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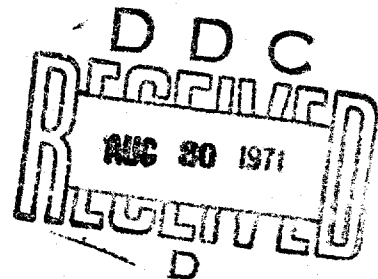
COMPETITIVE ADSORPTION OF PHENOL AND SODIUM
DINONYLNAPHTHALENESULFONATE ON NICKEL OXIDE POWDER

by

PAUL KENNEDY
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Competitive Adsorption of Phenol and Sodium

Dinonylnaphthalenesulfonate on Nickel Oxide Powder

by Paul Kennedy,* Marco Petronio, and Henry Gisser

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The adsorption of phenol at the nickel oxide-cyclohexane interface and the displacement of adsorbed phenol by sodium dinonylnaphthalenesulfonate were studied. The presence of physisorbed water on nickel oxide increased phenol adsorption. From adsorption isotherm plateaus, it was found that the cross-sectional area for phenol was $33.4 \text{ \AA}^2$ on "dry" nickel oxide and $24.3 \text{ \AA}^2$ on "wet" nickel oxide, corresponding approximately to tilted and vertical configurations in the adsorbed state. Adsorption on "wet" nickel oxide was not Langmuirian, but did follow the Frumkin isotherm, and it was found to be partly reversible, roughly corresponding to the excess adsorption promoted by physisorbed water. On "dry" nickel oxide, the adsorption was of the Langmuir-type. Competitive adsorption studies of phenol and sodium dinonylnaphthalenesulfonate on "dry" nickel oxide have indicated that competitive adsorption at high surface coverages deviated from Langmuir behavior. An approximate competitive adsorption equation, based on the Flory-Huggins isotherm, was developed to correct for the effect of adsorbate size on competitive adsorption. Competitive adsorption data fit this modified equation.

Introduction

High molecular weight alkylarylsulfonates, such as the salts of dinonylnaphthalenesulfonic acid, are effective corrosion inhibiting compounds for hydraulic and lubricating fluids. Although the actual mechanism is not well understood,¹ corrosion inhibition is related to close-packed monolayer formation which retards diffusion of corrodants to the surface and oxidation products from the surface. We have recently found² that the adsorption of salts of dinonylnaphthalenesulfonic acid on metal oxide powders follows a Langmuir model, and that close-packed monomolecular films (which may act as barriers) were formed at low concentrations. In technologically important lubricating systems, however, there is a multiplicity of polar additives that compete for adsorption, and this indicates that the composition of the mixed monolayer is a parameter of importance. In a study of competitive adsorption, Smith, Gordon, and Nelson³ found that calcium dinonylnaphthalenesulfonate is displaced from the gold-white oil interface by a polyalcohol and poly(dodecylmethacrylate), and report that this adsorption is Langmuirian.

The purpose of this investigation was to study competitive adsorption and mixed film formation in technologically important situations (e.g., mixed additive systems) on nickel oxide. Specifically, the competitive adsorption of phenol and sodium dinonylnaphthalenesulfonate in cyclohexane on nickel oxide powder was studied. The uv spectrum of phenol is sufficiently different from sodium dinonylnaphthalenesulfonate to facilitate mixture analysis. (Although phenol is not an effective antioxidant, this study was undertaken as

preliminary to more extensive work on hindered phenols.) In this work, the adsorption characteristic of phenol was also determined in order to compare adsorption data for phenol with previously obtained adsorption data for sodium dinonylnaphthalenesulfonate, and thus develop a better insight into the competitive adsorption mechanism. Attention was also given to the effect of physisorbed water on phenol adsorption.

Experimental Section

Materials. The nickel oxide powder (Vitro Laboratories) used was prepared by a metal vaporization technique. The surface area as determined by BET measurements, using N_2 adsorption, was $36 \text{ m}^2/\text{g}$. "Intra-analyzed" grade cyclohexane (J. T. Baker) was used without further purification. Mallinckrodt reagent grade phenol (with H_3PO_2 preservative) was recrystallized three times from distilled water and after initial distillation of the aqueous azeotrope, a middle cut of the fraction distilling at 180° was taken. The absence of impurities was confirmed by vpc analysis. Sodium dinonylnaphthalenesulfonate was prepared from a purified sample of dinonylnaphthalenesulfonic acid (R. T. Vanderbilt) by a method previously described.² Analysis indicated that the purified salt contained $4.73 \pm 0.02\%$ sodium (calcd 4.76).

