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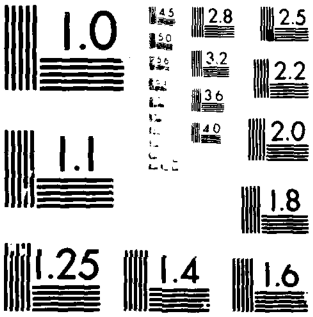

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Chemical Demulsification of Tanker Crude Emulsions

RALPH C. LITTLE

Combustion and Fuels Branch
Chemistry Division

February 13, 1980

NAVAL RESEARCH LABORATORY
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The chemical demulsification of tanker crude emulsions was studied as a function of oil type (light vs. heavy crude), demulsifier concentrations, and temperature. Aerosol OT shows promise as a chemical demulsifier of tanker crude emulsions provided that ambient temperatures are not too cold and that an appropriate concentration range is used for specific oil. The evaporation rates and viscosities of the six crudes studied are also reported in the text.

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SUMMARY

The chemical demulsification of tanker crude emulsions was studied as a function of oil type (light vs. heavy crude), demulsifier concentrations, and temperature. Aerosol OT shows promise as a chemical demulsifier of tanker crude emulsions provided that ambient temperatures are not too cold and that an appropriate concentration range is used for a specific oil. The evaporation rates and viscosities of the six crudes studied are also reported in the text.

CHEMICAL DEMULSIFICATION OF TANKER CRUDE EMULSIONS

I. INTRODUCTION

The successful resolution of oil spill problems requires that the available clean-up equipment be quickly transported to the site of the spill, weather permitting. The Navy is involved in an effort to develop a worldwide oil spill response capability through the use of strategically located pollution response centers (1). A matrix of such centers worldwide would insure that a given center would be reasonably accessible to the site of a given oil spill. In general, oil spill equipment may be rapidly transported from these centers to the spill with one notable exception - the oil barges or their equivalent which are required to store and transport the collected material. It is obvious that the initial functioning of oil spill clean-up equipment is dependent upon the available barge capacity in the vicinity of the oil spill while awaiting additional units from the response center. Efficient use of the available barge units then is central to the success of the oil clean-up operation.

Unfortunately, as a result of weather conditions or equipment limitations, significant quantities of seawater can be entrained or emulsified with the collected crude oil. With seawater concentrations in the collected emulsions averaging 50% but running as high as 75% the efficient use of the available barges is seriously compromised. Unless this water is separated from the recovered oil, the barge oil storage capacity would be needlessly taken up by seawater rather than oil. If an oil/water separator system, either mechanical, chemical, or some combination

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of the two, can be devised to separate the seawater from the oil and return the sea water to the environment at the oil spill location then efficient barge use will be maintained. This report deals with a chemical method to assist the separation of oil and seawater under ambient conditions of temperature. In order to provide as broad a base as possible, a variety of tanker crudes representing oil fields in different parts of the world have been selected for the purpose of providing a realistic test of the chemical demulsification technique. This report is concerned with the results of those tests.

II. EXPERIMENTAL

Materials

Six 1 gallon samples of crude oils were kindly supplied by the Exxon Corporation, Baytown Texas Facility. Thev were labeled as Prudhoe Bay, BCF44, Ivory Coast, English, Arabian Heavy and Nigerian Mix.

The sodium dioctyl sulfosuccinate was obtained from American Cyanamid as a 75% active "Aerosol OT" solution. The remainder was water and approximately 5% of a lower alcohol to provide fluidity.

The artifical seawater used was made up by dispersing and dissolving the recommended amount of "sea salt" (Lake Products Company) in distilled water.

Methods

The processes used in emulsion production and destabilization may be represented as follows:

Emulsion Making

Water/Oil System $\xrightarrow{\text{Homogenizer}}$ w/o Emulsion $\xrightarrow{\text{Time}}$ Aged w/o Emulsion

Emulsion Breaking

Aged w/o Emulsion + Demulsifier $\xrightarrow{\text{Mixing}}$ Destabilized Emulsion $\xrightarrow{\text{Time}}$ Water/Oil system

A previous report (2) suggested that aging the emulsion for one or two days greatly reduced the experimental variations found when fresh emulsions were demulsified. In addition, emulsions found in practice would likely be at least several days old before they were collected. Accordingly, all emulsions were aged before chemical demulisifier was applied.

A Virtis homogenizer was used to form the emulsion and an ultrasonic probe (Branson Sonic Power Model S-75) to mix demulsifier with 25 ml samples in 50 ml plastic vials followed by separation in 25 ml test tubes. Ultrasonic mixing was 30 seconds and the samples were precooled to avoid temperatures in excess of that desired. In each case, samples were placed in a constant temperature bath maintained at ± 0.1°C and volume readings of the separated water layer taken at selected time intervals and recorded.

All rheological measurements were made both with a Brookfield Model LVT rotary viscometer and a series of Cannon-Fenske Capillary viscometers.

Evaporation Studies

The evaporation experiments were of two types -- preparative, to obtain the required sample for viscosity and chemical demulsification measurements and analytic, to obtain information on the evaporation process. In the first case, 400 ml of crude oil were placed in 1000 ml beakers and allowed to evaporate for two weeks within the laboratory hood. Within the context of this report, a sample thus prepared was termed "an evaporated crude." The total loss of material from the sample (directly weighed by a 2 kg. capacity Torbal balance) during this period of time was designated as the percent "volatiles" lost. It is admitted that the process of evaporation is a continuing one and that had the evaporation period been increased to several months, some slight increase in percent "volatiles" lost would have been observed. In the second case, samples of crude oil were place in Petri dishes (7.25 cm. radius and 1.9 cm. wall height) to a thickness of 0.4 cm. The air flow over the sample was adjusted to a velocity of 5 mph. The loss in sample weight was monitored by a Statham transducer cell to which was attached a load cell accessory with its output feeding a recorder. It was found that the experimental data could be plotted as time/percent weight lost vs. time showing a strong linear dependence (equation discussed in later section). From such plots, an estimate of percent "volatiles" lost at infinite time could be made. Such estimates tended to be only one to three percent higher in absolute value than the two week beaker results, i.e., English crude 25.6% vs. 24.3%; Ivory Coast crude 19.2% vs. 18.1% etc.

Surface Tension - Log Concentration Calibration Curve

A calibration curve of surface tension vs. log concentration for solutions of Aerosol OT in artificial seawater was made up using an automated Whilemy plate method. In this method, the downward pull on a flat plate just touching the surface or interface is measured. The pull is then $F = 2 (l + t) \gamma$ where l is the length of the plate in the interface, t is its thickness and γ is the surface tension. The measurement of the force, F, in the NRL equipment was made by attaching the plate to a Statham transducer cell with its microbalance accessory. The output of the cell, via its readout device, was fed to a Hewlett-Packard recorder. The thin platinum plate used was sandblasted to promote wetting by the solutions tested. The plate was cleaned in hot chromic acid between surface tension measurements. Sensitivity of the method is limited to concentrations above 2.2×10^{-6} M/l (1 ppm). In order to make quantitative measurements accurately below 10^{-6} M/l, account must be taken of surfactant adsorption onto the glass surfaces used in making dilutions and in the container used for making the measurements. Calculations suggest that adsorbed surfactant will amount to approximately 10^{-8} moles of Aerosol OT (assuming monolayer coverage). Thus, this approximately sets the lower qualitative limit for the analysis technique. The critical micelle concentrations (CMC) for the surfactant is 1.63×10^{-4} M/l in artificial seawater. The CMC properties of this sample are reported in Table 1 in 0.633 N sodium chloride and in distilled water. Comparison of this sample with literature data for both commercial and pure species is also reported in the Table. Apparently, the present sample has CMC properties which more closely resemble that of the 2-ethylhexyl salt than the n-octyl salt. It is further noted that the CMC of the present sample is lowered by an order of magnitude in artificial seawater. Surface tension data for this sample in various solvents are reported in Figures 1 to 3. The absence of minima in the surface tension plots suggests a reasonable purity for the sample used in this study.

Aerosol OT Distribution Experiments

Ten ml of 3.4×10^{-3} molar solution of Aerosol OT were pipetted into a 30 ml wide mouth glass jar. Ten ml of raw tanker crude were then added. The jar was sealed using an aluminum foil liner and then vigorously shaken. Jars were set aside for a 6 day period before measurements were made.

Two ml of the aqueous layer were removed using a glass syringe with hypodermic needle. The needle penetrated the oil phase through the aid of a protective glass capillary to minimize contamination of the syringe needle. Several ml of solution were then filtered through a Millipore 0.1μ filter which prevented entry of any oil microdroplet which might cause sufficient surface contamination to produce anomalous surface tension readings. Additional calculations and experiments showed that the filter caused negligible removal of surfactant. One ml of filtered solution was next diluted to 10 ml of solution with artificial seawater and surface tension measurements subsequently made.

III. RESULTS AND DISCUSSION

Viscosity of Tanker Crudes

The viscosities of the tanker crudes varied greatly with their origins and were strongly affected by the temperature and the "volatiles" lost through evaporative processes (see Table 2). For example, the loss of volatile light fractions, which range from approximately 18% to 36% by weight depending on the crude oil, result in viscosity increases of the order of two to seven times at 50°C to as much as twelve to thirty-five times at 0°C. Such substantial changes in viscosity of well over an order in magnitude may significantly affect the resultant viscosity of water-in-oil emulsions and, subsequently the ease with which these emulsions may be broken through use of chemical demulsifiers, as will be shown later. The crudes were essentially Newtonian in their flow properties and their viscosities could be described by means of the Walther equation (3):

$$\text{Log}\,\log(\nu + \kappa) = A + B \log T$$

where κ = 0.6 for most oils

ν = kinematic viscosity (cs)

T = absolute temperature (°K)

A, B = constants to be determined for each oil

Table 3 lists data for the six crudes studied. Walther equation constants for both the raw crude and the evaporated crude are given in the Table together with limited data for the intermediate, partially evaporated crudes. Unfortunately, the constants A and B did not vary in a predictable fashion with the percent "volatiles" lost so that a Walther equation expressing viscosity-temperature relations as a function of "volatiles" lost could not be constructed easily. However, the viscous properties of the raw crude and the evaporated crude are of principal interest in this report. The Walther equation for the raw and evaporated crudes permits a reasonable estimation of viscosity in the 0° to 50°C range for these crudes.

Figure 4 features ASTM - derived viscosity-temperature plots for the six oils tested. For the purpose of this report, light crudes are considered to be those oils whose kinematic viscosities at 25°C are below 10 cs.; heavy crudes are those above 10 cs. In the figure, both the raw crudes and the evaporated crudes are plotted for purposes of comparison. The two crudes showing the higher temperature coefficient of the viscosity were the Ivory Coast and Nigerian Mix crudes both in the raw and evaporated states. These two crudes also show evidence of substantial wax content because on evaporation a surface crust was observed. The raw crudes range from slightly more than 3 cs. to nearly 27 cs. at room temperature while the evaporated crudes range from 21 cs. to 180 cs. On the average, the crudes increase 6-fold in viscosity through evaporation of "volatiles." Of special interest are the low temperature viscosities which range from slightly less than 7 cs. for the BCF41 crude to 3000 cs. for the evaporated Arabian Heavy crude at 0°C.

The viscosity of seawater-in-crude oil emulsions may be estimated by use of the Richardson equation (4). A previous report (2) suggested that the viscosity data of emulsions of seawater in residual type oils approximately followed the expression

$$\log \frac{\nu}{\nu_o} = 2.70\ \phi$$

where ν = kinematic viscosity of emulsion

ν_o = kinematic viscosity of oil

ϕ = volume fraction of seawater

Using this equation as a tool, Table 4 was generated to determine the approximate range of emulsion viscosities which might be expected from the crudes.

For example, high volume fractions of seawater in the evaporated Prudhoe Bay and Arabian Heavy crudes produce emulsions of extremely high viscosity, i.e., of the chocolate-mousse type especially at temperatures as low as 0°C. Such highly viscous emulsions may present additional problems in collection, handling, and chemical treatment. However, a warming of such emulsions to 25°C greatly reduces their viscosity and they should become less intractable as a result. Emulsions generated with the lighter crudes, i.e., BCF44, English and Nigerian Mix, remain quite fluid even at 0°C and therefore should be easily collected and treated.

The chemical demulsification of seawater in crude oil emulsions will be dependent upon the collision rate between particles. That is, after the chemical demulsifier is thoroughly mixed with the emulsion and steady state conditions are reached, the flocculation rate, a, may be approximated by (assuming each collision is beneficial).

$$a = \frac{2\kappa T}{3\rho\nu D}$$

Where κ = Boltzman Constant

T = absolute temperature

ν = viscosity of continuous phase

D = diameter of drop

ρ = density of continuous phase

It is clear that the flocculation process is a necessary precursor to coalescence (5) and that large values of viscosity will greatly inhibit flocculation. This will be developed further in the demulsification data to be discussed later.

Evaporation of Tanker Crudes

The evaporation of "volatiles" both contributes to the loss of hydrocarbon mass and to significant changes in the physical properties of the remaining oil. The remaining oil may become at once both more viscous and more concentrated in natural water-in-oil emulsifiers such as the asphaltenes (6). The evaporative flux of volatile crude oil components has been estimated through use of Raoult's law (7), the resultant equation having the form

$$N_i^e = K_e X_i \; P_i/RT$$

where N_i^e = evaporative flux of component i
K_e = evaporative mass transfer coefficient
X_i = mole fraction of component i
P_i = vapor pressure of pure component i
R = gas constant
T = air temperature above the oil

This relation assumes ideal solutions wherein the heat of mixing is zero. In practice, crude oils are non-ideal mixtures of components having widely varying solubility parameters (8). In such cases, the evaporative flux equation might perhaps best be modified to

$$N_i^e = K_e \gamma_i X_i \frac{Pi}{RT}$$

where γ_i is the activity coefficient defined by the relation

$$\ln \gamma_i = \frac{V_i}{RT} (\delta_i - \bar{\delta})^2$$

and V_i = molar volume of components

δ_i = solubility parameter of the component i

$\bar{\delta} = \sum_{i=1}^{n} \phi_i \delta_i$

and ϕ = volume fraction

At any rate, it was felt that the precise calculation of evaporation rates of non-ideal crude oil systems might be difficult to treat in such a manner. Therefore, evaporation experiments were performed in the laboratory hood to obtain the necessary data (see experimental section for details). It was found that the experimental data conformed rather well to an empirical equation of the type

$$\frac{W}{W_m} = \frac{t}{t_{1/2} + t}$$

where W = weight percent "volatiles" lost at time t

W_m = initial weight percent "volatiles" of oil

$t_{1/2}$ = time when 50% of "volatiles" have evaporated

Figure 5 illustrates the plots obtained for two different crudes. The reciprocal of the slope yields the percent "volatiles." The half life is determined from the reciprocal of the slope times the intercept at t = 0. Table 5 lists the data obtained from the evaporation experiments. The initial evaporation rates, R_e, were estimated by differentiating this expression and incorporating the area of the Petri dish i.e.

$$R_e = \frac{t_{1/2}\, W_m}{A\,(t_{1/2} + t)^2}$$

where W_m = original weight of "volatiles" in sample

$t_{1/2}$ = half life in seconds

t = time in seconds

A = area of dish in cm^2

$$R_{t=o} = \frac{W_m}{At_{1/2}}$$

In general, the initial evaporation rates of the crudes were quite similar and varied only by a factor of 2 with the exception of the Prudhoe Bay sample where the evaporation rate was an order of magnitude lower. Figure 6 presents evaporation rate curves for the six crudes, over a three-hour period. In spite of differences in origin and viscosity, the five samples form a fairly narrow envelope of curves with the exception of the Prudhoe Bay sample. After three hours, at 25°C (approximately 1/2 day at 0°C), essentially 95% of the "volatiles" have evaporated from the 4 mm layers of the 5 crude oil samples at the 5 mph wind condition.

Evaporation rates at lower temperatures, for example 5°C, may be estimated by application of the earlier expression relating evaporative flux and the other physical factors together with the Clausius-Clapeyron equation as follows:

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H_{vap}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Since $\Delta H_{vap} \cong 100$ cal gm for most organic components and the expected molecular weight range for "volatiles" is in the range of 60 to 110, an approximate change in total vapor pressure for such a mixture would be

$$\ln \frac{P_2}{P_1} = -1.02, \text{ hence } P_2 \cong 0.36\ P_1.$$

Correcting for temperature leads to a decrease in the initial evaporation rate of $\cong 0.38$. The half life, $t_{1/2}$, would therefore be 2.6 times longer at 5°C than at 25°C. The Petri dish data might also conceivably be extrapolated to larger pool sizes representative of oil spills and to higher wind velocities through use of Sutton's equation (9) for the mass transfer coefficent, κ_e, i.e.

$$\kappa_e = C\ U^{0.78}\ D^{-0.11}$$

Where C is a constant, U is the velocity and D is the pool diameter.

The Mackay-Leinonen Oil Spill Model

Mackay and Leinonen (7) have developed a mathematical model which describes the spread of oil spills on water and which accounts for the loss of volatile oil components into the air phase and the dissolution of oil components into the water phase. These processes have been developed as a function of sea state and temperature for a model crude oil (7). The equations developed for these processes are relatively simple and a computer program has been written to determine critical data -- in terms of remaining oil, slick diameter, evaporative and dissolution losses etc. -- as a function of sea state, temperature and time. The results of the analysis conform to expectations and are not in conflict with reality. In the words of the authors, "numerical solutions of the equations for evaporation, dissolution and dispersion, combined with solutions of the spreading and horizontal diffusion equations as empirical correlations, might yield reasonable results" with regard to the fate of oil components and spreading of the slick.

The treatment of Mackay and Leinonen, however, was restricted by the authors to a non-emulsified oil slick. The authors avoid emulsions considering that processes such as evaporation would be seriously affected by emulsion formation. Therefore, it is of interest to determine to what extent the presence of seawater in a 50% water-in-oil emulsion will affect the evaporation process. If a gross effect obtains then it will be necessary to devise an empirical factor or function (if possible) to modify the evaporation equation bringing it into coincidence with experimental observations.

If the perturbation is minimal it will be possible to use the Mackay-Leinonen analysis virtually unchanged to determine vital oil spill parameters. In principle, then, it may be possible to insert the required physicochemical data into their model (i.e., ASTM distillation curve, oil component solubility data etc.) and estimate the remaining oil characteristics as a function of temperature, sea state and time. A knowledge of residual oil characteristics will be useful in estimating the oil slick threat and planning for its removal and processing.

Evaporation of Volatile Hydrocarbon Components from a Seawater-in-Oil Emulsion

The evaporation of a crude oil slick is important in that the loss of volatile components tends to (1) increase the viscosity of the remaining crude and (2) increase the concentration of natural emulsifiers in the crude, perhaps further changing the solubility characteristics of these emulsifiers. The net effect of the evaporative process will result in a greater amount of chemical demulsifier being required to break a water-in-oil emulsion formed with the evaporated crude as compared with the raw freshly spilled crude. There are two extreme cases which may be considered in the combined evaporation-emulsification process (assumed to take place under isothermal conditions). They may be represented schematically as follows:

Case I

$$\text{Raw Crude} \xrightarrow[\substack{t_v \\ \text{S.S.}\,(\leq 1)}]{\text{Evaporation}} \text{Evaporated Crude} \xrightarrow[\substack{t_E, E_m \\ \text{S.S.}\,(\geq 2)}]{\text{Seawater}} \text{Emulsion}_E$$

Case II

$$\text{Raw Crude} \xrightarrow[\substack{t'_E, E_m \\ \text{S.S.}\,(\geq 2)}]{\text{Seawater}} \text{Emulsion}_R \xrightarrow[\substack{t'_v \\ \text{S.S.}\,(\leq 1)}]{\text{Evaporation}} \text{Emulsion}_E$$

In Case I, the raw crude first evaporates losing its volatile components over the time interval, t_V, under calm conditions (sea state $\leq 1.$). After completion of this process, the sea state is sufficiently increased so that the mixing energy, E, supplied to the evaporated crude in the time interval, t_E, produces a seawater-in-evaporated crude emulsion (emulsion$_E$). In Case II, sea water is immediately emulsified into the fresh crude under appropriate sea state conditions (S.S. ≥ 2) over the time period t'_E producing a seawater-in-fresh crude oil emulsion (emulsion$_R$). After emulsification, the sea state returns to calm conditions and evaporation occurs over the interval t'_V producing a seawater-in-evaporated crude emulsion (emulsion$_E$). The most generalized case, of course, is a combination of Cases I and II with evaporation and emulsification taking place concurrently. Diffusion and dissolution processes into the water column will be neglected in the following discussion. It is clear that if the dispersed water significantly impedes the evaporative process, $t'_V >> t_V$, Case I would then appear to have the capability to produce more viscous emulsions at a given volume fraction of seawater than Case II since $\log \frac{\nu_E}{\nu_o} = 2.70\phi$ (3). Clearly, an increase in oil viscosity, ν_o (as a result of evaporation) at constant volume fraction, ϕ would significantly increase emulsion viscosity, ν_E, thus greatly favoring the probability of producing a chocolate-mousse type emulsion. The distinction (or lack of distinction) between these cases is considered in the next section.

Evaporation of Volatile Hydrocarbons from a Emulsion-Experimental Data

Evaporation experiments were devised simulating a 5 mph wind blowing over a 4mm thickness of (a) a raw crude oil, BCF 44 and (b) an emulsion of 50% ethylene glycol in BCF 44. Ethylene glycol was chosen because of its negligible vapor pressure and the ease with which reasonably stable glycol-in-oil emulsions could be made, thus avoiding additional complicating evaporative weight losses had water been used. The mean droplet size of the dispersed glycol was observed in the microscope to be roughly 10 microns and was thus comparable to a seawater-in-oil dispersion. The crude oil and the emulsion were placed in Petri dishes whose weights were monitored by Statham load cells.

Figure 7 reports the evaporative loss data as a function of time for both the raw crude and the emulsion. It is clear that the evaporation losses in the emulsion (based on the oil content) are nominally the same as with the raw crude. The incorporation of micro-droplets of ethylene glycol into the fluid medium apparently does not sufficiently lower the diffusivity of the volatile components to the surface layer to the point that transport across the interface into the gas phase is affected. Figure 8 is a re-plot of the same data into a form consistent with conformity to the proposed earlier equation in this report. At any rate, the evaporation of emulsions may, to a good approximation, be treated exactly as the raw crude. Moreover, the distinction between Case I and Case II of the previous section becomes minor and the mass transport of "volatiles" into the gas phase is not influenced by the sequence of the emulsification and evaporation steps.

Figure 9 shows the computed growth of emulsion viscosity with time for a raw Arabian crude emulsion at two temperatures, 0°C and 25°C. The solid line represents a 75% emulsion wherein evaporation difficult to separate demulsifier concentration effects with the equipment used and the statistical design, therefore, was not pursued further. The evaporated BCF 44 emulsion was quite stable and the effect of added demulsifier is shown in Figure 11. Small amounts of demulsifier of the order of 0.1% work best; larger amounts are tolerated but at lower emulsion breaking efficiency. While the raw crude was easily demulsified in several hours, even at 1°C, the evaporated crude requires about a day at the 0.1% demulsifier level. While the curves suggest that lower concentrations would work better, it was found that slightly lower concentrations were quite ineffective. It is concluded that light crudes require minimal amounts of demulsifier and that small amounts in 0.02% increments be cautiously added to determine optimum working concentrations.

On the perhaps arbitrary basis of viscosity, Ivory Coast, Arabian Heavy and Prudhoe Bay crudes are classified as heavy crudes for the purposes of this report. Ivory Coast was somewhat unusual in that its raw crude emulsions appeared slightly more difficult to break than in its evaporated form (see Figures 12, 13 and Table 8). Nevertheless, very minimal amounts of demulsifier - in the range of 0.04% to 0.1% - are effective in breaking its emulsions over a wide range of temperatures. The Prudhoe Bay and Arabian raw crude emulsions offer more substantial resistance to demulsification at 34°C (Fig. 12). The demulsification characteristics of both crudes are quite similar with respect to concentration. Separation of oil and water at this temperature is achieved in an hour or less at demulsifier concentrations as low as 0.1%.

Some mild acceleration in demulsification rate occurs above the 0.5% level but not enough, perhaps, to justify the economics of such an increase. At 1°C (Fig. 13), the Prudhoe Bay emulsion sample appears most resistant to demulsification. Periods of several weeks are required to separate the oil and sea water at concentrations as high as 0.7% demulsifier. The Arabian Heavy raw crude emulsion sample may still be broken at this temperature well within a 24-hour period. The evaporated heavy crude emulsions - with the exception of the Ivory Coast sample - represent the most difficult case for the chemical demulsifier technique. Figure 14 reports the demulsification curves at 1°C for emulsions of Prudhoe Bay, Arabian Heavy together with the residual type oils, #6 fuel oil and Navy Special Fuel Oil (NSFO). When working with heavy evaporated crudes and residual oils, it is extremely difficult to mix the demulsifier with the emulsion since viscosities of several hundred thousand or more are involved. For the evaporated crude and residual oil data, it was necessary to double the mixing time to properly dispense the demulsifier through the thick chocolate-mousse like mass - otherwise separation would not take place. At such low temperatures, however, emulsions of residual type oils and probably some aged weathered heavy crude emulsions will give responses similar to the upper two curves of Fig. 14. Such emulsions are thoroughly intractable at such low temperatures and cannot be broken at ambient conditions. Both heat and mixing energy are required in substantial amounts, in addition to demulsifier, to bring about phase separation. Interestingly, the Arabian Heavy and Prudhoe Bay emulsion samples could be demulsified if the 30 second ultrasonic mixing period was doubled to 1 minute - otherwise phase separation would not take place.

