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The Behavior of o-Nitrophenol on Alkaline Earth Oxides

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A study of the behavior of *o*-nitrophenol adsorbed on alkaline earth oxides has revealed displacements of the wavelength maxima in the visible diffuse reflectance spectra of the two component systems. The shifts, which are bathochromic in order of increasing size of cation, beryllium providing an exception, are interpreted in terms of polarization theory. Moisture contamination studies show enhancement of bathochromic shifts upon progressive elimination of adsorbed water molecules in competition with the phenol for active adsorbent sites.

INTRODUCTION

Recent studies on two-component solid systems prepared by mixing or grinding in the dry state various organic and inorganic species with an active adsorbent have revealed, upon interaction, spectral changes in the visible diffuse reflectance spectra of the optically absorbing species (*1–8*). The changes arising as a result of the adsorption or spreading upon the surface of the adsorbent are detected spectrally by an increase in intensity of an absorption peak which may be accompanied by displacements of its wavelength maximum. Visually, the solid system undergoes a color change or an increase in intensity of the original color.

Attempts have been made to explain the spectral changes in terms of the polarization theory (*1, 9*) which has been employed successfully for the interpretation of shifts occurring in transmittance spectra of liquid systems through solute–solvent interaction.

Kortüm and Vogel (*10*) in a study of the spectral behavior of colorless malachite green-*o*-carbonic acid lactone, which turns blue upon spreading on the surface of a series of alkali metal halides, found that the intensity of the blue color varied inversely with the size of the cation (nuclear charge) in the order $Li^+ > Na^+ > K^+ > Cs^+$. Shifts, however, in the wavelength maxima were not considered significant. In contrast to these findings, Zeitlin and co-workers (*8*), in a study of the color changes occurring in the mononitrophenols adsorbed on the alkali metal carbonates, have reported that intensification of color was accompanied by sizeable displacement of the wavelength maxima varying regularly with the size of the cation in the order, $Li^+ < Na^+ < K^+$.

In light of the foregoing, it seemd pertinent to extend the examination of the spectral behavior of *o*-nitrophenol when mixed with a series of alkaline earth oxides and to include a study of the role of moisture contamination which, as shown by Kortüm (*1, 10, 11*), is able to cause modification of reflectance spectra.

EXPERIMENTAL

The chemicals used were from the following sources: beryllium oxide, anhydrous, purified grade, Fisher Sci. Co.; magnesium oxide, reagent grade, Baker Chem. Co.; calcium oxide, reagent grade, Baker Chem. Co.; strontium oxide, anhydrous, purified grade, Fisher Sci. Co.; barium oxide, anhydrous, purified grade, Fisher Sci. Co.; *o*-nitrophenol, reagent grade, Eastman Kodak Co. The *o*-nitrophenol was recrystallized several times until its melting point indicated satisfactory purity. The alkaline earth oxides of Be, Mg, Ca, Sr, and Ba used as adsorbents were ground for approximately 15 min in an agate mortar to achieve a fine state of subdivision which results in sharper absorption peaks in the reflectance spectra. Following grinding the adsorbents were sieved through fine mesh screens and powders of 100 to 140 mesh were retained for use. Tests with powders of this particle size range revealed no anomalies in the form of spurious peaks in the reflectance spectra. Separate samples of the pure adsorbent were dried carefully at temperatures of 200°C, 600°C, and 1000°C in order to evaluate the effect of moisture on the systems to be examined. Additional samples were obtained in an "air dry" state by allowing them to be exposed to ambient temperatures and humidity.

Samples of preheated adsorbent ranging in weight from 1 to 4 g depending upon the oxide were transferred without delay to a vacuum desiccator containing P_2O_5 evacuated to *ca.* 1 mm Hg. The desiccator containing the adsorbent, *o*-nitrophenol, and the predried equipment required to prepare the samples were transferred to a dry box which was dried by dynamic adsorption through activated silica gel for 12 hr. This procedure minimized atmospheric moisture although the absolute exclusion of moisture is extremely difficult and was probably not completely achieved in this study.

In the dry box quantities between 10 and 20 mg of the *o*-nitrophenol were mixed thoroughly with each of the adsorbents in a mortar for about 1 min to attain uniform distribution of the two components. The completeness of the interaction between *o*-nitrophenol and adsorbent was examined by mixing the two components thoroughly as described and measuring the reflectance spectrum of the system over a period of time up to a maximum of several days. Interaction was extremely rapid, as shown by color change and spreading of the *o*-nitrophenol over the surface of the adsorbent and appeared to be complete in 5 to 10 min. Spectrally the major change observed was a gradual decrease in reflectance (increase in absorbance) until a constant value, not altered materially with time, was attained. However, of greater significance to this study was the observation that during the 2-day period, there was no detectable change in the positions of the minima and maxima of the absorption peaks. In light of this preliminary work it was decided to measure the spectra of the systems in all subsequent experiments after 1 hr of interaction, upon the premise that equilibrium had been attained for all practical purposes by this time. While in the dry box the powder was packed into a special cell described by Barnes and co-workers (*12*) in which the edges of the aluminum planchet were coated with silicone grease.

The diffuse reflectance spectra (350–750 mμ) were measured with an automatic recording DK-2 Beckman spectrophotometer equipped with the standard reflectance attachment. A Beckman standard reference MgO plate served as the reference standard blank. Adsorbent blanks were investigated by measuring the reflectance spectra (350–750 mμ) of all pure adsorbents (100–140 mesh) against the MgO reference standard. The spectra obtained were smooth, gradually declining curves from long to short wavelengths without any characteristic minima or maxima. In addition, the spectra of *o*-nitrophenol adsorbed on each of the alkaline earth oxide adsorbents determined with use of the MgO plate were compared with those obtained with the same samples using the respective pure adsorbents as reference standards. The comparison showed that the use of the pure adsorbent in place of the MgO plate had no detectable effect on the position of the reflectance minima. Approximately 1 min was required for the recording of the spectrum. Time recording tests with sample systems carried out previously showed that practically no water was picked up during the brief recording interval. Reproducibility was studied by measuring four replicates under similar conditions. Deviations were reproducible with a maximum uncertainty of ± 3 mμ.

The reflectance spectra of the preheated samples were measured again following exposure to the atmosphere for 24 hr in order to compare them with those obtained from similar systems in which the adsorbents had been "air dried."

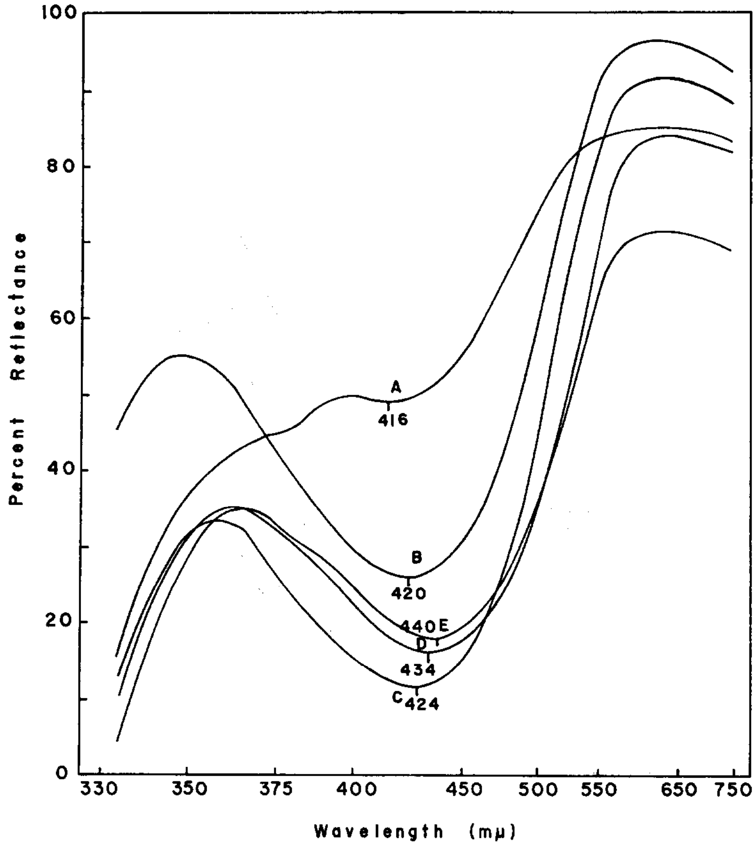

FIG. 1. The reflectance spectra of *o*-nitrophenol adsorbed on alkaline earth oxides measured in the "air-dry" state: A, on BeO; B, on MgO; C, on CaO; D, on SrO; E, on BaO.

Transmittance spectra were recorded with the DK-2 Beckman spectrophotometer in 1-cm matched quartz cells.

DISCUSSION

Figures 1–4 give typical graphs obtained from solid systems measured at equilibrium in which per cent reflectance (*R*) is plotted versus wavelength. Table 1 contains wavelength absorption maxima of the diffuse reflectance spectra of *o*-nitrophenol adsorbed on alkaline earth oxides measured at equilibrium under various conditions. Table 2 contains a compilation of transmittance data on absorption maxima measured in various solvents.

TABLE 1

WAVELENGTH MAXIMA (mμ) OF THE REFLECTANCE SPECTRA OF *o*-NITROPHENOL ADSORBED ON ALKALINE EARTH OXIDES

Oxide	"Air-dry"	200°C[a]	600°C[a]	1000°C[a]
BeO	416 ± 2	434 ± 3	440 ± 3	444 ± 3
MgO	420 ± 2	420 ± 2	427 ± 2	428 ± 3
CaO	424 ± 2	426 ± 2	428 ± 3	430 ± 3
SrO	434 ± 2	440 ± 2	452 ± 2	*ca.* 454
BaO	440 ± 2	447 ± 2	458 ± 3	—

[a] Temperature at which adsorbent is preheated and allowed to cool before mixing with phenol.

The technique of spectral reflectance is particularly useful in the study of chemical phenomena occurring on solid surfaces (*1–11*). The inherent experimental difficulties, however, associated with the application of this tool to solid systems, which are imposed by the need for rigid control of moisture and allied variables, are formidable. The present status of this area of research is such that it is exceedingly difficult to gather

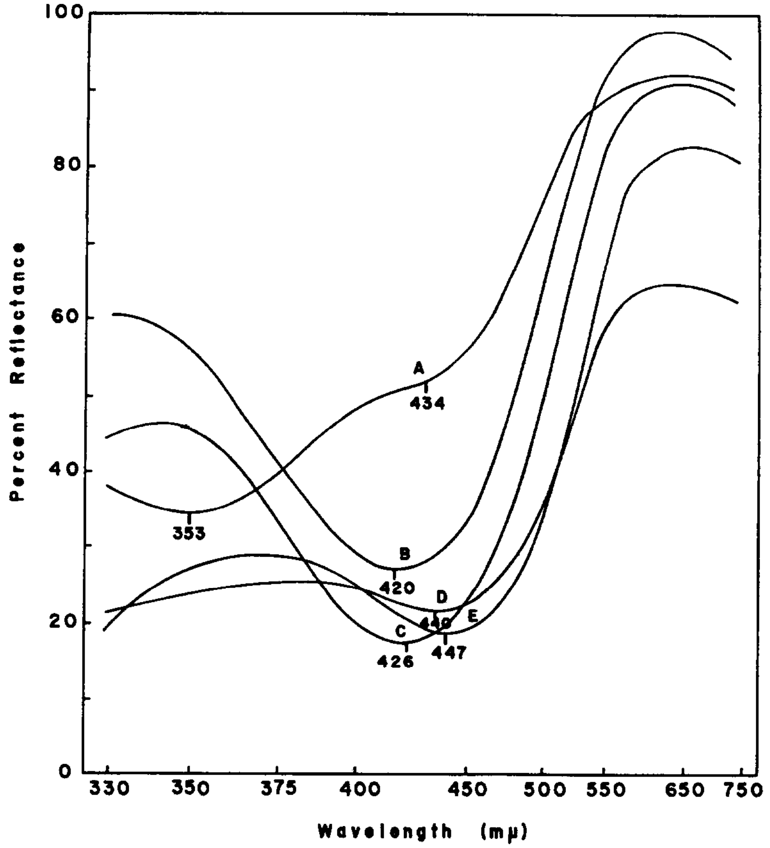

Fig. 2. The reflectance spectra of *o*-nitrophenol adsorbed on alkaline earth oxides preheated to 200°C: A, on BeO; B, on MgO; C, on CaO; D, on SrO; E, on BaO.

valid quantitative data of the kind available in transmittance spectroscopy. Consequently, the discussion below is necessarily qualitative in nature with the hope that improved instrumentation and techniques will make possible a quantitative treatment of these phenomena.

A comparison of the values (Table 2) for the absorption peaks in the two neutral solvents, benzene and ether, with those in the basic solvents shows the shifts which result through the formation of the *o*-nitrophenoxide anion in the latter solvents. The corresponding peaks at lower wavelengths in the two neutral solvents are ascribed to the presence of the undissociated acid species which upon conversion to the phenoxide should be expected to absorb at considerably longer wavelengths, a conclusion confirmed by the data. The results also show

TABLE 2

Wavelength Maxima of the Transmittance Spectra of *o*-Nitrophenol in Various Solvents

Solvent	Molar concentration	wavelength (mμ) of absorption maximum
Benzene	3.81×10^{-5}	354
Ether	3.48×10^{-5}	338
Saturated calcium hydroxide	2.88×10^{-5}	416
Saturated barium hydroxide	4.42×10^{-5}	417

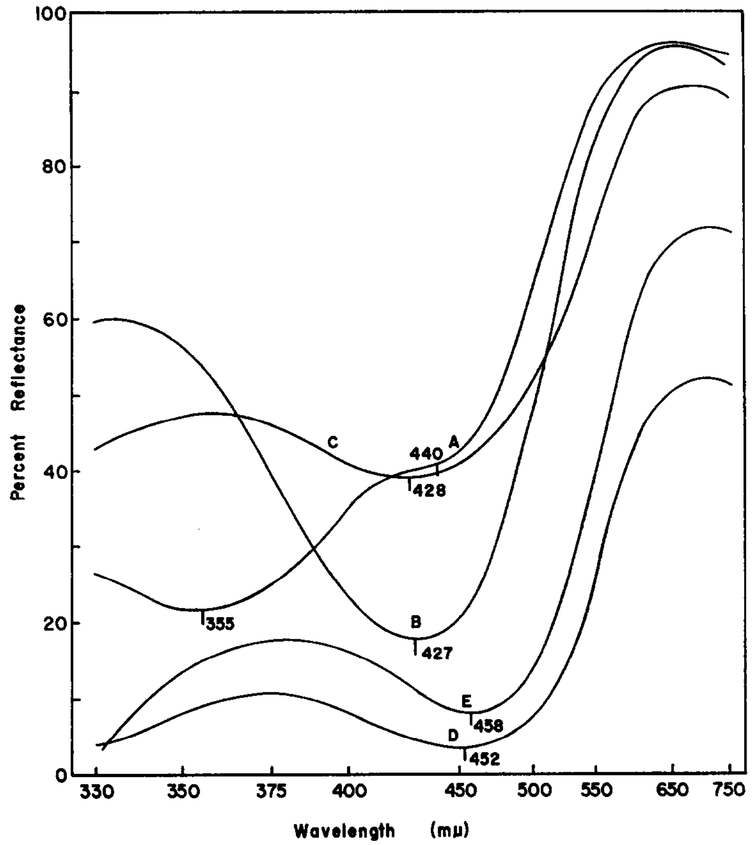

FIG. 3. The reflectance spectra of *o*-nitrophenol adsorbed on alkaline earth oxides preheated to 600°C: A, on BeO; B, on MgO; C, on CaO; D, on SrO; E, on BaO.

that the transmittance spectrum of the phenol is similar in solutions of the two alkaline earth hydroxides tested. This spectrum is also identical with those which were obtained previously for *o*-nitrophenol dissolved in an aqueous solution of lithium, sodium, and potassium carbonate (*8*). It is concluded that the five cations concerned exert no experimentally detectable differentiating influence on the phenoxide ion in solution. The cations apparently are shielded effectively by hydration so that they are not able to impose an appreciable polarizing effect on the anion by means of their nuclear charges. Moreover, hydration of the phenoxide anion and mobility in solution of both cationic and anionic species contribute to the same end. The situation is quite different in the solid state.

Reflectance spectra (Figs. 1–4) and data (Tables 1, 2) reveal bathochromic displacements in going from transmittance to reflectance, a shift which has been reported by a number of investigators (*13–15*). An examination of the values for the phenol adsorbed on the alkaline earth oxides again shows a bathochromic shift, regular in nature, in the order BaO > SrO > CaO > MgO > BeO. The beryllium salt, however, falls in the expected order only in the "air dry" state and deviates in the other systems (Table 1). The following interpretation is advanced to account for the effect of the cations on the phenol in the adsorbed state. When the alkaline earths are arranged in the order of increasing cationic size, i.e. Be through Ba, the effective nuclear charge decreases in this order due to increased screening by additional electron levels. The cation in the crystal lattice of the adsorbent exerts a

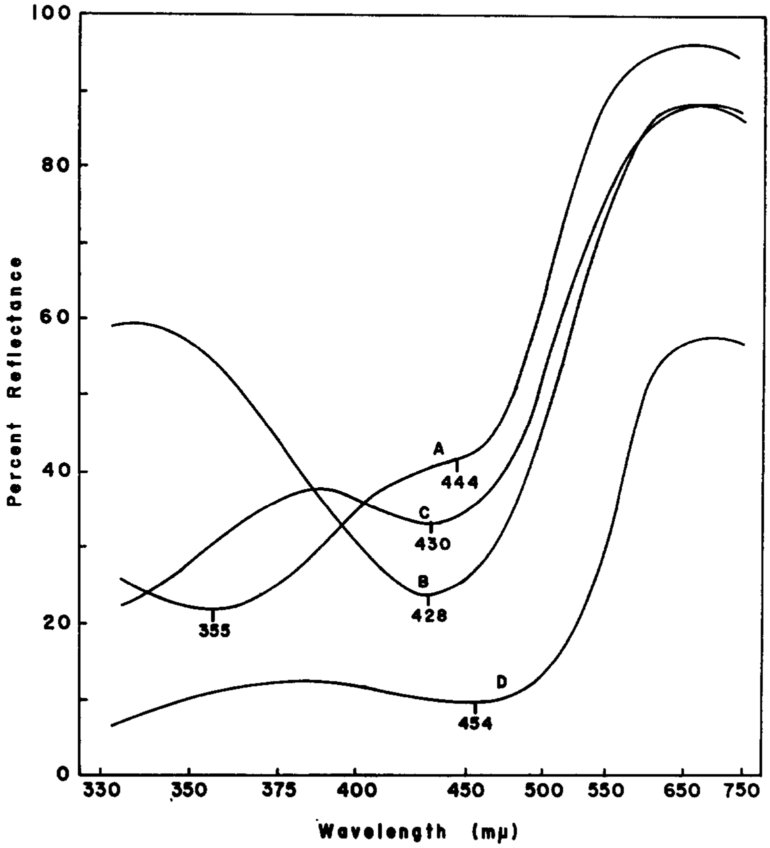

FIG. 4. The reflectance spectra of *o*-nitrophenol adsorbed on alkaline earth oxides preheated to 1000°C. A, on BeO; B, on MgO; C, on CaO; D, on SrO.

polarizing action on the phenol which is followed forthwith by adsorption on the surface of the adsorbent, presumably as a result of a Lewis acid-base type of interaction. The polarizing effect of the alkaline earth cations on the highly nonlocalized pi bond system of the phenol should then increase in the expected order of $Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Be^{2+}$, with the effective nuclear charge increasing accordingly. Such a polarization should result in a partial freezing or localization of the electron cloud of the phenol in the series studied, rendering electronic excitation more difficult and thereby accounting for the regular shift of the absorption peaks toward the more energetic shorter wavelengths.

The bathochromic displacements observed upon going from transmittance to reflectance (Tables 1, 2) are more difficult to interpret on the basis of the argument presented above. In aqueous solution electronic delocalization in all probability is at a maximum since the phenoxide ion is protected by hydration, and excitation energy is at a minimum. The anion on the other hand, upon being subjected to a solid ionic environment with subsequent localization, should result in an increase of excitation energy and a hypsochromic shift to wavelengths less than 417 mμ. The experimental evidence to the effect that bathochromic shifts do occur implies, instead, that delocalization takes place as a result of adsorption and interaction between the anion and cation of adsorbent. There exists the possibility that the increased delocalization indicated as compared to that in solution arises through a molecular orbital overlap between the phenoxide anion and the active site on the adsorbent, accounting for the shifts to the longer wavelengths. It is also possible, of course, that other factors not yet taken into account may be involved and be responsible to a major degree for this phenomenon.

The results with the various oxides are in agreement with a similar trend reported recently for the three mononitrophenols adsorbed on lithium, sodium, and potassium carbonate (*8*). Bathochromic shifts took place in each case in the order $K_2CO_3 > Na_2CO_3 > Li_2CO_3$ which were more pronounced, as might be expected, than those observed with the alkaline earth oxides. We are of the opinion that in this series the species undergoing adsorption is the phenoxide anion, which is polarized to varying degrees by the alkali and alkaline earth metal cations, resulting in displacements of the wavelength maxima. This hypothesis has not yet been definitely established.

Kortüm's findings (*10*) with malachite green *o*-carboxylic acid lactone have been explained by him on the following basis. The blue color of the otherwise colorless lactone adsorbed on the alkali metal halides is due to cleavage of the lactone ring resulting from the polarizing action of the cations with the formation of a zwitterion. The intensity of the blue color depends upon the position of the equilibrium attained between chemisorbed and physically adsorbed molecules, which in turn is a function of the size of the cation. In Kortüm's system chemisorption arises at the interphase from the bond between the negative end of the zwitterion and the cation with the result that localization of the electron cloud in the vicinity with the carboxylate anion occurs. The positive charge associated with the malachite green cation is, however, delocalized and can be distributed over the molecule, in contrast with our postulated behavior of the phenol in which localization takes place with the effect on the maximum absorption peak described above. The increased intensity of the blue color of malachite green implies displacement of the equilibrium in favor of chemisorption due to increasing polarizing action of the cation and an increase in concentration of the blue malachite green cationic species with no significant displacement of the absorption peak.

Table 1 shows the effect of moisture and provides some insight into the role of this agent. The color change, which can be followed spectrally by the displacement of a wavelength maximum, is dependent upon humidity. As the temperature of the preheat treatment of the adsorbent increases a regular bathochromic shift takes place in the reflectance spectrum of the phenol–alkaline earth oxide system. These findings are in accord with those of Kortüm (*1, 10, 11*) and support his interpretation that a competition for the active adsorption sites exists between the species undergoing adsorption and water molecules which is in favor of the latter. The heat treatment of the adsorbent before mixing with the phenol results in a gradual but progressive elimination of the adsorbed water molecules. The phenol with the concentration of the otherwise favored water molecules diminished is more effectively and directly exposed to the polarizing action of the cations. The changes are reversible since all the sample mixtures prepared by preheating of the adsorbent upon exposure to atmospheric humidity changed visually, with the result that they resembled in appearance the "air dry" sample. Spectrally, the wavelength maxima of the samples so exposed were observed to undergo a hypsochromic shift. The wavelength maximum at equilibrium with the atmosphere was identical with that of the "air dry" sample.

