarded approximation is given by Hamaker-Lifshitz theory, expressed as an integral over a “dummy” variable $x$ \cite{2}.
\[ F_{132}(d) = \frac{kT}{8n^2d^2} \sum_{n=0}^{\infty} \int_0^{\infty} x \, dx \, \ln(1 - \Delta_1 \Delta_2 e^{-x}) \]  \hspace{1cm} (VI-2)

The prime on the summation indicate that the n=0 term is given by half weight.

where

\[ \Delta_{jk} = \frac{\varepsilon_j(i \xi_n) - \varepsilon_k(i \xi_n)}{\varepsilon_j(i \xi_n) + \varepsilon_k(i \xi_n)} \]  \hspace{1cm} (j,k=1,2,3)  \hspace{1cm} (VI-3)

\[ \xi_n = n \left( \frac{2\pi kT}{\hbar} \right) \]  \hspace{1cm} (\hbar \text{ is Plank's constant and } \xi_n \text{ is in rad s}^{-1})  \hspace{1cm} (VI-4)

Substituting equation (VI-2) into equation (VI-1), we have

\[ A_{132} = -\frac{3kT}{2} \sum_{n=0}^{\infty} \int_0^{\infty} x \, dx \, \ln(1 - \Delta_1 \Delta_2 e^{-x}) \]  \hspace{1cm} (VI-5)

The Hamaker constant depends on the material properties of the system through the functions \( \varepsilon(i \xi) \). Since \( \Delta_1 \Delta_2 e^{-x} < 1 \), the log term in equation (VI-5) can be expanded in power series, and the integral can be performed term by term to obtain

\[ A_{132} = \frac{3kT}{2} \sum_{n=0}^{\infty} \sum_{\text{reel}} \frac{(\Delta_1 \Delta_2)^n}{n!} \]  \hspace{1cm} (VI-6)

The Hamaker constant in a non-retarded approximation is calculated by this equation from the FORTRAN program given by M.L. Gee.

The dielectric function, \( \varepsilon(i \xi) \), for alkane is calculated by \([11]\)

\[ \varepsilon(i \xi_n) = 1 + \frac{C_{IR}}{1 + \left( \frac{\xi_n}{\omega_{IR}} \right)^2} + \frac{C_{UV}}{1 + \left( \frac{\xi_n}{\omega_{UV}} \right)^2} \]  \hspace{1cm} (VI-7)
and for water, $\varepsilon(i\xi)$ is calculated by [11]

$$
\varepsilon_{H_2O}(i\xi_n) = 1 + \sum_i \frac{C_i}{1 + \left(\frac{\xi_n}{\omega_i}\right) + \frac{\xi_n^2}{\omega_i^2}}
$$  \tag{VI-8}

where $C_{IR}$, $\omega_{IR}$, $C_{UV}$, $\omega_{UV}$ are estimated as in Section III.

From equation (VI-6), since $\Delta_3 \Delta_{23} < 1$, the error in truncating the $s$ sum at first term will be less than 15%, in practice less than 5% [2], and equation (VI-6) can be rewritten as:

$$
A_{132} = \frac{3kT}{2} \sum_{m=0}^{\infty} (\Delta_3 \Delta_{23})
$$  \tag{VI-9}

or

$$
A_{132} = \frac{3kT}{2} \sum_{n=0}^{\infty} \left[ \frac{\varepsilon_1(\xi_n) - \varepsilon_3(\xi_n)}{\varepsilon_1(\xi_n) + \varepsilon_3(\xi_n)} \right] \left[ \frac{\varepsilon_2(\xi_n) - \varepsilon_3(\xi_n)}{\varepsilon_2(\xi_n) + \varepsilon_3(\xi_n)} \right]
$$  \tag{VI-10}

After replace the sum by an integral over $n$, viz., $dn = (\hbar/2\pi kT) d\xi_n$ from equation (VI-4), so that

$$
kT \sum_{n=1}^{\infty} \rightarrow \frac{\hbar}{2\pi \xi_1} \int d\xi_n
$$  \tag{VI-11}

The Hamaker constant expression becomes

$$
A_{132} \approx \frac{3}{4} kT \left( \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \right) \left( \frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3} \right)
$$

$$
+ \frac{3\hbar}{4\pi \xi_1} \int \left[ \frac{\varepsilon_1(\xi_n) - \varepsilon_3(\xi_n)}{\varepsilon_1(\xi_n) + \varepsilon_3(\xi_n)} \right] \left[ \frac{\varepsilon_2(\xi_n) - \varepsilon_3(\xi_n)}{\varepsilon_2(\xi_n) + \varepsilon_3(\xi_n)} \right] d\xi_n
$$  \tag{VI-12}
Assume that the dispersion energy can be estimated by the electronic absorption in the UV only. Equations (VI-2) and (VI-1) become

$$\varepsilon(\tilde{\varepsilon}_n) \approx 1 + \frac{n_0^2 - 1}{1 + \left(\frac{\tilde{\varepsilon}_n}{\omega_{UV}}\right)^2}, \quad n \geq 1$$

(VI-13)

where: $\omega_{UV}$ is the electronic absorption frequency in the UV ($\sim 1.8 \times 10^{16}\text{rad.s}^{-1}$ for hydrocarbon)

One can substitute equation (VI-13) into equation (VI-12) for each medium and integrate using the definite integral

$$\int_0^\infty \frac{dx}{(a^2 + x^2)(b^2 + x^2)} = \frac{\pi}{2ab(a + b)}$$

(VI-14)

Also, assume the absorption frequencies of all three media are the same (see Table VI-1). The Hamaker constant can be estimated as

$$A_{Total} = A_{v=0} + A_{v>0}$$

$$\approx \frac{3}{4} kT \left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3}\right) \left(\frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3}\right)$$

$$+ \frac{3\hbar \omega_{UV}}{8\sqrt{2}} \frac{(n_0^2 - n_0^2)(n_0^2 - n_0^2)}{(n_0^2 + n_0^2)^{0.5}(n_0^2 + n_0^2)^{0.5}} \left\{\frac{(n_0^2 + n_0^2)^{0.5} + (n_0^2 + n_0^2)^{0.5}}{(n_0^2 + n_0^2)^{0.5} + (n_0^2 + n_0^2)^{0.5}}\right\}$$

(VI-15)

This is the same as equation 11.13 in *Intermolecular & Surface Forces* by Jacob Israelachvili [12].
Table VI-1: Absorption frequencies (obtained by Cauchy plots)

<table>
<thead>
<tr>
<th>Media</th>
<th>Absorption frequency in $[s^{-1}]$</th>
<th>Absorption frequency in $[rad/s]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>$3.01 \times 10^{15}$</td>
<td>$1.89 \times 10^{16}$</td>
</tr>
<tr>
<td>n-alkane</td>
<td>$2.96 - 2.98 \times 10^{15}$</td>
<td>$1.863 - 1.877 \times 10^{16}$</td>
</tr>
</tbody>
</table>

From equation (VI-15), the zero-frequency term of Hamaker constant is calculated by the dielectric constants of the media. The non-zero-frequency term in Hamaker constant is calculated by the refractive index extrapolated to zero frequency estimated from visible range of the media. This equation, equation (VI-15), is derived from the Hamaker-Lifshitz theory by using the following assumptions. The absorption frequency is assumed to be the same for all three media. The summation in equation (VI-6) is calculated by the first term only. Other estimations are using in equation (VI-11), (VI-14), and (VI-15).