Adsorption Measurements. Adsorption data for phenol were obtained over the concentration range of

(1) R. R. Annand, R. M. Hurd, and N. Hackerman, *J. Electrochem. Soc.*, **112**, 138 (1965).

(2) P. Kennedy, M. Petronio, and H. Gisser, *J. Phys. Chem.*, **74**, 102 (1970).

(3) M. L. Smith, B. E. Gordon, and R. C. Nelson, *ibid.*, **69**, 3833 (1965).

0.02 to 1.0%. Volumes (10 ml) of the phenol-cyclohexane solution in small glass vials (fitted with Teflon liners) were equilibrated with 500 mg of nickel oxide (18 m^2) for 5 days. (Initial adsorption of both phenol and sulfonate is very rapid. However, completion of the sulfonate required 2 hr as contrasted to several days for phenol.) This large surface area-volume ratio minimized the effect of any trace adsorption. The supernatant liquids, after separation as ascertained by the absence of the Tyndal effect, were analyzed spectroscopically at $278 \text{ m}\mu$, using a Beckman DK-2 recording spectrophotometer with matching 1-cm cells. Surface coverage was calculated from equilibrium data. Techniques used in the studies of the rate of adsorption, desorption by dilution, and effect of temperature were previously described.²

Competitive adsorption measurements require an accurate method of mixture analysis. The phenol-sulfonate system was found to be suitable for mixture analysis since phenol has a spike-like adsorption maximum at $278 \text{ m}\mu$ with essentially no overlapping adsorption at $284 \text{ m}\mu$, which is an adsorption maximum for the sulfonate. In most experiments, phenol solution was added to the metal oxide and, after equilibration, sulfonate solution was added. Data from reverse addition and simultaneous addition were similar. Sulfonate addition always resulted in the expected desorption of phenol and the amount of phenol desorbed increased with increasing sulfonate concentration in general accord with Langmuir theory. Experimentally, it is helpful to keep the initial concentration of one component constant so that the amount of desorption associated with an increase in the concentration of the other component could be accurately measured. The competitive adsorption experiments were run at less than full surface coverage in the range of fractional surface coverage values from 0.65 to 0.98.

Results and Discussion

The adsorption of phenol at the nickel oxide-cyclohexane interface was found to be complex and influenced by the amount of physisorbed water on the nickel oxide substrate. Phenol adsorption was measured on nickel oxide powder at varying states of dryness. These isotherms are shown in Figure 1. Nickel oxide powder in equilibrium with atmospheric moisture ($14 \text{ }\mu\text{mol of } \text{H}_2\text{O/m}^2$) was used in determining isotherm III. This amount of water corresponds approximately to monolayer coverage and considerably complicates the interpretation of adsorption data since this amount of water considerably in excess of the amount of water (0.015% weight) necessary to saturate the phenol-cyclohexane solution. (This problem is not encountered in the sulfonate-cyclohexane system because the water is readily solubilized by sulfonate micelles.) The nickel oxide was partially dried at 110° for 1 hr (resulting in $1 \text{ }\mu\text{mol/m}^2$) for determination of isotherm II and

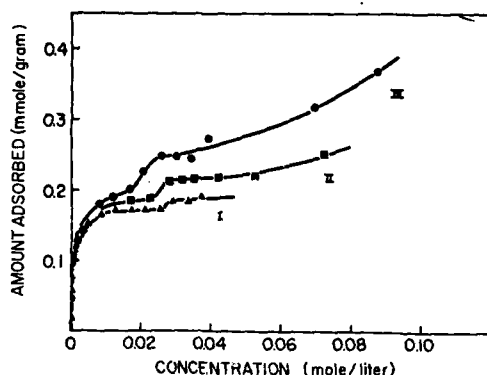


Figure 1. Phenol adsorption on nickel oxide powder. The three isotherms represent various amounts of physisorbed water on the surface: extensively dried powder (isotherm I), moderately dried powder (isotherm II), most of the surface covered by physisorbed water (isotherm III).

more vigorously dried at 120° under N_2 to constant weight (resulting in less than $1.0 \text{ }\mu\text{mol/m}^2$) for determination of isotherm I. Yao⁴ reported a BET V_n value of $10.05 \text{ }\mu\text{mol/m}^2$ for physisorbed water on nickel oxide. Using this value, the surface coverage for the residual physisorbed water on the nickel oxide powders used in isotherms II and I were approximately 0.3 and less than 0.1, respectively.

Adsorption on Dry Nickel Oxide. Phenol adsorption on "dry" nickel oxide (isotherm I) is shown in Figure 1. Neglecting for the moment the presence of the small secondary plateau, isotherm I resembles a Langmuirian adsorption, and, indeed, follows the Langmuir relationship

$$\theta = KC(1 - \theta) \quad (1)$$

where θ is the fraction of the surface covered, $(1 - \theta)$ is the fraction uncovered, C is the equilibrium concentration, and K is the adsorption coefficient or equilibrium constant. Equation 1 can be expressed as follows, and the data are shown in Figure 2.

$$C/(x/m) = 1/aK + C/a \quad (2)$$

where x is the weight in grams of adsorbate on m grams of nickel oxide and a is the maximum value of x/m . Although it is realized that the system under study is much too complex to be explained in terms of the simple assumptions involved in the derivation of this relationship, Figure 2 does show that the ratio of the amount in solution to the amount on the surface does vary linearly with concentration. Adsorption constants were $33.4 \text{ }\text{\AA}^2/\text{molecule}$ (as compared with $33.9 \text{ }\text{\AA}^2/\text{molecule}$ as calculated from the first plateau of isotherm I, Figure 1) and $1.40 \times 10^3 \text{ l./mol}$. They represent the adsorption at full and half surface coverage. In our opinion, phenol adsorption is due in part to attraction arising from the hydroxyl group. Thus, the orientation of

(4) Y.-F. Y. Yao, *J. Phys. Chem.*, **69**, 3930 (1965).

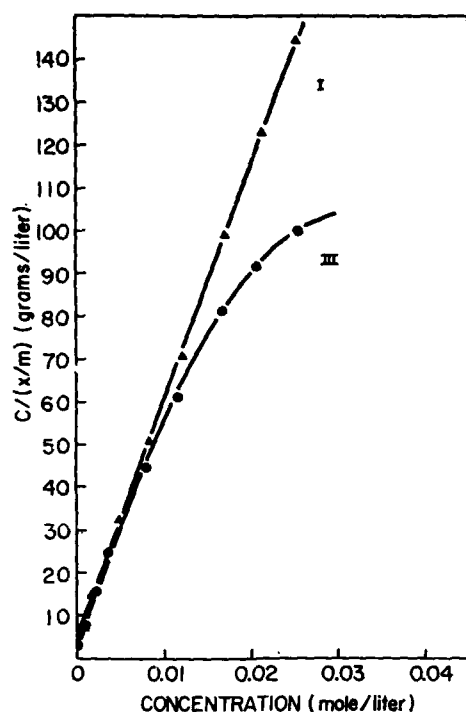


Figure 2. Langmuir plots of phenol adsorption: "dry" nickel oxide (isotherm I), "wet" nickel oxide (isotherm III).

phenol is probably tilted with the hydroxyl group pointed towards the surface. Theoretical cross-sectional areas for phenol (based on van der Waals radii) have been reported⁸ as 21.7 and 41.0 Å² in the vertical and flat configurations, respectively. Our cross-sectional area compares closely with the value of 30.6 Å² as reported by Bykov and Presnyakova⁵ where a similar orientation has been proposed.

For the adsorption of one component on more than one kind of elementary space, the adsorption isotherm developed by Langmuir⁶ indicates that if the energies of adsorption on different sites are markedly different, adsorption will occur in definite steps as the concentration increases. Alternately, stepped isotherms on inorganic oxides have been attributed to reorientation of the molecules on the surface to become vertically oriented, thus increasing their lateral interaction.⁷ The amount of physisorbed water introduced into the system via the metal oxide powder is in excess of the amount that can be solubilized by cyclohexane and suggests that at least some of the water remains on the metal oxide surface and that it participates in the adsorption process. Figure 1 indicates that phenol adsorption increases with increasing amount of physisorbed water on the surface. This observation is reasonable if it is assumed that the physisorbed water is only distributed over the surface and that the tilted configuration is the favored configuration for adsorption, but in the vicinity of a water molecule, phenol is forced to adsorb in a more tilted configuration. Hair

and Hertl⁸ have shown that adsorbed water acts as a specific adsorption site for other molecules (e.g., benzene, ammonia).

Adsorption on Partially Dry Nickel Oxide. Isotherm II suggests a multilayer adsorption. Phenol adsorption on partially dry nickel oxide corresponds to a partially flat adsorption (32.0 Å²) with exposure of the polar group for further hydrogen bonding. This decrease in the cross-sectional area for phenol suggests that as the concentration of physisorbed water at the interface increases, phenol assumes a more vertical orientation. Using molecular models, it can be shown that adsorption in the immediate vicinity of a bulky water molecule results in considerable steric hindrance.

Adsorption on Wet Nickel Oxide. The Langmuir plot (Figure 2) of the wet nickel oxide (isotherm III) is of interest because as θ increases, the adsorption coefficient decreases. As a first approximation, a linear variation of adsorption energy was assumed, since, in chemisorptive processes, a linear variation of the free energy of adsorption with coverage is frequently observed. A convenient relationship proposed by Biegler and Woods⁹ (i.e., the basic assumption of the Frumkin isotherm) is

$$\Delta G^\circ_\theta = \Delta G^\circ_{\theta=0} + f_0 RT \theta \quad (3)$$

where ΔG°_θ is the standard free energy of adsorption at a surface coverage θ and f_0 is a constant related to an adsorption parameter such as a neighbor-neighbor interaction or a two-dimensional second virial coefficient.¹⁰ $\Delta G^\circ_{\theta=0}$ represents the free energy of adsorption on the bare surface. Since the equilibrium constant in eq 1 is equal to $\exp(-\Delta G^\circ_\theta/RT)$, substitution of (3) into (1) gives the form of the Frumkin isotherm.

$$\frac{\theta}{1-\theta} \exp(f_0 \theta) = KC \quad (4)$$

Or in the more convenient logarithmic form, we have

$$\log C \frac{(1-\theta)}{\theta} = f_0 \theta \log e - \log K \quad (5)$$

The Frumkin plot of phenol adsorption on wet nickel oxide is shown in Figure 3 and suggests that the assumption of a variation in adsorption energy with respect to θ is reasonable. The adsorption coefficient was 3.25×10^3 l./mol compared with 1.40×10^3 l./mol on dry nickel oxide. This difference probably reflects the difference in configuration of phenol on the "dry" and "wet" surfaces. The linear variation of ΔG°_θ can

(5) V. T. Bykov and O. E. Presnyakova, *Kinet. Katal.*, **3**, 784 (1962).

(6) I. Langmuir, *J. Amer. Chem. Soc.*, **40**, 1361 (1918).

(7) S. A. Selim, R. Sh. Mikhail, and R. I. Razouk, *J. Phys. Chem.*, **74**, 2944 (1970).

(8) M. L. Hair and W. Hertl, *ibid.*, **73**, 4269 (1969).

(9) T. Biegler and R. Woods, *ibid.*, **73**, 3502 (1969).

(10) J. Lawrence and P. Parson, *ibid.*, **73**, 3577 (1969).

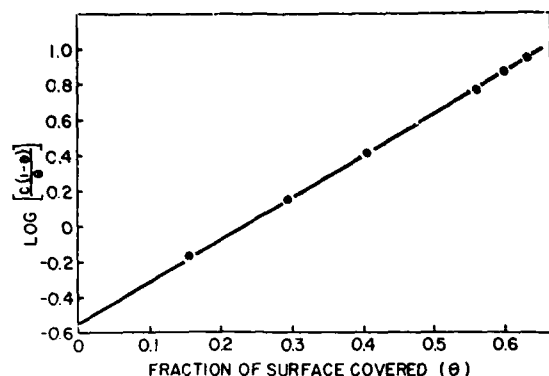


Figure 3. Frumkin plot of phenol adsorption on "wet" nickel oxide.

is made somewhat consistent with our model if it is assumed that Δf° is orientation dependent and that initial adsorption is flat, and subsequent adsorption results in progressively greater tilt. Comparison of the Langmuir and Frumkin adsorption coefficients is of questionable value. The Langmuir adsorption coefficient is an average value obtained at moderate surface coverages, and it is tacitly assumed that the adsorption coefficient on the bare surface is the same as on a moderately covered surface. The Frumkin adsorption coefficient applies only to initial adsorption and should theoretically be equal to the Langmuir coefficient; however, it can reasonably be assumed that initial adsorption on high-energy sites not reflected in the Langmuir equation is responsible for the difference in the two coefficients. The effect of adsorbed water and orientation on the value of the adsorption coefficient must be considered. The parameter f_0 , which reflects the effect of physisorbed water on phenol adsorption, is 2.30. The positive slope indicates decreasing free energy with respect to coverage and is consistent with the above model.

Desorption Studies. The effect of an increased equilibrium temperature on promoting phenol desorption from dry nickel oxide was studied by determining the phenol isotherms at 22.5 and 34.6°. (Several hours was allowed for attainment of equilibrium at the higher temperature.) No significant difference was found, indicating that if there is any desorption at the elevated temperature, it takes place at a very low rate. Figure 1 suggests that a certain fraction of the phenol adsorbed on "wet" nickel oxide should be rapidly desorbable. Phenol desorption from "wet" nickel oxide as studied, using a dilution technique. The amount of phenol desorbed from the monolayer by each dilution is shown in Figure 4. Approximately $1/2$ of the monolayer was found to be desorbable by successive dilution of the equilibrium solution in contact with the monolayer. Approximately 13 mg of phenol per gram of nickel oxide was apparently irreversibly adsorbed. The plateau associated with adsorption on "dry" nickel

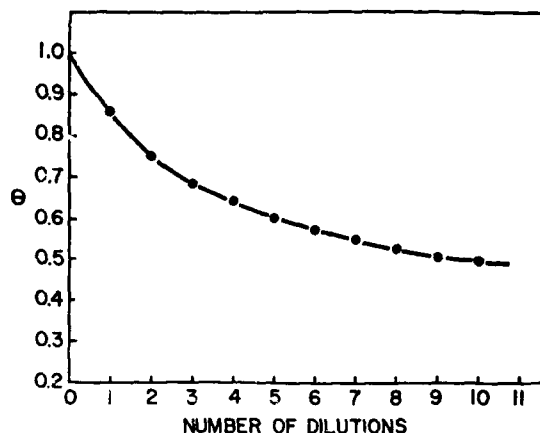


Figure 4. Desorption of phenol from nickel oxide powder. Each dilution represents a 75% reduction of the equilibrium concentration.

oxide (Figure 1) corresponds to approximately 17 mg per gram of nickel oxide. These studies suggest that the increased adsorption promoted by physisorbed water is a significantly weaker adsorption and is the reversible portion. A rough estimate of the equilibrium concentration at $1/2$ desorption indicates an adsorption coefficient of at least an order of magnitude less than the corresponding coefficients obtained from phenol adsorption measurements.

Competitive Adsorption. Langmuir adsorption theory can be applied to the special case of competitive adsorption in a system containing n components.³ The rates of adsorption and desorption respectively of the i th component are given by

$$\begin{aligned} r_{a,i} &= k_i C_i (1 - \sum \theta_i) \\ r_{d,i} &= k_{-i} \theta_i \end{aligned} \quad (6)$$

Equating rates and letting the ratio of the specific rate constants equal the adsorption coefficient, an adsorption equation similar to eq 1 is obtained

$$K_i C_i = \frac{\theta_i}{(1 - \sum \theta_i)} \quad (7)$$

For the i th and j th component in competitive adsorption eq 7 leads to

$$\frac{\theta_i}{K_i C_i} = \frac{\theta_j}{K_j C_j} \quad (8)$$

Competitive adsorption data for phenol and sodium dinonylnaphthalenesulfonate are shown in Figure 5, the broken line representing ideal behavior as predicted by eq 8. (The broken line in Figure 5 was drawn from the origin to the point of lowest surface coverage value obtainable with spectroscopic methods with the assumption that phenol-sulfonate interactions were negligible at this value.) The experimental points were obtained by keeping the initial concentration of phenol

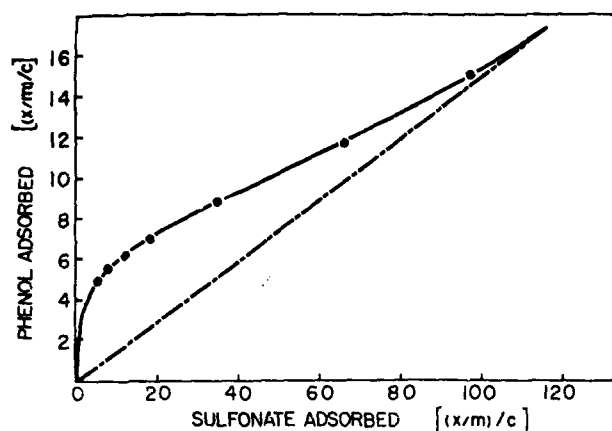


Figure 5. Competitive adsorption of phenol and sodium dinonylnaphthalenesulfonate. Dashed line represents behavior predicted by unmodified Langmuir theory.

constant at 1.13×10^{-3} mol/l. The point farthest from the origin represents a mixed monolayer consisting of 0.70 sulfonate, 0.03 phenol, and 0.21 cyclohexane. As the initial concentration of sulfonate was increased, while keeping the initial concentration of phenol constant, the amount of phenol on the surface steadily decreased. The experimental deviation from ideality becomes clear when we consider the actual experimental system. If the adsorption of a minute quantity of phenol and sulfonate on a finite surface is considered, eq 8 would be valid since reduction of surface area available for adsorption is responsible for competitive effects. With increasing surface coverage, molecular interactions (attributed to the size effect) increase and result in a deviation from ideal behavior. The slope of the broken line in Figure 5 predicts that sulfonate adsorption is 6.5 to 13 times as strong as phenol adsorption. This is a reasonable estimate and can be compared with a value of 9.6 (on a weight basis) obtained from the ratio of the Langmuir coefficients which is obtained in turn from independent adsorption measurements.

Competitive adsorption was also studied at less than full monolayer coverage, and it was found that holding the initial concentration of one component constant was approximately equivalent to holding that surface coverage value constant. The per cent change in surface coverage was experimentally small. Because of this, Langmuir isotherms for phenol and sodium dinonylnaphthalenesulfonate could be derived from competitive adsorption data. These isotherms are shown in Figure 6. Data followed eq 2 except that a is now a reduced maximum adsorption equal to $a_i(1 - \Sigma\theta)$ when the initial concentration of one component is varied and the fraction of the surface covered by second component is considered constant. For example, in Figure 6, the maximum adsorption value is 6.14 mg/g for phenol compared with 16.84 mg/g for phenol from

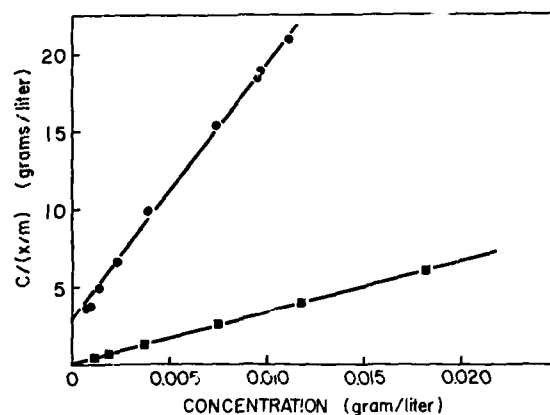


Figure 6. Langmuir isotherms derived from competitive adsorption data: —●—, phenol; —■—, sodium dinonylnaphthalenesulfonate.

