Adsorption of Lubricating Oil Additives on Solid Surfaces (Part 3)

Influence of Polar Compounds on the Adsorption and Desorption of Additives

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Lubricating oil additives are expected to perform in the presence of polar organic compounds in functioning lubrication system. The present study deals with the influence of polar solvent on the adsorption phenomena of DNNS and other additives on metal surfaces using ellipsometry. The results show that BaDNNS film adsorbed on gold surface from *n*-hexane solution is not easily desorbed with *n*-hexane, whereas the film is desorbed with acetone. The same result was obtained with CaDNNS; succinimide dispersant is not easily desorbed by acetone rinse. The same tendency was obtained with chromium, and iron alloy. On the other hand, when BaDNNS is adsorbed from acetone solution on gold surface, the adsorbed film consists of two layers, that is, one is easily desorbed with acetone and the other is not. The contact angle measurement suggests that the adsorbed film of BaDNNS from *n*-hexane solution is different from that for acetone in orientation. The adsorption behavior of BaDNNS on gold from mixed *n*-hexane/1-propanol solution is different from that on carbon black.

1. Introduction

Lubricating oil additives are expected to perform in the presence of polar organic compounds that occur in functioning lubrication systems, such as that of an automotive engine. These polar compounds may be present because of oxidation of the oils or its nitration, caused by high ambient temperature and/or blow-by gas. It is to be expected that the adsorption behavior of such additives will be greatly influenced by these polar compounds, but little has been reported on this matter. In a preceding paper¹⁾, the adsorption of dinonylnaphthalenesulfonate (DNNS) on carbon black was reported, including in the presence of polar compounds, and the influence of which was confirmed. A second paper reported on the adsorption of various additives on flat metal surfaces, as measured ellipsometrically²⁾. In the present study, the effect of polar compounds such as alcohols and ketones on the adsorption of various additives is reported for gold, chromium, and iron alloy adsorbent surfaces. The additives used were BaDNNS, CaDNNS, poly-decylmethacrylate (PDMA), Zn-diisobutyl-dithio-phosphate (ZnDiDP), and other com-

mercial products. Ellipsometry is again used.

2. Experimental

Adsorbed film thicknesses were measured by means of a Rudolph & Sons Model 436/200E ellipsometer, the same as used in part 2 of this series²⁾. In addition, some measurements were made with a Shimadzu EP-10 ellipsometer. All experiments were at 25°C. The schematic diagram of the adsorption cell is shown in Fig. 1.

Fig. 1 Adsorption Cell for Ellipsometric Measurement of Adsorbed Film Thickness

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In a typical adsorption procedure, *n*-hexane was added first to the sample cell containing the surface specimen, followed by addition of the additive, to give a final concentration of 1×10^{-3} mol/l. The solution was stirred, with periodic ellipsometric readings until equilibrium was obtained or the experiment terminated.

At the end of the adsorption procedure, the solution was removed by draining it out of the cell compartment, without disturbing the specimen. The surface of the specimen was rinsed with a small amount of *n*-hexane, and then, in some cases, with some second solvent, and the specimen was then dried under vacuum. Film thickness measurements could be made at various stages during this procedure.

The lubricating oil additives used were BaDNNS, CaDNNS, ZnDiDP, poly-decyl methacrylate (PDMA), and a commercial ashless dispersant. Their purification was as described in parts 1¹⁾ and 2²⁾ of this series.

The organic solvents used were of analytical grade. They were additionally purified by silica gel chromatography followed by fractional distillation. Finally, any adventitious water was removed by adsorption on molecular sieve material.

The specimens involved consisted of gold, chromium, and iron alloy surfaces, which were obtained and cleaned as described in part 2²⁾.

3. Results

3.1 Film Adsorbed from *n*-Hexane Solution

Figure 2 shows some typical adsorption and desorption results for BaDNNS on a gold surface, using *n*-hexane solution. Adsorption is seen to reach completion within a few minutes. The gold

surface was then rinsed with *n*-hexane, but there was no desorption, that is, no detectable change in film thickness occurred. If, however, the specimen was rinsed with a polar solvent, acetone or 1-propanol, and then re-immersed in *n*-hexane (to return to the original solvent index of refraction condition), we found that desorption had occurred. Duplicate experiments gave the same result; also, the same behavior was found with CaDNNS. Similarly, Kennedy and co-workers³⁾ reported that BaDNNS was not desorbed easily from a metal oxide surface ($\text{Fe}_2\text{O}_3/\text{Ni}_2\text{O}_3$) by cyclohexane.