As discussed earlier, the wetting transition occurs when the Hamaker constant is equal to zero (or changes its sign from positive to negative). According to Israelachvili [12], the zero-frequency term in Hamaker constant is small for most of the cases. Therefore, when the refractive indices of the substrate and the liquid layer are identical, the Hamaker constant is equal to the zero frequency term which is small and negative in most cases if water is the substrate. The liquid layer already spreads in this case (negative Hamaker constant). Using this approach, Hamaker constant can be estimated from...
refractive index and dielectric constant for other systems for which there is not
enough information available for calculating the Hamaker constant using the full
Lifshitz theory. Wetting behavior of the system can also be predicted from the
refractive indices of the substrate and the film phase.

Later, the Hamaker constant of the brine/alkane/vapor system will be
estimated by using equation (VI-15). The spreading behavior of H₂S at the
water/sulfur interface will be estimated by the refractive indices of H₂S and water
(substrate).
VII. Retardation Effects:

When the separation between two atoms is large, the time taken for the electric field of the first atom to reach the second and return is comparable to the period of fluctuating dipole itself. When this happens, the orientation of the instantaneous dipole of the first molecule is different upon return of the electromagnetic field and is less favorably disposed to an attractive interaction. Therefore, the dipole moment component antiparallel to the field of the first molecule will be smaller than in the non-retarded case. The energy decrease of the first molecule will be less. In our calculation, retardation is taken into account in the calculation of disjoining pressure isotherm for the long-range interaction. The calculation result will be shown in a later section.
VIII. Experimental procedure - Contact angle and Spreading coefficient determination:

1. Purification of hydrocarbon liquids and water:

The hydrocarbon liquids used in this work were straight-chain alkanes. The alkanes were supplied by Eastman Kodak Company and Fisher Chemical Company with the mole % purity of 99%. Following the purification procedure that Cerro and Jameson [17] and Takii and Mori [26] used to remove polar compounds, each alkane was passed through a 30 cm long by 1.5 cm diameter glass chromatography column. The lower half of the column was packed with 150 mesh activated chromatographic grade silica gel (Aldrich Chemical Company) and the upper half with 70-250 mesh activated alumina (basic, standard grade, Aldrich Chemical Company). Silica gel and alumina were heated up to 160°C for 24 hours before using.

The alkane-water interfacial tensions were measured before and after the alkane passed through the column for purity testing purpose. For unclean alkanes (from old bottles that have been opened), the interfacial tensions change with time. After the alkanes have been passing through the column, the interfacial tensions remain constant with time (See Fig. VIII-1). The surface tensions of alkanes were also measured for purity test (See Table VIII-3 in the spreading coefficient determination from contact angle section).
Water used in this work was distilled twice and deionized. According to Endoh, Mikami, and Mori [26], the surface properties of water can be affected appreciably by a trace amount of surface-active contaminant. It possibly results in an significant change in the spreading behavior of alkanes on water. The "bubbles persistence test" [27] was performed for our double distilled and deionized water. The result agrees with the result described by Endoh, Mikami, and Mori [26]; air bubbles burst immediately (within 0.5 s) when they rise to the free surface, indicating that the surface is free of surface-active material. The surface tension of water was also measured for purity test (See Table VIII-3 in the spreading coefficient determination from contact angle section).

2. Glassware cleaning:

The glassware was cleaned by firstly soaking in liquid detergent (Alconox detergent) and then rinsing with copious amount of water. This was followed by soaking in sulfuric acid plus nochromix cleaning solution (Godax Laboratories, Inc.), and a final rinse with large amount of double distilled and deionized water before using.
3. Experimental procedure and measurement:

a. Apparatus:

The experimental apparatus used in this study consisted of an optical interference microscope and a glass cell containing substrate water and a hydrocarbon lens. The temperature was controlled by a Thermal Microscope Stage (Sensortek).

An Aus JENA Epival Interphako microscope was used to make the contact angle measurements. This microscope is capable of viewing objects in transmitted or in reflected light. Reflected light could not be used because of the reflection from the cover glass. The cover glass is needed to maintain saturated conditions for the glass cell. Transmitted light with the wavelength of $\lambda = 0.546 \mu m$ was used in this study. The microscope is equipped with a rotary wedge slide which splits the original beam of the image into two beams of different optical paths which give a shearing type differential interference fringes between the split images. These fringes are used to determine the contact angle. A special designed glass cell held the water substrate in which the alkane droplet floated on the water surface. The construction of the cell is shown in Figure VIII-2.
Side view

**Figure VIII-2:** Schematic of the cylindrical cell with cover glass.

**b. Experiment measurements:**

The main parameter required to determine the contact angle of the alkane lens is the distance between two adjacent interference fringes, $\Delta x$. By measuring the splitting distance of the contact line, $d_s$, and the total number of interference fringes between the split contact lines, $N_f$, the distance between two adjacent interference fringes, $\Delta x$, is obtained by $\Delta x = \frac{d_s}{N_f + 1}$. 
c. Obtaining the splitting distance of the contact line, \( d_x \), and total number of interference fringes between the split contact lines, \( N_f \):

After the glass cell had been cleaned, it was filled with liquid substrate (double distilled and deionized water or brine solution). A drop of alkane was introduced onto the substrate surface. The glass cell then was covered by a microscope cover glass and placed into the microscope slide-holding clips with the Thermal Microscope Stage beneath. The temperature was set at 20°C. Without the Thermal Microscope Stage controlling the temperature of the cell, the liquids were heated by the microscope light. After awhile, the contact line could not be observed due to the liquid vapor condensed on the cover glass. The cell was assumed to have reached saturation when the contact line observed by the microscope became motionless. At saturation, the image of the contact line was split such that images of the contact line coincided with dark fringes (See Fig. VIII-3). Turning the light filter (which has dark stripes on it) would make the fringes parallel to the images of the contact line. Also, by adjusting the micrometer knob (the knob \# 19 in the microscope manual book) or the pinion head for moving the specimen in y direction (knob \# 50), the images of the contact line would align with the dark fringes. By doing this, whole number of white fringes were observed between the images of the contact line. The cell and the Thermal Microscope Stage then were removed from the microscope. A micrometer slide was placed into the microscope slide-holding
clips and used to measured the splitting distance. The splitting distance of the contact line was determined by the splitting distance between the scale's images (See Fig. VIII-4).

