

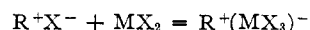
sorption on the resin, with several differences. The "knee" of the curve is more rounded, so that with absorptions approximating 0.9 mM./g., the residual concentration of salt in the acetone may be 0.010–0.015 *M*. There is also a definite slope to the plateau, perhaps related to the rounding of the knee. The most marked difference, however, is the essential independence of the water content of the resin, the absorptions of nitrate onto resin with 4% and 6.8% of water being essentially the same, and equal to that of the chloride on resin of 22% water content. Levels of cobalt on the resin as high as 1.4 mM./g. have been found for solutions of residual concentration 0.11 *M*.

One may also absorb chloride on nitrate resin, and nitrate on chloride resin. Thus, absorption of cobaltous chloride on nitrate with 8.4% water resin may be as high as 1.5 mM./g. with a residual concentration of 0.05 *M*. The absorption on resin with only 4% water is depressed to about 0.72 mM./g. at 0.025 *M* residual concentration. Cobaltous nitrate in acetone, on chloride resin, with 22% water, shows absorption to 0.5 mM./g. at 0.05 *M* residual concentration, 1.0 mM./g. at 0.1 *M* and 1.5 mM./g. at 0.15 *M* residual concentration. Against the resin with 6.8% water, the level is about 0.1 mM./g. resin at 0.015–0.03 *M* residual concentration, significantly less.

Chlorides have been shown to be capable of forming complexes with cobaltous chloride in acetone.¹⁰ The effects of lithium chloride on the absorption of cobaltous chloride from acetone have not been demonstrable with any certainty, and the same may be said of pyridinium chloride. Lithium nitrate likewise shows no clear effect on the absorption of cobaltous chloride or nitrate. These statements are to be understood to apply to a concentration range up to about 0.2 *M* in the added salt. Pyridine, which also associates with

the cobaltous salts in acetone solution, and which is able, in at least some cases, to displace coordinated chloride,¹⁰ does have a strong effect on the absorption of the cobalt salts. Thus, 1.5–3 equivalents of pyridine almost completely inhibit the absorption of 0.07 *M* cobaltous nitrate on nitrate resin, while 0.4–0.9 equivalent of pyridine will reduce the absorption of cobaltous chloride on the same resin to some 20% or so of the value with pyridine absent.

In summary, therefore, it is seen that substances as diverse as HCl, LiCl and the chlorides and nitrates of the divalent transition elements can be absorbed from acetone solution onto anion exchange resins, the molecule as a whole disappearing from solution. A single mechanism, it is conceivable, may cover all the cases; it is possible, on the other hand, to point to possible specific (and different) factors in several of the cases. Thus, for HCl, the hypothesis is tenable that a large factor at least in its absorption is the presence of weakly basic nitrogen groups in the resin which dissociate acid in the procedures of washing the resin with water, but take it up again from the (undoubtedly) high activity acetone solutions. The transition element salts are known to participate in equilibria in which higher complexes are formed with anions, and therefore a mechanism for their absorption may be written in terms of the equilibrium



in which R^+ represents the resin cation. Lithium chloride does not obviously follow either of these two explanations, and therefore represents a potential third class, though it is conceivable that its absorption may represent evidence for complexes of the type $(LiCl_2)^-$ and $(Li(NO_3)_2)^-$, and perhaps even the HCl case may be due in part to an analogous phenomenon.

CHICAGO, ILLINOIS

(10) L. I. Katzin and E. Gebert, *THIS JOURNAL*, **72**, 5464 (1950).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

Infrared Spectra of Heavy Water Adsorbed on Silica Gel

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A technique has been developed for the determination of the infrared absorption spectrum of adsorbed D_2O . The experiments were performed with D_2O adsorbed on silica gel. In the 1900–3400 cm^{-1} region, the spectra of samples with surface coverages from 0.35 to 1.8 monolayers are similar to the spectrum of D_2O in the liquid phase. Exchange of the adsorbed D_2O with the H_2O in the gel has been observed.

I. Introduction

Spectroscopic studies of adsorbed materials provide information which aids in understanding the properties of surfaces as well as the nature of processes occurring at interfaces.¹ Some studies have been made using visible and ultraviolet light,^{1,2} but the results have been limited by experimental difficulties peculiar to adsorption systems: insufficient

adsorbate to provide definitive spectra or excessive light scattering by the adsorbent. These experimental difficulties are encountered in infrared spectroscopy; in addition, there is the problem of putting the sample in a suitable form for infrared study while maintaining a known surface coverage. Apparently the only studies of this kind in the infrared spectral region are those of Kurbatov and Neufmin.³ Their technique is such that the surface coverage is not known. The present work indicates experi-

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(1) H. Volkringer and S. Valladas-Dubois, *J. chim. phys.*, **46**, 388 (1949).

(2) G. Jura and M. W. Nathans, unpublished studies.

(3) L. N. Kurbatov and G. G. Neufmin, *Akad. Nauk Leningrad, LXVII*, No. 2, 341 (1949).

mental conditions which allow the study of a portion of the infrared spectrum of known amounts of D_2O adsorbed on silica gel suspended in paraffin. It is likely that these procedures can be modified to allow study of other systems under conditions more favorable for theoretical interpretation.

Since it was necessary to develop experimental techniques, the initial studies were made on a system selected to provide optimum opportunity for spectroscopic study. Silica gel is an adsorbent readily available with high specific surface and it has reasonable transparency in a portion of the infrared region. The adsorbate, D_2O , was selected for its high surface coverage at low pressures on silica gel at room temperature and its high spectral absorption in an infrared region where atmospheric absorption does not interfere. The suspending medium, paraffin, was chosen to provide a supporting agent which gives mechanical properties suitable for preparation of thin samples, which is transparent in the infrared region to be studied, and which prevents or delays change in the adsorbed material due to contact with the atmosphere.

II. Materials and Experimental Procedure

The silica used was obtained from Dr. M. Corrin, who in turn had obtained it from the du Pont Co. The du Pont designation is RS-1. The area was found to be $89 \text{ m}^2/\text{g.}^{-1}$ by nitrogen adsorption at 77.3°K. The heat treatment used on the sample for area determination was identical with that used prior to the adsorption of the heavy water. The BET theory was applied to the adsorption data to obtain the area. The D_2O was taken from a previously unopened ampoule of 99.9% D_2O supplied by California Isotope Co. (lot No. 112). The paraffin was ordinary household paraffin manufactured by Socony-Vacuum Oil Co., Inc. The D_2O was degassed by freezing under vacuum several times. The paraffin was used without further treatment.

The container for the solid and paraffin, shown in Fig. 1, was mounted with the silica gel in the vertical tube and the paraffin in the horizontal tube. The gel was degassed at 475° for about 15 hours in a vacuum of 10^{-5} to 10^{-6} mm. The sample was then cooled to room temperature and the desired amount of D_2O was admitted from a gas buret.

After adsorption equilibrium had been reached the entire assembly was sealed at the constriction C_1 and removed from the vacuum line. The silica gel was then poured onto the solid paraffin and the tube was sealed off at constriction C_2 to reduce dead volume. The mixture was immersed in boiling water to melt the paraffin and the melt was shaken to obtain approximately uniform distribution of the gel in the paraffin. The mixture was then permitted to cool. For all results reported here the infrared spectrum was taken within four hours of opening the tube. A few minutes before spectroscopic study a sample of the desired thickness was prepared by compressing a small piece of the mixture between the jaws of a micrometer caliper. The maximum ratio of silica gel to paraffin which retained the desired mechanical properties, one to two by weight, was used for all samples except no. 3, for which the ratio was one to five. Using this technique, samples were prepared with the surface coverages and thicknesses indicated in Table I. An attempt to prepare a sample of the gel saturated with D_2O failed because the paraffin did not wet the gel.

The samples were mounted just in front of the thermocouple window of a Perkin-Elmer, model 12C infrared spectrometer and in this location transmitted 40-60% of

the incident light in the spectral range $1900\text{--}3400 \text{ cm.}^{-1}$. A LiF prism was used in the frequency range $2100\text{--}3400 \text{ cm.}^{-1}$ and a NaCl prism at frequencies below 2100 cm.^{-1} . Calculations of I/I_0 were made only in regions free of the background interference caused by the paraffin, atmospheric CO_2 and atmospheric H_2O .

III. Results and Discussion

For each sample with an amount of D_2O adsorbed in the range 0.35 to $1.82 v_m$, a very broad band with a distinct maximum was found in the spectral region $2200\text{--}2800 \text{ cm.}^{-1}$, where the unsymmetrical OD stretch, ν_3 , of liquid D_2O is found. The symbol v_m refers to the calculated amount of water necessary to form a monolayer using a specific area of 10.6 \AA^2 for D_2O . The band attributed to adsorbed D_2O is, within the precision of the present measurements, identical to the ν_3 band of liquid D_2O .

Figure 2 shows the comparison between the spectrum of a blank, gel and paraffin alone, and the spectrum when $1.09 v_m$ is adsorbed upon the gel.

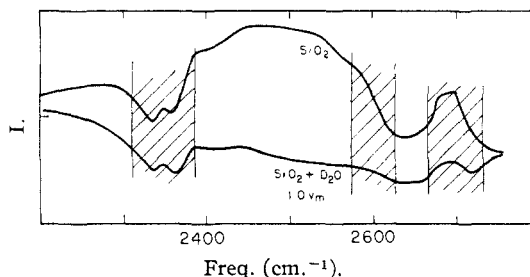


Fig. 2.—Spectra of silica gel in paraffin, $2200\text{--}2800 \text{ cm.}^{-1}$, with no adsorbed D_2O and with $1.0 v_m$ adsorbed D_2O .

Figure 3 shows the spectra of the adsorbed D_2O as a function of surface coverage. The curves have been vertically displaced. Maximum absorption occurs at $2510 \pm 15 \text{ cm.}^{-1}$ for samples no. 3, 4 and 5. The absorption curve for no. 2 was not well defined but the maximum absorption was taken to be at $2590 \pm 100 \text{ cm.}^{-1}$. For comparison, the spectrum of liquid D_2O has been included.⁵ Table I lists the pertinent data for each sample.

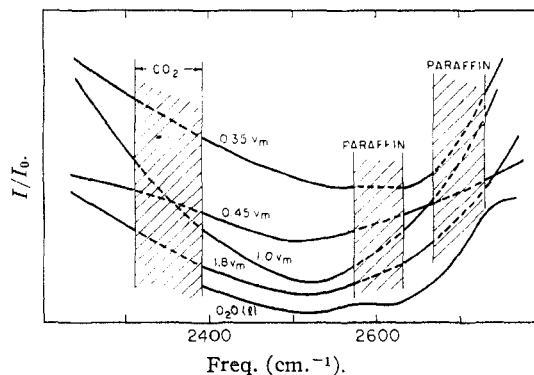


Fig. 3.—Spectra of liquid D_2O and of D_2O adsorbed on silica gel in paraffin: $2200\text{--}2800 \text{ cm.}^{-1}$.

(4) In the early stages of this work it was hoped that this location of the sample would result in capture of a fraction of the scattered light, but later experiments showed that the sample could be located at the entrance slit with comparable transmission.

(5) We wish to thank Mr. William A. Klemperer for providing this spectrum.

TABLE I

Sample No.	Thickness, mm.	Surface coverage, ^a v_m	Max. absorption, cm.^{-1}
1	0.12	0.1	
2	.12	0.35	2590
3	.12	0.45	2505
4	.025	1.0	2515
5	.06	1.8	2515

^a There is a small uncertainty in the surface coverage arising in the operation of coating the solid with paraffin at an elevated temperature. A correction was made based on the estimated dead volume above the solid and an assumed heat of adsorption of D_2O on the gel equal to the measured heat of adsorption of H_2O on TiO_2 . The volume in which the paraffin and solid were mixed was made as small as practicable. The maximum correction is of the order of 10% and this figure is probably not in error by more than a factor of two.

Similarity of the absorption spectrum of liquid D_2O to the spectra of the samples is evident in the location of the maximum of absorption as well as in the band width. In view of this similarity, it seems desirable to review the arguments which indicate that the spectrum is not due to droplets of liquid present as a separate phase in the paraffin.

1. It is well known that silica gel adsorbs water preferentially to hydrocarbons. On this basis it would be surprising if a significant fraction of the water were to desorb and form a separate phase.

2. Since the contact angle of water against paraffin is greater than 90° , the vapor pressure of a small droplet of water in paraffin must exceed the vapor pressure of bulk liquid. Since the vapor pressure of the adsorbed D_2O is always below that of bulk D_2O , it is evident that small drops could not grow by distillation.

3. It was observed that the spectral absorption in the region near 2500 cm.^{-1} decreased as the sample aged for a few days and a new absorption appeared in the region $3240\text{--}3650 \text{ cm.}^{-1}$. This behavior is attributed to exchange between D_2O and H_2O . If the D_2O were present in the form of suspended drops, H_2O would have access for exchange only by diffusion through the solid paraffin. It seems unlikely that such diffusion could occur in a period as short as one week. Furthermore, the droplets should merely evaporate by diffusion whereas the appearance of infrared ab-

sorption which can be attributed to HDO suggests exchange rather than loss of the absorbing material. If the D_2O were present as adsorbent on silica gel, the water in the gel provides an ample supply of H_2O distant only a few molecular layers. It is believed that the exchange takes place with the H_2O in the gel. To verify this proposal the following experiment was performed. A sample of the degassed silica gel was placed in contact with D_2O vapor and at intervals up to 80 hours aliquots of the gas phase were removed for mass spectrometric isotopic analysis.⁶ This experiment indicated that in the first four hours, about 5% exchange $(\text{H}/\text{H} + \text{D}) \times 100$ occurred above that observed in blank experiments (in which the silica gel was omitted) and about 12% in 48 hours.

4. The spectrum of sample no. 1 seems to differ from the other spectra. This sample and another sample of surface coverage near $0.1 v_m$ showed an apparent absorption with such a broad and indistinct maximum that their spectra were not included here. These apparent spectral changes though not definitely established, could reasonably be attributed to an adsorbed sample at a surface coverage so low that the high energy sites predominate. The forces of binding at these sites would be expected to be less homogeneous and quite different from liquid forces.

To show that the observed spectra cannot be attributed to D_2O dissolved in paraffin, a blank experiment was performed. The spectrum of paraffin which was melted in contact with liquid D_2O failed to show absorption in the spectral region near 2500 cm.^{-1} comparable to that of the samples with silica gel present.

In recent years it has been postulated that adsorbed molecules in the second and higher layers closely approximate the liquid state. With respect to this one accessible vibrational mode of D_2O on silica, this contention is apparently substantiated to coverages even less than that required to form a monolayer. These results are in accord with those of Kurbatov and Neuimin.³

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(6) These analyses were very kindly performed by Dr. Amos Newton of the Radiation Laboratory, University of California.