Movement of Oil Under Sea Ice

L.W. ROSENEGGER

Technical Report No. 28

2



THE MOVEMENT OF OIL UNDER SEA ICE

L.W. Rosenegger

Production Research and Technical Research Laboratory Imperial Oil Limited Calgary, Alberta

Beaufort Sea Technical Report #28

Beaufort Sea Project Dept. of the Environment 512 Federal Building 1230 Government St. Victoria, B.C. V8W 1Y4

December, 1975

TABLE OF CONTENTS

ABSTRACT

	ABST	RACT				1
1.	INTR	ODUCTION				1
	1.1 1.2	Objectives Outline of Present Work				1 1
2.	SURF	ACE TENSION				2
	2.1 2.2 2.3	General Analytical Development Experimental Procedure	¥.			2 2 4
		2.3.1 Sessile Drop Method 2.3.2 Ring Detachment Method				4 6
	2.4	Results				7
		2.4.1 Sessile Drop Method 2.4.2 Ring Detachment Method				7 9
	2.5	Conclusions				10
3.	MOVE	MENT OF OIL DROPS				11
	3.1 3.2 3.3 3.4 3.5	General Analytical Development Experimental Procedure Results Conclusions				11 11 12 13 13
4.	OIL	MOVEMENT IN A LEAD				13
	4.1 4.2 4.3	General Spreading Analysis Conclusions				13 14 15
5.	SOLU	TE REDISTRIBUTION AND OIL PENETRATION				15
	5.1	Solute Redistribution				15
		5.1.1 General 5.1.2 Methods and Results 5.1.3 Conclusions				15 16 17
	5.2	Oil Penetration				17
6.	CONC	LUSIONS				18
7.	REFE	RENCES				20
8.	BIBL	IOGRAPHY				23
	TABL	ES 1 to 6 inclusive		24	to	28
	FIGU	RES 1 to 39 inclusive		29	to	65

Page

APPENDIX A - DEVELOPMENT OF THE EQUATION FOR THE PROFILE	Page
OF A SESSILE DROP	66
APPENDIX B - TEST RESULTS FROM RING DETACHMENT METHOD	69
APPENDIX C - DATA FOR CALCULATING THE SPREADING COEFFICIENTS	75
APPENDIX D - TEST METHOD USED IN DETERMINING SALT CONTENT OF CRUDE OILS	79

ABSTRACT

This report presents the results of laboratory tests to determine the interfacial tension and motion of crude oil bubbles under sea ice. Two different crude oils were used in these experiments (Swan Hills and Norman Wells). An assessment has also been made of; a) the ability of oil to penetrate sea ice from beneath, b) the equilibrium thickness of a crude oil film on water under arctic conditions, and c) the redistribution of solutes in the oil.

1. INTRODUCTION

This report presents the results of a laboratory investigation into certain aspects of the behaviour of oil under ice. The topics studied were recommended by the Frozen Sea Research Group, Ocean and Aquatic Sciences, Environment Canada, as part of the Beaufort Sea Project (Oil in Ice Studies). Funding for this study was provided jointly by the Frozen Sea Research Group (DSS Contract OSZ4-0344) and by Imperial Oil Limited.

1.1 Objectives

The major objectives of this study can be summarized as follows:

- To determine the interfacial tension between oil and water at the temperature of freezing water for Norman Wells and Swan Hills crude oils by the sessile drop method.
- To study the movement and/or absorption of sessile oil drops at an interface between sea ice and water in response to gravitational and drag forces produced by ice sheet tilt.
- 3. To determine the movement of an oil film in a lead in response to a continuous oil input at a given point in the lead.
- To determine whether oil will penetrate from beneath into a growing sea ice sheet due to buoyancy forces and to assess the effects of the redistribution of solutes in the oil on the ice sheet.

The work outlined above constitutes a small portion of the input information necessary for a better understanding of the effects and ultimate disposition of arctic offshore oil spills. Its main purpose is to serve as useful input information to the Beaufort Sea Project covering the 'Behaviour of Oil in an Ice-Covered Area'.

1.2 Outline of Present Work

In each Chapter, a brief discussion of previous work and of the significance of each study objective is presented. Experimental and analytical procedures used in this study are then described, followed by a presentation of the results obtained. The significance of the results is discussed and conclusions based on the results are presented. A final chapter summarizing the overall results and conclusions of this work is also presented.

2. SURFACE TENSION

2.1 General

The surface tension parameter is used extensively in calculations concerning the rise and breakup of buoyant plumes and in determining whether one liquid will spread on another. Both of these situations could be encountered in the event of an accidental release of oil in an arctic environment. The first would be the case of a blowout at the sea bottom, while the second would pertain to the spread of oil under ice or on the water surface.

For the blowout case, in which a buoyant gas and oil plume rises through a water column, one is interested in determining (Topham, 1976); a) whether the gas jet will penetrate the surface, b) the fluid velocity distribution, c) the entrained flow, d) the interaction with surface currents, and, e) the behaviour of the oil in the rising plume. Since there are two immiscible fluids (oil and water) present, one would expect the surface tension (possibly in the form of a Weber number) to be an important parameter involved in the solution of each of the above mentioned points (Hinze, 1955; Christiansen and Hixson, 1957). The surface tension parameter will likewise play an important role in the determination of whether and how extensively oil will spread at an interface. The current literature contains many examples of such applications (eg. Fay, 1969; Chen et al, 1974; Gleaser and Vance, 1971; Keevil and Ramseier, 1975; and Garrett, 1973, to mention only a few).

Our primary aim in this part of the work was to determine the interfacial tension between the two crude oils (Norman Wells and Swan Hills) and brine at the interface between ice and brine using the sessile drop method. An attempt was also made to assess the effects of aging (if any) on the surface tension. Several other parameters (eg. equilibrium bubble thickness and diameter, contact angle, etc.) were also measured in the course of this work.

2.2 Analytical Development

Surfaces can be classified according to the physical state of the matter separated by them. Thus, one is really dealing with interfaces between liquid-gas, liquid-liquid, solid-gas, solid-liquid, and solid-solid surfaces.

When one normally talks of the surface tension of a substance, one is actually referring to the interfacial tension between two substances. Interfacial tension acts along the interface and tends to minimize the interfacial area. The concept of interfacial (surface) tension can be developed from mechanistic or energy considerations. Both yield the same dimensions, expressed as either force per length, or energy per area. References cited in the bibliograpy give a detailed discussion of these viewpoints.

The earliest comprehensive work on determining interfacial tensions using the sessile drop method was by Bashford & Adams (B&A), 1883. B&A studied the form of sessile liquid drops (mercury) and were able to relate the coordinates (x,y) of points P(x,y) on a meridional profile of the drop to the first and second derivatives $y' \equiv dy/dx$ and $y'' \equiv d^2y/dx^2$ and to a constant parameter, β , given by

$$\beta = \frac{g_{\rho}b^2}{\gamma} \qquad \dots (1)$$

where

g is gravitational acceleration

ρ is the density difference of the fluids γ is the interfacial tension between the fluids

b is the radius of curvature at the origin of the coordinate system

The above are related by the equation [9]

$$\frac{d^2y}{dx^2} + \left\{1 + \left(\frac{dy}{dx}\right)^2\right\} \frac{dy}{xdx} = (2 + \beta y) \left\{1 + \left(\frac{dy}{dx}\right)^2\right\}^{3/2} \dots (2)$$

where x, y, are defined as $\frac{\overline{x}}{b}$ and $\frac{\overline{y}}{b}$ respectively, \overline{x} and \overline{y} being the actual physically measurable dimensions of the drop.

The above equation is applicable to drops resting on top of horizontal surfaces and also to the case of hanging drops as long as the density differences are taken as shown in the mathematical development of the above equation such that β is positive (see Appendix A).

B&A prepared a series of tables so that β could be determined from the geometry of the sessile drop. A second set of tables was used to obtain values of b which were then used to calculate γ from equation (1).

More recently, Staicopolus (1962, 1963, 1967) and Parvatikar (1966, 1967) have verified and extended the B&A results to cover a larger range of β values. For the present study, the empirical equations explicitly relating the interfacial tension, γ , to the experimentally obtainable quantities \mathbf{x} and \mathbf{y} as presented by Staicopolus (1962) have been used. These are:

 $\gamma_{=} \frac{g_{\rho}}{B_{\phi}G_{\phi}^{2}} (\overline{y})_{\phi}^{2}$

$$\gamma = \frac{g_{\rho}}{B_{\phi}F_{\phi}^2} (\overline{x})_{\phi}^2 \qquad \dots (3)$$

and

where $B_{\phi} = \beta$, $F_{\phi} = (\overline{x}/b)_{\phi}$ and $G_{\phi} = (\overline{y}/b)_{\phi}$ are obtained in terms of fourth order polynomials of the quantity $\overline{z} = \frac{(\overline{x}/\overline{y})_{\phi} - A_{\phi}}{C}$

as follows:

$$B_{\phi} = \exp\{[P_{B}(Z)]_{\phi}\} - D_{\phi} \qquad \dots (5)$$
$$F_{\phi} = [P_{F}(Z]_{\phi} \qquad \dots (6)$$

$$G_{\phi} = [P_{G}(Z]_{\phi} \qquad \dots (7)$$

Table I, taken from Staicopolus (1962) gives the values of the coefficients of the powers of Z for ϕ = 45° and ϕ = 90° together with the corresponding constants A_{ϕ} , C_{ϕ} and D_{ϕ} . Measurements of \overline{x} and \overline{y} on the maximum periphery of a sessile drop (ϕ = 90°) will therefore yield values of the interfacial tension between oil and water.

In hindsight, it may be stated that the sessile drop method of analysis was perhaps not the best method to use in this study since measurement errors can have relatively large effects on the results (this is discussed in the next section). As a check on the work and in order to obtain some additional information not available from the sessile drop method, several tests were run at room temperature using the du Noüy ring detachment technique. A derivation of this method can be found in Freud and Freud (1930); Harkins and Jordan (1930); and Fox and Chrisman (1952), and a general explanation in any of the surface chemistry books listed in the bibliography.

2.3 Experimental Procedure

2.3.1 Sessile Drop Method

The general procedure used in this study to determine the surface tension by the sessile drop method can be summarized as follows:

- 1. A brine solution $(12^{\circ}/_{\circ\circ}$ salinity for this experiment) was prepared and allowed to freeze in the cold room in clear plexiglass tanks which were insulated on all sides except the top. A heating tape was placed directly below the tank so that a temperature gradient could be maintained in the water.
- 2. The tank was removed from the cold room once an ice sheet of approximately 5 cm thickness had grown. A hole was drilled through the ice and oil was injected under the ice with a clean stainless steel syringe. This usually resulted in several bubbles of various sizes as it was very difficult to control the injection process.