![Diagram](image)

**Figure VIII-3:** Image of the contact line before and after splitting.

![Diagram](image)

**Figure VIII-4:** View of the micrometer scale when the image had been split.
d. Contact angle determination:

![Diagram of contact angle determination](image)

a) Real liquid surface  
b) Assumed liquid surface

**Figure VIII-5:** Profile of the liquid surface

Assume that the liquid surface of the substrate (water) and the alkane are flat as Figure VIII-5b. The assumption is made because, upon splitting the contact line, fringes could be seen within the images of the contact line but could not be seen anywhere else (substrate or alkane surface) (See figure VIII-7). This indicates that the angles of the curved substrate surface and the alkane surface with the horizontal surface are small (See Figure VIII-6).

![Diagram of substrate and alkane surfaces](image)

**Figure VIII-6:** Profile of the substrate and alkane surfaces.
Figure VIII-7: Calculation of contact angle from interference fringes

Let us consider the interference of the ray at point C (See Figure VIII-7). The difference in the optical path for the rays from the first and second images occurs because, for the first ray, the path BC passes in the liquid substrate (water), while, for the second ray, the path passes in the alkane liquid. Maximum interference occurs at point C if the difference in optical paths of the two images is equal to a multiple wavelength of the light [20] then

$$BC(n_w - n_o) = \Delta y(n_w - n_o) = k\lambda \quad \text{where} \quad k = 0, 1, 2, 3, \ldots \quad \text{(VIII-1)}$$

The transition from the preceding maximum interference to the subsequent one corresponds to a change in the difference of the optical path by \(\lambda\). Let the first interference from the second image of the contact line occurs at point C then
\[ \Delta y = \frac{\lambda}{n_w - n_o} \]  
\hspace{1cm} (VIII-2)

Let \( \theta \) be the angle of the alkane lens, and \( \Delta x \) is the difference between adjacent bands then

\[ \tan \theta = \frac{\Delta y}{\Delta x} \]  
\hspace{1cm} (VIII-3)

From (VIII-2) and (VIII-3), the contact angle can be determined as

\[ \tan \theta = \frac{\lambda}{(n_o - n_w)\Delta x} \]  
\hspace{1cm} (VIII-4)

where: \( \theta \) is the contact angle, \( \lambda \) is the light wavelength (\( \lambda = 0.546 \text{ \mu m} \) for this study), \( n_o \) and \( n_w \) are the refractive indices of alkane and water, respectively, \( \Delta x \) is the distance between two adjacent fringes.

The refractive indices for alkanes and water used in the calculation are shown in Table VIII-1. Table VIII-2 shows the measured values of the splitting distance, contact angle, and spreading coefficient.

Octane and lower alkanes contact angles were not measured in this study because the lens of these alkanes were either evaporated (too small) or touched the glass cell wall (too big) before the system became saturated.
**Table VIII-1**: Refractive indices of Alkanes and Water at $\lambda = 0.546 \, \mu m$.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Refractive index at $\lambda = 0.546 , \mu m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1.334</td>
</tr>
<tr>
<td>n-Octane</td>
<td>1.397</td>
</tr>
<tr>
<td>n-Decane</td>
<td>1.412</td>
</tr>
<tr>
<td>n-Hexadecane</td>
<td>1.435</td>
</tr>
</tbody>
</table>

(Values from Texas A&M University, American Petroleum Institute Research Project 44)

**Table VIII-2**: Measured splitting distance, contact angle, and spreading coefficient for the water/alkane/vapor system.

<table>
<thead>
<tr>
<th>System</th>
<th>$\Delta x$ ((\mu m))</th>
<th>Contact angle</th>
<th>Spreading coefficient (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C10/pure water</td>
<td>7.97</td>
<td>$49.59 \pm 11.251$</td>
<td>$-6.16 \pm 2.591$</td>
</tr>
<tr>
<td>C12/pure water</td>
<td>3.89</td>
<td>$58.58 \pm 2.652$</td>
<td>$-8.31 \pm 0.865$</td>
</tr>
<tr>
<td>C16/pure water</td>
<td>3.09</td>
<td>$61.56 \pm 8.030$</td>
<td>$-10.27 \pm 2.333$</td>
</tr>
</tbody>
</table>
e. Spreading coefficient determination from contact angle:

The equilibrium spreading coefficient of alkane (o) on water (w) is defined as the following equation (v is the vapor phase):

\[ S_{ov/w}^{eq} = \sigma_{vw}^{eq} - \sigma_{vo} - \sigma_{ow} \]

(VIII-5)

where: \( \sigma_{vw}^{eq} \) and \( \sigma_{vo} \) are the equilibrium surface tensions of water (w) and liquid hydrocarbon (o) respectively, and \( \sigma_{ow} \) is the interfacial tension between the two liquids.

The contact angle can be determined by using Neumann's triangle [20] as follow:

\[ \cos \theta = \frac{(\sigma_{vw}^{eq})^2 - (\sigma_{vo})^2 - (\sigma_{ow})^2}{2\sigma_{vo}\sigma_{ow}} \]

(VIII-6)

The equilibrium surface tension of water, \( \sigma_{vw}^{eq} \), can be eliminated from equation (VIII-5) and (VIII-6), then spreading coefficient is determined as follow:

\[ S_{ov/w}^{eq} = 2\sigma_{vo}\sigma_{ow}\cos \theta + (\sigma_{vo})^2 + (\sigma_{ow})^2 - \sigma_{vo} - \sigma_{ow} \]

(VIII-7)

From equation (VIII-7) above, the equilibrium spreading coefficient is obtained by measuring the contact angle, the surface tension of the alkane, and the interfacial tension of alkane/water. The measured contact angle are listed in Table VIII-2 from the earlier section. The surface tension of alkane and the interfacial tension were measured by using the pendant drop apparatus available in our laboratory. The values are listed in the following table (Table
VIII-3). Densities of alkanes and water were needed for the surface and interfacial tension measurements. The measured values for densities of alkanes and water are listed in Table VIII-4.

The measured contact angle and spreading coefficient results will be plotted and discussed in the result section.

Table VIII-3: Measured values of surface tensions and interfacial tensions compared to literature values.

<table>
<thead>
<tr>
<th>System</th>
<th>Measured Value (mN/m)</th>
<th>Literature data (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decane in air</td>
<td>23.37 ± 0.137</td>
<td>23.9&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Decane in water</td>
<td>50.71 ± 0.421</td>
<td>51.2&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Dodecane in air</td>
<td>24.96 ± 0.323</td>
<td>25.1&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Dodecane in water</td>
<td>52.01 ± 0.621</td>
<td>52.8&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Hexadecane in air</td>
<td>27.70 ± 0.838</td>
<td>27.3&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Hexadecane in water</td>
<td>52.54 ± 0.651</td>
<td>53.3&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Water in air</td>
<td>72.05 ± 0.536</td>
<td>72.75&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Note: Measured values were obtained at room temperature which was about 22°C.

<sup>a</sup> data from Girifalco and Good (1957) at 20°C.

