MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS-1963-A

# LEVEL II

THE MECHANISM OF CORROSION INHIBITION
BY DINONYLNAPHTHALENESULFONATES

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## I    INTRODUCTION

Operability of combat and combat support equipment can be
seriously compromised by rusting of power train components. As a
preventative measure, most lubricants in the Army Supply System are
rust inhibited. Sulfonates, such as the petroleum sulfonates and salts
of dinonylnaphthalenesulfonic acid, have proven to be effective rust
preventatives for Army lubricants, however, their use is limited due
to their high temperature instability and viscosity. New rust inhib-
itor systems are needed for formulation into a variety of fluids such
as turbine engine oils, aircraft hydraulic fluids and the newer
synthetic nonhydrocarbon fluids. A basic understanding of the rust
inhibition mechanism is needed in order to accomplish this task and
to keep pace with potential rust problems associated with advanced
Army systems.

Most, although not all investigators, believe that rust
inhibition is the result of rust inhibitor adsorption on metal
surfaces. Adsorption of a monomolecular layer on the metal surface
could act as a barrier toward diffusion of corrodants such as water
and oxygen to the surface and oxidation products from the surface (1).
Our previous work (2) on the mechanism of rust inhibition indicated
that sulfonates are strongly and irreversibly adsorbed on metal oxide
surfaces and form close-packed monolayers at low solution concen-
trations. These findings support a barrier-type mechanism for
corrosion inhibition, however, the actual mechanism is probably of
much greater complexity. The effect of micelles in bulk solution,
co-adsorption of the base lubricant, competitive effects of other
additives in the lubricant system and chemical modification of the
base metal by adsorption needs to be considered.

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Our present studies are directed towards a better understanding of the rust inhibition mechanism through an investigation of the thermodynamics associated with the chemical processes that occur in a typical rust inhibiting system. The first part of this investigation was concerned with the competitive adsorption of water with sulfonates on iron oxide in order to better understand the corrosion process. The second part of this investigation is concerned with measuring the heat liberated by sulfonate adsorption since this is a measure of the extent of interaction between the sulfonates and the metal oxide substrate.

II    EXPERIMENTAL SECTION

Materials used in this investigation included sodium dinonyl-naphthalenesulfonate (Na(DNNS)) and barium dinonylnaphthalenesulfonate (Ba(DNNS)$_2$); cyclohexane (J. T. Baker Chemical Company, Instra-Analyzed Grade) was used as received and also as a "dry" solvent by treatment over 4Å molecular sieve. The iron (III) oxide powder was of relatively high purity and had a surface area of 28 m$^2$/g as determined by the BET gas adsorption method. The method of preparation for the sulfonates was previously described (2).

.Information on the mechanism of corrosion inhibition was obtained by use of a flow microcalorimeter (Microseal Ltd., England). The principal of operation of this flow calorimeter is very similar to that of a column chromatograph except that thermistors are inserted in the adsorbent bed to detect temperature changes due to either adsorption or desorption of material from the column. In our experimental work, the iron oxide powder is used to form the adsorbent bed. In the continuous flow mode of operation, the carrier liquid (pure cyclohexane) is pumped through this miniaturized bed by special mircrpumps at a flow rate of 0.05 ml/min. so as to establish temperature equilibrium. After establishment of temperature equilibrium, a dilute solution of sulfonate in cyclohexane is percolated through the adsorbent bed until the heat effect associated with adsorption of sulfonate on iron oxide powder is dissipated. The flow of the pure cyclohexane carrier liquid is then resumed in order to measure any heat effects associated with the desorption of sulfonates. In the pulsed adsorption mode of operation, small amounts of dilute sulfonate solution are periodically injected directly into the carrier liquid stream to determine associated heat effects.