- 3. The insulation was removed from one side of the tank and photographs were taken of the oil bubbles. During this time, insulation was placed on top of the tank so as to reduce heat losses and to keep the temperature as uniform as possible.
- 4. Pictures were taken with a 200 mm fixed-focus lens (at various reproduction ratios). Once developed, the film was put into slide mounts. These were then projected on an optical comparator and measurements were taken directly from the slides.
- 5. Measurements were taken of the diameter at the meridional plane, 2X, of the height from the apex to the meridional plane, Y, of the height from the apex to the interface between oil and ice, and of the contact angles α and β measured through the water phase. Average values of α and β were used for calculation purposes. These parameters are shown schematically in Figure 1.
- The interfacial tension was then calculated from the measurement data according to the method described in the previous section.

The camera was mounted on a cathetometer stand to which a special bracket had been added to allow for full 3-axis positioning of the camera. This was particularly useful for rapidly focusing on a particular bubble. Figures 2 and 3 show the camera and tank in position ready for testing.

A string of 21 thermistors spaced 0.5 inches apart was also constructed. It was usually frozen into one of the tanks, and when a test was run on the particular tank containing the thermistors, readings were taken both before and after the test to determine whether a significant temperature change had taken place during a test. Shown in Figure 4 are the temperatures as measured both before and after a test on April 11, 1975. Even though the temperature of the top layer of ice has warmed up considerably during the test, it may be noticed that both above and below the interface between the ice and water the temperatures before and after the test differ by at most 1°F. The freezing temperature for the $12^{\circ}/_{\circ\circ}$ brine solution can be seen from the graph to lie between 29.1 and 29.6°F.

Table 2 gives measured values and calculated surface tensions for the two bubbles shown in Figures 5 and 6. These pictures were taken at 70 seconds and 25.5 minutes after injection respectively. The differences in the interfacial tensions calculated for the bubble at 70 seconds can be due to errors in x and y of ± 0.001 inch or less. This is verified by taking the above values and recalculating for γ using x = 0.2896 inch and y = 0.1907 inch. Using these values in equations (3) and (4) results in values for γ of 27.952 and 27.972 dyne/cm respectively.

Although accuracies of ± 0.001 inch (± 0.0025 mm) can be obtained with the optical comparator, the critical factor in taking measurements is the operator's ability to judge exactly when the crosshair on the comparator screen is aligned with the interface. It was found that in practice, an uncertainty of up to 0.001 inch could occur depending on the sharpness of the picture. Such errors are then multiplied by the inverse of the reproduction ratio. Thus, as shown in Table 2, the surface tensions calculated by using equations (3) and (4) and the measurement data for the first bubble (70 sec., 1/2 x reproduction ratio) are in error relative to the lower value of 11.5% while the same calculations for the second bubble (25.5 min., 1 x reproduction ratio) are within 0.1% of each other. The inability to grow a truly flat ice sheet caused difficulties in this phase of the program. Flat ice sheets could have been achieved by growing ice and subsequently melting the bottom of the sheet until a flat surface was obtained. This was not done, since it was desirable to keep the structure of the underside of the ice essentially the same as would be found in nature. As a result, oil bubbles usually settled in a hollow making it difficult at times to make out the position of the interface between the ice and oil. Sufficient bubbles were photographed, however, so that a sufficient number of good bubbles still remained for measurement purposes. A more annoying problem in this experiment was the lip of ice that formed around the tank at the interface between the ice and water. This was usually 0.5 cm in depth and in most instances had to be melted by playing a heat gun on the tank along its length. The bond between the ice and plexiglass on that particular side was usually broken as a result and if bubbles subsequently rolled over to that side, they would spread up the interface due to capillary action and the presence of air.

2.3.2 Ring Detachment Method

Surface tensions were measured using the ring detachment method at a temperature of from 25.8 to 28.2°C. A Fisher Tensiomat model 21 was used for these tests. Four or five tests were run on each fluid and the apparatus was thoroughly cleaned between each test (see A.S.T.M., 1970, for cleaning procedures used between oil samples). The apparatus was calibrated both before and after the tests according to the procedure recommended in the users manual supplied. Figure 7 shows the average calibration curve used in this work. When using this instrument, the scale value indicates only an apparent surface tension which must be corrected for ring dimensions and density difference between the upper and lower phase being tested. This correction factor is shown in Figure 8 based on the dimensions of the ring used. The upper phase in all the tests was air and Table 3 gives the densities and density differences between the fluids and air. The specific gravities of the different fluids were measured separately and the results are presented in Figure 9 and 10. Since the specific gravity of the 6% brine solution had not been determined, its value was interpolated as shown in Figure 11. Figure 12 is based on data given by Kreith (1968) and was used to obtain a value for the density of air.

2.4 Results

2.4.1 Sessile Drop Method

A total of 200 oil bubbles under an ice sheet were measured in this experiment (111 with the Swan Hills crude and 89 with the Norman Wells crude). Interfacial tensions were calculated according to the method described in Section 2.2. From these calculations, it was found that 19 of the Swan Hills and 7 of the Norman Wells interfacial tensions fell outside the range 5 to 50 dynes per cm. A number of these measurements were rechecked and it was found that the photographs were out of focus or a low reproduction ratio had been used. This data was then discarded before further calculations were made and although the limits imposed may seem somewhat arbitrary, interfacial tensions less than 5 and greater than 50 dynes/cm are considered unlikely for oil/water systems (Timmons and Zisman, 1968).

Table 4 gives a summary of the experimental results obtained showing the means and their standard deviations. Histograms are given in Figures 13 and 14 for the Swan Hills and Norman Wells results respectively. As may be noted, the standard deviations are quite high as are the mean deviations. This led to some doubt as to the validity of the results and to the statement in Section 2.2 concerning more appropriate measurement techniques. These deviations are of little importance, however, and their causes and effects will be explained in the discussion that follows.

The first step in the analysis of these results was to determine the effects of variations in the physical dimensions on the surface tensions. Shown in Figure 15 and 16 are the results obtained for the interfacial tension using equations 3 (GAMMA X) and 4 (GAMMA Y) plotted as a function of X. Differences in values between GAMMA X and Y are almost indistinguishable on these graphs which is reasonable since equations 3 and 4 yield the same results. That they do, can be seen in Figure 17 and 18. More difficult to explain is the large spread in GAMMA for small X in both Figure 15 and 16. Although Figure 16 (Norman Wells results) doesn't show this decreasing variation too well due to the lack of data at intermediate values of X, one would expect the variation to be similar to that of Figure 15 (Swan Hills results). These large deviations about the apparent mean value are due to small errors in the measurement process. To explain properly how this happens,

one must first look at the variation of Y with X as shown in Figures 19 and 20 for the Swan Hills and Norman Wells crudes respectively. One may note that X and Y vary linearly up to $X \simeq 0.2$ cm and that both X and Y are very nearly equal up to this point. This is to be expected as the drops are still almost spherical. This means however, that X/Y is very nearly equal to +1 and as shown in Figure 21 and 22, B (equation 5) approaches zero while F and G (equations 6 and 7) both approach one as X/Y goes to one. Equations 3 and 4 are therefore, undefined at X/Y = 1. When X/Y is still very nearly equal to one, a small error in measurement can lead to quite large errors in the calculated value of the interfacial tension. Results of an error analysis are given in Table 5 for Swan Hills crude to demonstrate this fact. Values of Y were first calculated from the regression equation and error limits of ± 0.003 cm (\simeq .0012 inch) were assigned to both X and Y. Ratios of X/Y were taken so as to maximize (i.e. X increases and Y decreases) and minimize Z. Figure 23 is a graph of the data in Table 5, and clearly shows that the calculated error decreases with increasing X. If one allows for no error in X and only a +0.003 cm error in Y, the resulting error is actually increased even though there is a smaller relative error between X and Y. It is, therefore, concluded that the equations relating the interfacial tension to the bubble dimensions are not valid for values of X less than 0.2 cm.

Graphs showing the effects of an error in the constant C (equal to $g \cdot \Delta p$) have also been prepared for both Swan Hills and Norman Wells crudes (Figures 24 and 25). These figures were prepared using values of Y calculated from the regression equations given in Figures 19 and 20. For the Swan Hills crude (Figure 24) the values of the interfacial tension are approximately constant over the range 0.2 < X < 0.7. It can not be interpreted from Figure 24 that the surface tension decreases after X = 0.7, since the apparent reduction is a direct result of the uncertainty in Y calculated from the regression. A different type of regression procedure (eq. a quadratic spline fit with zero bending moment at the end points) would possibly have given a more uniform curve but some fluctuations would still have been present. Because of the smaller number of data points at the larger values of X, the value estimated for Y in the regression analysis will be either above or below the 'actual value' by a small amount, this error will cause a small error in the ratio X/Y which in turn will result in a large error in B (see Figure 21) with little effect on F^2 and G^2 . It is readily seen that B increases much more rapidly than either F^2 or G^2 decrease by comparing Figures 21 and 22.

As a result, the calculated surface tension will show the fluctuating variations shown in Figure 24 and 25. For the Norman Wells crude, this effect is even more apparent (Figure 25). The interfacial tension calculated at X = 0.3 compares favourably, however, with the average of the test

pair results (Table 4). This was to be expected, however, because the majority of data points for this crude are very close to X = 0.3. For values of X > 0.3, the calculated values of Y from the regression analysis and the resulting surface tensions would therefore, be highly suspect.

The value of the constant $(g \cdot \Delta \rho)$ was taken to be 160.7 and 158.3 for the Swan Hills and Norman Wells crudes respectively. Values for the interfacial tension of the Swan Hills and Norman Wells crudes at the temperature of freezing water (in this case, approximately 29.5°F for a $12^{\circ}/_{\circ\circ}$ water salinity) have therefore been taken as the average values obtained in our experimental programme. These are (see Table 4) 25.5 and 24.0 dynes/cm respectively for the Swan Hills and Norman Wells crude oils.