The hypsochromic shift noted above has been explained by Kortüm (*1, 10*) as being due to a transition from chemisorption (Lewis acid-base interaction) which takes place in the first monomolecular layer between adsorbent and adsorbed species to physical adsorption resulting from van der Waals forces. The data (Table 1) also show a relation between moisture effect and size of cation. The effect is greatest with the large cations, Ba^{2+} and Sr^{2+}, whereas the bathochromic shifts for Ca^{2+} and Mg^{2+} with increasing pretreatment temperatures up to 1000°C are only about 8 mμ. The behavior of beryllium oxide is anomalous. The cation is an exception in the series since it exhibits in the moisture effect tests an unexpectedly large shift of about 24 mμ and otherwise does not conform (Table 1). The behavior of this alkaline earth illustrates the well-documented fact that due to the tiny size of the ion and its high charge density many of its properties are distinctly apart from its congeners. The peculiarities shown in the study by beryllium oxide, apart from the "air dry" system, lend support to the polarization concept advanced for the phenomena observed.

The alkaline earth oxides, with the exception of Be, crystallize with the rock salt structure. In contrast, BeO has the 4:4 coordinated zincblende structure in which each beryllium atom is coordinated tetrahedrally by four oxygen atoms (*16*). The small size of the Be^{2+} permits accommodation comfortably of only four O^{2-} ions whereas six and possibly more can be accommodated around the much larger ions of the other metals. The beryllium ion is thus so shielded by the oxygen that, unlike the other members of the family where the situation is not applicable to the same extent, it is no longer in the position to act effectively as a polarizer. Any bond that might arise between it and the polarized *o*-nitrophenol upon chemisorption at the interphase would be expected to be relatively weak. This is substantiated experimentally by the fact that upon exposure of the various alkaline earth oxide-phenol systems to the atmosphere, desorption accompanied by sublimation of *o*-nitrophenol occurs by far the most rapidly in the beryllium oxide system. It is remarkable that, under the experimental conditions described above, adsorption of *o*-nitrophenol on beryllium oxide occurs at all.

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REFERENCES

1. KORTÜM, G., VOGEL, J., AND BRAUN, W., *Angew. Chem.* **70**, 651 (1958).

2. KORTÜM, G., *Trans. Faraday Soc.* **58**, 1624 (1962).

3. GRIFFITHS, T. R., LOTT, K. A. K., AND SYMONS, M. C. R., *Anal. Chem.* **31**, 1338 (1959).

4. GRIFFITHS, T. R., *Anal. Chem.* **35**, 1077 (1963).

5. ZEITLIN, H., AND GOYA, H., *Nature* **183**, 1041 (1959).

6. ANTHONY, P., AND ZEITLIN, H., *Nature* **187**, 936 (1960).

7. GOYA, H., WAUGH, J. L. T., AND ZEITLIN, H., *J. Phys. Chem.* **66**, 1206 (1962).

8. ZEITLIN, H., KONDO, N., AND JORDAN, W., *J. Phys. Chem. Solids* **25**, 641 (1964).

9. KORTÜM, G., AND BRAUN, W., *Z. Phys. Chem. (Frankfurt)* **18**, 242 (1958).

10. KORTÜM, G., AND VOGEL, J., *Chem. Ber.* **93**, 706 (1960).

11. KORTÜM, G., BRAUN, W., AND HERZOG, G., *Angew. Chem.* **2**, 333 (1963).

12. BARNES, I. L., GOYA, H., AND ZEITLIN, H., *Rev. Sci. Instr.* **34**, 292 (1963).

13. PRUCKNER, F., SCHULENBURG, M., AND SCHWUTTKE, G., *Naturwiss.* **38**, 45 (1951).

14. ZEITLIN, H., AND NIIMOTO, A., *Nature* **181**, 1616 (1958).

15. ZEITLIN, H., AND NIIMOTO, A., *Anal. Chem.* **31**, 1167 (1959).

16. ZACHARIASEN, W. H., *Z. Phys. Chem. (Leipzig)* **119**, 201 (1926).