On the relationship of the oil/water interfacial tension and the spread of oil slick under ice cover

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Abstract

Oil-spill experiments were carried out to observe the behavior of oil under ice cover in NMRI ice model basin. Oil/water interfacial tension and contact angle of oil/ice/water interface were also measured, using ADSA (Axisymmetric Drop Shape Analysis) method.

As a result, the authors figure out the following: The contact angle of the interface was 180deg., and on the assumption of this contact angle, the measured size of the oil slick under flat ice cover was almost equivalent to the size of a very large axisymmetric oil drop which shape obeys Laplacian equation.

The authors also investigated the past research work of this field, and figured out that the so-called "net interfacial tension" was equal to the twice of oil/ice interfacial tension, under the same assumption of the contact angle described above. The net interfacial tension was first introduced by Yapa and Chowdhury (1989) but its theoretical meaning was not known.

These results were successfully verified by the experiments.

Key words: ice cover, oil spill, slick, interfacial tension, Laplacian equation, ADSA.

1 Introduction

The risk of oil pollution has been arisen in the Sea of Okhotsk from the start of the crude-oil/gas production at the northern Sakhalin offshore. The production in winter season is not yet carried out, but is planned to start from 2004. Therefore the oil spill in the frozen ocean is not a groundless apprehension. However, research and preparation to cope with this serious situation seems not enough in Japan.

To take countermeasures against that, the research project was organized by five research institutes, including the authors, and is working to figure out the behavior and method of withdrawal of spilled oil in a frozen ocean. The authors are in charge of theoretical analyses and fundamental experiments. This study is a part of the research project.

If the oil spills under ice cover, the oil slick may behave under the effect of buoyancy, interfacial tensions between oil/water and oil/ice interfaces, friction from water and ice, and adhesion to the ice bottom. However, these important parameters were not yet formulated clearly, except the buoyancy. In the steady state the interfacial tension is the only force that restrain the oil slick from expanding to thin film so that the formulation of the tension is of vital requirement. Therefore the theoretical analyses in the past were introduced some empirical parameters, "the net interfacial tension" by Yapa and Chowdhury (1989) for example, to analyze the phenomena.

In this study the authors analyzed the effect of the oil/water interfacial tension theoretically, and proposed the formulation of the interfacial tension force and the method to estimate the oil slick size. To verify the theory, oil spill experiments were carried out to observe the behavior of oil under ice cover, in NMRI ice model basin. Oil/water interfacial tension and contact angle of oil/ice/water interface were also measured, using ADSA (Axisymmetric Drop Shape Analysis). These experimental results meet very well to the theory the authors proposed.

2 The state of the art

2.1 Measurement technique of the interfacial tension

There are many method proposed to measure surface or interfacial tension. Major methods are: ring method, hanging plate method, drop weight method, maximum bubble pressure method, capillary rise method, sessile drop method and pendant (hanging) drop method. If you want to measure the interfacial tension but the measurement system specialized in it is not available, the latter three, namely, capillary rise method, sessile drop method or pendant drop method, may be good choices. Because these methods are based on the visual information such as a drop shape, so that these do

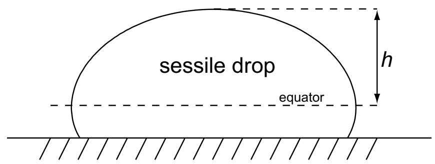


Fig. 1: Sessile drop method: the simplest version

not require accurate weight measurement, opposite to the other methods.

As the sessile drop method is used in this research, the following discussion forcuses on it. This method is based on two assumptions that a shape of a sessile drop is determined by the body force (gravity) and the interfacial tension, and that the shape is axisymmetric. Under these assumptions it derives the surface or interfacial tension from some feature of a shape of a sessile drop on a levelly flat plate. One of the simplest versions of the sessile drop method is measuring the height h from the equator of a drop to the apex, as shown in Fig. 1. Then the interfacial tension σ is derived as

$$\sigma = \frac{1}{2}(\Delta\rho)gh^2, \tag{1}$$

in which $\Delta\rho$ is the difference in the densities of the two bulk phases, and g is the gravitational acceleration.

This version is very simple, but restricted only when the drop size is large enough. In addition, this method requires determination of certain positions of the drop, the equator and the apex, and the accurate measurement of them is difficult. Padday and Pitt (1972) proposed an improved method which uses the height from the flat bottom to the apex. They also proposed the correction scheme to apply their theory to smaller drops.

The above methods make use of only a little information given from the drop shape. There are another versions which use whole points of the measured shape to determine the interfacial tension. The drop shape is a solution of nonlinear differential equations with two arbitrary parameters: a radius of curvature at the apex and the interfacial tension. Therefore the problem comes down to a curve-fitting problem. Rotemberg et al. (1983) proposed the method to determine the interfacial tension by solving the curve-fitting problem. Modern ADSA (Axisymmetric Drop Shape Analysis) is based on their analysis or its variants.

2.2 The interfacial tension of oil in a frozen sea

One of the earliest measurement of crude-oil/water interfacial tension and contact angle were done by Malcolm and Dutton (1979). They measured the interfacial tension using two kinds of crude-oil, flesh water and sea water, with the sessile drop method, and concluded that the interfacial tension was $20 \pm 5\,\mathrm{mJ/m^2}$ and that the contact angle was 180° in every case.

Liukkonen (1996) measured the contact angle of crude-oil/air/ice and crude-oil/water/ice interface, and concluded that the contact angle under ice cover was $159.92 \pm 7.83°$. The authors are doubtful of the accuracy of their measurement, since in their report they only mentioned that the contact angle was “measured by photographing.”

The above studies did not make use of the modern ADSA after Rotemberg et al. (1983). As far as the authors know, not any application of the modern ADSA to oil/water interface under ice cover is reported yet.

2.3 The relationship between the interfacial tension and the final slick radius

If the oil spills under flat ice cover, the oil forms a round slick, thus the slick size can be represented by its radius. The relationship between the interfacial tension and the final slick radius was discussed by Yapa and Chowdhury (1989). They introduced “the net interfacial tension” σ_n, which they considered to be derived from oil/water, ice/water, and ice/oil interfacial tensions and the contact angle. They also carried out the laboratory experiment, and found that these estimation met the experimental results. However, the physical meaning of the net interfacial tension and how to estimate it have not been known.

Here the authors try to formulate the net interfacial tension in different way with that of Yapa and Chowdhury (1989). The interfacial tension force f_t effecting on a unit length of the slick edge is expressed simply as

$$f_t = \sigma_n. \tag{2}$$

The gravity (buoyancy) effects F_g, which expands the slick, is represented as follows, on the assumption of hydrostatic conditions.

$$F_g = \pi(\Delta\rho)gRh^2.$$

The final slick radius can be determined as the radius with which the shrink force $2\pi R f_t$ and expansion force F_g are evenly balanced. That is to say,

$$\frac{1}{2}(\Delta\rho)gh^2 = \sigma_n. \tag{3}$$

Obviously, Eq.(3) corresponds to Eq.(1).

3 Theory of the ADSA

In this study the authors made use of the theory constructed by Rotemberg et al. (1983). The short summary of this theory is explained in this section.

3.1 Differential equations of the oil drop shape

The pressure difference across a curved interface is described by the classical Laplace equation

$$\sigma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = \Delta P, \tag{4}$$

where σ is the interfacial tension, R_1 and R_2 represent the two principle radii of curvature, and ΔP is the pressure difference across the interface.

In the absence of external forces, other than gravity, the pressure difference is a linear function of the elevation

$$\Delta P = \Delta P_0 + (\Delta\rho)gz, \tag{5}$$

where ΔP_0 is the pressure difference at a selected datum plane, $\Delta\rho$ is the difference in the densities of the two bulk phases, g is the gravitational acceleration, and z is the vertical height measured from the datum plane.

Hereafter the sessile drop is assumed axisymmetric, and the datum plane is placed levelly, tangent to the apex. The x and z axes are placed on this plane and on the axis of symmetry, respectively, as shown in Fig. 2. The origin is placed at the apex. Then from Eqs (4) and (5),

$$\sigma\left(\frac{1}{R_1} + \frac{\sin\phi}{x}\right) = \frac{2\sigma}{R_0} + (\Delta\rho)gz, \tag{6}$$

where R_1 turns in the plane of the paper and $R_2 = x/\sin\phi$ rotates in a plane perpendicular to the plane of the paper and about the axis of symmetry. R_0 is the radius of curvature at the origin of the x-z coordinate system. ($R_1 = R_2 = R_0$ at the origin.) ϕ is the turning angle measured between the tangent to the interface at the point (x, z) and the datum plane.

The meridian curve can be represented by the arc length s measured from the origin, as follows:

$$x = x(s), \qquad z = z(s).$$

A geometrical consideration yields the differential identities

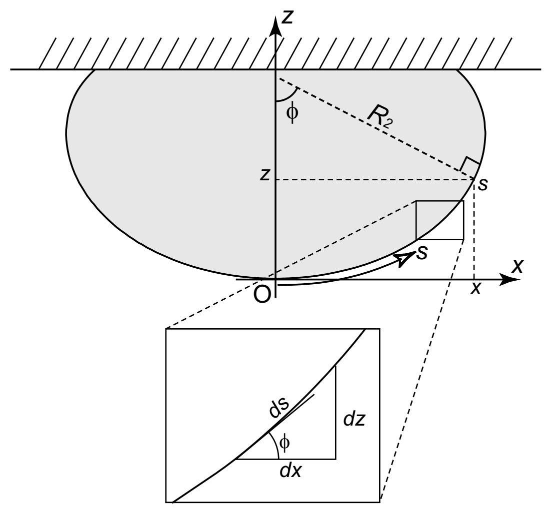


Fig. 2: Definition of the coordinate system

$$\frac{dx}{ds} = \cos\phi, \qquad \frac{dz}{ds} = \sin\phi. \tag{7}$$

By definition

$$\frac{1}{R_1} = \frac{d\phi}{ds} \tag{8}$$

is the rate of change of the turning angle ϕ with respect to the arc-length parameter s. Hence, combining Eq.(6) with Eq.(8) yields

$$\frac{d\phi}{ds} = \frac{2}{R_0} + \frac{(\Delta\rho)g}{\sigma}z - \frac{\sin\phi}{x}. \tag{9}$$

Eqs.(7) and (9), and the boundary conditions

$$x(0) = z(0) = \phi(0) = 0$$

form a set of first-order differential equations for x, z and ϕ as functions of the argument s. For given R_0 and given $(\Delta\rho)g/\sigma$ the complete shape of the curve may be obtained by integrating simultaneously these three equations.

To generalize the discussion, these variables can be non-dimensionalized by R_0, as

$$\bar{s} = \frac{s}{R_0}, \qquad \bar{x} = \frac{x}{R_0}, \qquad \bar{z} = \frac{z}{R_0}.$$

Hence the equations (7) and (9) can be rewritten as follows:

$$\begin{aligned} \frac{d\bar{x}}{d\bar{s}} &= \cos\phi \\ \frac{d\bar{z}}{d\bar{s}} &= \sin\phi \\ \frac{d\phi}{d\bar{s}} &= 2 + \frac{(\Delta\rho)g\,R_0^2}{\sigma}\bar{z} - \frac{\sin\phi}{\bar{x}}. \end{aligned} \tag{10}$$

Here $(\Delta\rho)gR_0^2/\sigma$ is the shape parameter and is often written as β.

3.2 The objective function and the calculation method

The differential equations (10) determine the drop shape with given R_0 and β. To determine the interfacial tension, σ, the reverse estimation, from the shape to R_0 and β, is required. In addition, the position of the apex should also be a parameter to be determined, since it is difficult to accurately measure the apex of the gently curved surface.

Suppose that u_n, $n = 1, 2, \ldots N$ are a set of experimental points which describe the meridian section of an interface and $v = v(s)$ is a calculated Laplacian curve from certain R_0 and β. The objective function is defined as

$$E = \frac{1}{2} \sum_{n=1}^{N} [d(u_n, v)]^2 , \qquad (11)$$

where $d(u_n, v)$ is the normal distance between u_n and the curve v.

Practical method to calculate this objective function is as follows. First, the the differential equations (10) are numerically integrated, using small intervals of s so that a set of points on the curve $(x, z) = (R_0\overline{x}, R_0\overline{z})$ is obtained. Then, the smallest distance d between u_n and (x, z) can be adopted as the normal distance:

$$d^2 = (x - (x_n - X))^2 + (z - (z_n - Z))^2 \qquad (12)$$

in which (X, Z) is the location of the origin.

X, Z, R_0 and β should be determined to minimize the objective function E, by making use of some optimization technique, for example, nonlinear least square method. Rotemberg et al. (1983) used the Newton-Raphson method to determine these parameters, and explained the method to calculate Jacobian and Hessian matrices of E analytically. These matrices are required for the nonlinear least square method. In this study the authors made use of a certain routine in the MINPACK optimization library (Moré et al. (1984)). This routine determines Jacobian and Hessian matrices numerically and implements the Levenberg-Marquardt method.

The differential equations (10) were integrated using 4th order classical Runge-Kutta method.

4 Results of the ADSA measurement

Fig. 3 shows the experimental apparatus to measure the meridian shape of the oil drop. Mechanical oil #10 was provided for the measurement, after blackened by oil-solvent dye. The size of drops was varied so that drops of different shapes were measured.

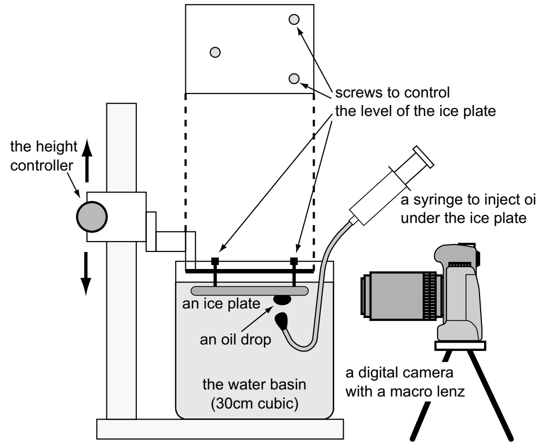


Fig. 3: Experimental apparatus to measure the oil drop shapes

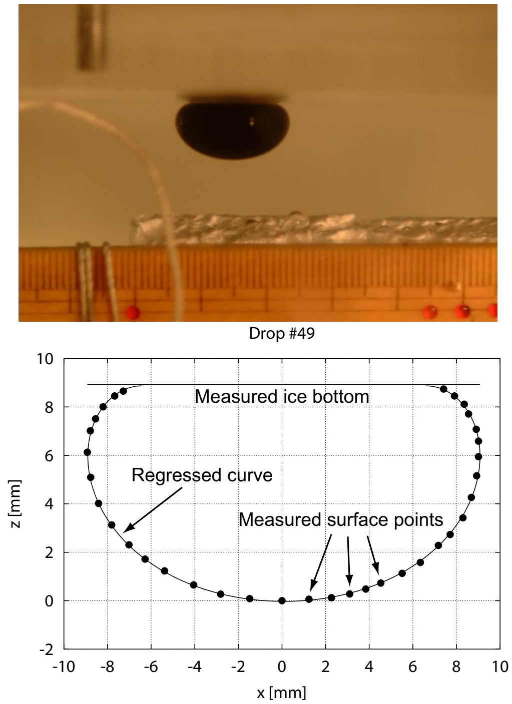
Examples of the drop shapes and measured results are shown in Fig. 4. The average of the oil/water interfacial tension of this oil was $0.0262\,\mathrm{J/m^2}$.

The flat lines in the lower graphs of Fig. 4(a) and (b) represent measured bottoms of the ice sheets. To measure the contact angle, the differential equations (10) is integrated until $z = R_0\overline{z}$ reaches the ice sheet. ϕ at that time is the contact angle. In this measurement, however, the curvature sometimes did not reach the line before ϕ reached 180°, as shown in Fig. 4(a). That was because it was hard to accurately determine the ice bottom from photographs such as Fig. 4.

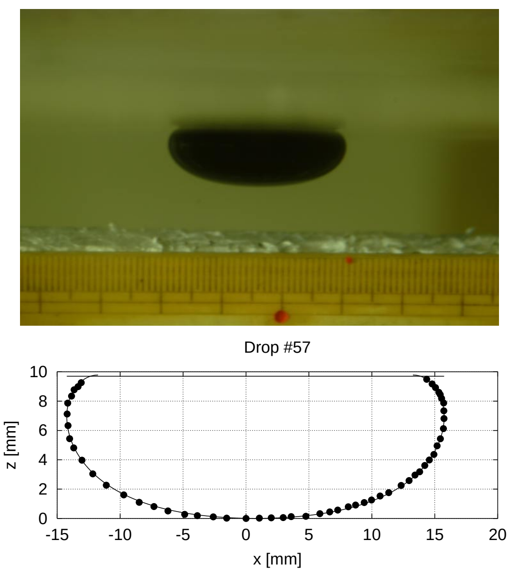
From limited results of the measurement, the authors concluded that the contact angle was near 180°. An evidence of this conclusion is Fig. 5. In this photograph there is a small oil drop which looks completely spherical. That was because the contacting surface is very narrow and can be regarded as a point. Therefore the contact angle comes down to 180°.

5 Prediction of the spread of the oil slick by way of Laplacian equation

From the above measurement, the interfacial tension σ and the contact angle were determined. If, in addition, the radius of curvature at the apex R_0 are given, the shape of the corresponding oil drop (slick) can be calculated by integrating Eqs.(10) from $s = 0$ until $\phi = 180°$. The radius of the slick is the maximum value of $x = R_0\overline{x}$. The volume of the slick can also be calculated by again integrating the shape of the meridian. By varying R_0 parametrically, the relationship between the volume and the radius of the oil slick is obtained.



(a) $R_0 = 13.9756\,\text{mm}$, $\sigma = 25.6086\,\text{mJ/m}^2$



(b) $R_0 = 40.3046\,\text{mm}$, $\sigma = 23.4607\,\text{mJ/m}^2$,
Contact angle: 164.5°

Fig. 4: Examples of the ADSA measurement

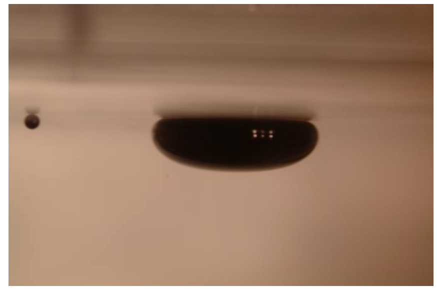


Fig. 5: A photograph of large and small oil drops

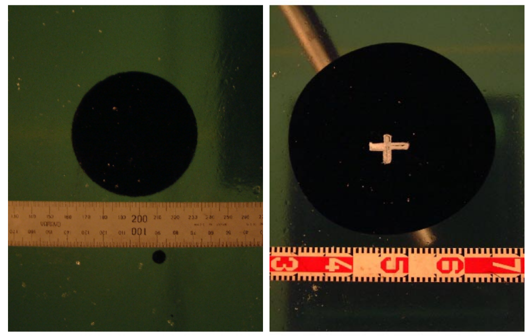


Fig. 6: Examples of photographs of the measured oil slick

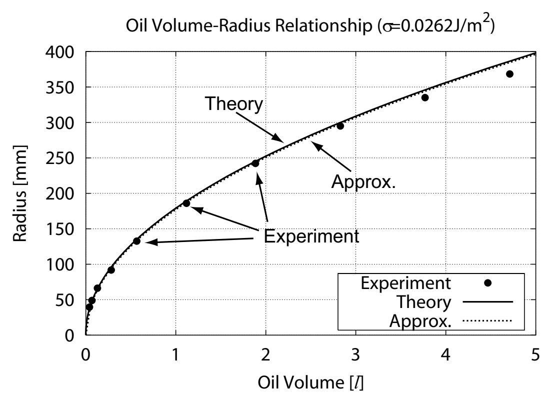


Fig. 7: Comparison of the theoretical estimation and the experimental results of the oil slick radii

The authors carried out the oil-spill experiments using The Ice Model Basin at National Maritime Research Institute. Experimental facilities, conditions and results are reported in Izumiyama and Konno (2002). In this paper the authors limit themselves to a consideration of the results of the experiments under flat ice covers. Fig. 6 shows examples of the oil slicks viewed from above.

Fig. 7 shows the measured results and theoretical estimation of the oil slick radii. The results ('Experiment' in Fig. 7) and estimation ('Theory') meet very well each other, especially in the small volume region. (The line 'Approx.' is discussed in the next section.) In the large volume region there are small descrepancies and the experimental results are smaller than the theoretical estimation. It might be because the radii of the oil slicks were not yet converged so that these were smaller than

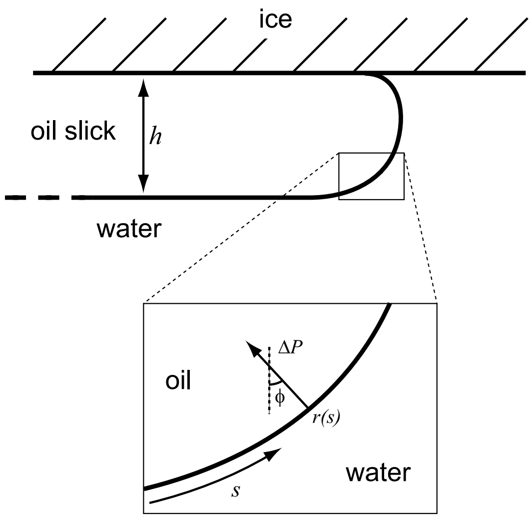


Fig. 8: The illustration of the edge shape of the oil slick and relationship between the position, the radius of curvature and the perpendicular direction of the surface

the final slick radii.

6 Physical meaning of the net interfacial tension

In the preceding section, the authors successfully estimated the relationship between the size and the volume of the oil slick, using only the interfacial tension between water and oil. Therefore it must be possible to identify "the net interfacial tension" σ_n, which was introduced by Yapa and Chowdhury (1989) and is discussed in Section 2.3, using only the oil/water interfacial tension. In this section the authors try to represent σ_n with σ. The following matters are assumed.

1. The bottom of the oil slick is flat, except near the edge, and the edge of the oil slick is smooth.

2. The thickness of the oil slick h is by far smaller than the radius R.

3. Contact angle on oil/water/ice interface is 180°.

By using the radius of curvature on the edge $r = r(s)$, which is defined as shown in Fig. 8, Eq.(4) can be transformed as follows:

$$\begin{aligned}\Delta P &= \sigma\left(\frac{1}{R_1}+\frac{1}{R_2}\right)\\ &\approx \sigma\left(\frac{1}{r}+\frac{1}{R_2}\right)\\ &\approx \frac{\sigma}{r}. \qquad (O(r/R_2) = O(h/R) \ll 1)\end{aligned}$$

In addition, from the geometrical relationship,

$$\frac{d\phi}{ds} = \frac{1}{r}.$$

Therefore,

$$\Delta P = \sigma\frac{d\phi}{ds}.$$

To get the interfacial tension force on a unit length of the slick edge, f_t of Eq.(2), the levelly component of this pressure difference should be integrated.

$$\begin{aligned}f_t &= \int_{\text{arc}} \Delta P \sin\phi\, ds\\ &= \int_{\text{arc}} \sigma\frac{d\phi}{ds}\sin\phi\, ds\\ &= \int_0^{\pi} \sigma\sin\phi\, d\phi\\ &= 2\sigma\end{aligned} \tag{13}$$

Comparing Eqs (2) and (13), the following conclusion is clearly obtained:

$$\sigma_n = 2\sigma. \tag{14}$$

That is to say, the net interfacial tension is twice as mach as the oil/water interfacial tension.

It should be mentioned that the upper limit of the interval of integration in Eq.(13) is equal to the contact angle. Therefore the net interfacial tension and the final slick radius are functions of the oil/ice interfacial tension and the contact angle.

To verify this result by the experiments explained in the preceding section, the approximate relationship between the oil slick volume and radius will be formulated. Suppose the oil slick is large and flat so that the volume V can be approximated to be the product of the thickness and the bottom area,

$$V = \pi R^2 h. \tag{15}$$

In Section 2.3, the relationship between h and σ_n are represented in Eq.(3), namely,

$$\frac{1}{2}(\Delta\rho)gh^2 = \sigma_n. \tag{3}$$

From Eqs.(3), (14) and (15), h is eliminated and the relationship between V and R is derived, as follows.

$$\frac{1}{2}(\Delta\rho)g\left(\frac{V}{\pi R^2}\right)^2 = 2\sigma$$
$$\Leftrightarrow R = \left(\frac{(\Delta\rho)gV^2}{4\pi^2\sigma}\right)^{1/4}. \qquad (16)$$

The comparison between this approximation and the experimental results is shown in Fig. 7, in which the line 'Approx.' shows Eq.(16). It is obvious that the line is very close to the 'Theory' line which is explained in the preceding section. Therefore this approximation meets both the theory and the experiments well.

The fact that the approximation is very close to the theoretical analysis will encourage research attempts at the numerical modeling and simulation of the oil spreading phenomena under ice covers. The interfacial tension should not be neglected for the modeling, since it has a strong effect on the phenomena. In this study its formulation was figured out, and it had not been reported before, as far as the authors know. And it is simple: $f_t = 2\sigma$. That is to say, the interfacial tension force is twice of the oil/ice interfacial tension par a unit length.

7 Conclusions

Theoretical analysis were carried out to clarify the relationship between the oil/water interfacial tension and the oil/water/ice contact angle, and the final slick radius. The results were verified by the experiments. The following conclusions were obtained.

1. The oil/water interfacial tension was successfully measured by the ADSA method.

2. The final slick radius can be estimated if and only if the oil/water interfacial tension is given.

3. The net interfacial tension, introduced by Yapa and Chowdhury (1989), is twice as much as the oil/water interfacial tension, on the assumption that the contact angle is 180°.

Acknowledgments

This study was supported by the Program for Promoting Fundamental Transport Technology Research from the Corporation for Advanced Transport & Technology (CATT).

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水・油界面の界面張力と平坦氷板下での油拡散との相関について

On the relationship of the oil/water interfacial tension and the spread of oil slick under ice cover

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サハリン沖の大陸棚における油・ガス田開発の本格化に伴い，オホーツク海における油流出事故に対する懸念が高まっている。現在は冬季の油採掘は行なわれていないが，2004 年からは冬季を含む通年での採掘が予定されている。そのために氷海域での油流出事故の危機が現実のものとして急浮上し，その対策が求められている。しかしながらこの問題に対する日本での研究や技術開発は例が少なく，まだ十分とは言えない。

この事態への対策を取るべく，5 研究期間からなる研究プロジェクト「氷海域における流出油の挙動と回収に関する基礎的研究」が組織された。著者らはそのプロジェクトの一員として，主に理論と基礎実験を担当している。

氷板下に油が流出した場合，その油層の挙動を支配する要因には，油の浮力，氷・水・油の各界面での界面張力，水および氷下面との摩擦力，氷下面への付着などがある。流れや氷の移動が無い静的な状態では，これらの要因のうち油の浮力と界面張力とが支配的である。しかしこれらの支配パラメタの明確な定式化は，浮力を除き，これまで行なわれていなかった。そのために例えば氷下面での油拡散を定量的な意味で予測したり，数値シミュレーションすることはできなかった。

本研究では，まず Rotemberg et al. (1983) によって開発された ADSA (Axisymmetric Drop Shape Analysis) と呼ばれる界面張力計測手法を適用し，供試油と水との界面張力および氷・水・油界面の接触角を測定した。接触角はほぼ 180° であった。次に ADSA の基礎理論を適用し，平坦氷板下に流出した油についてその体積と拡散半径との関係を理論的に導いた。導出された結論は，海上技術安全研究所にて行なわれた実験結果とよく一致した。なお実験の詳細は Izumiyama and Konno (2002) を参照されたい。

また，過去の研究で用いられていた「正味の界面張力」(net interfacial tension) と呼ばれる経験定数について，その物理的意味を検討した。この正味の界面張力は Yapa and Chowdhury (1989) が導入したものだが，これまで物理的な意味が明確でなかった。本研究で検討の結果，接触角が 180° との仮定の下に，正味の界面張力は水・油界面の界面張力の 2 倍で与えられることを見出した。この結果を用いて油の拡散範囲を近似的に求めたところ，上記の理論および実験結果とよく一致した。

本研究は平坦氷板下での油拡散について調査したものだが，得られた結論は一般的なものであるため，氷板下の油拡散の数値モデルを構成する際に利用できる。オホーツク海のような凹凸氷板下での油拡散を予測する場合，理論解析のみで予測するのは不可能なので何らかのモデル化を行ない数値計算に供する必要があるが，その際に重要な因子である界面張力のモデル化を提案するものである。具体的には，界面張力に起因する単位長さ当たりの収縮力は，水・油界面の界面張力の 2 倍に等しい。本研究の成果を踏台として，氷海域での油拡散予測に関する研究が推進されることを期待する。

本研究は運輸施設整備事業団「運輸分野における基礎的研究推進制度」による研究の一環として実施された。