No effects on the interfacial tension due to aging of the oils could be determined. If such effects do exist, they are well within the limits of accuracy of this method and would have to be determined in another manner. Some additional data relating the equilibrium thickness H to the parameters X and Y have also been prepared. Shown in Figures 26 and 27 are graphs of Y vs H for all measurable data pairs. Using these graphs and the asymptotic values for Y in Figures 19 and 20, one can readily arrive at an estimate for the equilibrium film thickness of the two oils. These are 0.80 and 0.88 cm for the Swan Hills and Norman Wells crude oils respectively. The latter number was determined by extrapolating the 'best line' through the available data and plotting on this line a value of Y = 0.6which was taken from Figure 20 as representative of the limiting Y value. Figures 28 and 29 have also been included here for ease in relating H back to X.

2.4.2 Ring Detachment Method

The test results for this part of the study are given in Appendix B and plotted in Figure 20. It should be noted that the interfacial tensions represented are with respect to the ambient air. To calculate oil/brine interfacial tension, one can use Antonow's Law (Adamson, 1960) which states that for mutually saturated liquids

$$\gamma_{ab} = \gamma_{a'} - \gamma_{b'} \qquad \dots (8)$$

This rule generally holds approximately, and in the absence of sufficient data, it is useful for estimation purposes. A more reliable method is that of Good et al, (1958) who have obtained a semi-empirical equation for the interfacial tension which is,

$$\gamma_{ab} = \gamma_a + \gamma_b - 2\phi(\gamma_a\gamma_b)^{\frac{1}{2}} \qquad \dots (9)$$

where

$$= \frac{4V_{a}^{1/3} V_{b}^{1/3}}{\left[V_{a}^{1/3} + V_{b}^{1/3}\right]^{2}} \dots (10)$$

and V is the molar volume of the phase in question.

For the Swan Hills crude $\Phi = 0.832$ while for the Norman Wells crude $\Phi = 0.831$. Using the average value shown in Figure 30 for the surface tension of the $12^{\circ}/_{\circ\circ}$ brine solution and the surface tensions of the Swan Hills and Norman Wells crude oils as given in Appendix B one obtains the following interfacial tensions between the oil/brine phases.

 γ_{ab} = 23.91 dynes/cm for the Swan Hills crude, and

 γ_{ab} = 24.32 dynes/cm for the Norman Wells crude.

These numbers compare favourably with those arrived at in the previous section but before a comparison can be made, the above values must be corrected for the temperature difference. Assuming a -0.1 change in tension per °C (Washburn, 1927), and a temperature difference of 27.4°C results in a correction of +2.74 dynes/cm to be added to each of the above tensions. Final interfacial tensions arrived at are therefore, 26.65 and 27.06 dynes/cm for the Swan Hills and Norman Wells crude oils respectively. Though these results cannot be considered as absolutely correct, they should be within 10% of the correct value allowing for errors in the ring detachment method itself and in the temperature correction factor. These results do, however, lend credence to the results obtained in the previous section and have, therefore, fulfilled their purpose.

2.5 Conclusions

From the preceding discussion, one may conclude the following:

a) The interfacial tension between the Swan Hills crude and a $12^{\circ}/_{\circ\circ}$ brine solution is 24.5 dynes/cm at approximately 29.5°F which was determined to be the average freezing temperature of the brine. The interfacial tension between the Norman Wells crude and a similar brine solution is 23.8 dynes/cm. These values are estimated to be correct to within 10% of the true value.

b) An alternative method has been established for determining the interfacial tensions between the oils and brine at salinities other than $12^{\circ}/_{\circ\circ}$ using the results obtained for the ring detachment method. One could also use Figures 24 and 25 by assuming that the bubble dimensions will not change significantly with a change in salinity. Since the constant $g \cdot \Delta \rho$ is dependent on salinity, one can therefore, arrive at interfacial tensions by interpolation on these graphs.

10

c) Data allowing an estimation of the equilibrium thickness for use in under-ice spreading calculations has been presented. These are 0.80 and 0.88 cm for the Swan Hills and Norman Wells crude oils respectively. It is estimated that these values are within 6% and 10% for the Swan Hills and Norman Wells crudes respectively.

d) The sessile drop method reported here (as per Staicopolous) breaks down at small values of bubble radius because the bubbles at this point are still very nearly spherical.

e) The use of polynomial least squares regression fit on the meridional height Y can be applied successfully up to values of X < 0.8 cm approximately. Beyond this point instabilities set in due to the numerical calculation technique.

3. MOVEMENT OF OIL DROPS

3.1 General

When a buoyant gas and oil plume rises through a water column as would be the case in an underwater blowout, the oil will break down into small droplets. At the underside of the ice, most of these droplets will coalesce to form an oil slick. Should this slick move along the bottom of the ice, bubbles of oil will break away from the periphery due to interfacial instability. This fact has been demonstrated recently by Norcor Engineering and Research Limited in films of their work on the behaviour of oil under ice which is part of the Beaufort Sea Project. In this work, we have endeavoured to determine the force required to set such bubbles in motion. This force can then be used to estimate the current necessary to initiate motion of an oil bubble. It should be noted that no attempt has been made here to define the flow conditions to the instability which causes these bubbles.

3.2 Analytical Development

Considering an oil bubble under an inclined ice sheet as shown in Figure 31, where R is the resultant buoyancy force, one can easily show that at the onset of motion

$$R' = \left[\frac{\rho W}{\rho o} - 1\right] M_{o}g \sin \alpha \qquad \dots (11)$$

It is this quantity that has been determined in the present study. In an idealized field situation, the bottom of the ice sheet would be horizontal, and the driving force initiating the motion would be the shear stress τ , exerted on the oil by the moving water. The shear stress required to initiate motion can then be represented by

$$R' = \int_{A} \tau dA \qquad \dots (12)$$

where A, for large bubbles, becomes the area over which the oil has

spread. For bubbles of the size studied here, assuming an area of $\pi \cdot \bar{x}^2$ and neglecting the edge effects would yield a good first approximation to τ . When considering large areas of oil, one can use the Blasius solution to flow over a flat plate (Schlichting, 1968) to relate the shear stress to U_{∞} . It should be noted that both of these approaches to the problem assume that the oil has spread to its equilibrium shape in the absence of any shear stress and that suddenly such a stress field is applied to the oil.

3.3 Experimental Procedure

This series of tests was run in a refrigerated trailer using essentially the same equipment as described in Section 2.3. One modification required was a mechanism for tilting the tank. A plywood platform was built for this purpose. It was hinged to the workbench at one end and at the other end a lead screw was installed through the bench which allowed the platform to be raised or lowered. The tank sat on this platform together with all the insulation. Both tanks were also modified by enclosing a dead air space, along the length of the tanks, between the original and additional outside walls. This was needed to prevent the freezing of brine down the inside surfaces of the tanks during a test.

Although the air gap did prevent the freezing of brine on the inside walls, it prevented one from thawing the lip of ice formed due to conduction along the wall. This made it almost impossible to obtain a good picture from which the height of the bubble could be measured accurately. Operation in the trailer presented several additional difficulties. The action of the cathetometer slides became very stiff in the cold making accurate focusing of the camera difficult. Growing flat ice sheets was also difficult. A way was however, found of growing plane sheets (not parallel) and these were then levelled by blocking up the entire workbench.

Once an ice sheet was ready for testing, a quantity of oil was injected under the ice. The bubbles were then photographed and the tank tilted until they started to move. This was determined visually and a measurement was then taken of the elevation of the tank at the lead screw. On a number of occasions, it was not possible to obtain a picture of the bubble and so an estimate of the volume was made based on the amount of oil injected and the relative size of other bubbles if any.

Velocity measurements were taken but were not indicative of the original bubble in most cases. This is because most of the bubbles broke into a number of smaller bubbles. In such cases, a large bubble would start slowly, then neck down, form a second bubble (which did not necessarily move at that angle) and then continue. The velocities that were recorded were for the first bubble to reach the finish marker and were, therefore, in no way representative of the original bubble that was measured.

3.4 Results

Tests were run on both the Swan Hills and Norman Wells crude oils. Results of the sessile drop experiments were used to calculate the mass of a bubble as a function of \overline{X} according to a method described by Staicopolus (1962). No significant difference could be determined between the two oils as shown in Figure 32 where the data for both oils has been plotted. Figure 33 shows this data on a log-log scale and reveals that the calculation method is limited to $\overline{X} \approx 1$. The exact reason for this is not known, but is is suspected that it is due to the polynomial functions used in the empirical equations given by Staicopolus. The mass of a cylinder of oil having a radius X and a height of 0.8 cm has also been plotted in Figure 33 for comparison purposes. For subsequent calculations, the straight line extrapolation through the calculated data points has been used. Figures 34 and 35 were then prepared using the experimental data and clearly show that the angle of inclination necessary to initiate motion decreases with the mass of the oil which was to be expected. Application of equation 11 then results in the data presented in Figures 36 and 37 which give the relationship between the force required to initiate motion of an oil bubble and its mass. Equations describing the best lines through the data are,

$$F = 48.5M^{0.486}$$
 ...(13)

$$F = 23.4M^{0.659}$$
 ... (14)

for the Swan Hills and Norman Wells crude oils respectively. It is seen that the force required increases with the mass of oil present.

3.5 Conclusions

and

The following conclusions may be drawn from the preceding discussions:

- a) The angle at which an oil bubble will move up an inclined ice sheet decreases as the mass of the bubble increases.
- b) The force required to initiate motion increases with the mass of the oil bubble as shown in Figures 36 and 37. For the Swan Hills crude, this force is given by $F = 48.5M^{0.486}$, while for Norman Wells crude it is given by $F = 23.4M^{0.659}$.

4. OIL MOVEMENT IN A LEAD

4.1 General

How far oil spilled on cold arctic waters will spread is of particular importance, especially at ambient winter temperatures. In an offshore environment such spreading will typically occur in a lead. The ultimate extent of the spread will, of course, be dependent on the amount of oil released. Since this parameter can only be determined once a spill has occurred and then only approximately, it was thought that the best approach to this problem would be to determine the initial and final spreading coefficients from which an equilibrium film thickness could then be calculated. This thickness could then be combined with the volume estimate to give an estimate of the maximum areal spread that could reasonably be expected. Determination of the rate of spread during the early life of the spill may be made using the methods described in the open literature (Christiansen and Hixson, 1969; Fay, 1971; Waldham et al, 1972; and, Fannelop and Waldham, 1972) and will not be presented here.