The heat adsorption of Na(DNNS) on iron oxide was determined by using a thermometric titration and solution calorimeter (Tronac, Inc.). Heat of adsorption measurements were made by titrating a suspension of iron oxide powder in cyclohexane with a dilute solution

of Na(DNNS) in cyclohexane at 30$^\circ$C using either a 25 ml or 50 ml isothermal reaction vessel. This data was augmented by ultraviolet analysis of the post run supernatant liquid to determine the extent of sulfonate adsorption on the iron oxide powder.

## III   RESULTS AND DISCUSSION

Water is a common contaminant in lubricating oils and would be expected to actively compete for adsorption with the other lubricant additives. The effect of water can be complex; it can either increase adsorption, decrease adsorption or have little or no effect on the adsorption of other additives. For example, we had found that water adsorbed on nickel oxide can act as sites for additional adsorption of phenol (3) or it can effectively block the adsorption of other additives such as phenyl disulfide. In the case of phenyl disulfide, room temperature adsorption studies indicated an adsorption of only 2 to 4 $\mu$g of disulfide per gram of iron oxide as received. Moderate drying of the iron oxide powder at 120$^\circ$C under vacuum conditions resulted in an increased adsorption of 24 $\mu$g/g. Intensive drying at 350$^\circ$C resulted in a further increased adsorption to 172 $\mu$g/g. In this latter case dehydroxilation of iron oxide surfaces with generation of highly active sites not present on the moderately dried sample were suspect. In the previous work (3), we had found that sulfonate adsorption isotherms were not noticeably effected by water and first studies were initiated without consideration for the effect that drying or the iron oxide powder would have on experimental results.

### Effect of Water

Data output from the flow calorimeter is similar to the output from a gas chromatograph in that detector response is recorded as a function of time. A typical recorder output from the flow calorimeter is shown in Figure I. Initially, a steady flow of cyclohexane is percolated through the iron oxide column in order to achieve a steady thermal base line and at this point, a flow of dilute Ba(DNNS), in cyclohexane is substituted for the flow of cyclohexane. The thermal effect produced by the adsorption of BA(DNNS)$_2$ on the column is recorded as a pen deflection corresponding to region "A" in Figure I. (Exothermic processes produce a pen deflection in the -Q direction and endothermic processes produce a pen deflection in the +Q direction.) The area under the curve is directly proportional to the heat of adsorption. Flow of the sulfonate solution is continued until the recorder returns to the initial thermal base line. The flow of sulfonate is then discontinued and replaced by a flow of pure cyclo-

hexane which allows the measurement of thermal effects associated with desorption. This cyclohexane wash corresponds to region "B". Regions "C" and "D" correspond to additional flow change-overs to Ba(DNNS)$_2$ in cyclohexane and pure cyclohexane, respectively.

Data initially obtained from the flow calorimeter (Figure I) using BA(DNNS)$_2$ as an adsorbate and iron oxide powder for the adsorbent bed was at first somewhat puzzling. Adsorption of sulfonate would be expected to produce an exothermic heat effect and further washing with pure cyclohexane should produce a very slight endothermic heat effect due to slight desorption of sulfonate. These types of heat effects were initially not found, in fact, the reverse of these heat effects were observed. The initial work indicated that sulfonate adsorption produced a slight exothermic heat effect as would be expected for sulfonate adsorption, however, this was rapidly over-shadowed by a very much greater endothermic heat effect of unknown origin. Washing with cyclohexane produced an exothermic heat effect suggesting an adsorption process rather than a desorption process. Further addition or sulfonate produced an endothermic heat effect of approximately the same magnitude as was found during the previous cyclohexane wash.