<sup>b</sup> data from Johnson and Dettre (1966) at 24.5°C.
Table VIII-4: Measured densities for alkanes and water at our laboratory.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Measured at our lab</th>
<th>Literature values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>at T = 22°C</td>
<td>(CRC and Perry Handbooks)</td>
</tr>
<tr>
<td>pure water</td>
<td>0.97825</td>
<td>0.997698</td>
</tr>
<tr>
<td></td>
<td>0.9797</td>
<td>(interpolated value at 22°C)</td>
</tr>
<tr>
<td>C10</td>
<td>0.7115</td>
<td>0.7300 (20°C)</td>
</tr>
<tr>
<td></td>
<td>0.714</td>
<td></td>
</tr>
<tr>
<td>C16</td>
<td>0.75365</td>
<td>0.7733 (20°C)</td>
</tr>
<tr>
<td></td>
<td>0.7565</td>
<td></td>
</tr>
</tbody>
</table>

*a Measured values by Kho Irani [31] at our laboratory.
IX. Results for the vapor/alkane/water system:

1. Spreading coefficient:

The calculated values for spreading coefficient of hexane, octane, and decane are shown in Fig. IX-1. The experimental values obtained at our laboratory and by Johnson and Dettre [13] agree with the calculated values.

Figure IX-2 shows the spreading coefficient of octane from this calculation and the experimental values from Akatsuka, Yoshihiga, and Mori [18]. According to Akatsuka, Yoshihiga, and Mori, the uncertainty for their experimental values are estimated to be ±3% at 0°C and ±8% at 50°C for octane. Comparing to our calculation, it is about 39% different at 50°C based on our calculated value. In Akatsuka, Yoshihiga, and Mori’s experiments, the spreading coefficient was obtained by measuring the film thickness of the alkane lens using the interference microscope viewing the object in reflected light.

Figure IX-3 shows the result of the calculated and experimental values for the spreading coefficients of alkanes on pure water substrate. From the initial and equilibrium spreading coefficient curve, it shows that pentane, hexane and heptane will initially spread on water but will not spread at equilibrium. The results confirmed the observation results conducted by Del Cerro and Jameson [3] (See Table IX-1 and its explanation).

The experimental spreading coefficient values for decane, dodecane and hexadecane were obtained by measuring the contact angle of those alkanes on
water (Figure IX-3). The results agree with the calculated values (the calculated values lie within experimental error or less than 10% difference for dodecane based on its calculated spreading coefficient.

Table IX-1 shows the observation of alkane on water from previous studies. According to Del Cerro and Jameson [3], at unsaturation, hexane and heptane formed a thin layer with undefined edges (spreading film) because, at the edges, the layer spread and evaporated rapidly. Interference fringes could be seen on the water surface by using tungsten light at a suitable angle. At saturation, the edges became clear and well defined (non-spreading lens). The interference fringes also disappeared. Del Cerro and Jameson introduced the alkane to the water surface from below. For pentane, Del Cerro and Jameson observed a floating islands with ill-defined border (spreading film) at unsaturation and a thick pentane island with a little tendency to retract into the circular lens (not form a stable lens or spreading film) at saturation were formed for this alkane. Hauxwell and Ottewill [15] observed that pentane, hexane, and heptane formed multilayer (spreading film) at saturation, but octane formed microlenses (non-spreading lens) at saturation. In Hauxwell and Ottewill’s experiments, alkanes were introduced onto the water surface from the vapor phase.
Fig. IX-1: Spreading Coef. vs. temperature
Alkane on water (h* = 2.3 Angstrom)

Temperature (deg. C)

Spreading Coefficient S, mN/m

--- = calculated values
■ = Johnson and Dettre [13]
▲ = measured value
Fig. IX-2: Spreading Coefficients of octane on water.

Temperature deg. C

Spreading coefficient S', mm/m

Octane

Octane (Mori [18])

Johnson & Detrie [13]
Figure IX-3: Comparison of calculated spreading coefficients with measurements at room temperature.

- Calc. Equilibrium Spreading coef.
- Measured Equilibrium Spreading coef.

C5, C6, and C7 initially spread on water.
<table>
<thead>
<tr>
<th></th>
<th>vapor phase</th>
<th>C5</th>
<th>C6</th>
<th>C7</th>
<th>C8</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Del Cerro &amp; Jameson [4]</td>
<td>unsaturated</td>
<td>spreading film</td>
<td>spreading film</td>
<td>spreading film</td>
<td>non-spreading lens</td>
<td>Introduce alkane to the water surface from below</td>
</tr>
<tr>
<td></td>
<td>saturated</td>
<td>not form stable lens or spreading film</td>
<td>non-spreading lens</td>
<td>non-spreading lens</td>
<td>non-spreading lens</td>
<td></td>
</tr>
</tbody>
</table>
2. Disjoining pressure isotherm:

The disjoining pressure isotherms of pentane, hexane, heptane, octane and decane on water at elevated temperature are shown in Fig. IX-4 to IX-8. Figure IX-9 shows the disjoining pressure isotherm for n-alkanes at 20°C, and Figure IX-10 shows the equilibrium film thickness of n-alkanes at 20°C. From these figures, Fig. IX-9 and IX-10, the equilibrium film thickness of the C5, C6 and C7 are higher than the interaction distance, \( h^* = 2.3 \) Angstrom, at 20°C. The interaction distance, \( h^* \), is defined as the distance from a flat surface to the center of an n-alkane lying on the surface.

The disjoining pressure isotherms of pentane, heptane, and octane on water at higher film thickness (0.5 - 100 nm) (retardation effect) at 20°C are shown in Fig. IX-11. From Figure IX-11, the disjoining pressure isotherm of pentane, hexane, and heptane do cross the x-axis. This reconfirms Del Cerro and Jameson's results [17] that when retardation is taken into account, thick, metastable, spreading films are possible for pentane, hexane, and heptane. For octane, the disjoining pressure isotherm also crosses the x-axis. More study about octane wetting behavior and calculated result are needed.
Fig. IX-4: Disjoining Pressure Isotherm for pentane on water

Vapor phase: water + alkane sat. vapor
h^v = 2.3 Ångstrom

Film Thickness (Å)

Disjoining Pressure (p_d)


Millions
Fig. IX.5: Disjoining Pressure Isotherm for hexane on water

Vapor phase: water + alkanesat. vapor

h* = 2.3 Angstrom

Film Thickness, (Å)

Disjoining Pressure, (Pa)

Millions
Fig. IX-6: Disjoining Pressure Isotherm for heptane on water

Vapor phase: water + alkane sat. vapor
h*=2.3 Angstrom

Disjoining Pressure, (Pa)
(Millions)

Film Thickness, (Å)

-8  -6  -4  -2  0  2  4  6
2  3  4  5  6  7  8  9  10

-  -  -  -  -  -  -  -  -
20 deg. C  60 deg. C  80 deg. C

-  -  -  -  -  -  -  -  -
120 deg. C  130 deg. C
Fig. IX-7: Disjoining Pressure Isotherm for octane on water

Vapor phase: water + alkane sat. vapor

$h^* = 2.3$ Angstrom

![Graph showing disjoining pressure isotherm for octane on water.](image-url)
Fig. IX-8: Disjoining Pressure Isotherm for decane on water.