4.2 Spreading Analysis

The profile of an oil lens floating on water is shown in Figure 38, where t represents the equilibrium film thickness. Usually this quantity is used to calculate the spreading coefficient S from an equation given by Langmuir (1933) as:

$$t_{\infty}^{2} = -2S\rho_{a}/g\rho_{b}\Delta\rho$$
(15)

where the subscript a represents the water phase and b the oil phase. In the present work, equation 15 is used to calculate t_{∞} by calculating values of S from the data presented in Section 2 of this report. It should be noted here that equation 15 is meaning-ful only if the spreading coefficient S is negative. The spreading coefficient is defined as follows (Adamson, 1960),

$$S_{b/a} = \gamma_a - \gamma_b - \gamma_{ab} \qquad \dots (16)$$

...(17)

where the surface tensions of a and b in equation 16 are those for the pure liquids. When two substances are in contact however, they will become mutually saturated, so that Υ_a and Υ_b will become $\Upsilon_{a'}$ and $\Upsilon_{b'}$ respectively. The corresponding spreading coefficient is then written as $S_{b'/a'}$ or just S'. It is this latter quantity which must be used in equation 15 to determine t_{∞} and is given by,

 $S' = \gamma_a - \gamma_b - \gamma_{ab}$

Values of these parameters for the Norman Wells and Swan Hills crude oils (corrected to 0°C) are presented in Appendix C along with calculated values of S and S'. The spreading coefficients listed in Appendix C are for a particular point in time and for the conditions indicated in the notes to Tables C-1 and C-2. Since the samples were kept in sealed bottles, negligible aging occurred. In reality, considerable evaporation of the light hydrocarbon fractions would occur, thereby not only reducing the volume of oil present, but also increasing the density of the remaining oil. This would lead to a lowering of the spreading coefficient because this coefficient is positive only for the lower molecular weight hydrocarbons (Pomerantz et al, 1967). In addition, natural surfactants present in the oil would diffuse into the water. Since these organic surface active constituents cause the spreading (Garrett, 1973), one would expect the spreading coefficient to eventually decrease and become negative. That this did not happen for the Swan Hills samples is most likely due to the fact that these samples were not thoroughly mixed with the brine as was the case with the Norman Wells samples. Attempts at

mixing the former samples yielded emulsions that couldn't be broken either by heating or centrifuging them. Even if a negative spreading coefficient had been measured for the Swan Hills samples, use of this in calculating an equilibrium film thickness would not be recommended because of the relatively high pour point of this crude (-9.5°C). Below this temperature, the oil becomes non-fluid in character (it gels) and spreading due to surface forces would be essentially halted (Garrett, 1973).

The film thickness calculated for the Norman Wells crude (Appendix C) should be regarded as a minimum to be expected. With evaporation, etc., this thickness would be increased. One should also note that these values were calculated for a 0°C mean water and oil temperature. At lower temperatures, the spreading coefficient will be decreased even further which will also result in an increase in the equilibrium film thickness.

4.3 Conclusions

From the preceding discussion, one may conclude the following:

- a) The minimum equilibrium thickness of the Norman Wells crude on water under arctic winter conditions will be approximately 0.25 cm (Appendix C).
- b) A similar minimum equilibrium thickness may be expected for the Swan Hills crude taking into account the effects of aging (evaporation) and the relatively high pour point of this crude.
- c) The equilibrium film thickness quoted is conservative insofar as one may reasonably expect this figure to increase as the oil weathers.

5. SOLUTE REDISTRIBUTION AND OIL PENETRATION

- 5.1 Solute Redistribution
 - 5.1.1 General

It is generally thought that many crude oils contain a certain amount of dissolved salt in their produced form. The problem posed, therefore, was whether or not the salt produced as a result of an underwater blowout would be transported by the oil to the under-ice surface where it may be released causing possible rotting of the ice sheet. Whether the ice sheet rots is also a function of the amount of salt, in excess of the equilibrium concentration already present, available at the under-ice surface for lowering the freezing temperature. This problem is important when one considers an oil well blowout in the winter during which time one would expect to be able to move considerable heavy equipment over the ice in a cleanup effort. Such movement could be impeded if significant rotting and weakening of the ice were to take place.

5.1.2 Method and Results

It was decided that an experimental inquiry was unnecessary as all of the pertinent information was in hand. The problem was reduced to that of: a) determining the amount of dissolved salt that may reasonably be expected in the oil, b) examining the method used in arriving at these figures, and c) discussing the problem with several people in our analytical chemistry group.

The property records of crude oils from 22 different locations were reviewed. Salt contents of these crudes are presented in Table 6 and in Figure 39 which shows the results as having an exponentially decreasing frequency distribution. A description of the test method used in determining the salt contents listed in Table 6 is given in Appendix D. It was pointed out in several discussions (personal communications with H.A. Jacobson, R.E. Heater and W.N. McKay) that this test does not necessarily indicate that salt is actually dissolved in the crude oil. Most of the salt actually produced from a well comes in the form of brine which is generally removed in the field before the crude as such is analyzed. Whether the salt subsequently measured is contained as dissolved salt in the oil or whether it is present as minute brine droplets dispersed in the oil is still subject to debate, although the latter seems more likely (personal communications with H.A. Jacobson and R.E. Heater). In either case the physical situation strongly mitigates against any of the salt reaching the under-ice surface. This is due to the violent agitation expected as the plume issues out of the pipe and rises through 15 to 60 metres of water. The ensuing breakdown of the oil stream into very fine droplets during its ascent should release any salt in the stream to the water phase.

If one assumes that this did not happen and that there was dissolved salt in the oil that was carried to the under-ice surface, then one can calculate an areal distribution of the salt due to the movement of the oil. Taking the average salt content as 27.1 pounds per M bbl, one obtains 40.65 pounds per day assuming that the oil is released at a rate of 1500 bbl/day. Taking an equilibrium thickness of 0.8 cm for the oil and ignoring any additional spreading due to water currents or ice movement, one obtains an areal spread of approximately 29.83 x 10^7 cm². One can also assume that the salt would be quite slow in coming out of solution if it hasn't done so during its ascent in the oil. On this basis, one obtains a figure of 6.2×10^{-5} gm of salt in the oil per square cm of ice covered by the oil. This can also be represented as a salinity of approximately 0.08°/00. Since the oil has now displaced the water, a reduction in the salinity at the interface has taken place. And assuming that a redistribution of the salt does take place)through some concentration diffusion process), then it would be reasonable

to expect the concentration in the oil to increase and that in the ice (brine drainage channels) to decrease.

5.1.3 Conclusions

Whether salt actually exists as a dissolved species in the oil is open to question. Assuming, however, that it does, then one may conclude from the preceding discussion that the dissolved salt will not cause the under-ice surface to rot. It is also suggested, since the salt is more likely to be present in dispersed water droplets, that the majority of the salt would be released to the water column during the oil's ascent.

5.2 Oil Penetration

This section considers whether or not the small oil bubbles that rise to the bottom surface of the ice will penetrate the ice structure due to their buoyancy force. If this were the case, then a considerable amount of the oil resulting from an underwater blowout in the winter would be retained by the ice. This could considerably limit the spread of the oil but could also hamper recovery operations due to the large areal distribution possible for such drops. A combination of observational evidence and physical reasoning has been used in formulating a solution to this question.

In performing the surface tension experiments, a large number of oil drops were studied from an even larger group of drops that had been injected under the ice. At no time was any bubble observed to disappear into the ice during an experiment. An examination was made of several ice sheets after an experiment to determine whether some oil had actually penetrated the ice. No traces of oil could be found. Wolfe and Hoult (1972, 1974) in their study of oil under sea ice also observed that negligible amounts of oil are entrapped in the ice brine matrix.

What was noticed, however, was that there were in many cases, small depressions left on the under-ice surface where the oil had been. These depressions are attributed entirely to our method of removing the ice from the test tanks which was to remove the tanks from the cold room and to allow sufficient ice around the edges to melt so that the ice block could be removed. This normally took quite some time and resulted in considerable heat gain by both the ice and the brine.

Such behaviour is easily explained by considering that the average radius of the brine drainage channels at the bottom ice surface is of the order of 0.1 mm (Assur, 1958; Eide and Martin, 1975) and this size generally increases somewhat as one moves up from the under surface of the ice. These brine channels can be likened to inverted ink bottles, having narrow necks and being wider inside. Even though the openings are not truly circular, generally they are more elliptical in shape (Assur, 1958), one can assume that they are circular. The pressure drop across the opening can be given by (Adamson, 1960).

$\Delta P = (2\gamma/r) \cos \theta$

Taking γ (the surface tension) as 25 dynes/cm and θ (the contact angle) as 150° for this sample calculation, one obtains a pressure drop ΔP (i.e. driving force required to penetrate the meniscus) dependent on orifice size as follows:

r(mm)	=	0.1	0.2	0.5	0.7
$\Delta P(dyne/cm^2)$	=	4330.	2167.	866.	617.

If one now takes an oil bubble thickness of 0.8 cm, this is equivalent to a ΔP across the oil (P at the interface between oil and ice is reference) of approximately 636 dyne/ cm^2 (using a specific gravity of 0.81 for the oil). One can easily see that if the orifice size is increased to 0.7 mm (ΔP equivalent to 671. dyne/cm²) that some oil can then be expected to move into the channel. In the case of Wolfe and Hoult (1974), it seems that the oil was not cooled prior to its injection under the ice. Heat transfer from the warmer oil to the ice could have caused some melting to take place with a resultant increase in the size of some of the brine drainage channel orifices. Alternatively, the temperature gradient between the oil and the ice could have resulted in a thermal diffusion of the salt in the brine channels towards the interface between the oil and ice. A reduction of the freezing temperature of the brine would result with the effect that melting at the brine drainage channel orifices could occur causing an enlargement of some of these orifices. A similar result could be expected in either case; a) increase in orifice diameter, and b) a corresponding decrease in ΔP .

One can draw the following conclusions from the preceding discussion:

- Assuming the oil to be in thermal equilibrium with its surroundings, one should not expect any significant penetration of oil into the ice.
- b) The limited penetration of oil that may occur will likely result from the oil encountering an oversized brine drainage orifice.
- c) Penetration will occur in the spring as melting proceeds and the drainage channels open.