Continuing with the BaDNNS system, Table 1 reports the percent reduction in film thickness, and hence percent desorption⁴⁾, on washing a film covered gold surface with various solvents. The general finding was that non-polar solvents such as cyclohexane and *n*-hexane do not desorb BaDNNS, while the more polar solvents, such as 1-propanol, acetone, ethyl acetate and ethanol desorb.

Table 2 summarizes the desorption behavior of

Table 1 Desorption of BaDNNS Film Adsorbed on Gold Surface with Organic Solvent

No.	Solvent	%BaDNNS Desorbed	$\delta^a)$	$\epsilon^b)$	$\mu^c)$
1	<i>n</i> -Hexane	<10	7.3	1.890	0.0
2	Cyclohexane	<10	8.2	2.023	0.0
3	Benzene	60	9.15	2.284	0.0
4	Ethyl acetate	75	9.9	6.02	1.810
5	2-Butanone	50	8.9	18.51	2.747
6	Acetone	>90	9.9	20.7	2.720
7	1-Propanol	80	11.7	20.1	1.657
8	Ethanol	90	12.9	24.3	1.68
9	<i>n</i> -Heptane	<10	7.45	1.924	0.0

^{a)} : Solubility parameter from Ref. 8, ^{b)} : Dielectric constant, ^{c)} : Dipole moment in Debye units. Values for ϵ and μ obtained from the Handbook of Physical Chemistry, Chemical Rubber Publishing Co.

Fig. 2 Adsorption of BaDNNS from *n*-Hexane Solution followed by Desorption with Acetone, and Adsorption of BaDNNS from 1-Propanol Solution; BaDNNS Concentration, 1×10^{-3} mol/l

Table 2 Desorption of Lubricating Oil Additives with Organic Solvent on Gold Surface (The adsorption was made from *n*-Hexane)

No.	Additives	% Desorption		
		<i>n</i> -Hexane Rinse	1-Propanol Rinse	Acetone Rinse
1	BaDNNS	<10	80	>90
2	CaDNNS	<10	80	>90
3	Polyalkenyl Succinimide	<10	30	30
4	PDMA ^{a)}	<10	50	60
5	ZnDiDP	30	60	70

^{a)} : Polydecyl methacrylate, $\bar{M}_w$ 170,000

other additives, again from a gold surface. There is some variation in behavior with the type of adsorbate, particularly with polar solvents. Thus polyalkenyl succinimide and PDMA are relatively less desorbable. Interestingly, ZnDiDP is somewhat more easily desorbed by *n*-hexane than are the DNNS salts, and less easily desorbed by polar solvents.

Other adsorbing surfaces were also studied. **Tables 3** and **4** show the behavior found for a chromium and an iron alloy surface, respectively. These surfaces behaved similarly to gold in that there was little desorption by *n*-hexane (the adsorbing solvent). With acetone as the desorbing solvent, BaDNNS was easily desorbed from the iron alloy surface and chromium surface. The behavior of CaDNNS was similar. The polyalkenyl succinimide was more easily desorbed from both surfaces than from gold, using acetone.

3.2 Films Adsorbed from a Polar Solvent Solution

Since polar solvents could generally desorb a

Table 3 Desorption of Lubricating Oil Additives on Chromium Surface at 25°C Adsorbed from *n*-Hexane

No.	Additives	% Desorption	
		<i>n</i> -Hexane Rinse	Acetone Rinse
1	Ca-sulfonate A	20	80
2	Ca-sulfonate B	20	80
3	BaDNNS	<10	>90
4	CaDNNS	<10	>90
5	Polyalkenyl Succinimide A	<10	50

Table 4 Desorption of Lubricating Oil Additives on Iron Alloy at 25°C Adsorbed from *n*-Hexane

Additives	% Desorption	
	<i>n</i> -Hexane Rinse	Acetone Rinse
BaDNNS	<10	80
Polyalkenyl Succinimide A	<10	40

BaDNNS film that had been adsorbed onto gold from *n*-hexane solution, it is expected that there would be little adsorption, if any direct adsorption from such solvent solutions takes place. This was indeed the case with 1-propanol as solvent, as illustrated in **Fig. 2**, where there was a small apparent initial adsorption, which then dropped essentially to zero.

A rather more complex behavior was found in the case of acetone solution, however. This is illustrated by the sequences shown in **Fig. 3**. Curve (I) in the figure shows that the final adsorbed film thickness rose to about the same level as with *n*-hexane as solvent. There was, thus, no indication of reduced adsorption. Note, however, that the rate of adsorption was much smaller than with *n*-hexane as the solvent; the half time of approach to equilibrium was about 15 min., and some sixty minutes were required to approach a limiting value. Rinsing with acetone effected about a 30% desorption (much less than with a film adsorbed from *n*-hexane solution), so that there now appeared to be an adsorbed film present that was resistant to desorption with acetone. On re-introducing a solution of BaDNNS in acetone to the cell, further adsorption took place, to a level exceeding that originally reached. This readsorption occurred more rapidly than did the previous adsorption, with a half time of about 10 min.

Qualitatively, it appears that two layers or two types of adsorbed films are involved. Layer A in **Fig. 3** adsorbs strongly onto the clean gold surface, and does not desorb easily. Layer B adsorbs to about an equal final extent as layer A, and is readily desorbed by the same solvent, acetone.

Curve (II) in the figure shows the results of a further exploration of the situation. Adsorption of BaDNNS from acetone solution was allowed to occur for a few minutes only. On now rinsing with acetone, slight desorption occurred. On re-introducing a solution of BaDNNS in acetone into the cell, further adsorption occurred, up to about the same level as reached in sequence (I) with the same total adsorption time, and with a half time of about 10 min. Continuing with sequence (II), on now rinsing with acetone, there was again about 30% desorption, or as much as occurred in sequence (I).

3.3 Contact Angle Measurements

The desorbability of film A by acetone was quite different from the desorbability of a film originally adsorbed from *n*-hexane solution. We can call

Sequence (I) : a-b : adsorption from 1×10^{-4} mol/l solution; at point b the solution was removed from the cell, the surface of the gold specimen was rinsed with acetone, and acetone was put in the cell; b-c : effect of the rinse; c-d : no further desorption occurred; at point d, the cell was filled with 1×10^{-4} mol/l BaDNNS solution; d-e : further adsorption of BaDNNS.

Sequence (II) : a-b' : adsorption from 1×10^{-4} mol/l BaDNNS solution for 3 min; at point b' the solution was removed from the cell, the surface of the specimen rinsed with acetone, and acetone was put in the cell; b'-c' : effect of the rinse; c'-d' : no further desorption occurred; at point d', the cell was filled with 1×10^{-4} mol/l BaDNNS solution; d'-e' : further adsorption of BaDNNS; at point e', the solution was removed, the specimen rinsed with acetone, and the cell filled with acetone; e'-f' : effect of the rinse; f'-g' : no further desorption.

Fig. 3 Adsorption of BaDNNS on Gold from Acetone Solution at 25°C

this *n*-hexane adsorbed film, film C. It seemed worthwhile to see whether or not the surface properties of films A and C also differed, as determined by contact angle measurements.

A sample of film C was prepared by immersing a cleaned gold surface into a 1×10^{-4} mol/l *n*-hexane solution of BaDNNS for either 2 min. or 10 min. The specimen was then taken out and rinsed with *n*-hexane, and air dried. The sample of film A was prepared following the same general procedure,

but now with adsorption from a 1×10^{-4} mol/l acetone solution, followed by rinsing with acetone and air drying.

The contact angle of water on films A and C was measured by placing a drop of water on the film covered specimen, and using a goniometer telemicroscope. The results are given in **Table 5**. The clean gold surface gave an angle of about 25°; there are literature indications that the water contact angle on absolutely pure gold surface is

Table 5 Influence of Adsorption on Contact Angle of Gold Surface

Surface Treating Method	Immersing Time	Contact Angle of Water ^{a)}		
		θ_1	θ_2	av.
1. Clean gold surface	—	24 28 25	26 26 27	25 27 26
2. After immersing gold surface in hexane and air drying	2 min 10 min	23 23	28 29	25.5 24.5
3. After immersing gold surface in hexane and air drying	2 min 10 min	22 25	24 28	23 26
4. After immersing gold surface in solution (BaDNNS 10^{-4} mol/l in hexane), rinse with hexane and air drying	2 min 10 min	52 50 50	54 58 50	53 54 50
5. After immersing gold surface in solution (BaDNNS 10^{-4} mol/l in acetone), rinse with acetone and air drying	2 min 10 min	34 35	36 37	35 36

^{a)} : θ_1 and θ_2 are the angles measured for the left and right drop profile

zero (see Refs. 5 and 6). Under ordinary handling procedures, however, results similar to ours are found; there is evidently some surface reaction with atmospheric gases which make a gold surface incompletely wet by water. Film C shows the contact angle of 50° , while with film A, it was 35° . It is thus apparent that the film C/air interface is less polar than the film A/air interface.

3.4 Adsorption from Mixed Solvent Systems

It was reported in part 1 of this series¹⁾ that the adsorption of BaDNNS on carbon black varies with the composition of a polar/non-polar solvent mixtures. A similar study is reported here for the case of BaDNNS adsorbed on the gold surface, using 1-propanol/*n*-hexane mixtures. As shown in **Fig. 4**, the surface coverage decreased linearly to zero with increasing percent of 1-propanol; this is consistent with the showing in **Fig. 2** of negligible adsorption from 1-propanol solution. For comparison, the previous results¹⁾ with carbon black as adsorbent are included in the figure. In this case, however, the adsorption was greatly reduced by only a small addition of 1-propanol.

These results indicate that BaDNNS is adsorbed more tenaciously on a gold surface than on one of carbon black. This observation is consistent with the general experience that sulfonates are more effective in metal surface detergency than in the dispersion of carbons or related insoluble products in deteriorated automotive engine oils.

- : Adsorption on Gold from 1-Propanol/*n*-Hexane solution, at 25°C
- : Adsorption on Gold from 1-Propanol/*n*-Heptane solution, at 30°C
- : Data from Ref. 1, Adsorption on Carbon Black from 1-Propanol/*n*-Heptane solution, at 30°C

Fig. 4 Adsorption of BaDNNS on Gold and Carbon Black from mixed 1-Propanol/*n*-Hexane(or *n*-Heptane) Solution, at Room Temperature and using 1.3×10^{-3} mol/l Solutions

4. Discussion

There are several aspects of interest in our results. The adsorption should be of the physical type, that is, it should be due to van der Waals forces rather than to strong chemical bond formation between adsorbent and adsorbate. This should certainly be true of the gold and chromium surfaces; even hydrogen bond formation with the iron oxide surface would be classified as a van der Waals type interaction. Since the films could be easily desorbed with suitable solvent, it is believed that no direct chemical bond formation is involved.

The first point of interest is that, while physical adsorption is generally considered to be rapid and reversible⁷⁾, the data shown in **Fig. 2** indicate a rather slow adsorption process to be occurring, and the adsorption is not highly reversible. The type C films(adsorbed from *n*-hexane solution) are not desorbed by *n*-hexane, although they are largely desorbed by polar solvents. There is thus a question as to whether or not adsorption isotherms determined for *n*-hexane solutions are truly ones in equilibrium.

A second aspect of interest is that the same adsorbent-adsorbate system can give apparently different types of films, depending on the solvent used. It has been necessary to designate films A and B in the case of adsorption from acetone solution, and film of type C, in the case of adsorption from *n*-hexane solution.

Turning to **Table 1**, there is some correlation between the ease of desorption of a type C film by a given solvent with the δ solubility parameter (Ref. 8). As might therefore also be expected, there is some correlation as well with the solvent dipole moment or dielectric constant.

There are many cases of irreversible adsorption of polymers by various adsorbents reported (Refs. 9—12).

A possible explanation of the solvent effect follows. There must be a potential difference between the metal surface(gold or chromium) and solution, and hence a surface charge and associated diffused double layer, note Refs. 4, 13. The relaxation distance of this double layer will be much smaller in a polar solvent than in a non-polar solvent,⁷⁾ and it can be supposed that the surface charge adsorbed by an adsorbate in a non-polar solvent is much larger than that in a polar solvent. In addition, the adsorbate used here should be more soluble in the polar solvents than in the non-polar

Fig. 5 Illustrations of Possible Molecular Orientations of BaDNNS in Films A, B, and C, and their Desorption Behavior

ones, note Refs. 14, 15. For example, δ for BaDNNS is 11.3¹⁵⁾ or close to the values for ethanol and 1-propanol. If the adsorption is taken as a partitioning between a surface phase and a solution phase, then the adsorption from a polar solvent solution should be weaker and more easily desorbable by a polar solvent, than that for a non-polar solvent.