Vapor phase, water + alkane sat. vapor

\( h^* = 2.3 \text{ Å} \)
Fig. IX-9: Disjoining Pressure Isotherm for n-alkanes on water at 20 deg. C.

Vapor phase: water + alkane sat. vapor
$H^+ = 2.3$ Angstrom

Disjoining Pressure, (pA)

Film Thickness, (Å)
Fig. IX-10: Equilibrium film thickness of n-alkanes on water at 20 deg. C
Fig. IX-11: Disjoining pressure isotherm
Long-range interaction

At 20 deg C

Film Thickness, (nm)

Disjoining Pressure, (P_d)

n-pentane
n-hexane
n-heptane
n-octane
3. Hamaker constant:

The Hamaker constant calculated by equation (VI-15) and exact solution calculated by equation (VI-6) are shown in Fig. IX-12 to IX-15. The Hamaker constants values obtained by equation (VI-15) are overestimated compared to the exact solution for all alkanes.

Exact solution from equation (VI-6), and estimated Hamaker constant from equation (VI-15) are both calculated for the system of water (1), saturated vapor (2), and liquid film n-alkane (3). For n-pentane, the Hamaker constant curve increases at high temperature near to its critical temperature due to phase 2 (saturated pentane vapor) and phase 3 (liquid film pentane) becoming nearly identical (see Table IX-2 for critical temperature).

Table IX-2: Critical temperature of n-alkane (source from Introduction to Chemical Engineering Thermodynamics by Smith and Van Ness, 5th ed.)

<table>
<thead>
<tr>
<th>Alkane</th>
<th>Critical temperature in degree C</th>
<th>Critical temperature in degree K</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-pentane</td>
<td>196.45</td>
<td>469.6</td>
</tr>
<tr>
<td>n-hexane</td>
<td>234.25</td>
<td>507.4</td>
</tr>
<tr>
<td>n-heptane</td>
<td>267.05</td>
<td>540.2</td>
</tr>
<tr>
<td>n-octane</td>
<td>295.65</td>
<td>568.8</td>
</tr>
</tbody>
</table>
4. Wetting transition temperature estimation:

The wetting transition temperature can be predicted from the plot of Hamaker constant versus temperature. The wetting transition temperature occurs when Hamaker constant equals to zero. When the Hamaker constant equals to zero, the multilayer part of the disjoining pressure is also equal to zero. The area between the x-axis and the disjoining pressure curve is positive. When the initial or equilibrium spreading coefficient is positive; the liquid hydrocarbon will spread on the water surface.

However, for some systems, there is not enough information available to calculate the Hamaker constant. An alternative way to estimate the wetting transition temperature is when the refractive index of water and alkane become identical, but it overestimates compare to the exact wetting transition temperature.

Figure IX-12 to IX-15 are plots of refractive Index, negative of 1st and 2nd terms in equation (VI-15), and Hamaker constant versus temperature for n-pentane, n-hexane, n-heptane, and n-octane. The negative of the 1st term is shown in the middle panels because the Hamaker constant goes to zero where the curves cross.

Figure IX-16 is the plot of predicted wetting transition temperature of n-alkane as a function of temperature. The wetting temperature predicted by
equation (VI-15) and by refractive index of water and alkane overestimate the value from the exact solution (See Table IX-3 for wetting transition temperature).

**Table IX-3:** Wetting temperature of alkane on water (the temperatures are in degree C and were rounded up)

<table>
<thead>
<tr>
<th>Alkane</th>
<th>From exact solution</th>
<th>From Hamaker constant by eq. VI-15</th>
<th>When refractive index identical</th>
</tr>
</thead>
<tbody>
<tr>
<td>pentane</td>
<td>43</td>
<td>55</td>
<td>70</td>
</tr>
<tr>
<td>hexane</td>
<td>84</td>
<td>98</td>
<td>118</td>
</tr>
<tr>
<td>heptane</td>
<td>125</td>
<td>146</td>
<td>168</td>
</tr>
<tr>
<td>octane</td>
<td>160</td>
<td>185</td>
<td>208</td>
</tr>
<tr>
<td>decane</td>
<td>233</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From the study of the Hamaker constant, we see that:

1. Equation (VI-15) (same as equation 11.13 in *Intermolecular & Surface Forces* by Jacob Israelachvili [12]) can be used to estimate Hamaker constant and wetting temperature if the absorption frequencies of all media are the same. However, it will overestimate the Hamaker constant compared to the exact solution for the system water/alkane/vapor.

2. Wetting temperature predicted when refractive indices of the substrate and the thin film become identical will be higher than the exact wetting temperature if the zero-frequency term in the Hamaker constant is negative and
vice versa. In other words, when the refractive index of substrate and thin film become identical, the non-zero-frequency term in the Hamaker constant equals zero, but the total Hamaker constant is negative (since it equals to zero-frequency term).

3. For systems where dielectric properties are not available, the wetting transition temperature prediction using refractive index can be used; however, it may overestimate the wetting transition temperature.
Fig. IX-12: n-pentane

Refractive Index vs. Temperature

-1st and 2nd terms in Eq. VI-15

Hamaker constant vs. Temperature
System of Vapor/n-Pentane/Water
Fig. IX-13: n-hexane

Refractive Index vs. Temperature

-1st and 2nd terms in Eq. VI-15

Hamaker constant vs. Temperature
Fig. IX-14: n-heptane

Refractive Index vs. Temperature

-1st and 2nd terms in Eq. VI-15

Hamaker constant vs. Temperature
Fig. IX-15: n-octane

Refractive Index vs. Temperature

-1st and 2nd terms in Eq. VI-15

Hamaker constant vs. Temperature
System of Air/n-Octane/Water
Figure IX-16
Predicted wetting temperature of n-alkanes on water as a function of carbon number

Calculating interfacial constant by eq. 14.15

When refractive indices are identical

Exact solution
X. Prediction of the spreading behavior for other systems:

1. Effect of NaCl concentration to the dielectric properties of water:

   a. Determination of the dielectric constant for salt water:

   The effect of salinity on the dielectric constant of water is defined by [28]:

   \[ \varepsilon = \varepsilon_w + 2c\dd \]  \hspace{1cm} (X-1)

   where: \( \varepsilon_w \) is the static dielectric constant of water, \( \varepsilon \) is that of the solution,

   \( \dd \) is the molar depression of dielectric constant of water by electrolytes

   \( \dd = -5.5 \text{ L/mol for NaCl} \)

   \( c \) is the concentration in mole per liter.