6. CONCLUSIONS

An evaluation of some of the parameters affecting the flow and areal distribution of crude oil under a sea ice canopy has been presented. It was found that the interfacial tensions between oil and brine $(12^{\circ}/_{\circ\circ})$ for Swan Hills and Norman Wells crude oils were 24.5 and 23.8 dynes/cm respectively. Interfacial tensions at salinities other than $12^{\circ}/_{\circ\circ}$ have also been presented. Effects of aging on the interfacial tension could not be determined due to the scatter in the measured data. The equilibrium thickness of these two crude oils under ice was found to be 0.80 and 0.88 cm for the Swan Hills and Norman Wells samples respectively. Expressions relating the force required to initiate motion of an oil bubble have also been presented. For the Swan Hills crude, this force is given by $F = 48.5M^{0.486}$ while for Norman Wells crude it is given by $F = 23.4M^{0.659}$. In these expressions, the force, F, is in dynes and the mass, M, is in grams. Data relating the mass of oil to the shape of the bubble has also been presented. This will enable calculations of the minimum currents required to initiate motion of an oil bubble to be made.

When considering the spread of oil on water under arctic conditions, as would be the case of oil spreading in a lead, it was found that a minimum equilibrium film thickness of 0.25 cm should be expected for the two crudes tested. Taking into account the effects of evaporation and the leaching of natural surface active agents present in the oil into the water, it is reasonable to expect this figure to be conservative in most cases. A determination of the maximum areal spread of the oil, barring any external forces (e.g., effects of currents, etc.), is therefore possible.

It was also concluded that the presence of dissolved salt in the oil, if indeed it does exist as a dissolved species in the oil, would not cause the under-ice surface to rot. Penetration of the oil into the ice sheet is not normally expected. When the oil encounters an oversized brine drainage channel of approximately 0.7 mm radius, limited penetration will likely result. As melting proceeds in the spring, and the brine drainage channels open, a significant amount of oil penetration should be expected.

7. REFERENCES

- Adamson, A.W., 1960. Physical Chemistry of Surfaces. Interscience Publishers Inc., New York, N.Y.
- Assur, A., 1958. Composition of Sea Ice and Its Tensile Strength. Reprint from National Academy of Sciences, National Research Council Publication 598 - Arctic Sea Ice.
- A.S.T.M., 1970. Standard Method of Test for Interfacial Tension of Oil Against Water by the Ring Method. Designation D971-50, Annual Book Book of ASTM Standards, Part 29.
- Bashford, F. and J.C. Adams, 1883. An Attempt to Test The Theories of of Capillary Action by Comparing the Theoretical and Measured Forms of Drops of Fluid. Cambridge University Press, Cambridge, England.
- Chen, E.C., J.C.K. Overall and C.R. Philips, 1974. Spreading of Crude Oil on an Ice Surface. Can. J. of Chem. Eng., Vol. 53. p 71.
- Christiansen, R.M. and A.N. Hixson, 1957. Breakup of a Liquid Jet in a Denser Liquid. Industrial and Engineering Chemistry. Volume 49, No. 6. pp 1017 - 1024.
- Eide, L.I. and S. Martin, 1975. The Formation of Brine Drainage Features in Young Sea Ice. J. of Glaciology, Vol. 14, No. 70.
- Fannelop, T.K. and G.D. Waldman, 1972. Dynamics of Oil Slicks. AIAA Journal, Vol. 10, No. 4. p. 506.
- Fay, J.A., 1969. The Spread of Oil Slicks on a Calm Sea. In Oil on the Sea. D.P. Hoult, Editor. Plenum Press, N.Y. p. 53.
- Fay, J.A., 1971. Physical Processes in the Spread of Oil on a Water Surface. Proceedings of the Joint Conference on Prevention and Control of Oil Spills. American Petroleum Institute, Washington, D.C. p. 463.
- Fox, H.W. and C.H. Chrisman, 1952. The Ring Method of Measuring Surface Tension for Liquids of High Density and Low Surface Tension. J. Phys. Chem. 56, 284.
- Freud, B.B. and H.Z. Freud, 1930. A Theory of the Ring Method for the Determination of Surface Tension. J. Am. Chem. Society 52. 1772.
- Garrett, W.D., 1973. The Surface Activity of Petroleum and its Influence on the Behavior of Oil at Sea. In Background Papers for a Workshop on Inputs, Fates and Effects of Petroleum in the Marine Environment. NTIS Report AD 783990.
- Girifalco, L.A. and R.J. Good, 1957. A Theory for the Estimation of Surface and Interfacial Energies. I. Derivation and Application to Interfacial Tension. The Journal of Physical Chemistry. Vol. 61, p. 904.

Gittens, G.J., 1969. Variation of Surface Tension of Water with Temperature. J. of Colloid and Interface Science. Vol. 30, No. 3, p. 406.

- Gleaser, J.L. and G.P. Vance, 1971. A Study of the Behavior of Oil Spills in the Arctic. NTIS Report AD 717 142, U.S. Coast Guard, Washington, D.C.
- Good, R.J., L.A. Girifalco and G. Kraus, 1958. A Theory for Estimation of Interfacial Energies Application to Surface Thermodynamics of Teflon and Graphite. The Journal of Physical Chemistry. Vol. 62 p. 1418.
- Harkins, W.D. and H.F. Jordan, 1930. A Method for the Determination of Surface and Interfacial Tension from the Maximum Pull on a Ring. J. Am. Chem. Society 52, 1751.
- Hinze, J.O., 1955. Fundamentals of the Hydrodynamic Mechanism of Splitting in Dispersion Processes. A.I.Ch.E. Journal, Vol. 1, No. 3 pp 289-295.
- Keevil, B.E. and R.O. Ramseier, 1975. Behavior of Oil Spilled Under Floating Ice. In Proceedings 1975 Conference on Prevention and Control of Oil Pollution. p. 497. Sponsored by EPA, API, USGG, San Francisco, March 25-27, 1975.
- Kreith, F., 1968. Principles of Heat Transfer. 2nd Ed. International Textbook Company, Scranton, Pennsylvania.

Langmuir, I., 1933. J. Chem. Phys. 1, 756.

- Parvatikar, K.G., 1966. Verification of Empirical Equations in Computing Surface Tension by the Sessile-Drop Method. J. of Colloid and Interface Science 22. pp 298-299.
- , 1967. Verification of Empirical Equations in Computing the Contact Angle by the Sessile-Drop Method. J. of Colloid and Interface Science 23. pp. 274-276.
- Pomerantz, P., W.C. Clinton and W.A. Zisman, 1967. Spreading Pressures and Coefficients, Interfacial Tensions and Adhesion Energies of the Lower Alkanes, Alkenes and Alkyl Benzenes on Water. J. of Colloid and Interface Science. Vol. 24, No. 1. pp 16-28.
- Schlichting, H., 1968. Boundary Layer Theory. Sixth Edition. McGraw Hill Book Co., New York, N.Y. p. 128.
- Staicopolus, D.N., 1962. The Computation of Surface Tension and of Contact Angle by the Sessile-Drop Method. J. of Colloid Science, 17. 539-447.

, 1963. The Computation of Surface Tension and of Contact Angle by the Sessile-Drop Method (II). J. of Colloid Science 18. 793-794.

, 1967. The Computation of Surface Tension and of Contact Angle by the Sessile-Drop Method (III). J. of Colloid and Interface Science 23. 453-456.

- Timmons, C.O. and W.A. Zisman, 1968. The Relation of Initial Spreading Pressure of Polar Compounds on Water to Interfacial Tension, Work of Adhesion and Solubility. J. of Colloid and Interface Science. Vol. 28, No. 1. p. 106.
- Topham, D.R., 1974. Hydrodynamic Aspects of an Oilwell Blowout Under Sea Ice. Beaufort Sea Project Study G2a, Interim Report, December 1974. Dept. of the Environment, Victoria, B.C.
- Waldman, G.D., T.K. Fannelop and R.A. Johnson, 1972. Spreading and Transport of Oil Slicks on the Open Ocean. Reprints of the 1972 Offshore Technology Conference. Vol. 1, p. 353. ASME, Houston, Texas.
- Washburn, E.W., 1927. International Critical Tables. McGraw Hill Book Co., New York, N.Y. Vol. 2, p. 146.
- Wolfe, L.S. and D.P. Hoult, 1972. Effects of Oil Under Sea Ice. Fluid Mech. Lab. Publication. No. 72-10. Dept. Mech. Eng. MIT.
- Wolfe, L.S. and D.P. Hoult, 1974. Effects of Oil Under Sea Ice. J. of Glaciology. Vol. 13, No. 69.

8. BIBLIOGRAPHY

Bikerman, J.J.	2nd Edition, Academic Press, New York, 1958.
Davies, J.T. Rideal, E.K.	Interfacial Phenomena. Academic Press, New York, 1961.
Harkins, W.D.	The Physical Chemistry of Surface Films. Reinhold Publishing Co., New York, 1952.
Adams, N.K.	The Physics and Chemistry of Surfaces. 3rd Edition Oxford University Press, London, 1941.
Gregg, S.J.	The Surface Chemistry of Solids. 2nd Edition, Chapman and Hall Ltd., London, 1961.
Gould, R.F. (editor)	Contact Angle, Wettability and Adhesion. Advances in Chemistry Series 43, American Chemi- cal Society, Washington, D.C. 1964.
Burdon, R.S.	Surface Tension and Spreading of Li q uids. 2nd Edition. Cambridge University Press, Cambridge, England, 1949.
Adamson, A.W.	Physical Chemistry of Surfaces. Interscience

TA	RI	F	1
11	D		-

Quantity Elapsed Time	2R (in.)	x=R (in.)	y (in.)	^B 90	F90	G ₉₀	γ(eq 3) dyne/cm	γ(eq 4) dyne/cm
70. sec.	0.5772	0.2886	0.1917	7.7607	0.6557	0.4598	28.141	25.237
25.5 min.	0.5902	0.2951	0.1955	8.1312	0.6371	0.4218	29.745	29.770

Numerical Values of Coefficients (a_k) and Constants A_{ϕ} , C_{ϕ} , D_{ϕ} used in Equations (5), (6) and (7). (From Ref. 10).

TABLE 2

Quantity	ø	Polynomial Coefficients						Constants			
6		^a 0	al	^a 2	^a 3	ali	Aø	С¢	Dø		
^Β ø ^F ø ^G ø	45 90 45 90 45 90	3.1713 2.5924 0.4443 0.5864 0.1425 0.3684	1.596 2.1838 -0.2027 -0.3512 -0.0979 -0.3555	-0.1064 -0.1302 0.0509 0.0859 0.0408 0.1857	-0.0526 -0.1347 -0.009 0.00898 -0.0124 -0.07188	0.0464 0.1141 -0.01415 0.01838	3.11 1.5922 3.11 1.5922 3.11 1.5922	0.6958 0.5922 0.6958 0.5922 0.6958 0.5922	4.8		

Measurements and Calculated Interfacial Tension of Sessile Drop at Two Times After Injection (Fig. 5 and 6).