At 34°C (Fig. 15), all of the emulsion samples could be easily broken in several hours using 0.3 to 0.4% demulsifier. Both the NSFO and #6 fuel oil have reversed their position with respect to the evaporated crudes at this higher temperature. In short, the chemical demulsification of a large variety of light, heavy, raw or evaporated crudes is achievable under ambient conditions provided temperature conditions are not too severe. Chemical demulsification will proceed easily in ambient tropic conditions. Under artic conditions, however, chemical demulsification will become much more difficult with additional heat and mixing energy being required to bring about phase separation.

Agent Solubility and Toxicity

The fate of the chemical demulsifier is of some importance. If the demulsifier goes predominately into the salt water phase, economic and ecological considerations will obviously be of concern. If the demulsifier concentrates in the oil phase, some reuse of the demulsifier may be possible. Specifically, admixing the separated agent-containing oil with incoming untreated emulsion may be sufficient to either break the emulsion or require lower increments of agent for demulsification. For example, a rough calculation suggests that the admixing of 1 part agent-containing oil (separated from a 75% water-in-oil emulsion) to 2 parts of untreated 75% emulsion would require one half as much demulsifier for effective demulsification (assuming all the agent goes into the oil).

Preliminary studies of the distribution of Aerosol OT between various tanker crudes and artificial seawater suggest that the demulsifier overwhelmingly goes into the oil. The experiment was performed as follows. Equal volumes of seawater (containing 0.15% OT) and tanker crude were vigorously shaken together in small jars and allowed to stand for 6 days at 25°C. Samples from the aqueous layer were withdrawn and analyzed by surface tension measurements. In spite of the fact that OT is a powerful surface tension lowering agent - even at several parts per million - only extremely minute amounts were present in the seawater phase. Table 9 summarizes the results for the six EXXON tanker crudes. The concentrations of OT in the seawater phase range well below 1 ppm. At such low concentrations, heroic measures must be taken to account for and to minimize adsorption of surfactant on the containers of the equipment being used. For all intents and purposes, the demulsifier is quantitatively extracted into the oil phase. It is clear that the use of this demulsifier will not result in any observable toxicity problem to the environment. While data do not appear to be available for marine species, laboratory experiments indicate the oral LD_{50} for mice to be approximately 1 gm./kg. Various species of laboratory animals have been fed doses as high as 0.87 gm./kg. daily for as long as six months without evidence of toxic effect (10).

Proposed Test for Seawater Content in Crude Oil Emulsion

It is of some importance to determine the seawater content of suspected oil slick emulsions. While some emulsions may obviously suggest high water content, e.g. the chocolate-mousse type, other emulsions may be relatively thin and nearly black in color yet contain high levels of seawater. There are, then, two basic reasons for the determination of emulsion seawater content: (a) to estimate the level of seawater in the emulsion for pre-treatment purposes and (b) to help establish the feasibility of demulsification treatment when considered with other factors.

The proposed test for seawater level in tanker crude emulsions is based on chemical demulsification experiments performed on residual type oils (NSFO and No. 6 fuel oil) and on the various tanker crude emulsions featured in this report. The experience with a large variety of seawater-in-oil emulsions suggests that a reliable chemical demulsifer such as Aerosol OT or Aerosol GPG may be used as an integral part of the seawater content test. Demulsification tests have shown that emulsions based on light crudes generally require less chemical agent for emulsion breaking than do the heavy crudes. As a rule of thumb, concentrations of Aerosol OT or GPG in the 0.04% to

0.1% active range (based on total emulsions volume) are sufficient for the lighter crude emulsions whereas 0.2% to 0.6% may be needed for the heavier crudes (at room temperature conditions). For the purposes of the proposed test, light crudes are defined as less than 10 cs. kinematic viscosity; heavy crudes are considered to be greater than 10 cs. in viscosity. The rate of phase separation is also influenced by temperature, hence the accelerated test procedure would involve separations at or near the boiling point of water.

A. Equipment

1. 70 → 75% Aerosol OT or GPG solution
2. Two 100 ml ASTM-type conical graduated centrifuge * tubes with stoppers
3. Beaker, 1000 ml or equivalent
4. Eye dropper
5. Stirring rod, 1/8" diameter (approx.)

B. Method

1. Fill each centrifuge tube to 50 ml mark with emulsion.
2. Using eye dropper, add 1 drop of OT or GPG to one tube and 5 drops to the other tube.
3. Thoroughly mix the agent with emulsion in each tube with aid of stirring rod (emulsion should thin significantly).
4. Stopper tubes and handshake vigorously 10 times to insure good mixing of demulsifier and emulsion.
5. Remove stoppers and place tubes in gently boiling water bath for a 15 minute period.

*Conical tubes will better resolve small quantities of separated water.

6. After 15 minutes, remove tubes and read highest water level in either tube. Record percent seawater as twice the measured water level.

IV. CONCLUSIONS

1. Crude oils exhibit a 5 to 10 fold increase in viscosity (at room temperature) upon evaporative loss of their "volatiles" content.

2. Seawater emulsions generated from light crudes are less stable and more easily broken than emulsions from heavy crudes.

3. Chemical demulsification at low temperature i.e. near freezing point or lower may be arrested by the high viscosity of the oil phase.

4. In spite of differences in viscosity and origin, five of six crudes studied had similar evaporation rates.

5. After three hours essentially 95% of the "volatiles" have evaporated from 4 mm layers of oil ($25^{\circ}C$ and 5 mph air velocity).

6. The evaporation of "volatiles" from crude oil emulsions is not significantly different from their evaporation from the raw crudes.

7. Aerosol OT is an effective demulsifier for seawater-in-crude oil emulsions when used within the appropriate concentration range for a given crude oil emulsion.

8. Temperature and mixing energy (to disperse demulsifier and promote droplet collisions) greatly aid the demulsification process.

9. Demulsifier concentrations in the range of 0.01% to 0.1% are useful for light crude emulsions; concentrations of 0.1% to 1% may be needed for stubborn heavy crude emulsions.

10. Aerosol OT is almost quantitatively extracted into the oil phase and should present no toxicity problem when used as a chemical demulsifier of seawater-in-crude oil emulsions.

Acknowledgment

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Table 1. Critical Micelle Concentrations of Sulfosuccinate Salts

Sample	Solvent	CMC (M/l)	Reference
2-ethylhexyl	Distilled Water	2.5×10^{-3}	Dixon et al. (1)
n-octyl	Distilled Water	6.8×10^{-4}	Dixon et al. (1)
Commercial OT	Distilled Water	1.6×10^{-3}	Am. Cyan. Bulletin (2)
Aerosol OT	Distilled Water	3.3×10^{-3}	Little, this report
Aerosol OT	0.633N NaCl	1.3×10^{-4}	Little, this report
Aerosol OT	Artificial Seawater	1.6×10^{-4}	Little, this report

(1) Williams, E. F., Woodberry, N. and Dixon, J. K., J. Colloid Sci. 12, 452 (1957).

(2) American Cyanamid Bulletin No. PR 102, May 1972.

Table 2. Viscosity of Raw and Evaporated Crudes (cs)

	Raw Crude				Evaporated Crude			
Source	Number	$\nu_{0°C}$	$\nu_{25°C}$	$\nu_{50°C}$	Number	$\nu_{0°C}$	$\nu_{25°C}$	$\nu_{50°C}$
BCF44	1	6.86	3.53	2.21	1'	84.0	21.2	8.53
Nig. Mix	2	9.59	4.61	2.74	2'	359	28.8	7.51
English	3	19.5	6.18	2.95	3'	168	32.5	11.2
Ivory C.	4	81.3	12.6	4.26	4'	1430	55.5	9.91
Arab. H.	5	85.7	28.3	12.9	5'	3000	384	92.6
Prudhoe Bay	6	104	26.5	10.5	6'	1960	176	37.6

Table 3. Walther Equation Constants as Function of Percent "Volatiles" Lost

Crude Oil	% $Lost_1$	A	B	% $Lost_2$	A	B	% $Lost_3$	A	B	% $Lost_4$	A	B
Prudhoe Bay	0	9.85	-3.92	11.9	9.25	-3.63	14.3	10.04	-3.93	17.8	11.14	-4.36
BCF 44	0	9.60	-3.96	31.9	8.89	-3.57	36.2	9.95	-3.98	38.4	10.42	-4.16
Ivory Coast	0	15.16	-6.11	11.7	15.17	-6.07	15.0	15.92	-6.35	18.1	16.92	-6.74
English	0	12.63	-5.14	19.7	10.42	-4.16	22.4	10.74	-4.28	24.3	10.97	-4.36
Arabian H.	0	8.09	-3.20	17.6	8.55	-3.30	20.6	8.74	-3.37	22.5	8.85	-3.41
Nigerian Mix	0	9.51	-3.90	15.7	12.06	-4.86	19.1	14.60	-5.86	22.9	16.00	-6.40

1 Raw Crude
2 After 72 hours
3 After 168 Hours
4 Evaporated Crude (2 weeks in laboratory hood)

Table 4: Predicted Water-in-Oil Emulsion Viscosities* from Raw and Evaporated Crudes

No.	Raw Crudes	Viscosity of Oil $\nu_{0°C}$	$\nu_{25°C}$	25% Emulsion $\nu_{C°}$	$\nu_{25°C}$	50% Emulsion $\nu_{0°C}$	$\nu_{25°C}$	75% Emulsion $\nu_{0°C}$	$\nu_{25°C}$
6	Prudhoe Bay	104.3	26.46	493	125	2,335	592	11,000	2,800
1	BCF 44	6.86	3.53	32.4	16.7	154	79.0	727	374
4	Ivory Coast	81.30	12.61	385	59.7	1,820	282	8,620	1,340
3	English	19.50	6.18	92.3	29.2	437	138	2,060	655
5	Arabian Heavy	85.70	28.31	405	134	1,920	634	9,080	3,000
2	Nigerian Mix	9.59	4.61	45.4	21.8	215	103	1,020	488
	Evaporated Crudes								
6'	Prudhoe Bay	1,960	176	9,290	835	4,400	4,000	208,000	19,000
1'	BCF 44	84.0	21.2	397	100	1,900	475	8,900	2,200
4'	Ivory Coast	1,430	55.5	6,800	263	32,000	1,240	152,000	5,900
3'	English	168	32.5	794	154	3,800	730	17,800	3,400
5'	Arabian Heavy	3,000	384	14,400	1,800	68,000	8,600	350,000	51,000
2'	Nigerian Mix	136.3	19.0	645	89.9	3,050	425	14,400	2,000

* - Viscosities are in centistokes.

Table 5: Evaporation of Crudes* in a Simulated 5 mph Wind at 25°C

Crude Oil	Percent "Volatiles"	Half Life (minutes)	Initial Evaporation Rate (g/cm^2-sec)
Prudhoe Bay	17.8	152	5.54×10^{-6}
BCF 44	35.8	16.5	9.40×10^{-5}
Ivory Coast	19.2	15.4	5.72×10^{-5}
English	25.6	19.2	5.71×10^{-5}
Arabian Heavy	23.6	8.7	1.33×10^{-4}
Nigerian Mix	24.6	10.3	1.09×10^{-4}
Toluene	-	-	1.15×10^{-4}
Water	-		1.85×10^{-5}

* - Approximately 4 mm thickness in a low wall Petri dish of 14.5 cm. diameter.

Table 6: Two Variable Second Order Design Matrix

x_o	x_1	x_2	Y
1	1	1	Y_1
1	1	-1	Y_2
1	-1	1	Y_3
1	-1	-1	Y_4
1	$\sqrt{2}$	0	Y_5
1	$-\sqrt{2}$	0	Y_6
1	0	$\sqrt{2}$	Y_7
1	0	$-\sqrt{2}$	Y_8
1	0	0	Y_9
1	0	0	Y_{10}

Variable Code:

$x_1 = A\ (\% - B)$

$x_2 = E\ (°C - D)$

A, B, E, D values chosen to conform to design matrix

$Y = \text{Log}_{10}$ demulsification time

$$S^2 = \frac{R^2}{N-K}$$

Where R = residuals
N = number of Y values
K = number of coefficients
S = standard deviation

Statistical Equation:

$$Y = b_o + b_1x_1 + b_2x_2 + b_{11}x^2{}_1 + b_{22}x^2{}_x + b_{12}x_1x_2$$

Table 7: Typical Data Sample: Chemical Demulsification of 50% Emulsions of Seawater in Arabian Heavy Crude

Run #	Temp. (°C)	Agent Conc'n (%)	Log_{10} Exp'l Demuls. Time (min)	Log_{10} Calc'd* Demuls. Time (min)	Residual
1	18.4	0.40	2.550	2.48	0.067
2	23	0.20	2.550	2.498	0.052
3	23	0.60	1.740	1.871	-0.131
4	34	0.117	2.041	2.190	-0.149
5	34	0.40	1.919	1.949	-0.030
6	34	0.40	1.978	1.949	0.029
7	34	0.683	1.204	1.100	0.104
8	45	0.20	2.000	1.821	0.179
9	45	0.60	0.903	0.903	0
10	49.6	0.40	1.204	1.320	-0.116

* $Log_{10}t = 1.949 - 0.386X_1 - 0.411X_2 - 0.152X_1^2 - 0.024.3X_2^2 - 0.0718X_1X_2$

$$S^2 = \frac{R^2}{N - K} = \frac{0.1046}{10-6} = 0.02615$$

$S = 0.1617$

Table 8: Statistical Equations Used in Demulsification Experiments

Oil	Equation
BCF 44, raw	$\mathrm{Log}_{10}\ t = 1.792-0.221X_1-0.271X_2+0.0474X_1^2-0.0484X_2^2-0.0222X_1X_2$
Nigerian, raw	None, emulsions unstable
English, raw	None, emulsions unstable
Ivory Coast, raw	$\mathrm{Log}_{10}\ t = 0.328-0.128X_1-0.483X_2 + 0.00582X_1^2-0.209X_2^2-0.160X_1X_2$
Arabian Heavy, raw	$\mathrm{Log}_{10}\ t = 1.949-0.386X_1-0.411X_2-0.151X_1^2=0.0236X_2^2-0.0718X_1X_2$
Prudhoe Bay, raw	$\mathrm{Log}_{10}\ t = 2.106-0.177X_1-0.438X_2-0.118X_1^2-0.128X_2^2-0.0152X_1X_2$
BCF 44, Evap.	$\mathrm{Log}_{10}\ t = 0.517 + 0.358X_1-0.453X_2-0.0440X_1^2 + 0.336X_2^2-0.260X_1X_2$
Nigerian, Evap.	None, Emulsions rapidly unmix in presence of small amounts of demulsifier $\sim$ 0.08%
English, Evap.	None, Emulsions rapidly unmix with demulsifier concentration $\sim$ 0.02%
Ivory Coast, Evap.	None, Emulsions rapidly unmix at 0.04% demulsifier
Arabian Heavy, Evap	$\mathrm{Log}_{10}\ t = 2.488 + 0.0166X_1 + 0.0321X_2-0.0692X_1^2-0.0486X_2^2 + 0.111X_1X_2$
NSFO	$\mathrm{Log}_{10}\ t = 0.256 + 0.246X_1-0.825X_2 + 1.014X_1^2 + 0.204X_1X_2$
No. 6 Fuel Oil	$\mathrm{Log}_{10}\ t = 1.302-0.504X_1-0.812X_2 + 0.273X_1^2 + 0.379X_2^2 + 0.460X_1X_2$

Table 9: Distribution of Aerosol OT Between Seawater and Tanker Crudes

Oil	Conc'n OT in Seawater (M/l)	Conc'n OT in oil (M/l)	K apparent
Prudhoe Bay	$<10^{-8}$	3.4×10^{-3}	$<10^{-6}$
Ivory Coast	$<10^{-8}$	3.4×10^{-3}	$<10^{-6}$
English	10^{-7}	3.4×10^{-3}	$\sim 10^{-5}$
Nigerian Mix	10^{-7}	3.4×10^{-3}	$\sim 10^{-5}$
BCF-44	10^{-7}	3.4×10^{-3}	$\sim 10^{-5}$
Arabian Heavy	$<10^{-8}$	3.4×10^{-3}	$<10^{-6}$

Note: 10^{-8} M/l is detectability limit.

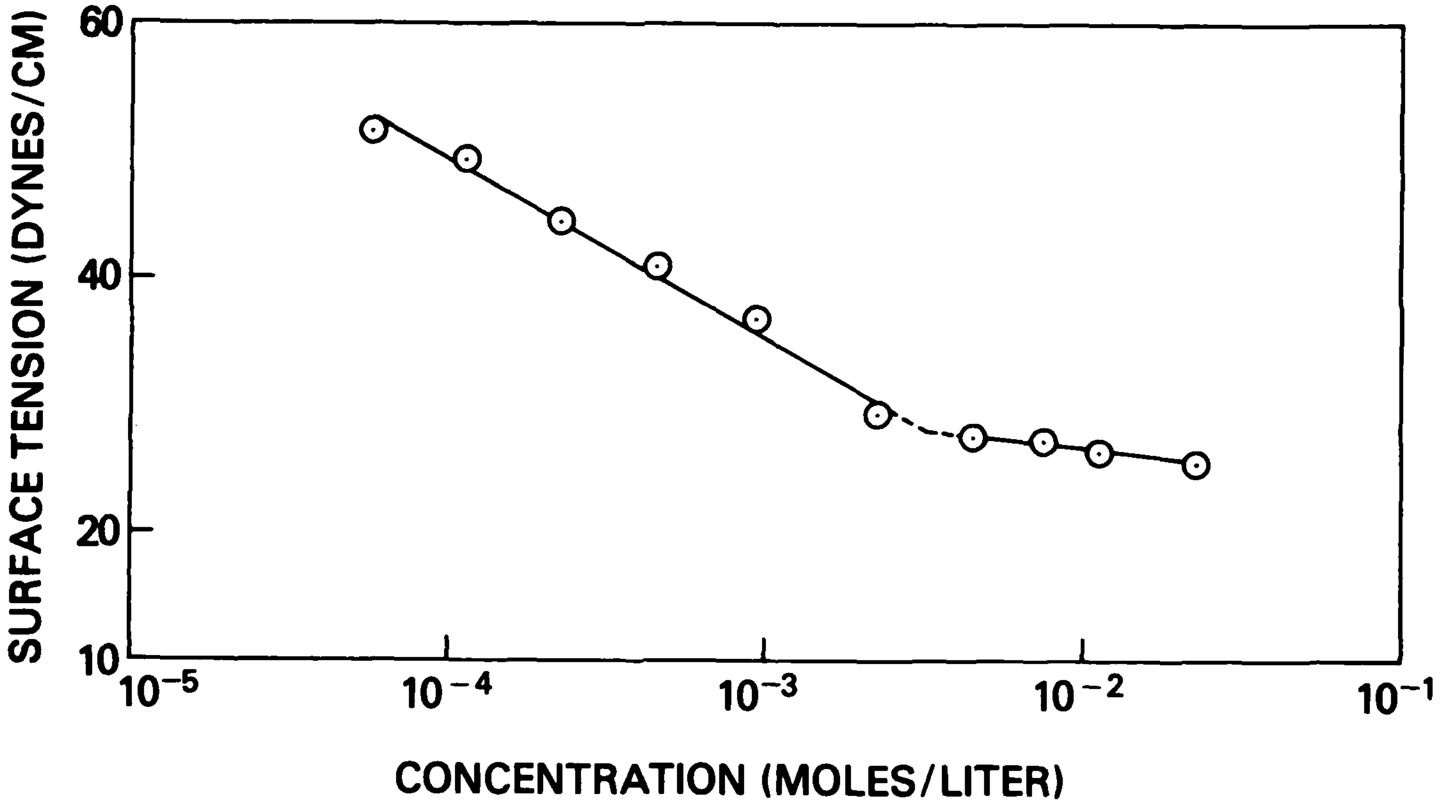

Fig. 1 - Surface Tension - Concentration plot for Aerosol OT in distilled water at 25°C.

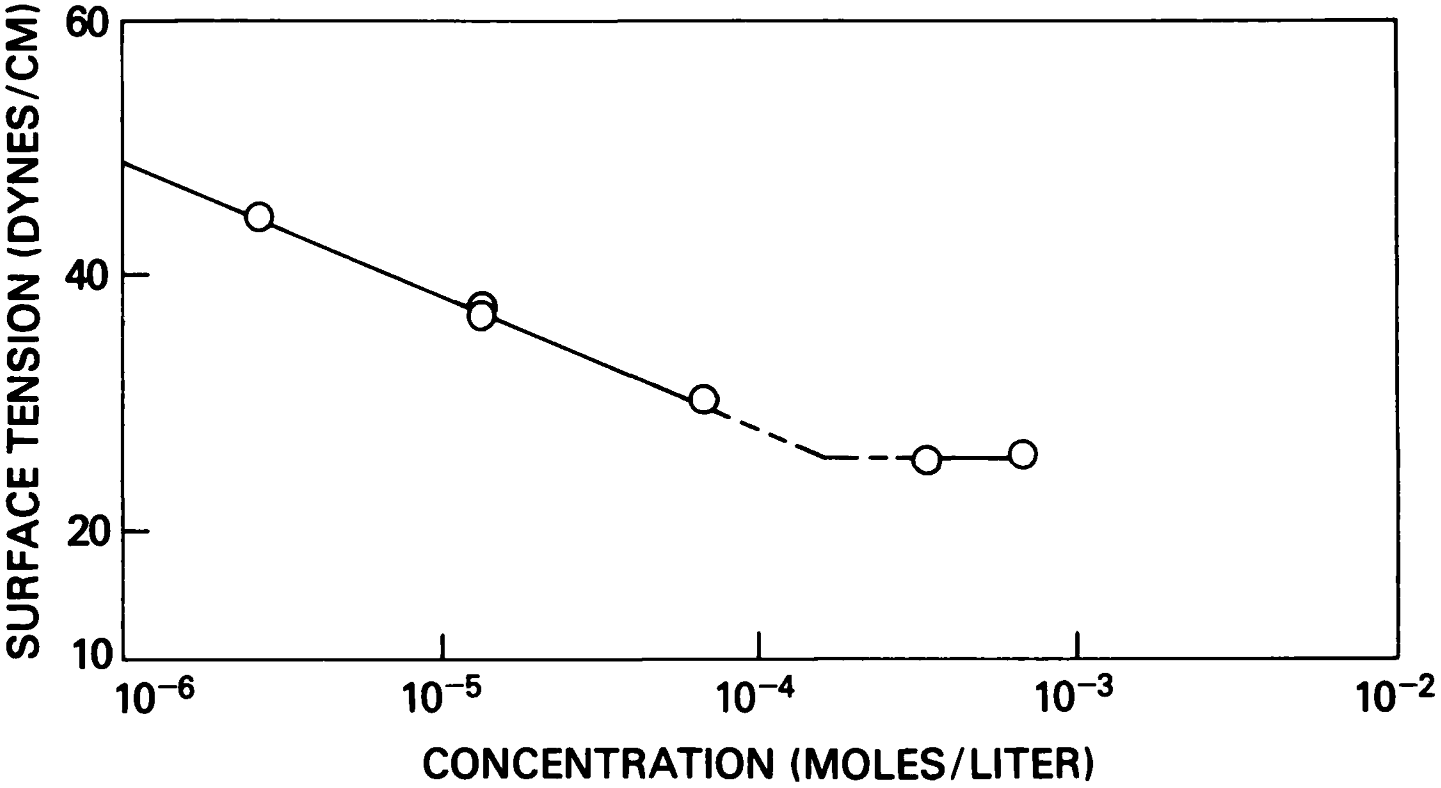

Fig. 2 - Surface Tension - Concentration plot for Aerosol OT in Artificial Seawater at 25°C.

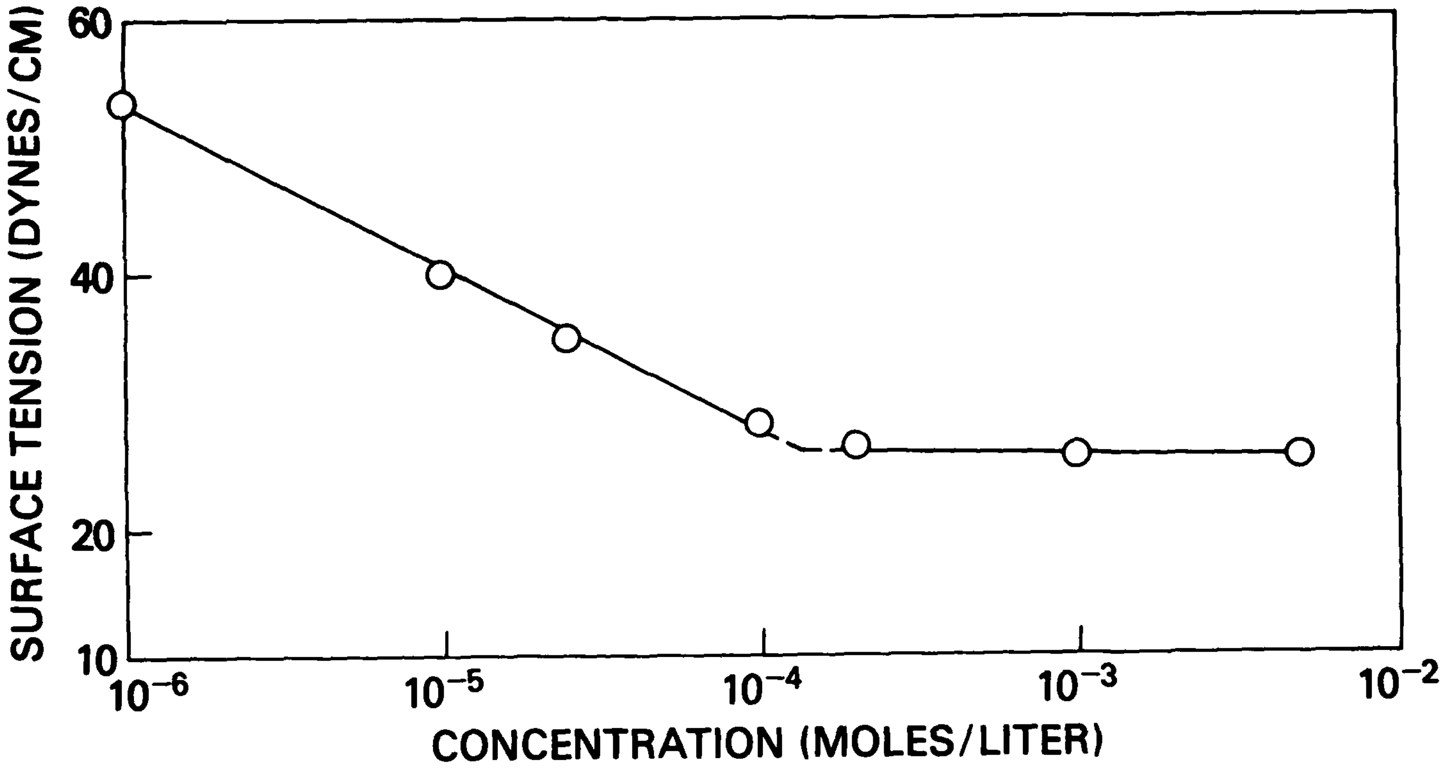

Fig. 3 - Surface Tension - Concentration plot for Aerosol OT in 0.633 molar NaCl at 25°C.

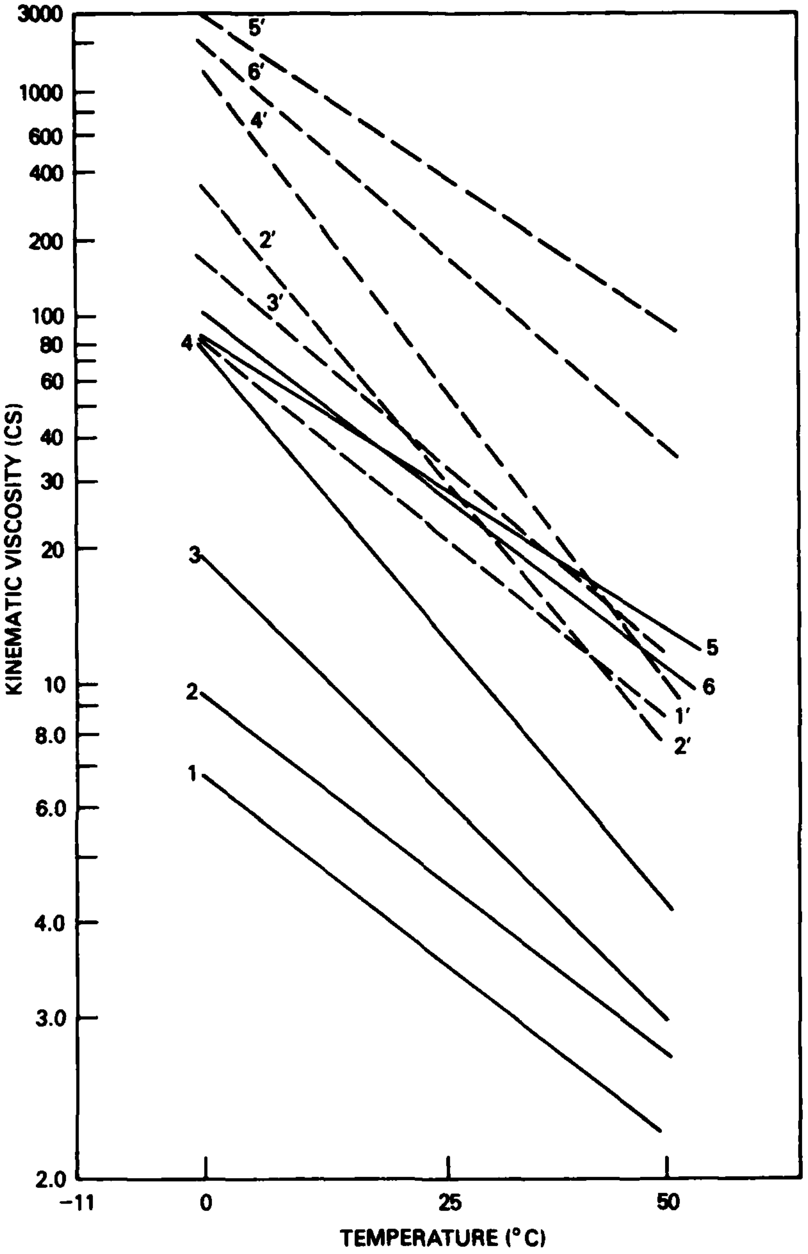

Fig. 4 - ASTM-type viscosity temperature plots for raw and evaporated tanker crudes studied. 1-BCF44; 2-Nigerian Mix; 3-English; 4-Ivory Coast; 5-Arabian Heavy; 6-Prudhoe Bay. Primes refer to evaporated samples of same.

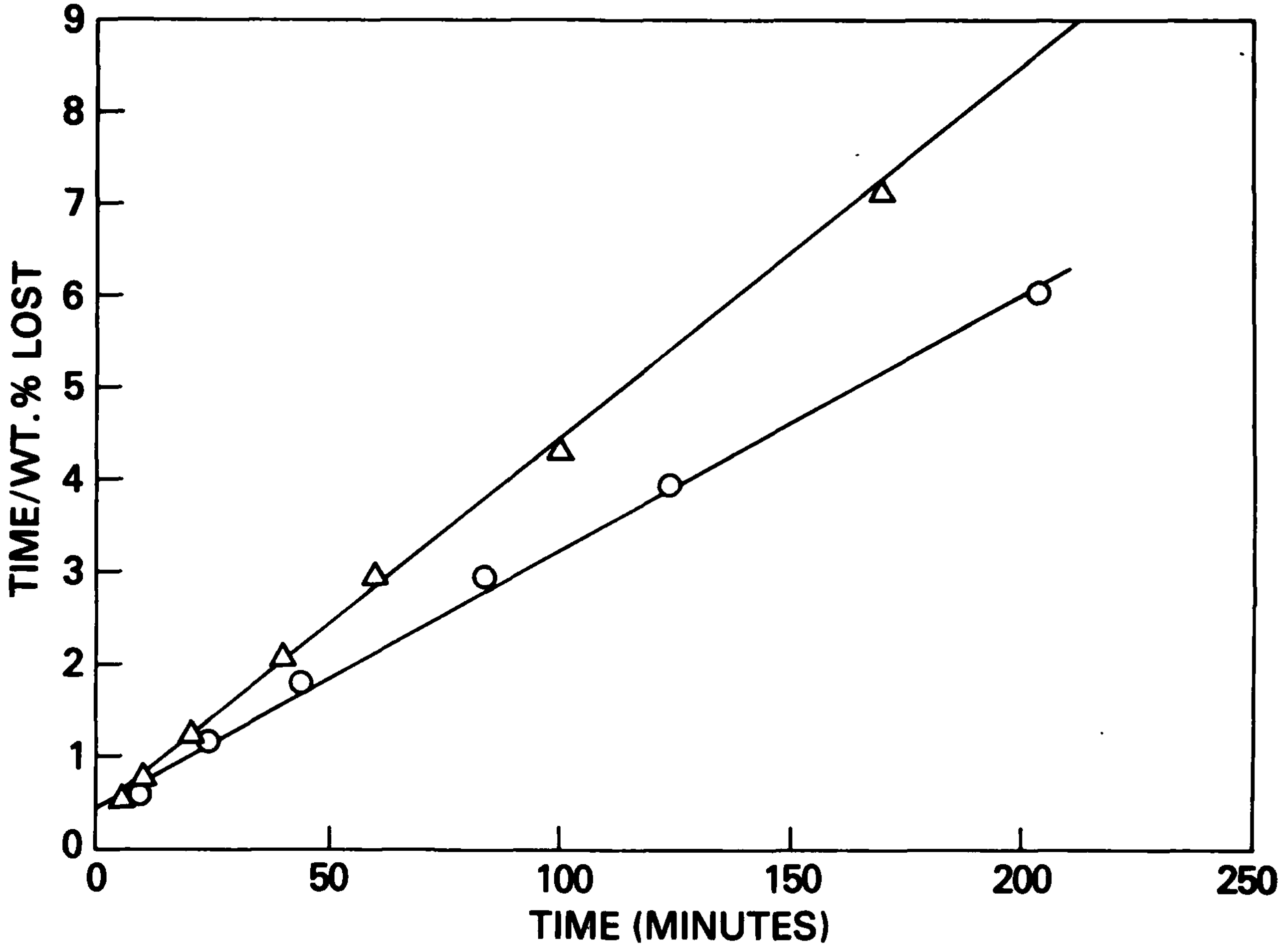

Fig. 5 - Test of Empirical Equation $\frac{W}{W_m} = \frac{t_{1/2}}{t + t_{1/2}}$ for Nigerian Mix (△); for BCF44 ⊙ ; 25°C, 5 mph air velocity.

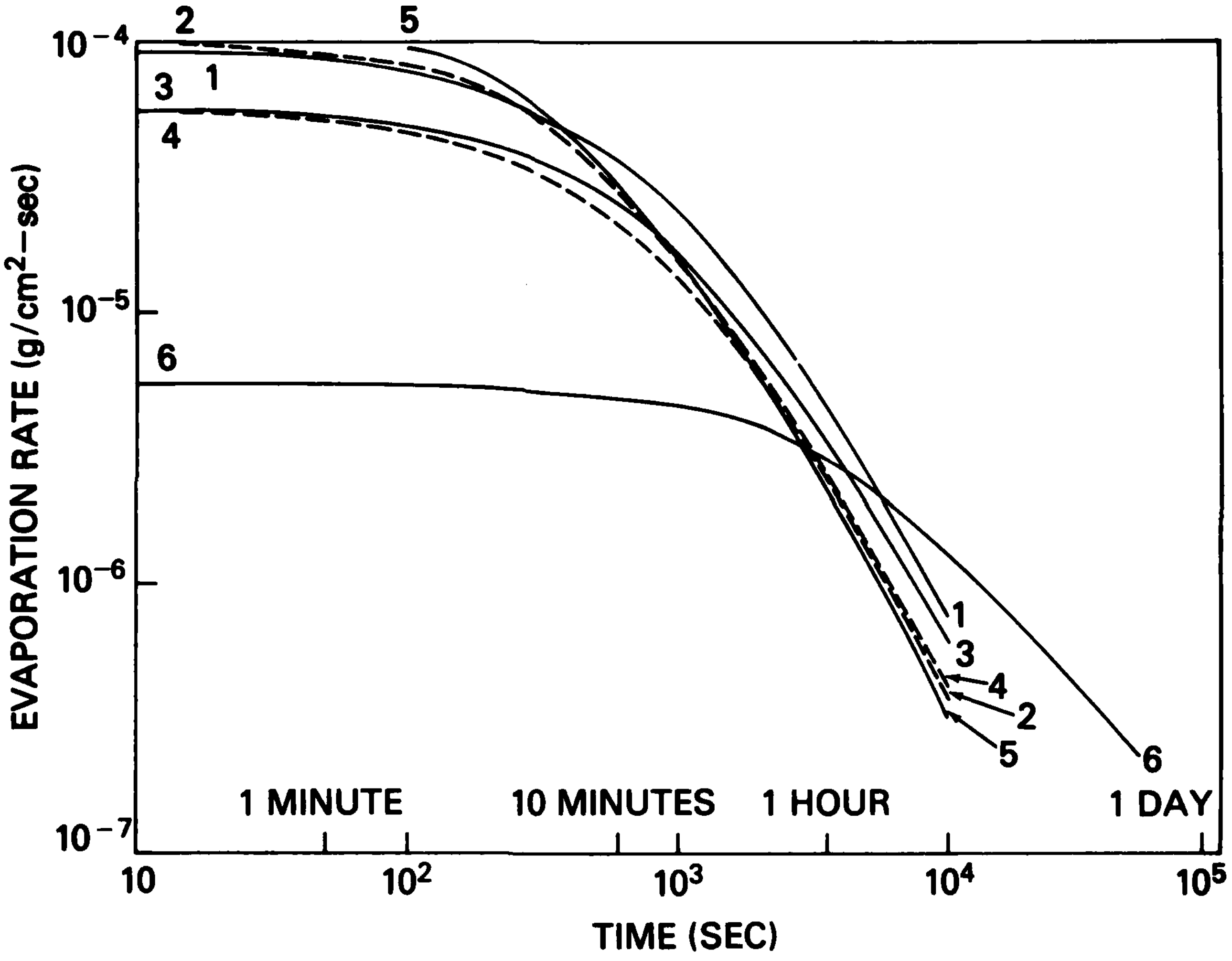

Fig. 6 - Evaporation of crudes from 4mm layers in laboratory Petri dishes (25°C, 5 mph air velocity).

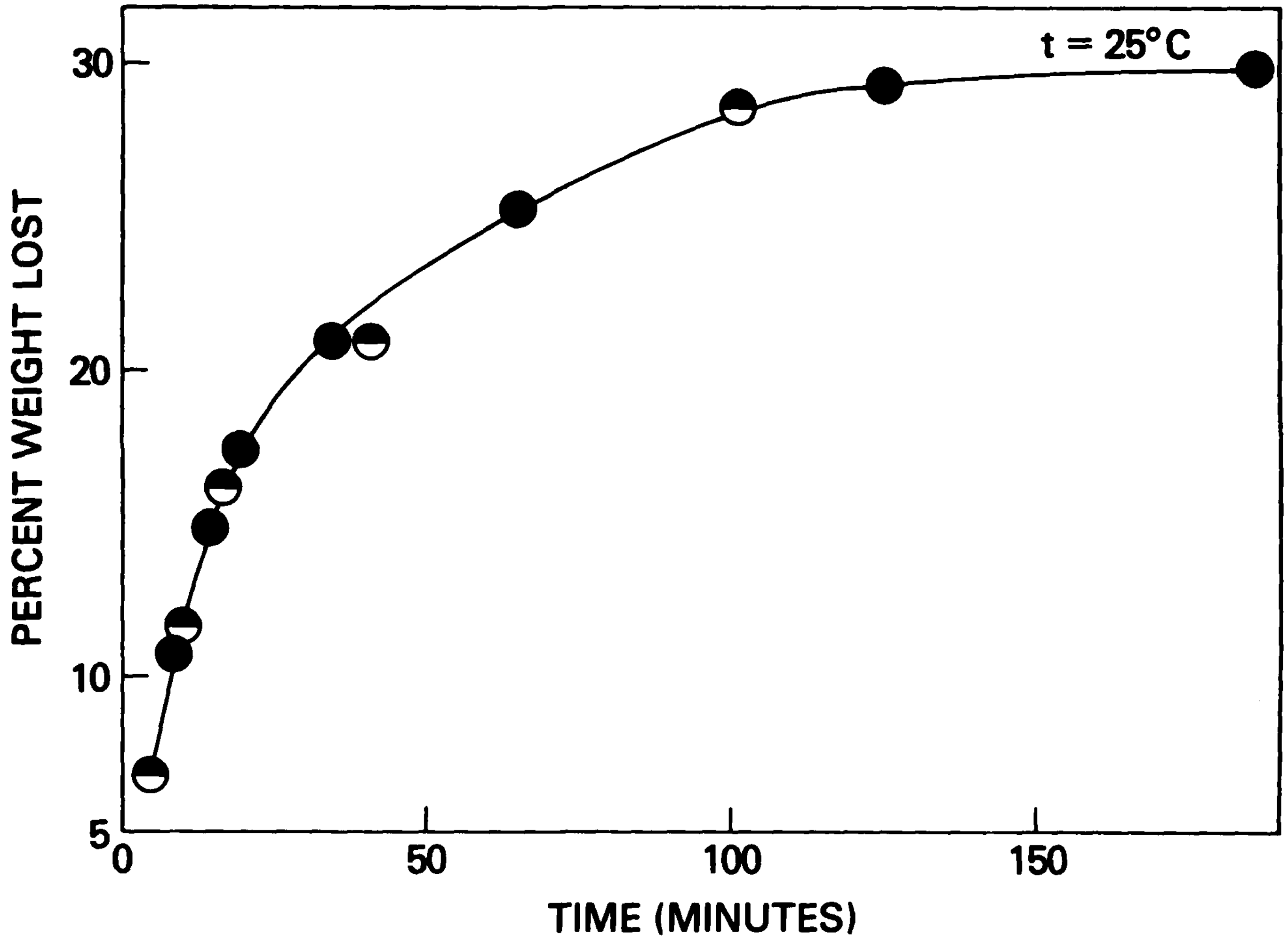

Fig. 7 - Comparative evaporation of "volatiles" from a raw crude (BCF44) and its 50% emulsions containing glycol (evaporation from emulsions based on its crude content). ● - crude; ◓ - emulsion; 25°C, 5 mph.

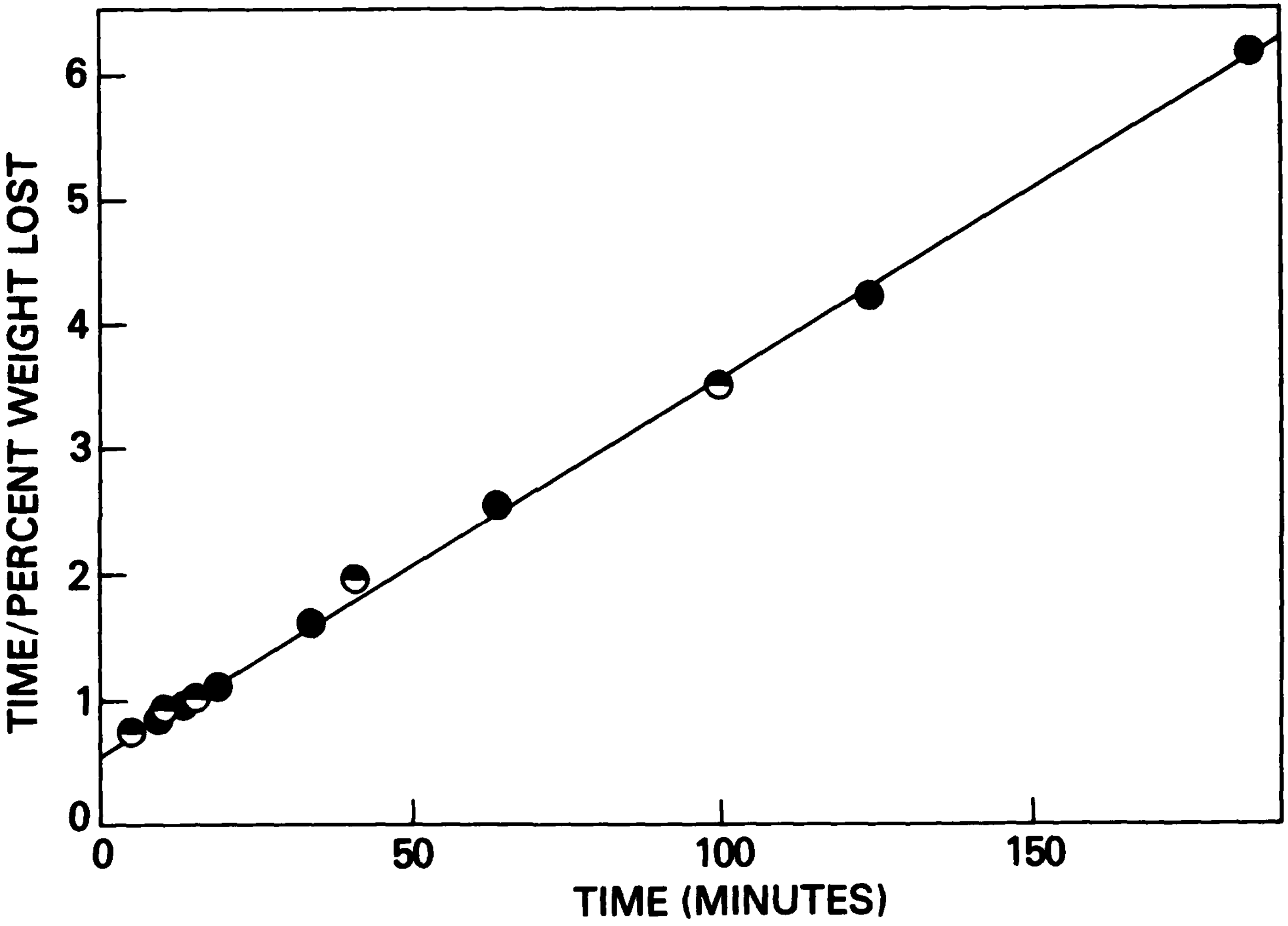

Fig. 8 - Test of Empirical Equation $\frac{W}{W_m} = \frac{t}{t_{1/2} + t}$ for both crude and its emulsions (25°C, 5 mph). ● - crude; ◒ - emulsion.

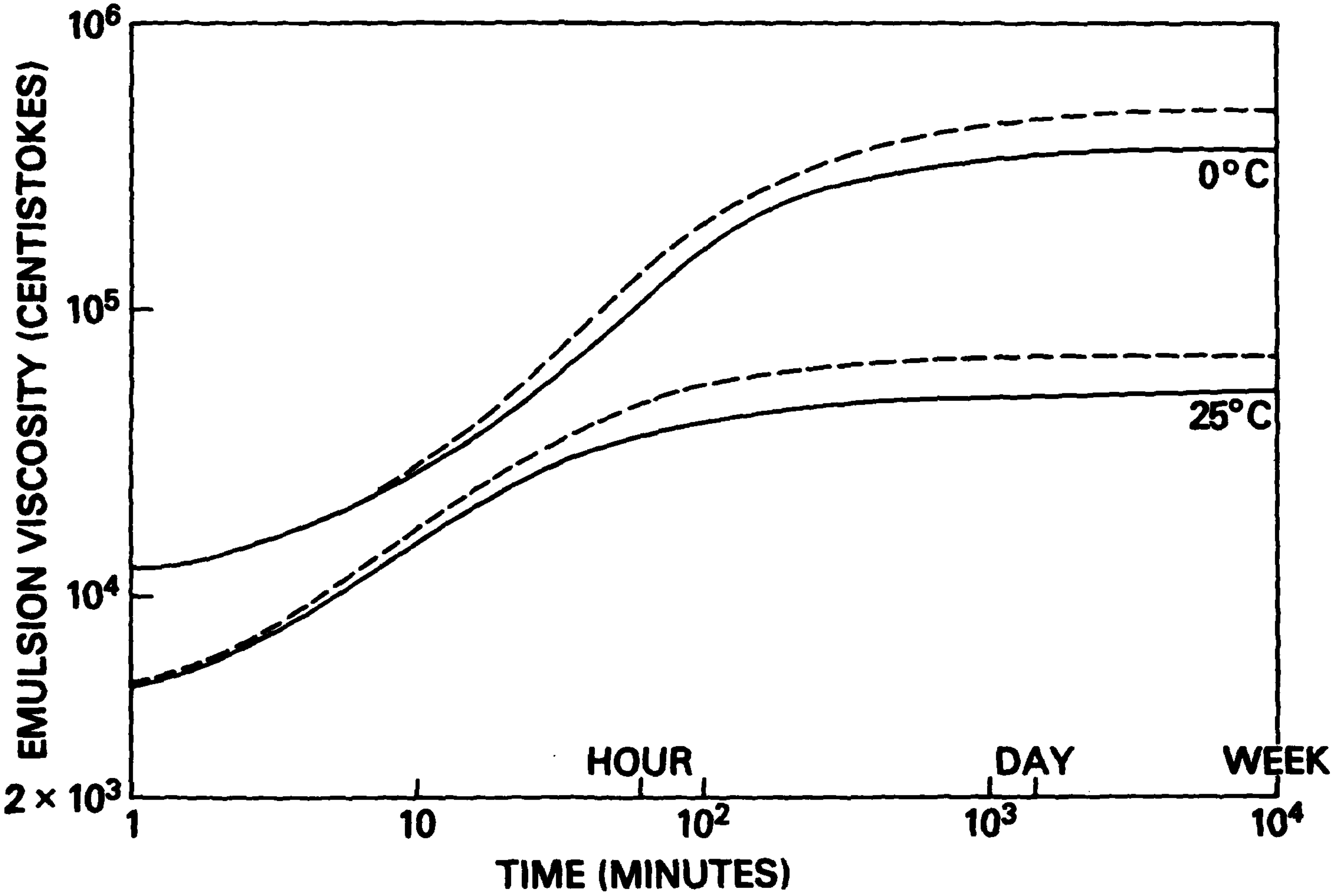

Fig. 9 - Computed emulsion viscosities as a function of time at 0° and 25°C (See text for equations used).

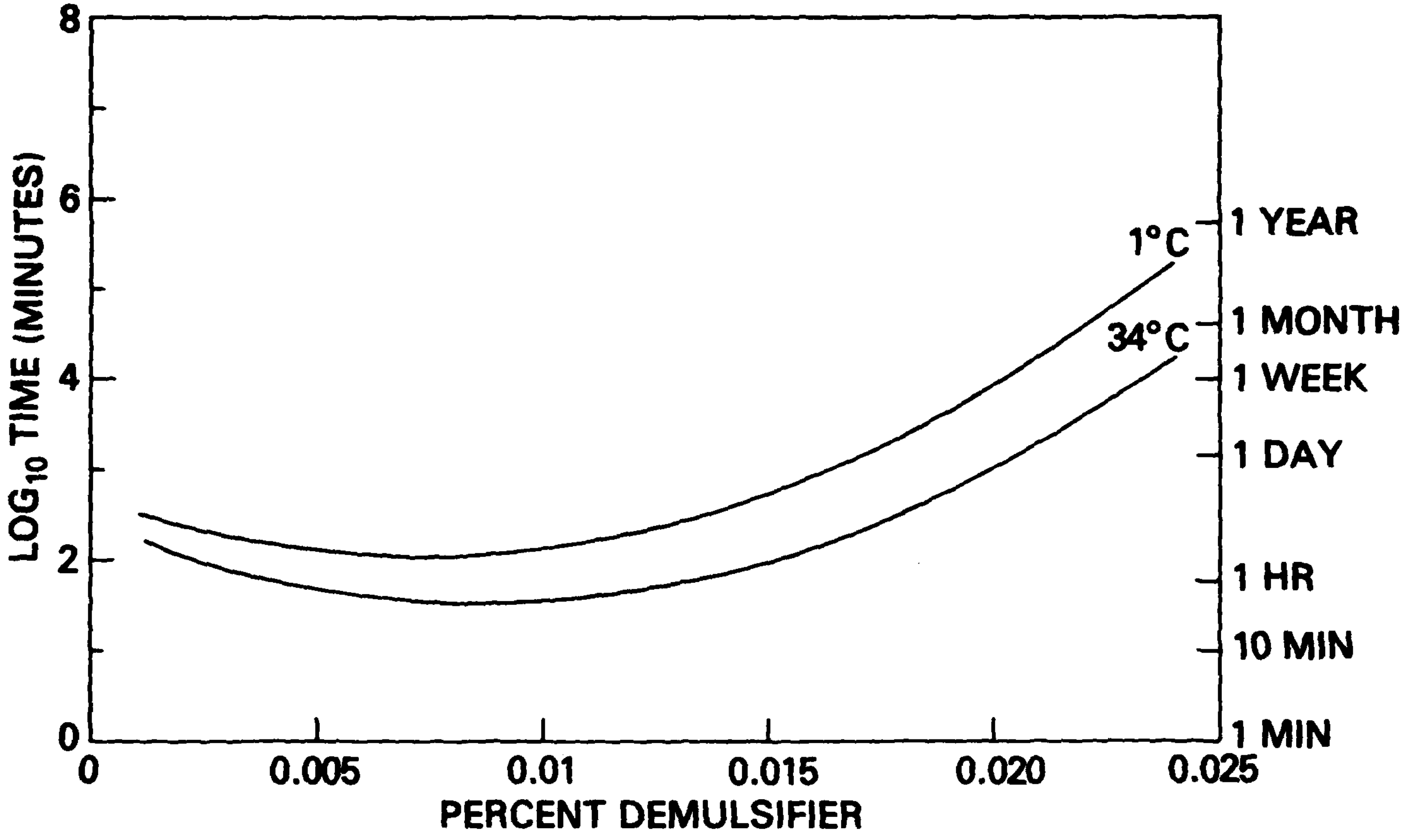

Fig. 10 - Demulsification of raw BCF44 emulsions at 1°C and 34°C.

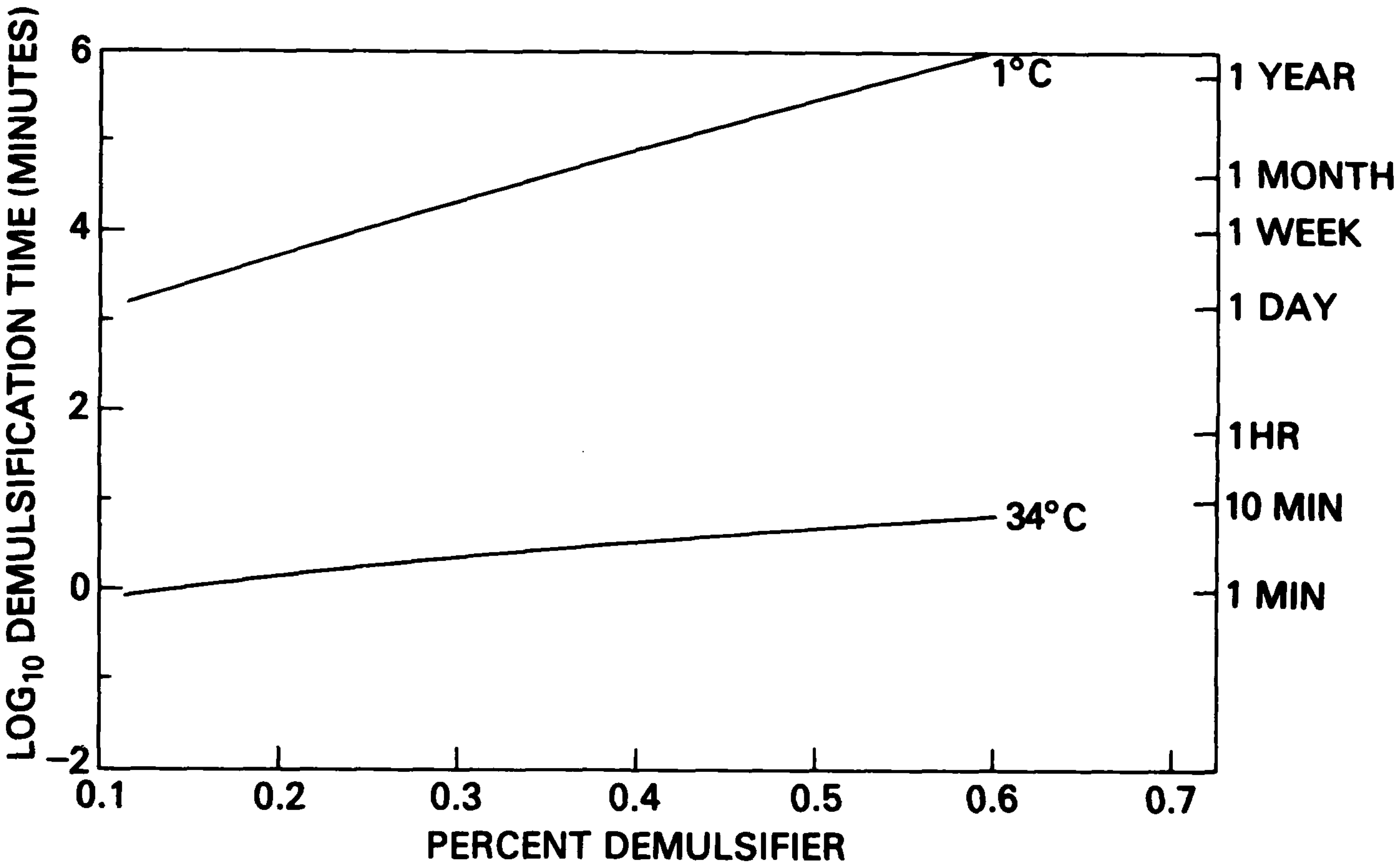

Fig. 11 - Demulsification of evaporated BCF44 emulsions at 1°C and 34°C.

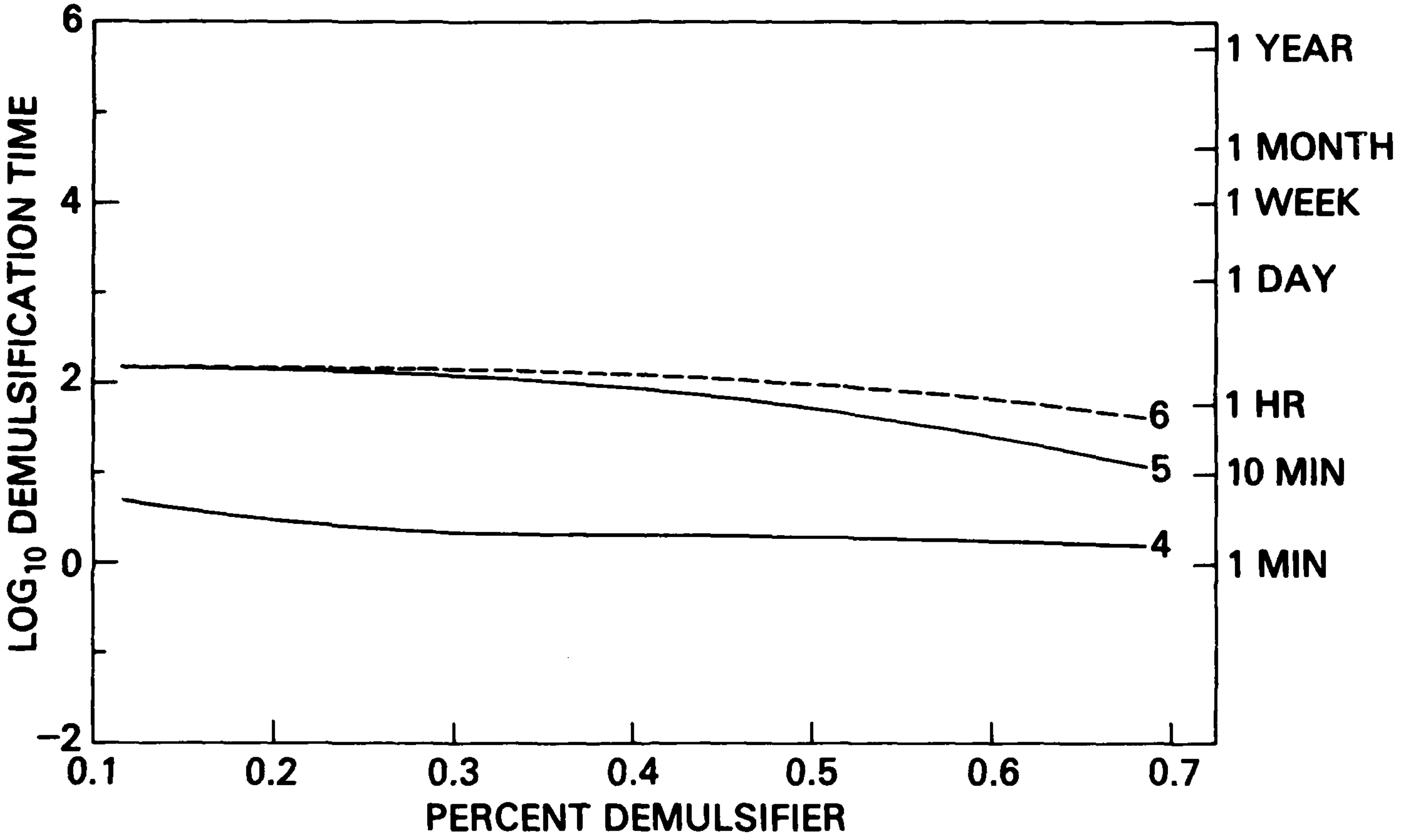

Fig. 12 - Demulsification of heavy raw crude emulsions at 34°C
4-Ivory Coast; 5-Arabian Heavy; 6- Prudhoe Bay.

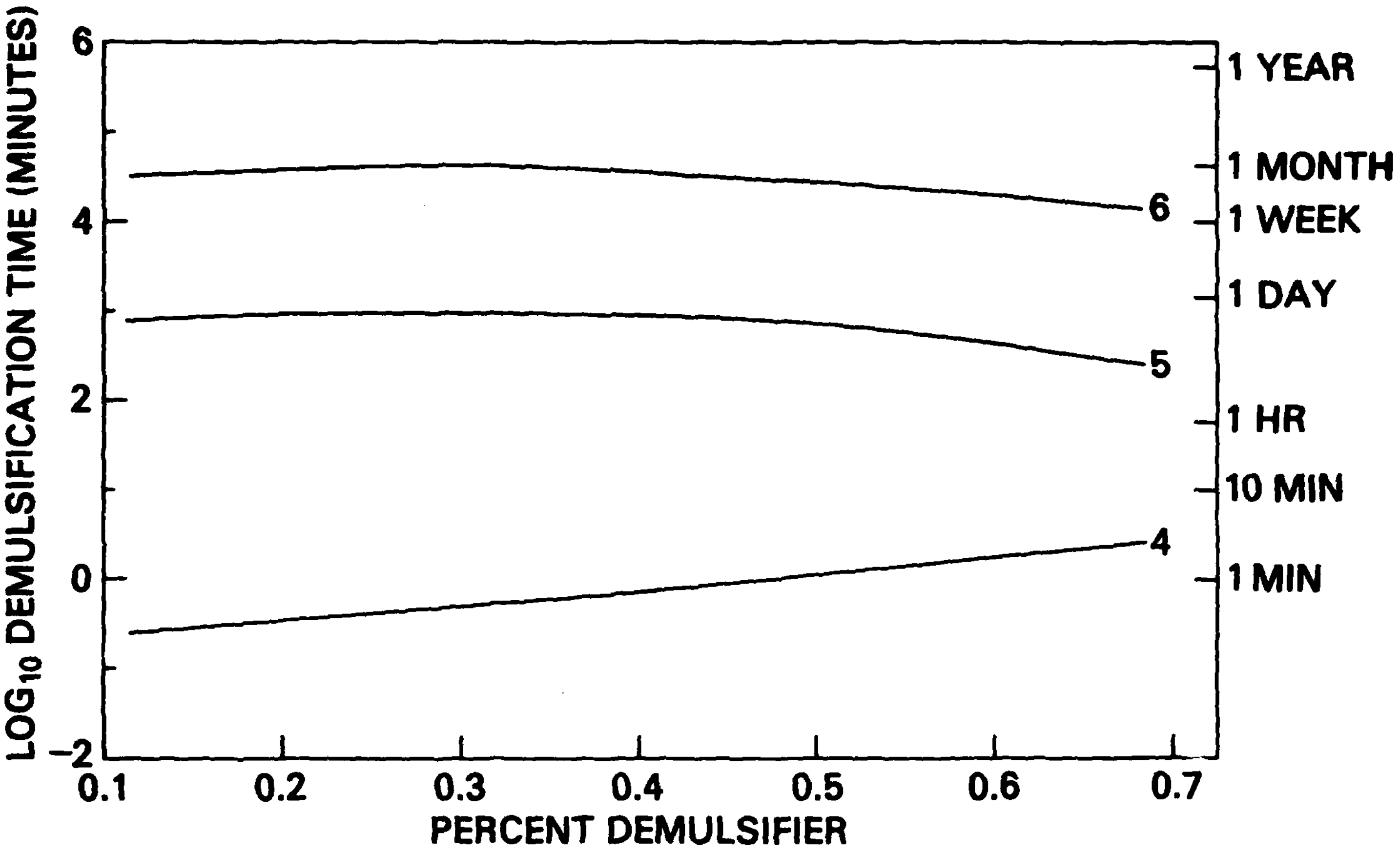

Fig. 13 - Demulsification of heavy raw crude emulsions at 1°C 4-Ivory Coast; 5-Arabian Heavy; 6-Prudhoe Bay.

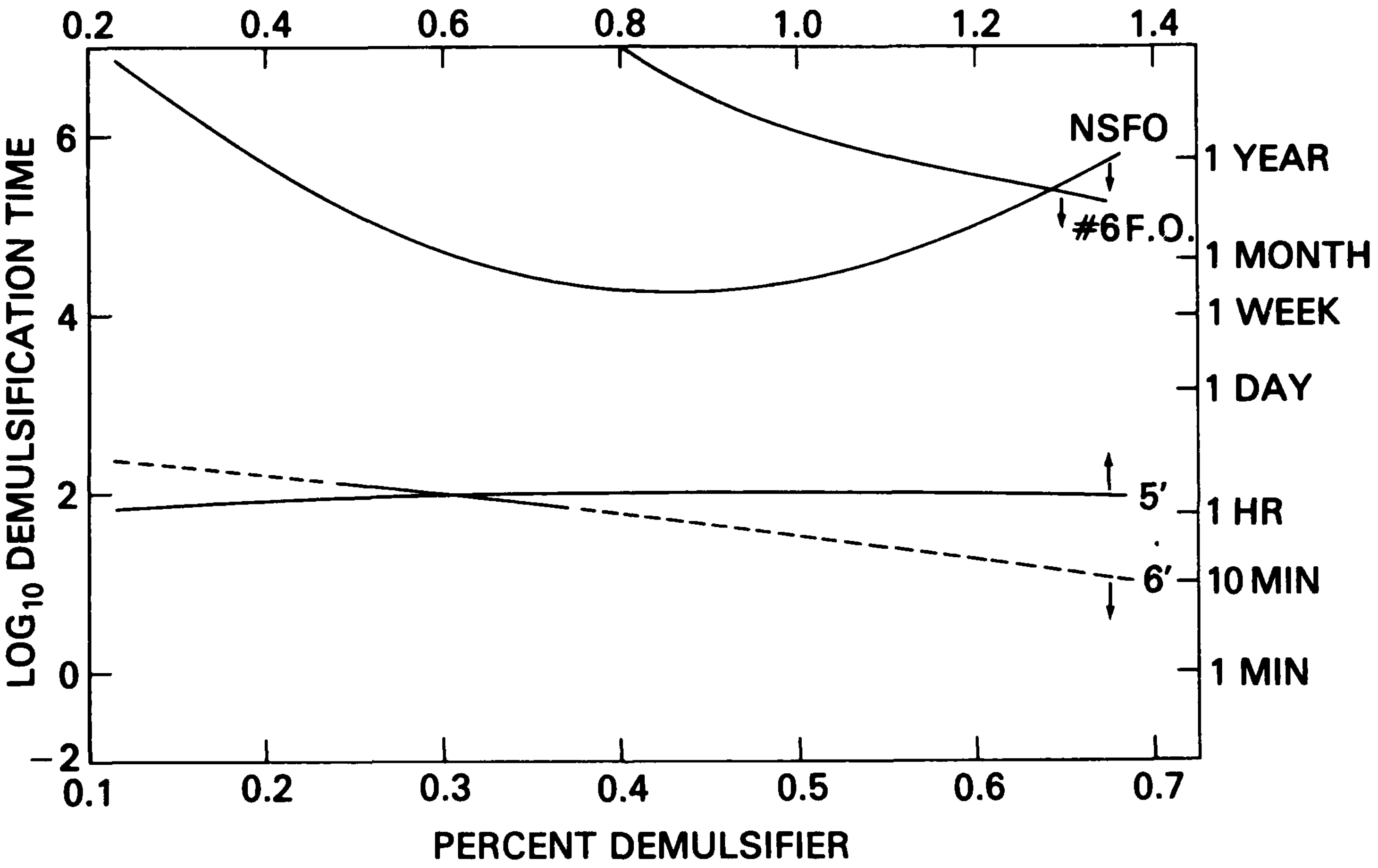

Fig. 14 - Demulsification of evaporated heavy crude emulsions at 1°C . 5' - Arabian heavy (evaporated); 6' Prudhoe Bay (evaporated); NSFO - Navy Special Fuel Oil; #6 F.O. - No. 6 Fuel Oil Emulsions.

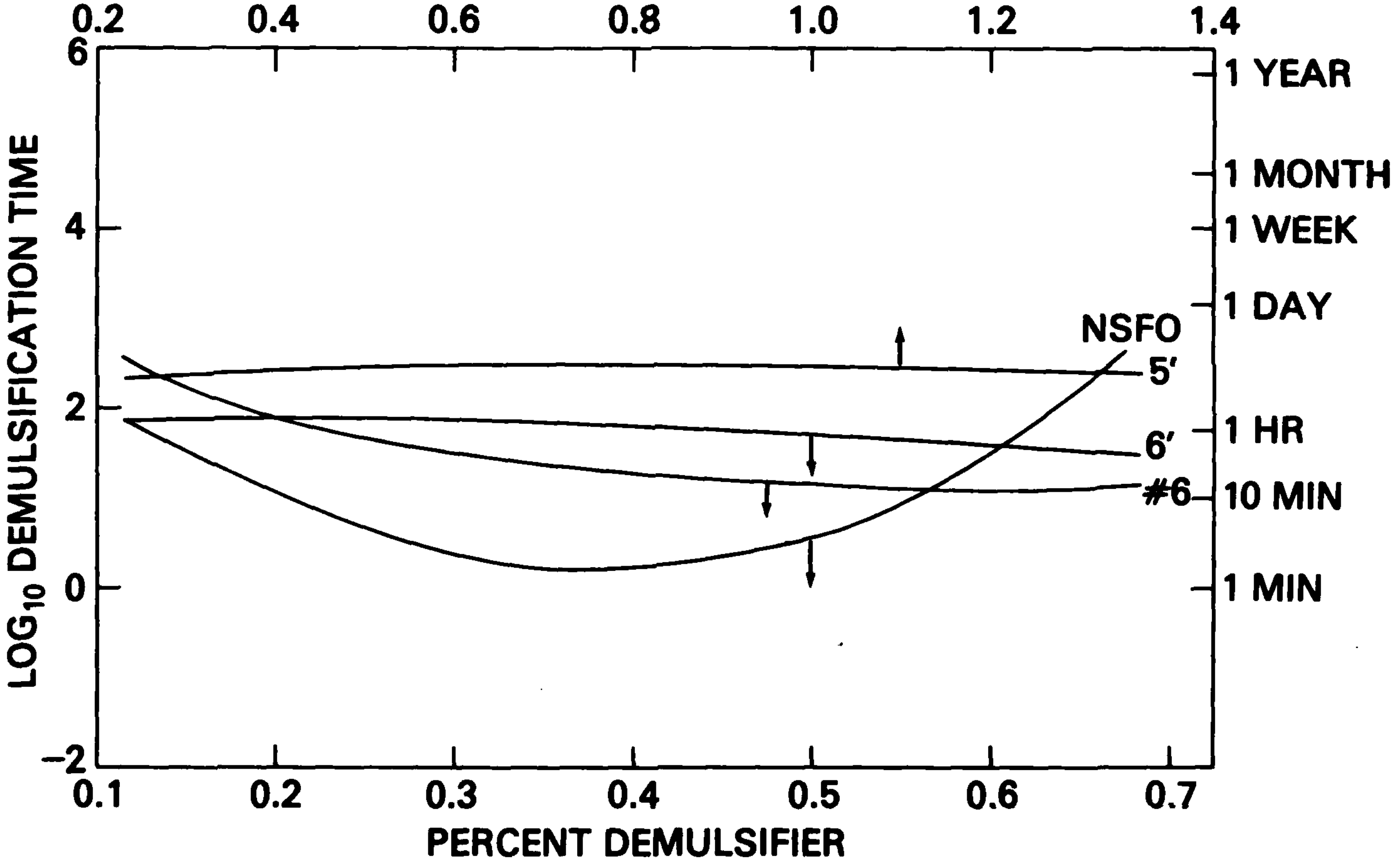

Fig. 15 - Demulsification of Evaporated heavy crude emulsions at 34°C. 5' - Arabian heavy (evaporated); 6' Prudhoe Bay (evaporated); NSFO - Navy Special Fuel Oil; #6 F.O. - No. 6 Fuel Oil.