The cause of these unusual thermodynamic effects was soon discovered. The solubility of water in cyclohexane at room temperature is approximately 15 ppm and the reagent grade cyclohexane used in this work contained 10 ppm of water. Thus, the initial flow of "wet" cyclohexane over the iron oxide powder column that was necessary to establish temperature equilibrium also produced a water saturated iron oxide surface. This suggested a possible explanation for the unusual heat effects shown in Figure I. Region "A" can be interpreted as indicating an exothermic sulfonate adsorption process that is over-shadowed by an endothermic heat effect associated with desorption and solubilization of water by sulfonate micelles. Washing the sulfonate monolayer with "wet" cyclohexane as in region "B" indicates an exo-thermic effect that can only be associated with water adsorption through the sulfonate monolayer. (It had previously been shown that concentrations of Ba(DNNS)$_2$, much less than 0.5%, produce close-packed monolayers.) Further addition of sulfonate as in region "C" produces an endothermic heat effect that again can be attributed to solubiliza-tion of adsorbed water by the micelles.

This possible explanation was then investigated by studying the effect that drying of the cyclohexane and sulfonate solutions had on the heat of sulfonate adsorption. Initial work involved the use of cyclohexane dried over 4Å molecular sieve for establishment

of thermal equilibrium and subsequent washing.  No attempt was made
to dry the sulfonate solution for this part of the study.  This data
is shown in Figure II.  Region "A" indicates an exothermic adsorption,
region "B" indicates no desorption or an extremely slow desorption,
but region "C" which corresponds to a re-wash of the adsorbed sulfonate
monolayer with sulfonate indicates an exothermic heat effect.  This
was again attributed to water adsorption.  This was verified by use
of both dried solvent and dried sulfonate solution.  These last studies
indicated an exothermic heat effect in region "A" and no heat effects
in region "B", "C", and "D".  This particular recorder tracing is not
shown since it is identical in shape to Figure II except that no heat
effect was observed in region "C".

Table I quantitates the effect of water on sulfonate adsorp-
tion and represents data obtained under the above described
conditions.  It is interesting to note that the net heat effect
obtained by summing the heats of adsorption and desorption is a
constant independent of run conditions.

TABLE I.  Effects of Water on the Adsorption of Sulfonates

| Run No. | Heat of Adsorption for Na(DNNS) on $Fe_2O_3$ (mcal) | Heat of Desorption from $Fe_2O_3$ (mcal) | Net Heat Effect (mcal) |
|---|---|---|---|
| A. "Wet" Cyclohexane/"Wet" Sulfonate Adsorption | | | |
| 1 | -16.9, +2.4 | -8.6 | -23.1 |
| 2 | -21.7, +5.7 | -8.2 | -24.2 |
| 3 | -22.0, +5.1 | -5.8 | -22.7 |
| 4 | -19.6, +1.8 | -5.1 | -22.9 |
| B. "Dry" Cyclohexane/"Wet" Sulfonate Adsorption | | | |
| 5 | -58.2 | +--- | --- |
| 6 | -62.0 | +42.7 | -19.3 |
| 7 | -55.0 | +--- | --- |
| C. "Dry" Cyclohexane/"Dry" Sulfonate Adsorption | | | |
| 8 | -22.7 | N.D. | -22.7 |
| 9 | -23.3 | N.D. | -23.3 |
| 10 | -23.2 | N.D. | -23.2 |
| 11 | -22.5 | N.D. | -22.5 |

These unusual results indicate some of the complexities involved in the rust inhibition mechanism. It had previously been reported that sulfonates are strongly and irreversibly adsorbed to form close-packed monolayers at solution concentrations significantly less than used in this work (2). The irreversible nature of sulfonate adsorption is verified by results under condition "C" of Table I. This strongly suggests that water is the chemical species that is being either adsorbed or desorbed under the other test conditions. For Run Nos. 1-4, we are dealing with an initially water saturated surface and the endothermic heat effect is most probably the result of water solubilization in the sulfonate micelles. In the second series of experiments (Run Nos. 5-7) we are dealing with an initially dry surface and the large exothermic heat effect suggests co-adsorption of water with the sulfonate. This type of behavior could be explained by assuming that an equilibrium exists between adsorbed water and micellar water and that the direction of this equilibrium is determined by the amount of adsorbed water initially on the metal surface. Thus, in a dry system, water solubilization in the sulfonate micelle might be considered as the first step in the corrosion inhibition mechanism.