Figure 2. This reflects the reduction in surface area due to adsorption of 23.4 mg/g of sodium dinonylnaphthalenesulfonate. Using the above relationship, it is possible to calculate a value for the maximum adsorption of sulfonate close to the experimental value of 35.8 mg/g. Data shown in Figure 6 apparently contradict the data shown in Figure 5. Figure 6 indicates phenol and sodium dinonylnaphthalenesulfonate adsorption follow the Langmuir equation, but apparently do not follow eq 8 at high surface coverage values. This indicates that the basic assumptions made in the derivation of eq 8 need to be reconsidered, especially the assumption that at equilibrium a phenol molecule sees exactly the same number of sites as a sulfonate molecule. This would be true if the adsorbates are of the same molecular dimensions. However, it is known that the cross-sectional area of sodium dinonylnaphthalenesulfonate is considerably greater than phenol. (Sulfonate in the extended position² would occupy an area of ca. 100 Å² compared with 21.7–41.0 Å² for phenol depending on orientation.)³ This size factor is not taken into consideration in eq 8. The sulfonate molecule is three times as large as the phenol molecule based on the experimentally found cross-sectional area of 33.4 Å². The failure of the competitive adsorption eq 8 to account for size differences can best be illustrated by considering the displacement of a phenol molecule from its close-packed monolayer by a sulfonate molecule. The probability that the vacant site (resulting from the desorption of one phenol molecule) will be occupied by a sulfonate molecule is zero and not some real value as predicted by the competitive adsorption eq 8. Three adjacent phenol molecules must desorb in order to have a site that is available to accommodate the sulfonate molecule.

The Flory-Huggins¹⁰ isotherm takes into account the variation in size of the adsorbing species and has the form of

$$\frac{\theta}{r(1-\theta)^r} = KC \quad (9)$$

where r is the molecular size ratio of adsorbate to adsorbed solvent. Since phenol and cyclohexane have approximately the same cross-sectional area ($r = 1$), eq 1 is adequate in describing the adsorption of phenol and indicates that the quantity θ_p/C_p varies linearly with $(1 - \theta_p)$. For sulfonate adsorption eq 9 predicts that the quantity $(\theta_s/C_s)^{1/2}$ varies linearly with $(1 - \theta_s)$. This suggests that a competitive adsorption equation can be found by expressing both (θ_s/C_s) and (θ_p/C_p) as functions of the fraction of the surface area available for adsorption $(1 - \Sigma\theta)$. Equation 7 is approximately valid for phenol but not for sulfonate since its rate of adsorption is apparently not linearly dependent on the surface area available for adsorption. If experimental conditions are such that θ_s is considerably greater than θ_p , then $(1 - \theta_s)$ is approximately equal to $(1 - \Sigma\theta)$ and under these conditions an approximate competitive adsorption equation is

$$\left[\frac{\theta_p}{K_p C_p} \right]^3 = \frac{\theta_s}{2K_s C_s} \quad (10)$$

This equation, useful only under restricted conditions, does reflect the "decreasing" adsorption of sulfonate at

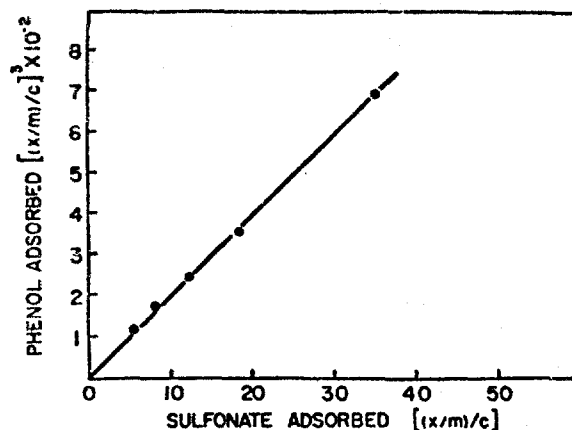


Figure 7. Competitive adsorption of phenol and sodium dinonylnaphthalenesulfonate using a modified competitive adsorption equation taking into account the relative difference in size of the two adsorbates.

high surface coverage values, which is the suspected cause of the nonideal competitive adsorption behavior. A plot of competitive adsorption data according to eq 10 is shown in Figure 7. The data are also shown in Figure 5 when plotted according to eq 8. This indicates that the cross-sectional area of the adsorbates is a parameter of importance in competitive adsorption studies.