A problem with the above kinds of explanation is that the final film thickness was actually greater for adsorption from a polar solvent than from a non-polar one (**Figs. 2** and **3**). Nor is adsorption strength in itself an explanation for non-desorbability if only van der Waals forces are involved. There is an element of passiveness to the adsorbed film that suggests that more than individual molecule-adsorbent interactions are involved. Possibly, for example, type C films have assembled into some kind of condensed or even ordered surface phase which resists desorption. The contact angle result suggests that C type films are largely oriented with the non-polar portion of the adsorbate towards the solution, as illustrated in **Fig. 5(a)**. A similar conclusion was reached in the case of DNNS salts adsorbed on stainless steel.¹⁶⁾

Turning to the results using acetone as solvent, the A type film obtained is more polar than the C type, judging from the contact angle measurement, and this suggests that the A type film may be one with the polar portion largely oriented toward the solvent, as illustrated in **Fig. 5(b)**. The rather slow rate with which this type of film forms certainly suggests structural ordering in the adsorbed phase, as does also its resistance to desorption by acetone. The B type film may now be due to a second layer adsorption. As shown in **Fig. 5(b)**,

this second layer might be oriented with the non-polar portion directed towards the solvent, and thus resemble the C type film. This orientation is consistent with the easy desorbability of the C-type film by acetone.

5. Summary

(1) The barium and calcium salts of DNNS, dinonylnaphthalenesulfonate, adsorb readily on to gold, chromium, and iron alloy surfaces from *n*-hexane solution. These are not easily desorbed using the same solvent. The films are readily desorbed, however, by polar solvents.

(2) The ashless dispersant, polyalkenylsuccinimide, is not easily desorbed even by polar solvents.

(3) If BaDNNS is adsorbed onto gold from *n*-hexane solution, it is readily desorbed by acetone, yet if it is adsorbed from acetone solution the film is now not readily desorbed by acetone. Indications, including contact angle measurements for water on adsorbed films, are that films adsorbed from *n*-hexane solution are oriented differently than those adsorbed from a polar solvent solution.

(4) The adsorption of BaDNNS on gold decreases linearly with 1-propanol concentration in mixed 1-propanol/*n*-hexane solvent mixtures. The behavior is quite different from that with carbon black as adsorbent for which case very low concentrations of 1-propanol are sufficient to inhibit adsorption.

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要 旨

潤滑油添加剤の固体表面への吸着 (第3報)
添加剤の吸着および脱着におよぼす極性物質の影響

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潤滑油添加剤は現実の系では酸化劣化などの影響のため極性物質の存在下で作用することが多いと考えられる。第1報でカーボンブラックへの DNNS の吸着現象におよぼす極性物質の影響を報告した。本報告では金属表面への DNNS などの吸着現象におよぼす極性物質の影響をエリプソメトリー法で調べた。金属としては金のほかに、クローム、鋳鉄も用いた。溶媒については無極性溶媒として *n*-ヘキサンを用い、また極性溶媒としてアセトン、1-プロパノールその他を用いて検討した。

BaDNNS は *n*-ヘキサン溶液から金表面に速やかに吸着し、Fig. 2 に示すようにこの吸着膜は *n*-ヘキサンによる洗浄では脱着し難い。しかしアセトンにより脱着する。さらに Table 1 のように 1-プロパノールその他の極性溶媒によっても脱着することがわかった。他の添加剤について試みた結果 Table 2 のように CaDNNS は BaDNNS と同一傾向を示した。しかしコハク酸イミド系無灰型分散剤は強固に吸着し極性溶媒によっても脱着し難い。以上の傾向は Tables 3 および 4 のようにクロームおよび鋳鉄に対しても同様であった。

アセトンは *n*-ヘキサン溶液からの BaDNNS 吸着膜を脱着させたが、次にアセトン溶液からの BaDNNS の吸着性を調べたところ予想に反し吸着が起こった。これは Fig. 3 のようにアセトンで脱着する膜と脱着しない膜の二つから成ると推定された。この現象は Table 5 に示す吸着表面の水の接触角測定から、溶媒として *n*-ヘキサンを用いた場合とアセトンを用いた場合とでは Fig. 5 のように吸着する BaDNNS のオリエンテーションが異なることが一因と推察された。

他方、1-プロパノール溶液からは BaDNNS の金表面への顕著な吸着は観察されなかった。そこで *n*-ヘキサン/1-プロパノール混合系からの金表面への吸着を試みた結果、Fig. 4 のように BaDNNS の吸着量は 1-プロパノールの濃度に反比例した。これに対してカーボンブラックへの吸着では 1-プロパノールの低濃度域から既に BaDNNS の吸着が阻害された。

以上のように吸着表面の種類によっても BaDNNS の吸着に対する極性溶媒の影響は異なることがわかった。

Keywords

Adsorption behavior, Contact angle measurement, Ellipsometry, Metal surface, Polar compound