Another factor that needs to be considered is the unusual shape of the sulfonate molecule. This molecule is umbrella shaped and is quite bulky (ca. 100 $A^2$/molecule) and would thus be expected to interact with only a relatively few of the metal oxide sites capable of adsorption even in keeping with the formation of close-packed monolayers. This would explain the ability of small water molecules to penetrate the sulfonate monolayer and adsorb on the metal oxide surface. It is reasonable to assume that these sites would be available to interact with the hydrocarbons of the bulk lubricant and would thus explain the influence of the structure of the bulk lubricant on the mechanism of corrosion inhibition.

The effect of trace amounts of water on the adsorption process is illustrated in Figure III. In this work, Na(DNNS) in cyclohexane is stored over molecular sieve in order to prevent water adsorption from the atmosphere. The syringe used to inject the Na(DNNS) into the carrier stream is usually freshly loaded before the start of the run. In Figure III, the first four injections were from a Na(DNNS) solution that was allowed to stand overnight in the syringe. After the fourth injection of sulfonate, fresh Na(DNNS) solution was drawn into the syringe and used for the remaining injections. It appears that the amount of water in the micelle, the degree of dryness of the cyclohexane and the amount of water on the metal oxide surface determine to a great extent the "apparent" heat effect associated with adsorption. This complex water equilibrium is probably the key to the understanding

of why sulfonates are effective in some base fluids and not in others.

## Heat of Adsorption

Analysis of data obtained by thermometric titration of suspended $Fe_2O_3$ in cyclohexane with Na(DNNS) can be difficult since total heats evolved (~0.3 cal) are small compared to other potential side reactions. A program has been written to reduce the effect of any initial spurious heat effects and to facilitate data reduction. Typical titration data as obtained from the solution calorimeter is shown in the bar graph (Figure I). The curved line in this graph represents the heat that would be evolved for a theoretical Langmuir adsorption with $\Delta H$, $K_2$ and "a" equal to 9 Kcal/mole, $1.05 \times 10^4$ liter/mole and 0.32 $\mu$ mole/$m^2$, respectively. The fit of the theoretical curve to all parts of the bar graph is good. Although the adsorption constants obtained from the solution calorimeter indicate strong adsorption and close-packing, these values are somewhat lower than previously reported (2).

Initial work indicated a relatively large uncertainty in the measured value for the heat of adsorption of sulfonates on iron oxide powder. In order to reduce this uncertainty, work was done on the effect of various parameters (e.g., the weight of iron oxide powder and effect of water) on the measured heat of adsorption. Heats of adsorption measurements on iron oxide powder dried under vacuum at $120^{\circ}C$ were not highly reproducible. On the other hand, experiments with iron oxide powder that were not subjected to drying gave very reproducible results. However, the measured heat of adsorption decreased with the weight of iron oxide powder. This effect can be seen in Figure V.

The graph shows the amount of heat liberated (mcal) during the titration of various weights of iron oxide powder in 25 ml of dry cyclohexane with a 0.0321 m solution of sodium dinonylnaphthalene-sulfonate. In Figure V, the solid lines represent actual data points and the dashed lines (e.g., 1.0 and 0.5 g run) are straight line extensions of the initial slopes. At the start of these thermometric titrations, nearly all sulfonate molecules are adsorbed. As the surface coverage increases, the fraction of sulfonate molecules that adsorb on the iron oxide powder decreases and this results in a general falling off of the heat evolved with respect to ml titrated. This can be seen in Figure V for the 1.0 and 0.5 g samples. If all molecules were adsorbed, then the experimental points would be expected to lie on the dashed lines. The initial slope in this type of plot (heat evolved/amount adsorbed) would be equal to the heat of adsorption and should be completely independent of the amount of iron oxide

powder used in the experiment. This is obviously not true in this experimental work. Calculated heats of adsorption were 8.5, 8.2, 7.8, 7.1, 3.9, and 2.1 Kcal/mole for 2.5, 2, 1.5, 1, 0.5, and 0.25 gram samples.

This unusual effect can be attributed to an endothermic heat effect (associated with water desorption) that occurs along with the exothermic heat effect associated with sulfonate adsorption. According to competitive adsorption theory, the concentration of water and sulfonate in solution are dependent on the fraction of the total surface covered by sulfonate molecules and this would fully account for this unusual effect. This hypothesis can be tested by assuming that the actual measured amount of heat ($Q_m$) is equal to the exothermic heat of adsorption ($Q_a$) and the endothermic heat associated with water desorption ($Q_d$).

$$Q_m = Q_a - Q_d \tag{1}$$

Dividing both sides of equation (1) by grams of adsorbent (g), we have:

$$Q_m/g = Q_a/g - Q_d/g \tag{2}$$

If equation (2) is valid, a plot of $Q_m/g$ vs $1/g$ should give a straight line having an intercept of $Q_a/g$ and a slope of $Q_d$. A plot of experimental data according to equation (2) is shown in Figure VI for a surface coverage value of 19.3 $\mu$ moles/g. This plot indicates that the true heat of sulfonate adsorption is 10.1 Kcal/mole.
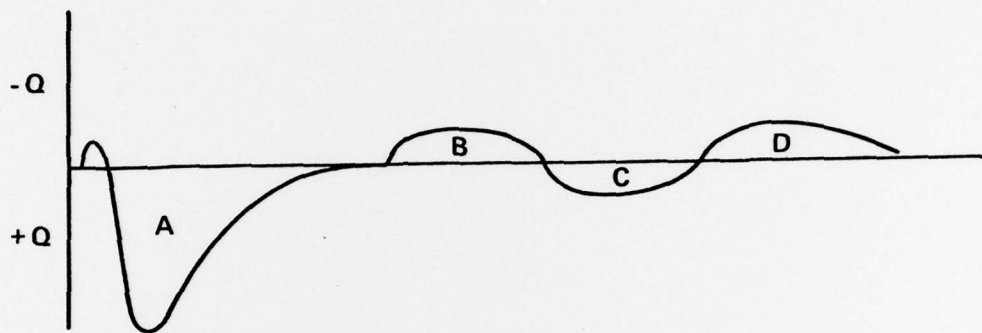
## IV    CONCLUSIONS

Previous studies (2,3) have indicated that sulfonates are strongly adsorbed on metal oxide powders. This work supports this previous finding in that a large heat of adsorption was found (10.1 Kcal/mole) for sulfonate adsorption on iron oxide powder. This indicates a relatively strong interaction between sulfonate and the metal oxide surface. This work also pointed out other areas that need consideration for possible interpretation of the mechanism of corrosion inhibition. Other types of rust inhibitors (e.g., long chained organic acids) have molecular dimensions that approximate the spacing of sites on the metal oxide surface, however, salts of dinonylnaphthalenesulfonic acid have an unusual umbrella-like shape and are quite bulky by comparison having molecular areas ranging from 200$A^2$ to 125 $A^2$ at 40 dyn/cm (4,5). Thus, sulfonate molecules will interact with only a relatively few of the sites available for

adsorption. This would explain the ability of the small water molecules to penetrate the sulfonate monolayer and adsorb on these free sites. It appears that in dry systems, water absorption in the micelle is favored over adsorption on the metal surface and that this factor would also tend to inhibit the corrosion process. The cyclohexane molecule is apparently too sterically hindered or lacking in adequate polarity to interact with these sites. A facile equilibrium between surface water and micellar water was indicated. In actual corrosion inhibiting systems, the solvent is normally an oil containing polar components and it would be expected that these polar components would be capable of interacting with these "free" sites which would tend to block this water equilibrium process.

## REFERENCES

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3. P. Kennedy, M. Petronio, and H. Gisser, Ibid., 75, 1975 (1971).

4. M. L. Smith, B. E. Gordon, and R. C. Nelson, Ibid., 69, 3833 (1965).

5. F. M. Fowkes, Ibid., 66, 1843 (1962).

A   0.5% Ba (DNNS)$_2$ in C$_6$H$_2$
B   C$_6$H$_{12}$ with 0.01% H$_2$0
C   0.5% Ba (DNNS)$_2$ in C$_6$H$_{12}$
D   C$_6$H$_{12}$ with 0.01% H$_2$0

Figure I.  Adsorption of Ba (DNNS)$_2$ on Fe$_2$0$_3$ with "wet" C$_6$H$_{12}$
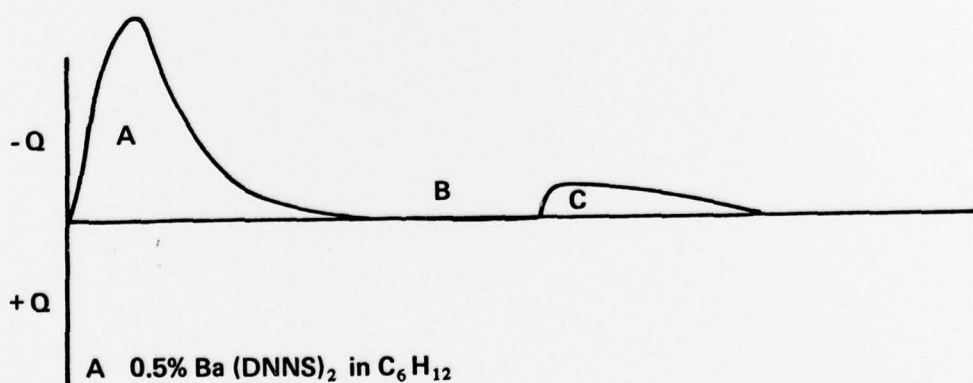


A   0.5% Ba (DNNS)$_2$ in C$_6$H$_{12}$
B   C$_6$H$_{12}$ (dried)
C   0.5% Ba (DNNS)$_2$ in C$_6$H$_{12}$

Figure II.  Adsorption of Ba (DNNS)$_2$ on Fe$_2$0$_3$ with "dry" C$_6$H$_{12}$
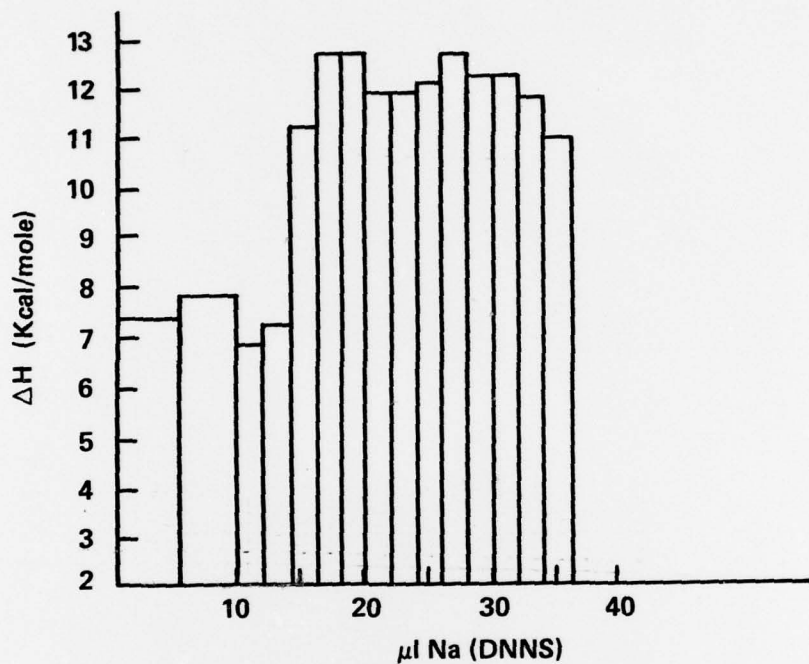
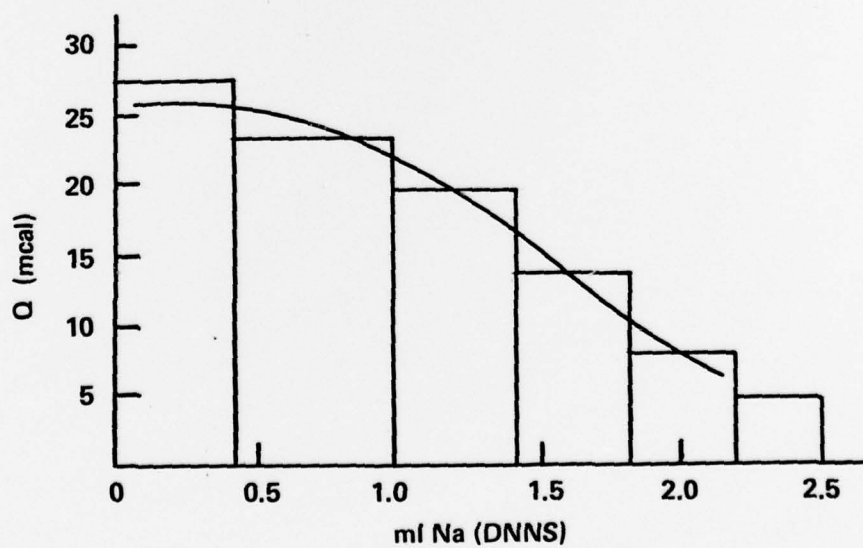Figure III. Effect of Water on Na (DNNS) Adsorption



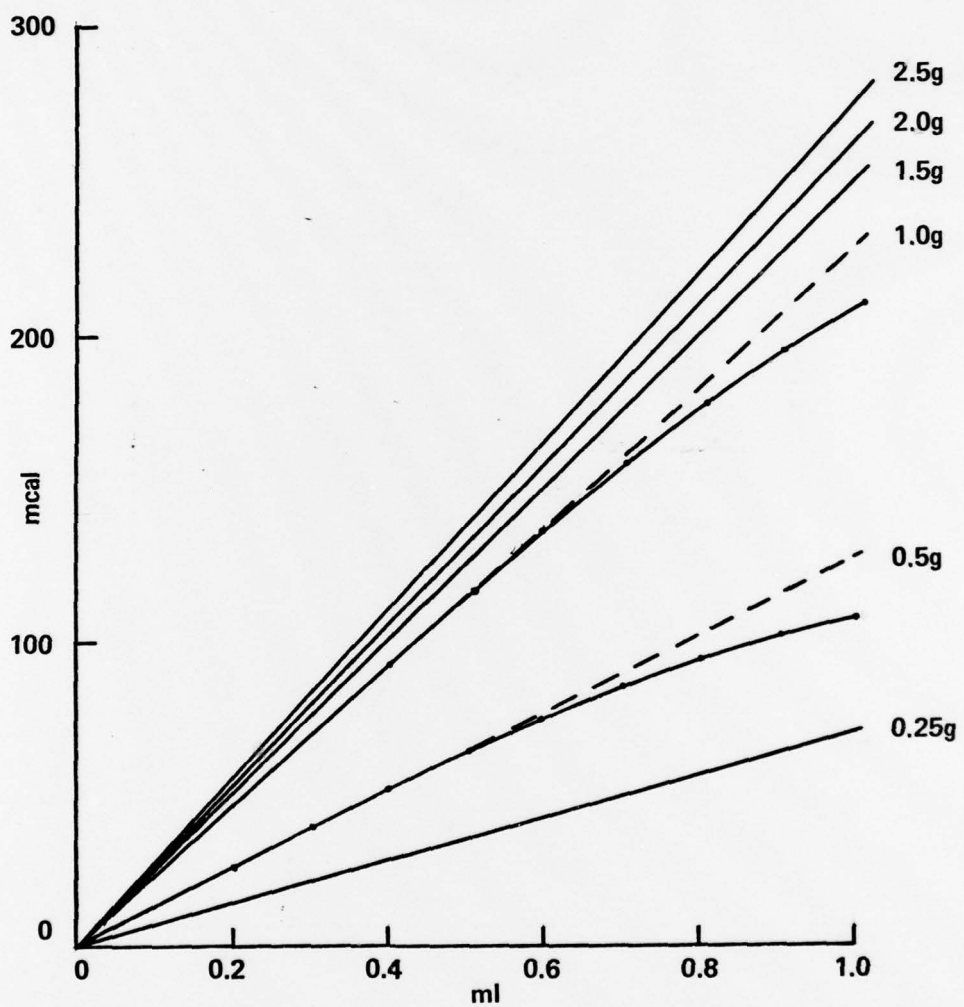Figure IV. Thermometric Titration of $Fe_2O_3$ with Na (DNNS)