   From equation (X-1), dielectric constant of salt water is decreased with the increasing of NaCl concentration.

   b. Determination of the refractive index for salt water:

   The refractive index of salt water as a function of temperature, pressure, and salinity is defined by [29]:

   \[ \left( \frac{n^2 - 1}{n^2 + 2} \right) = A_t \exp(-C_nT) \left( \frac{V_{\nu}^{(p)}}{V_{\nu}^{(w)}} \right)^{b_n} + \Delta f(n) \]  \hspace{1cm} (X-2)

   at \( \lambda = 5892.6 \text{ A}^\circ \), \( A_t = 0.2064709 \); \( B_n = 0.88538 \); \( C_n = 6.2037 \times 10^{-5} \) and

   \[ \Delta f(n) = a + bS_n/\nu_t \]  \hspace{1cm} (X-3)

   \[ \nu_t = 0.54214 - 0.0021896T \]  \hspace{1cm} (X-4)
with $a = 3.11905 \times 10^{-5} + 6.91429 \times 10^{-7}T$ and $b = 2.5667 \times 10^{-5} + 1.29817 \times 10^{-7}T$ ($T$ in degree C)

$$\psi_{w}^{(p)} = \psi_{w}^{(1)} \left[ 1 - 0.315 \log \frac{B + p + p_{e}}{B + 1} \right]$$  \hspace{1cm} (X-5)

$$\psi_{w}^{(1)} = 1.000028 \left( \frac{(T-a_{1})^{2}(T-a_{2})}{a_{3}(T-a_{3})} \right) [g \ cm^{-3}]$$  \hspace{1cm} (X-6)

where: $a_{1} = 3.9863$, $a_{2} = 288.9414$, $a_{3} = 68.12963$, $a_{3} = 508929.2$

$$p_{e} = 6.8966S_{s} - 0.0703S_{s}T \hspace{1cm} \text{bars}$$  \hspace{1cm} (X-7)

where: $p$ is the system pressure in bar, $p_{e}$ is called constant effective pressure, and $S_{s}$ is salinity in ppt (part per thousand).

$$B = 26718 + 19.45T - 0.27028T^{2} + 0.00097987^{3} \hspace{1cm} \text{bars}$$  \hspace{1cm} (X-8)

From equation (X-2), the refractive index of salt water is increased with the increasing concentration of NaCl in water. According to Leyendekkers [29], the refractive index calculated by equation (X-2) should be reliable to 0.0001. Leyendekkers compared his results with the available experimental data up to 1380 bars and up to 60°C.

Figure X-1 shows an example of the calculated refractive index of pure water obtained from equation (X-2) compared to the experimental data of Waxler et al. (1964) [32] at 24.8°C. Figure X-3 shows the plot of the brine solution's refractive index versus salinity at 20°C.
Figure X.1: Calculated and experimental values of refractive index vs. pressure

- Pure water at 24.8° deg. C
- Wavelength = 5875.6 ångstroms

Reflective Index

Pressure (bars)

1.348  1.346  1.344  1.342  1.34  1.338  1.336  1.334  1.332

0  200  400  600  800  1000  1200

Calculated values + Experimental values
2. Hamaker constant estimation for vapor/alkane/brine system:

a. Calculation results:

The values of the dielectric constant and refractive index (at Na-D line) of brine solution can be used to estimate the Hamaker constant of the brine/alkane/vapor system by using equation V-15. The calculated results are shown in Fig. X-2. It shows that octane and decane will spread when the concentration of NaCl in water exceeds 4.5M and 6.17M respectively at 20°C (the maximum concentration of NaCl in water is 6.17M at 20°C).

Figure X-3 shows the plot of refractive indices of brine solution as a function of salinity and alkanes’ refractive indices. As discussed before, spreading behavior predicted by refractive indices becoming equal will overestimate the actual transition. In this plot, refractive index of octane does not cross the refractive index of the brine solution even though octane already spreads on the brine substrate as predicted by the Hamaker constant estimation.

b. Observation results:

Figure X-4 shows the observation results for octane and decane on a salt water surface. It confirms the calculation result above for octane that it will spread on salt water surface at concentrations of NaCl greater than 4.5M. Detailed observations are discussed below.

For octane, when the concentration of NaCl is less than 4.0M, some lenses of octane are formed and float beside the original octane lens on the salt
water surface at saturation. These new lenses are formed by the octane vapor condensing (the original octane lens evaporates until the vapor phase in the observation cell becomes saturated with octane). For NaCl concentration greater than 4.5M, at near saturation some new lenses of octane are formed on the salt water surface (same as the observation for lower NaCl concentration). Then the liquid surfaces of the original octane lens and salt water become identical; the contact line between them disappears. Later, for those new lenses formed at near saturation, their contact lines also disappear; the liquid surface of the lenses and the surroundings become identical. At saturation, a uniform surface is observed for the liquid surface. There are no lenses or contact lines on the water surface. This indicates that the octane spreads and forms a uniform octane layer on top of the salt water phase. When the observation cell is opened into the air, the octane layer shrinks to form an octane lens with a define contact line.

For decane, when the concentration of NaCl is less than 5.5M, no new lenses of decane are formed. The original decane lens floats on the salt water surface by itself at saturation. When concentration of NaCl is 6.17M (maximum concentration of NaCl in water at 20°C), some small new lenses are formed and floating beside the original decane lens at saturation.
Figure X-3: Plot of refractive index
Fig. X-4: Observation results: alkane on salt water at saturation (20 deg. C)

(Note: the concentration interval is 0.5 M)
3. Contact angle and spreading coefficient determined by experiment for vapor/alkane/brine system:

Contact angle of alkane at the brine/vapor interface was obtained by using the microscope. The experimental procedure and calculation are the same as the water substrate case. The refractive index for brine solution was obtained by using Leyendekkers' equations [29].

Figure X-5 shows the experimental results for the contact angle of decane on brine solution. The contact angle of decane could not be obtained at higher NaCl concentration by using the method of this study because when the contact angle of decane becomes small, no interference fringes can be observed upon splitting the contact line. This problem might be caused by the limitation of the method and equipment or by the refractive indices of decane and brine solution becoming almost identical. In the same figure, the estimated Hamaker constant of decane at brine/vapor interface was also plotted (secondary y-axis). As the NaCl concentration in water substrate increases, the contact angle of decane decreases as well as its Hamaker constant. In conclusion, decane is approaching the spreading transition as the salinity increases.

Similar results are shown for hexadecane (see Fig. X-6). Contact angle of hexadecane and its Hamaker constant decrease with increasing salinity.

The spreading coefficients of vapor/alkane/brine system were obtained by using equation VIII-5. The interfacial tensions of decane and hexadecane with
5M brine solution (5 molar NaCl in the solution) were measured. These values and the interfacial tension of decane and hexadecane with pure water were used to interpolate for the interfacial tension of the brine solution at other salinity (See Table X-1). The surface tension of decane was assumed to be constant with the change of the substrate's salinity. These measured spreading coefficients from contact angle were plotted with the calculated values from the Hamaker constant and the values obtained from the definition of spreading coefficient, $S_{ow} = \sigma_{vw} - \sigma_{vo} - \sigma_{ow}$ (See Figure X-7 and X-8). The results confirm our method of measuring the spreading coefficient from the contact angle.

Table X-1 shows the measured values of splitting distance, contact angle, interfacial tension, and spreading coefficient.
Table X-1: Measured values of the splitting distance, contact angle, interfacial tension, and spreading coefficient (calculated from Hamaker constant).