FLUID	SPECIFIC GRAVITY	DENSITY 16.m/ft ³	DENSITY gm/cm ²	DENSITY DIFFERENCE
Air		0.074	0.001185	
Norman Wells Crude	0.8245	51.4488	0.8241	0.8229
Swan Hills Crude	0.8190	51.1056	0.8186	0.8174
6% Brine	1.0041	62,6558	1.0036	1.0024
12% Brine	1.0082	62,9117	1.0077	1.0065
18% Brine	1.0112	63.0989	1.0107	1.0095
24% Brine	1.0163	63.4171	1.0158	1.0146
30% Brine	1.0201	63.6542	1.0196	1.0184
36% Brine	1.0241	63,9038	1.0236	1.0224

TABLE 3: Fluid Densities Used in Calculations (at $25^{\circ}F$)

[†] Density difference = Fluid Density - Air Density in gm./cm.³

† Taken from Figure 11.

Crude Type	No. Observ.	Mean	Standard Deviation	Max. Value	Min. Value	Range	Mean Deviation
Swan Hills	92	25,456	7.009	47.693	6.925	40.768	4.960
Norman Wells	82	23.982	7.904	49.151	5.686	43.465	6.103

TABLE 4: Interfacial Tensions Between Oil and12% Brine Calculated From Experimental Data

X (cm.)	Y (cm.)	X/Y	Z	В	F ²	G ²	x^2/BF^2	Y^2/BG^2	cx ² /bf ^{2^d}	сү ² /вс ^{2^d}
.1	a .0966	1.0352	9406	.1675	.9490	.8860	.0629	.0629	10.066	10.061
. 3	.2680 ^a	1.1194	7984	.7129	.8303	.6636	.1520	.1518	24.326	24.291
. 5	.3874 ^a	1.2907	5092	2.6585	.6168	. 3700	.1525	.1526	24.394	24.411
.097 ^b	b .0996	0.9739	-1.0441	1170	1.0398	1.0934	0773	0775	-12.372	-12.404
.103 ^b	b .0936	1.1004	8304	.5717	.8564	.7082	.0217	.0216	3,467	3.462
.297 ^b	ь .2710	1.0959	8380	.5400	.8626	.7192	.1894	.1891	30.297	30.253
. 303 ^b	.2650	1.1434	7579	.9088	.7980	.6113	.1266	.1264	20.255	20.227
.497 ^b	ь . 3904	1.2731	5389	2.3894	.6368	. 3928	.1623	.1624	25.973	25.984
.503 ^b	b .3844	1.3085	4790	2.9519	.5969	3483	.1436	.1437	22.974	22.995
.100	.0996	1.0040	9932	.0125	.9948	.9860	.8009	.8015	128.137	128.242
									and the second s	

TABLE 5: Error Analysis For Swan Hills Crude

a Y Value taken from regression equation (see Figure 19)

b Error of ±0.003 cm. Maximum error difference used.

c Error of +0.003 cm. in Y only.

d C is the constant g- $\Delta\rho$ in equations 3 and 4. Taken here as 160.

CRUDE OIL ORIGIN	GRAVITY	SALT AS NaC1
	API	1b./M bb1.
Midale (Sask.)	27.9	1.58
Leduc-Woodbend (Alta.)	39.7	28.6
Sturgeon Lake (Alta.)	37.1	14.8
Norman Wells (N.W.T.)	40.8	2.3
Pembina (Alta.)	37.3	1.2
Redwater (Alta.)	34.7	40.8
Roselea (Man.)	35.5	NIL
Stettler (Alta.)	27.2	32.6
Smiley (Sask.)	33.0	15.1
Acheson (Alta.)	36.6	14.2
Ratcliff (Sask.)	31.3	193.0
Cantuar (Sask.)	20.3	57.0
Bonnie Glen (Alta.)	42.5	1.8
Forget (Sask.)	31.4	23.3
Wapella (Sask.)	26.5	NIL
Success (Sask.)	21.1	4.0
Fosterton (Sask.)	24.1	1.0
Coleville (Sask.)	13.8	64.0
Virden (Man.)	32.6	14.5
Wizard Lake (Alta.)	37.2	1.0
Ivik (N.W.T.) ⁺	· · · ·	5.9
Atkinson Point (N.W.T.)*		80.0

TABLE 6: SALT CONTENTS OF VARIOUS CRUDE OILS*

* These analyses are from the mid 50's. These figures change with time.

+ From recent analyses.





FIGURE 1



Figure 2. Close-up of Camera and Lens.



Figure 3. Camera and Tank in Test Position.



TYPICAL TEMPERATURE DISTRIBUTION IN TEST TANK

FIGURE 4

31



Figure 5. Bubble No. 6 of test on March 27, 70 seconds after injection (1/2X Reproduction Ratio).



Figure 6. Bubble No. 6 of test on March 27, 25.5 minutes after injection (1X Reproduction Ratio).






1.028 SPECIFIC GRAVITY OF BRINE SOLUTIONS x 1.026 X XX 1.024 0 - 12 % 0 × - 18 %-1.022 Δ 24 % ۰ ۰ - 30 %. X -36%. Δ 1.020 4 SPECIFIC GRAVITY ۵ Δ 1.018 Δ Δ 1.016 * * 1.014 × ×× 1.012 00 1.010 Ð 0 0 1.008 80 40 50 70 30 60 90 TEMPERATURE (*F.) FIGURE 10



AIR DENSITY vs TEMPERATURE AT ATMOSPHERIC PRESSURE [20]





SURFACE TENSION FREQUENCY DISTRIBUTION SWAN HILLS CRUDE

FIGURE 13

SURFACE TENSION FREQUENCY DISTRIBUTION NORMAN WELLS CRUDE



FIGURE 14











GRAPH OF \overline{Y} vs. \overline{X} FOR SWAN HILLS CRUDE (FOR ALL TIMES)



GRAPH OF \overline{Y} vs. \overline{X} FOR NORMAN WELLS CRUDE (FOR ALL TIMES)

Figure 20







GRAPH OF ERROR LIMITS FROM TABLE 5

FIGURE 23

GRAPH OF SURFACE TENSION vs. X FOR SWAN HILLS CRUDE

















SCHEMATIC OF THE FORCE R' CAUSING MOTION IN THE X DIRECTION



WATER : Pw

 $R^1 = R \sin \alpha$



FIGURE 32

GRAPH OF X vs. MASS



FIGURE 33



MASS . SIN a vs MASS FOR SWAN HILLS CRUDE



MASS · SIN a vs MASS FOR NORMAN WELLS CRUDE





FIGURE 36





PROFILE OF AN OIL LENS ON WATER

and the state	011	
	LENS to Po	
WATER Pw		



HISTOGRAM OF SALT CONTENT FROM 22 LOCATIONS



APPENDIX A

DEVELOPMENT OF THE EQUATION FOR THE PROFILE OF A SESSILE DROP



 D_2

Consider first a point A on the surface of the bubble with P₁ the pressure on the concave side of A and P₂ the pressure on the convex side. Let D₁ be the density on the lower side and D₂ that on the upper. Let P₁ - P₂ = C, C being determined by the curvature at A. Now the pressures at P will be

$$P_1 - gD_2y$$
 and $P_2 - gD_1y$

where P is a point on the surface at a level y above A.

Now from (9) $\frac{1}{R} + \frac{1}{R^1} = \frac{\Delta P}{\gamma_0/w}$

where R and R^1 are the principal radii or curvature at any point, then at point P

$$\frac{1}{R} + \frac{1}{R^{1}} = \frac{P_{1} - P_{2} + gy(D_{1} - D_{2})}{\gamma_{0/W}}$$

or

 $\frac{1}{R} + \frac{1}{R^{1}} = \frac{C + gy(D_{1} - D_{2})}{\gamma_{0/W}} \dots (A-1)$

Let x be the horizontal and y the vertical coordinate of any point in a meridional section of the surface of the fluid, r the radius of curvature of the meridional section at that point, and ϕ the angle which the normal to the surface makes with the axis of revolution (i.e., y axis). Then the length of the normal terminated by the axis is x/sin ϕ and

$$_{\circ}^{\circ}_{\circ}$$
 R = r and R¹ = $\frac{x}{\sin\phi}$

Eq. (1) then becomes

$$\frac{1}{x} + \frac{\sin\phi}{x} = \frac{C + gy(P_w - P_o)}{\gamma_{o/w}}$$

67

...(A-2)

Let b be the radius of curvature at the origin, so that at that point we have r = b and $lim(x/sin\phi) = b$

 $\circ^{\circ} \circ$ when y = 0 one gets

$$\frac{2}{b} = \frac{C}{\gamma}$$
 or $C = \frac{2\gamma}{b}$

Substituting into (2) we get

$$\frac{b}{r} + \frac{\sin\phi}{\left(\frac{x}{b}\right)} = \frac{2 + gb^2(P_W - P_O)(\frac{y}{b})}{\gamma_{O/W}} \dots (A-3)$$

$$\frac{gb^2(P_w - P_o)}{\gamma_{o/w}} \equiv \beta \qquad \dots (A-4)$$

$$\overline{r} = \frac{r}{r} : \overline{x} = \frac{x}{r} : \overline{y} = \frac{y}{r}$$

Let

$$=\frac{r}{b}$$
; $\overline{x}=\frac{x}{b}$; $\overline{y}=\frac{y}{b}$

Equation (3) then simplifies to

$$\frac{1}{\overline{r}} + \frac{\sin\phi}{\overline{x}} = 2 + \beta \overline{y} \qquad \dots (A-5)$$

Also, when $\phi = 0$, $\overline{y} = 0$, $\overline{r} = 1$ and limit $\left(\frac{\overline{x}}{\sin\phi}\right) = 1$ $d^2\overline{y}$

$$\frac{1}{r} = \frac{\frac{d\overline{y}}{d\overline{x}^{2}}}{\left\{1 + \left(\frac{d\overline{y}}{d\overline{x}}\right)^{2}\right\}^{3/2}}$$
and $\sin\phi = \frac{\frac{d\overline{y}}{d\overline{x}}}{\left\{1 + \left(\frac{d\overline{y}}{d\overline{x}}\right)^{2}\right\}^{1/2}}$
and letting $\frac{d\overline{y}}{d\overline{y}} = x^{1}$ and $\frac{d^{2}\overline{y}}{d\overline{y}} = x^{2}$

and letting
$$\frac{d\overline{y}}{d\overline{x}} = y'$$
 and $\frac{d^2\overline{y}}{d\overline{x}^2} = y''$

Then equation (5) becomes

$$\frac{y''}{[1 + (y')^2]^{3/2}} + \frac{y'}{[1 + (y')^2]^{1/2}\overline{x}} = 2 + \beta \overline{y}$$

or

$$y'' = (2 + \beta \overline{y})[1 + (y')^2]^{3/2} - \frac{y'}{\overline{x}}[1 + (y')^2] \dots (A-6)$$
APPENDIX B

TEST RESULTS FROM RING DETACHMENT METHOD

Abbreviations used in the following table are:

a,	A	-	The automatic mode was used for tensiomat operation.
m,	M	-	The tensiomat was operated manually.
nc		-	Indicates that the apparatus was not cleaned between tests.

Notes to the following table are:

+

- From data in Table 3.

 P is the calibration corrected value of the measured tension in dynes/cm.

- Taken from Figure 8.

FLUID TYPE	TEMP. °C	TEST V	ALUES ON TEST 2	TENSION TEST 3	MAT DYNE TEST 4	S/CM TEST 5	AVG.OF TEST VALUES	CALIBRATION CORRECTED VALUE DY/CM	D-d + GM./CM ³	$P/(D-d) \neq$ DY.CM ² /GM	CORRECTION FACTOR*	SURFACE TENSION DY./CM.
Brine 6%	26.65	67.6(m)	68.4(m)	68.3(m)	68.0(m)		68.075	67,626	1.0024	67.4617	0.9280	62.76
6%	27.2	70.7(m)	73.6(m	74.7(A)	75.2(A)	75.4(A)	73.92	73.432	1.0024	73. 254	0.9339	68.57
12%	26.65	68.7(m)	69.3(m)	68.8(m)	68.7(m)	-	68.875	68.420	1.0065	67.9761	0.9286	63.53
12%	26.25	75.4(m)	76.0(A	76.0(A)	76.0(A)	75.5(m)	75.78	75.28	1.0065	74.791	0.9353	70.41
18%		71.2(m)	69.6(m	69 (m)	68.7(m)		69.70	69.240	1.0095	68.5861	0,9292	64.34
18%	26.5	65.5(m)	72.8 (A	74.0(A)	76.8(A)	75.5(m)	72.92	72.439	1.0095	71.755	0.9324	67.54
24%	-	73.6(m)	73.7(M)	73.5 (M	73.8(M)	-	73.65	73.164	1.0146	72.1089	0.9325	68.23
- 24%	25.95	66.9(m)	68.2(A)	73.5(A	75.9(A	75.9 (M)	72.08	71.604	1.0146	70.572	0.9 312	66.68
24%	-	76.3(A)	76.4(<mark>A</mark>)	76.4(A	76.5 (M	76.1(M)	76.34	75.836	1.0146	74.743	0.9352	70.92
24%	-	76.0(m)	75.9(M)	76.4(A	76.4(A	75.9(M)	76.12	75.618	1.0146	74.528	0,9350	70.71
30%	-	73.8(M)	73.9(M)	73.9(M	73.8(M		73.85	73.363	1.0184	72.0350	0.9320	68.37
30%	-	71.9(M)	75.0 (M)	75.7(M	76.4 (A	76.2(A)	75.2	74.704	1.0184	73: 352]	0.9339	69.77
36%	26.85	73.2(M)	73.0 (M)	73.2 (M	73.1(M	-	73.125	72.642	1.0224	71.0489	0.9317	67.68
36%	26.7	66.8(M)	71.6 (A)	75.1(A	76.4(A	75.8(M) 76.4(A)	73.68	73.194	1.0224	71.589	0.9322	68.23
36%	1.4	71.5 (M)	75.2 (M)	75.7(M	75.8(M	75.7(M)	74.78	74.286	1.0224	72.657	0.9332	69.33
36%	-	75.8(M)	76.0 (M)	76.2(M	76.0 (M	76.6(A) 76.4(A)	76.17	75.667	1.0224	74.007	0.9345	70.71
N.W./S6%B	-	24.8	24.8	25.0	25.4(A	25.0	25.00	24.835	0.8229	30.1790	0.8871	22.03
N.W/S 6%	27.15	25.0 (M)	25.6(A)	25.6(A	25.6 (A	25.0 (M)	25.36	25.19	0.8229	30.610	0.8877	22.36

TEST RESULTS FOR RING DETACHMENT METHOD

FLUID	TEMP.	TEST V	ALUES ON	TENSIO	MAT DYNE	S/CM	AVG.OF TEST O	CALIBRATION	D-d +	P/(D-d) =	CORRECTION	SURFACE
TYPE	°C	TEST 1	TEST 2	TEST 3	TEST 4	TEST 5	DY./CM	VALUE DY/CM	GM./CM ³	DY. CM2/GM	FACTOR*	DY./CM.
N.W./S 12%B	27.8	24.8	25.3(A)	25.3(A)	24.5(M)	25.1(A)	25.00	24.835		30.1790	0.8871	22.03
N.W./S 18%8	27.65	25.4(A)	25.4(A)	24.8(M)	25.0(M)	25.4(A)	25.20	25.034		30.4209	0.8874	22.22
N.W./S 24%B	25.8	25.1(M)	25.7(A)	25.0(M)	25.8(A)	25.7(A)	25.46	25.292	72	30.7344	0.8878	22.45
N.W./S 30%E	25.95	27.9(M)	28.5(A)	28.6(A)	27.9(M)	28.0(M)	28.18	27.994		34.0178	0.8918	24.97
N.W./S 30%	27.1	28.0(M)	28.6(A)	28.5(A)	28.6(A)	28.1(M)	28.36	28.17	0.8229	34.232	0.8921	25.13
N.W./S 36%	27.0	28.0(M)	28.6(A)	28.6(A)	28.7(A)	28.2(M)	28.42	28.23	0.8229	34.305	0.8922	25.19
N.W./S 36%E	26.2	27.6(M)	27.9(A)	28.0(A)	27.5(M)	27.5(M)	27.70	27.517	-	33.4382	0.8911	24.52
6% B/S N.W.	26.85	46.4	45.0	44.4	43.5	-2- 0	44.825	44.529	1.0024	44.4208	0.9039	40.25
12% B/SN.W.	25.9	40.2	39.7	36.6	37.0		38.375	38.122	1.0065	37.8745	0.8964	34.17
12% B/S N.W.	26.7	49.1(M)	49.4(A	50.6(A)	50.9(A)	50.8(M	050.16	49.83	1.0065	49.506	0,8638	46.56
18% B/S N.W.	26.05	47.7	46.8	46.6	46.0		46.775	46.466	1.0095	46.0272	0.9057	42.08
24%B/S N.W	26.4	45.2	43.5	42 0	42.8		43.625	43.337	1.0146	42.7131	0.9020	39.09
24% B/S N.W	26.7	48.1(M)	56.7(A)	55.6(A)	55.5(A	55.4(M)54.26	53.90	1.0146	53.123	0.9134	49.23
30% B/S N.W	26.55	50.2.	49.2	48.8	48.7		49.225	48.900	1.0184	48.0152	0.9079	44.40
36% B/S N.W	26.8	50.8	50.7(N 51.9(A)	50.6	52.0(A) 51.4(M)		51.233	50.895	1.0224	49.7787	0.9098	46.31
S.H./S06% B		27.7(M)	28.4(A)	28,4(A)	28,4(A)	27.7(M)	28.12	27.93	0.8174	34.168	0.892	24.91
S.H./S12% B	27.9	27.7(M)	28.3(A)	28.3(A)	28.4(A)	27,8(M)	28.10	27.91		34.144	0.892	24.89
S.H./S18% B	28.1	27.3 (M	28.1(A)	28.1(A)	28.1(A)	27.6(M)	27.84	27.66	neer regime of treats	33.838	0.892	24.66

FLUID	TEMP.	TEST V	ALUES ON	TENSIO	MAT DYNE	S/CM	AVG.OF TEST VALUES	CALIBRATION CORRECTED	D-d +	P/(D-d) ‡	CORRECTION FACTOR*	SURFACE TENSION
		TEST 1	IESI 2	IESI 3	1E51 4	IESI 5	DY./CM	VALUE DY/CM	GM./CMP	DY. CM-/GM		DY./CM.
S.H./S 24%B	28.05	27.8(M)	28.4(A)	28.5(A)	28.4(A)	27.8(M)	28.18	27.99		34.242	0.892	24.97
S.H./S 30%B	28.1	27.8(M)	28.5(A)	28.4(A)	28.4(A)	27.8(M)	28.18	27.99	-	34.242	0.892	24.97
S.H./S 36%B	28.1	27.8(M)	28.5(A)	28.4(A)	28.4(A)	27.7(M)	28.16	27.97		34.217	0.892	24.95
6%B/S S.H.	27.4	58.3(M)	58.2(M)	60.0(A)	60.9(A)	61.7(A)	59. 82	59.425	1.0024	59.281	0.920	54.66
12%B/s S.H.	27.4	5515 (M)	55.1(A)	55.9(A)	56.4(N)	56.1(M)	55.802	55.432	1.0065	55.072	0.916	50.75
18%B/S S.H.	27.5	56.6(M)	57.3(A)	57.4(A)	57,8(A)	57.8(M)	57.38	57.001	1.0095	56.463	0.917	52.27
24%B/S S.H.	27.55	58.7(N)	59.7(A)	60.5(A)	60.9(A)	61.0(M)	60.16	59.763	1.0146	58.901	0,920	54.95
30%B/S S.H.	27.65	56.9(M)	57.3(A)	57.7(A)	58.4(A)	57.9(M)	57.64	57.260	1.0184	56.224	0.917	52.49
36%B/S S.H.	27.75	56.7(M)	56.9(A)	57.1(A)	57.7(A)	56.9(M)	57.06	56.683	1.0224	55.440	0.916	51.92
N.W.	26.9	27.5(A)	27.4(A)	26.8(M)	26.8(M)	27.5(A)	27.20	27.020	0.8245	32.7719	0.8903	24.06
S.H.	26.5	28.0(M)	27.7(M)	28.4(A)	28.4(A)		28.125	27.9393	0.8190	34.1139	0.8919	24.92
CENTRIFUGE S.H./S 24%E		27.8(M)	28.4(A)	28.3(A)	28.5(A)	27.8(M)28.16	27.9741	0.8190	34.1564	0.8920	24.95
DISTILLED H ₂ O	28.2	72.3(M)	73.3(M)	34.1(M)	73.9(M	73.9(M)	73.50	73.0148	0.9988	73.1014	0.9337	68.17
DISTILLED H ₂ O	28.2	74.4(A)	74.4(A)	74.4(A)	74.4(A	74.5(A)	74.42	43.9287	0.9988	74.0164	0.9345	69.09
DISTILLED H_0	27.5	74.6(M)	74.7(A)	74.4(A)	75.2(A	74.6(M)	74.7	74.207.	0.9988	74.295	0.9348	69.37
6%B/S S.H.	24.7	57.0 m	57.1m	57.9a	58.1a	57.5m	57.52	57.14	1.0024	57.00	0.9176	52.43
12%B/S S.H.	25.6	51.4m	51.9a	52.0a	51.9m	5166nc	51.82	51.48	1,0065	51.15	0.9112	46.91
18%B/ S S.H.	26.65	55.4 m	56.2a	56.4a	56.4a	56.1m	56.10	55.73	1.0095	55.20	0. 156	51.03

FLUID	TEMP.	TEST V	ALUES ON	TENSIO	MAT DYNE	ES/CM	AVG.OF TEST	CALIBRATION	D-d +	$P/(D-d) \neq$	CORRECTION	SURFACE
ТҮРЕ	°C	TEST_1	TEST 2	TEST 3	TEST 4	TEST 5	DY./CM.	VALUE DY/CM	GM./CM ³	DY. CM2/GM	FACTOR*	DY,/CM.
24%B/ S S.H.	25.75	59.4 m	60.1ac	60.3ac	60.5ac	60.0mc	60.06	59.66	1.0146	58.80	0.9194	54.85
30%B/ S S.H.	25.2	59.2m	59.1m	59.9a.	60.9m	60.8m	59.98	59.58	1.0184	58.50	0.9191	54.76
36%B/S S.H.	25.8	56.1m	56.8a	56.7a	57. 0 a.	5 6.9 m.	56.62	56.25	1.0224	55.02	0.9154	51.49
										10 .2	100	1
and the second second					10		· · · · · ·			and her	2. 2	
	No.		- 9							Section .		24. 1
		1						-	a	C. Starte		
	1		20				7		1.1		2 2 2	140
		-									1	
1997 100		-						W		N	1999 B.	10.0
												-
												13 E.
						1.1				-		
	_											
				2					-			
				-								
1						_					1	1
					1			8 8	1.5		1 H P 3	- Jul

APPENDIX C

DATA FOR CALCULATING THE SPREADING COEFFICIENTS

APPENDIX C

In preparing the following tables, values of the surface tensions of the pure liquids (γ_a and γ_b) and of the mutually saturated liquids ($\gamma_{a'}$ and $\gamma_{b'}$) have been taken from the best lines through the data in Figure 30. The values shown have been corrected to account for the 5 percent error in the average value of the measured surface tension of distilled water (68.88 dynes/cm) compared to an average value of 72.44 dynes/cm as reported on page 43 of Adamson (1960). For the mutually saturated liquids which were allowed to stand for twenty-four hours before the measurements, the notation $\gamma_{a'}$ and $\gamma_{b'}$ has been used while $\gamma_{a''}$ represents those samples measured after one week. These values were then corrected to 0°C and the temperature corrected values are shown as γ_a (TC), γ_b (TC), $\gamma_{a'}$ (TC), etc. Spreading coefficients corresponding to the unsaturated and mutually saturated states are represented as S, S' and S", respectively.

Salinity ppt	Υ _a dynes/cm	Υ _a ' dynes/cm	Υa" dynes/cm	Yb dynes/cm	Ϋ́b' dynes/cm	Υ _a (TC) 1 dynes/cm	Ya'(TC)1 dynes/cm	Y _{a"} (TC)1 dynes/cm	Yb(TC) ² dynes/cm	Y _{b'} (TC) ² dynes/cm	Υ _{ab} 3 dynes/cm	S 4 dynes/cm	S' 5 dynes/cm	S" 6 dynes/cm
6 %00	69.9	55.6	54.6		26.2	74.2	60.0	58.7		29.0	26.0	19.3	5.0	3.7
12 0/00	69.9	55.6	54.6		26.2	74.8	60.0	58.7		29.0	26.3	19.6	4.7	3.4
18 0/00	69.9	55.6	54.6		26.2	75.4	60.0	58.7		29.0	26.6	19.9	4.4	3.1
24 0/00	69.9	55.6	54.6		26.2	76.0	60.0	58.7		29.0	26.9	20.2	4.1	2.8
30 0/00	69.9	55.6	54.6		26.2	76.5	60.0	58.7		29.0	27.2	20.4	3.8	2.5
36 0/00	69.9	55.6	54.6		26.2	77.1	60.0	58.7		29.0	27.5	20.7	3.5	2.2
oil only				24.9		N			28.9					

TABLE C-1: DATA USED FOR CALCULATING THE SPREADING COEFFICIENTS FOR SWAN HILLS CRUDE

1. Using $\frac{\partial \gamma}{\gamma T}$ = -0.16 $\frac{dynes/cm}{C}$ [32].

2. Using
$$\frac{\partial \gamma}{\gamma T} = -0.1 \frac{dynes/cm}{C}$$
 [25].

- 3. Calculated using γ_a (TC) and γ_b (TC) in equation 9 with Φ = 0.832.
- 4. Calculated using γ_{a} (TC), γ_{b} (TC) and γ_{ab} in equation 16.
- 5. Calculated using γ_a' (TC), γ_b' (TC) and γ_{ab} in equation 17.
- 6. Calculated as follows: S'' = γ_a '' (TC) γ_b ' (TC) γ_{ab} .

Salinity pp:	Ya dynes/cm	Ya' dynes/cm	Yb dynes/cm	Yb' dynes/cm	Ya(TC) ¹ dynes/cm	γa'(TC) ¹ dynes/cm	Yb(TC) ² dynes/cm	Yb'(TC) ² dynes/cm	Yab 3 dynes/cm	S 4 dynes/cm	S' 5 dynes/cm	t∞ 6 cm
6 0/00	69.9	41.9	-	23.2	74.2	46.1		25.9	26.4	19.7	-6.2	0.29
12 0/00	70.5	43.2	6 1	23.2	74.8	47.4		25.9	26.7	20.0	-5.2	0.27
18 0/00	71.1	44.4		23.4	75.4	48.6		26.1	27.0	20.3	-4.5	0.25
24 0/00	71.7	45.7		23.6	76.0	49.9		26.3	27.3	20.6	-3.7	0.22
30 0/00	72.2	46.9		24.7	76.5	51.1		27.4	27.5	20.9	-3.8	0.22
36 0/00	72.8	48.2	.	26.9	77.1	52.4		29.6	27.8	21.2	-5.0	0.25
oil only		- <u></u>	24.1		24		28.1				. T.	

TABLE C-2: DATA USED FOR CALCULATING THE SPREADING COEFFICIENTS FOR NORMAN WELLS CRUDE

1. Using
$$\frac{\partial \gamma}{\gamma T}$$
 = -0.16 $\frac{dynes/cm}{°C}$ [32].

2. Using
$$\frac{\partial \gamma}{\gamma T} = -0.1 \frac{dynes/cm}{C}$$
 [25].

3. Calculated using $\gamma_a(TC)$ and $\gamma_b(TC)$ in equation 9 with Φ = 0.831.

4. Calculated using $\gamma_{a}(TC),~\gamma_{b}(TC)$ and γ_{ab} in equation 16.

5. Calculated using $\gamma_{a^{*}}(TC)$, $\gamma_{b^{*}}(TC)$ and γ_{ab} in equation 17.

6. Calculated using S' in equation 15 and density data from Table 3.

APPENDIX D

TEST METHOD USED IN DETERMINING SALT CONTENT OF

CRUDE OILS

APPENDIX D - MODIFIED BLAIR METHOD FOR DETERMINING TOTAL CHLORIDE CONTENT OF CRUDE OIL

Scope:

This method is intended as a rapid and reasonably accurate method of determining the total chlorides content of crude oil.

Reference: "Blair Method" ind. Engl Chem., Anal. Ed., 10, 207 (1938).

Apparatus:

- Separatory funnel, 500 ml. a)
- b) Beaker, 250 ml.
- c) Pipette, 100 ml.
- d) Graduate, 100 ml.
- Graduate, 50 ml. e)
- f) Funnel.
- g) No. 41 filter paper.

Regeants:

- a) Benzene, C.P.
- b) Silver nitrate 0.05 N.
- c) Potassium chromate indicator.
 d) Tret-O-Lite Destabilizer "A" or "B".
- e) Sodium bicarbonate, 10% soln.

Procedure:

- 1. 100 ml. of crude oil shall be pipetted from a well shaken sample into a 500 ml. separatory funnel.
- 2. 100 ml. of Benzene shall be added and a drop of Destablilizer A or B in concentrated form. The funnel and contents shall be shaken for 30 seconds.
- Exactly 100 ml. of boiling distilled water shall be added to the 3. funnel and the contents shaken gently, relieving pressure until safe.
- The separatory funnel and contents shall be shaken vigorously for 4. 5 minutes and allowed to settle. Any interface shall be cleared with a warm wire.
- 5. The separated aqueous solution shall be drawn off through filter paper into a 50 ml. graduate, until exactly 50 ml. are obtained.
- The contents of the graduate shall be transferred to a 250 ml. 6. beaker and the graduate rinsed with 25 ml. of distilled water. The washings are added to the beaker.

- 7. The pH of the solution shall be regulated to approx. 6.5 with sodium bicarbonate and the extract titrated with 0.5N silver nitrate using 5 drops of a 5% solution of potassium chromate as indicator.
- 8. The endpoint so obtained shall be matched with a titration using 75 ml. of distilled water and 5 drops of indicator. The volume of silver nitrate required shall be subtracted from the previous titration and the result expressed as pounds of NaCl per 1000 bbls. of crude by multiplying the remaining volume of silver nitrate by 19.8.

Note 1:

The factor, 19.8 takes into account the difference in volume between the water added and the extract withdrawn, due to difference in temperature.

Note 2:

An experimental determination will quickly show which type of destabilizer is most suitable to the crude under test.