Figure V. Thermometric Titration Data for Various Weights of $Fe_2O_3$ Titrated with 0.0321 $\underline{m}$ NaDNNS in $C_6H_{12}$
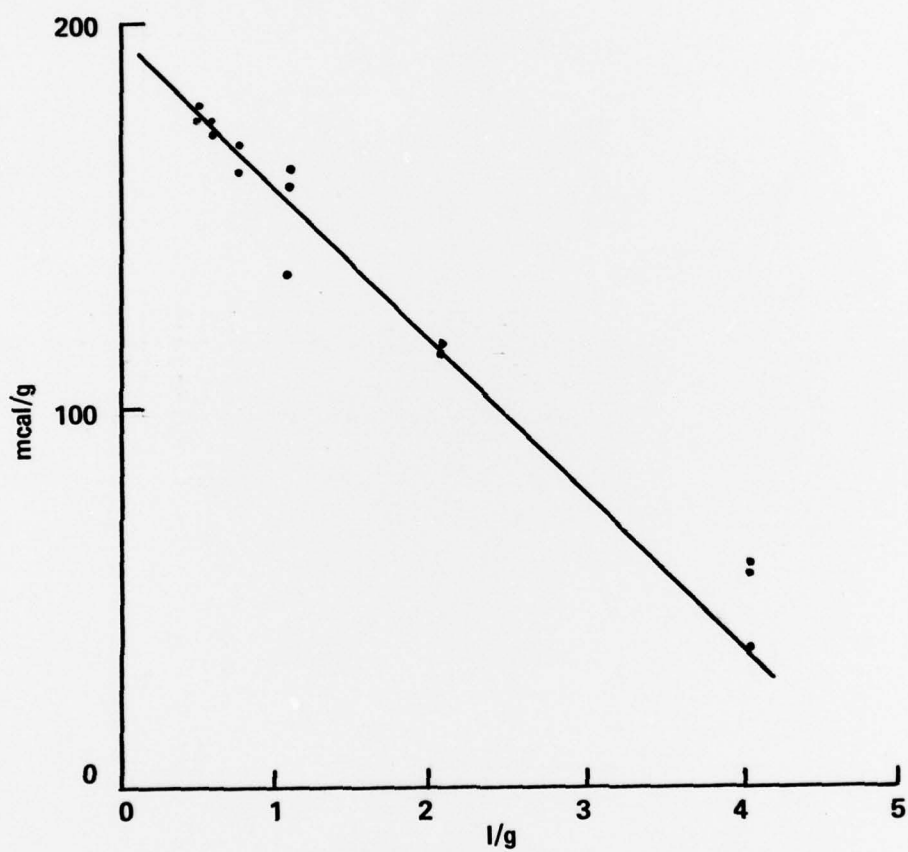
Figure VI. Plot of "mcal/g" vs. "l/g" at a Surface Coverage of 19.3 $\mu$ moles/gram