<table>
<thead>
<tr>
<th>System</th>
<th>$\Delta x$ ($\mu m$)</th>
<th>Contact angle</th>
<th>Interfacial tens. (mN/m)</th>
<th>Spreading coef. (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C10/pure water</td>
<td>7.97</td>
<td>49.59 ± 11.251</td>
<td>50.71 ± 0.421$^a$</td>
<td>-6.16 ± 2.591</td>
</tr>
<tr>
<td>C10/brine (1M)</td>
<td>15.12</td>
<td>40.39 ± 4.361</td>
<td>51.54$^b$</td>
<td>-3.71 ± 0.921</td>
</tr>
<tr>
<td>C10/brine (2M)</td>
<td>18.83</td>
<td>35.89 ± 2.658</td>
<td>52.37$^b$</td>
<td>-3.28 ± 0.534</td>
</tr>
<tr>
<td>C12/pure water</td>
<td>3.89</td>
<td>58.58 ± 2.652</td>
<td>-8.31 ± 0.965</td>
<td></td>
</tr>
<tr>
<td>C16/pure water</td>
<td>3.09</td>
<td>61.56 ± 8.030</td>
<td>52.54 ± 0.651$^a$</td>
<td>-10.27 ± 2.333</td>
</tr>
<tr>
<td>C16/brine (1M)</td>
<td>5.46</td>
<td>51.65 ± 2.383</td>
<td>53.47$^b$</td>
<td>-7.40 ± 0.558</td>
</tr>
<tr>
<td>C16/brine (2M)</td>
<td>7.82</td>
<td>45.79 ± 4.96</td>
<td>54.39$^b$</td>
<td>-6.03 ± 1.378</td>
</tr>
<tr>
<td>C16/brine (3M)</td>
<td>19.00</td>
<td>29.66 ± 12.48</td>
<td>55.32$^b$</td>
<td>-2.88 ± 1.649</td>
</tr>
<tr>
<td>C16/brine (4M)</td>
<td>27.25</td>
<td>27.41 ± 3.964</td>
<td>56.24$^b$</td>
<td>-2.99 ± 1.016</td>
</tr>
<tr>
<td>C16/brine (5M)</td>
<td>30.20</td>
<td>20.31 ± 0.796</td>
<td>57.17 ± 0.283$^a$</td>
<td>-1.26 ± 0.097</td>
</tr>
</tbody>
</table>

Note: Interfacial tension of C10/brine (5M) = 54.85 ± 0.708 (mN/m).

$^a$ measured values.

$^b$ interpolated values.
Fig. X-5: Measured contact angle and Hamaker constant of decane versus NaCl concentration (at 20 deg. C) (brine/decane/vapor system)
Fig. X-6: Measured contact angle and Hamaker constant of hexadecane versus NaCl concentration (at 20 deg. C) (brine/hexadecane/vapor system)

- Measured contact angle
- Calculated Hamaker constant

Graph with axes:
- X-axis: NaCl concentration (mol/L)
- Y-axis: Contact angle
- Y-axis: Hamaker constant (J)

Data points with error bars and a plotted line.
Fig X-7: Measured and calc. values of equilibrium spreading coefficient (Ct0)
Fig X-8: Measured and calc. values of equilibrium spreading coefficient (C16)

- Calc. from definition
- Measured from contact angle
- Calc. from Hamaker constant
XI. Spreading behavior of water/H₂S/sulfur system:

1. Problem statement:

Some natural gas reservoirs contain high concentrations of hydrogen sulfide (H₂S) and elemental sulfur. According to Coskuner [23], if elemental sulfur is dissolved in the gas, elemental sulfur will condense as the pressure in the reservoir decreases during the process of production of natural gas under isothermal conditions. It has been thought that the condensed liquid sulfur may impair the flow of natural gas in the reservoir causing a decline in deliverability. Coskuner performed laboratory experiments utilizing the flow of H₂S gas at the conditions of Bearberry reservoir, a reservoir in southwest Alberta, Canada. Coskumer’s experiments were conducted at 120°C and 31 MPa (310 bars). The pressure later was dropped to 10 MPa (100 bars). The glass micro-model is water-wet, hence, the pore walls are covered with a film of connate water. Coskuner observed that the presence of sulfur did not impair the flow of the gas. Hydrogen Sulfide (H₂S) gas can flow easily at the interface between the sulfur and water [23]. This suggested that H₂S was spreading between water and sulfur.

2. Spreading behavior prediction by using refractive index:

As mention earlier, if the refractive index of phase 3 becomes intermediate between the refractive index of phase 1 (substrate) and bulk phase 2, phase 3
will spread at the interface of phase 1 and 2. In Figure XI-1, the refractive indices of water, sulfur and H$_2$S versus pressure at 120°C are plotted. The refractive index of water was obtained by using Leyendeckers' equations [29] for zero salinity (See Figure X-1). The refractive indices of sulfur and H$_2$S were obtained by using Clausius-Mossoti's equation for high temperature and pressure. The values at 20°C for refractive indices of sulfur and H$_2$S are obtained from CRC Handbook of Chemistry and Physics [30]. Figure XI-1 shows that the refractive index of H$_2$S (gas) crosses the refractive index of water substrate at the pressure around 110 bars. This indicates that above the pressure of 110 bars the H$_2$S gas will spread at the water/sulfur interface. When spreading behavior occurs for H$_2$S gas, the gas becomes the intermediate phase between the water/sulfur interface; hence, H$_2$S can flow easily at the water/sulfur interface as the spreading occurs. Comparing with the results obtained by Coskumer as described above, the result of this study supports Coskumer's experiments and the field results.

According to Coskumer [23], there are no data in the literature for calculating the spreading condition of the system of water/H$_2$S/sulfur. The theory of this study will be a great estimation method to predict the spreading behavior for water/H$_2$S/sulfur system without gathering data from experiments.
XII. Conclusion:

A model of the disjoining pressure isotherm consisting of the Hamaker-Lifshitz theory of van der Waals interaction of two continuum film phases separated by a thin continuum film phase and the structural interactions due to submonolayer adsorption of discrete molecules is able to predict the disjoining pressure of alkanes at the water-gas interface including effects of the temperature and pressure. These calculation can be performed if the dielectric properties of each phase are available at various frequencies. Once the disjoining pressure is obtained, other values such as Hamaker constant, spreading coefficient, contact angle and wetting transition temperature of the system are also determined.

For systems for which only the static dielectric constant and refractive index at one wavelength are known, the Hamaker constant approximated from the Hamaker-Lifshitz theory assuming that the absorption frequencies of all three media are the same can be used to predict the spreading transition. Even though the spreading transition prediction using only the refractive index overestimates the exact calculation of the spreading transition, this method still can be used for system for which information about dielectric property is limited.

The contact angle can be obtained experimentally by using an interference microscope assuming the liquid surface is flat. The measured contact angle is used to determined the spreading.
At room temperature, for the system of water/alkane/vapor, the calculated spreading coefficient are confirmed by the experimental results from earlier works and our experimental values. At equilibrium calculations show that the spreading transition temperature of alkane at the water-gas interface increases with increasing of carbon number.

For the NaCl brine/alkane/vapor system, the spreading coefficients obtained from the Hamaker constant agree with the values obtained from the measured contact angle. This agreement demonstrates that the model using the Hamaker-Lifshitz theory to predict the spreading behavior is working, and the method for measuring contact angle is feasible. The calculation of Hamaker constant shows that octane will spread on brine solution at the concentration of NaCl of 4.5M or higher. Decane and hexadecane approach spreading as the NaCl concentration approach saturation.

For the water/H$_2$S/sulfur system, the spreading transition prediction using only the refractive index shows that H$_2$S spreads at the water/sulfur interface at the temperature of 120°C and the pressure of 110 bars or higher. This result is supported by Coskumer's experiments [23].
Appendix A:
Standard form of EOS

a. Standard form of Peng-Robinson [22]

\[ P = \frac{RT}{V-b} - \frac{a}{V^2 + 2bV - b^2} \]

Parameters:

\[ a = a' \left[ 1 + (0.37464 + 1.5422 \omega - 0.2699 \omega^2)(1 - T_c^{0.5}) \right]^2 \]

\[ a' = 0.45724 \frac{R^2 T_c^2}{P_c} \]

\[ b = 0.07780 \frac{R T_c}{P_c} \]

b. Standard form of Redlich-Kwong-Soave [22]

\[ P = \frac{RT}{V-b} - \frac{a}{V(V+b)} \]

\[ a = a' \left[ 1 + (0.480 + 1.574 \omega - 0.176 \omega^2)(1 - T_c^{0.5}) \right]^2 \]

\[ a' = 0.42748 \frac{R^2 T_c^2}{P_c} \]

\[ b = 0.08664 \frac{R T_c}{P_c} \]
Appendix B:

Dielectric Function estimation at elevated temperature

Following are plots of refractive index of water, pentane, hexane and heptane versus temperature using:

1. Cuv depends directly to the density of the material

\[ C_{\lambda T} = C_{\lambda 20^\circ C} \times \frac{\rho_{\text{by EOS at } T}}{\rho_{\text{at } 20^\circ C}} \]

and since

\[ n_0^2 = C_{UV} - 1 \]

2. Clausius-Mossoti equation: (See Section IV, equation 30). This approach gives a better estimate of the refractive index as a function of temperature.
Fig.B1: Refractive Index vs. Temperature for water

- **Refractive Index**
  - 1.335
  - 1.33
  - 1.325
  - 1.32
  - 1.315
  - 1.31
  - 1.305
  - 1.3

- **Temperature (deg C)**
  - 20
  - 40
  - 60
  - 80
  - 100
  - 120
  - 140
  - 160

- **Legend**
  - by Cuv
  - + Experiment data
  - by Clausius-Mossoti

**by Cuv**: Cuv proportional to density
Fig. B3: Refractive Index vs. Temperature for n-hexane

- Experiment data
- by Cuv
- by Clausius-Mossoti

by Cuv: Cuv proportional to density
Fig. B4: Refractive Index vs. Temperature for n-heptane

by Cuv: Cuv proportional to density
Appendix C:

Dielectric susceptibility estimation

The dielectric response function $\varepsilon(\omega)$ is a complex function which is defined as

$$\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega) \quad (C-1)$$

where $\varepsilon'(\omega)$ is the real component, and $\varepsilon''(\omega)$ is the imaginary component.

According to Hough and White [11], they are defined as

$$\varepsilon'(\omega) = 1 + \int_0^\infty f(\tau)\cos(\omega\tau)d\tau \quad (C-2)$$

$$\varepsilon''(\omega) = \int_0^\infty f(\tau)\sin(\omega\tau)d\tau \quad (C-3)$$

The function $f(\tau)$ contains all the information about electronic, vibrational, rotational and translational relaxation of the component molecules of the dielectric material. It describes the decay of an induced polarization with time. The function $f(\tau)$ tends to zero when $\tau$ becomes large, $\lim_{\tau \to \infty} f(\tau) = 0$.

In the visible frequency range where $\varepsilon''(\omega) = 0$, according to Landau and Lifshitz[10], the total dielectric response is purely real and equals to the square of the refractive index $n(\omega)$ of the medium

$$\varepsilon(\omega) = \varepsilon'(\omega) = n^2(\omega) \quad (C-4)$$
However, the quantity $\varepsilon(i\xi)$ according to modern dispersion theory has no physical significance. The function $\varepsilon(i\xi)$ arises from mathematical consideration in the evaluation of the free energy of a dispersive system. From Landau and Lifshitz [10], the physically meaningful $\varepsilon(\omega)$ can be allowed to take complex value of its argument. The function $\varepsilon(\omega+i\xi)$ of equations (C-1, C-2, and C-3) is defined as [11],

$$
\varepsilon(\omega+i\xi) = 1 + \int_0^\omega f(\tau)e^{i\omega\tau}e^{-i\xi\tau}d\tau \quad (C-5)
$$

This expression is evaluated on the imaginary axis as

$$
\varepsilon(i\xi) = 1 + \int_0^\infty f(\tau)e^{-\xi\tau}d\tau \quad (C-6)
$$

The quantity $\varepsilon(i\xi)$ is related to the dielectric response of the material by another relation, the Kramers-Kronig relation, [10]

$$
\varepsilon'(i\xi) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\varepsilon''(x)}{x^2 + \xi^2}dx \quad (C-7)
$$

From equation (C-7), the value of $\varepsilon(i\xi_n)$ is calculated from absorption data. However, it requires a knowledge of the absorption characteristics of material over the entire frequency spectrum. According to Ninham and Parsegian[3], $\varepsilon(i\xi_n)$ is estimated by

$$
\varepsilon(i\xi_n) = 1 + \sum_{n=1}^\infty \frac{C_n}{1 + \left(\frac{\xi_n}{\omega_n}\right)^2} \quad (C-8)
$$
For transparent materials, the behavior of $\varepsilon(i\xi_n)$ in the infra-red and the ultra-violet regions of the spectrum is important in the calculation of accurate interaction energy $F_{132}(d)$. $\varepsilon(i\xi_n)$ is approximated by single adsorption frequency in the infrared and the ultraviolet as

$$\varepsilon(i\xi_n) = 1 + \frac{C_{\text{IR}}}{1 + \left( \frac{\xi_n}{\omega_{\text{IR}}} \right)^2} + \frac{C_{\text{UV}}}{1 + \left( \frac{\xi_n}{\omega_{\text{UV}}} \right)^2}$$  \hspace{1cm} (C-9)

For water, $\varepsilon(i\xi_n)$ is determined by using the Gingell-Parsegian representation [8]

$$\varepsilon_{\text{H}_2\text{O}}(i\xi_n) = 1 + \sum \frac{C_i}{1 + \left( \frac{\xi_n}{\omega_i} \right)^2 + \frac{g_i\xi_n}{\omega_i^2}}$$  \hspace{1cm} (C-10)

where:

$g_i$ is the line widths of the absorption peaks

$C_i$ is oscillator strength constant for water which is also proportional to its density
References:


