

form solutions of very low viscosity. We have now found that the chloro compound can be prepared and is a non-thickener.

These results strongly suggest¹ that the thickening action is due to hydrogen bonding, but infrared absorption spectra⁵ seem to show that no hydrogen bonds are present in these systems, which eliminates this explanation.

Experimental

The Reaction of Aluminum Chloride with Lauric Acid.—Weighed amounts of distilled anhydrous aluminum chloride and lauric acid were placed in a three-neck flask. Upon addition of cyclohexane and stirring, the reaction proceeded smoothly at room temperature. Its progress was followed by titrating the hydrogen chloride evolved. The product was frozen and the solvent removed by sublimation *in vacuo*. With two or more equivalents of lauric acid present, two equivalents of hydrogen chloride were evolved, showing that the reaction proceeded only to the formation of AlCl_2 . Aluminum chloride gives a red color with tetralin. The products gave this same color with tetralin only when less than one equivalent of lauric acid was present. This suggests that an aluminum dichloromonolaurate as well as a monochlorodilaurate is formed. Because of the large solubility of reagents and products in hydrocarbons and their reactivity with polar solvents and traces of moisture, we have not been able to separate the components of the reaction mixture.

Aluminum Monochlorodilaurate.—Reaction of stoichiometric amounts yielded after lyophilization an extremely viscous liquid which froze at 2°. Due to this viscosity it stayed white for several days after being obtained by lyophilization. Upon standing for several weeks, or rapidly upon centrifugal compaction, it became transparent. Analysis indicated the presence of hydrolytic products and agreed with that expected if the product contained a small amount of the hydroxy dilaurate as shown by Table I.⁶ It reacted rapidly with atmospheric moisture evolving hydrogen chloride and forming a white brittle coating, but the reaction did not go to completion due to protective action of the coating.

TABLE I

	Found	Theoretical AlCl_2	Theoretical 89% AlCl_2 + 11% AlOHL_2
C	62.3	62.51	62.70
H	10.02	10.06	10.10
Al_2O_3	11.02	11.06	11.07
Cl	6.84	7.69	6.88

Solutions of Aluminum Chlorodilaurate.—Our product was very soluble in hydrocarbons and also soluble in acetone. Part of it reacted with any residual moisture present in dried acetone⁹ forming an insoluble product and the remainder dissolved. The acetone solution gradually darkened due to the formation of condensation products by the solvent.

All solutions were fluid. A few relative viscosities were estimated either in an Ostwald viscometer or by the rate of rise of air bubbles, with the following results: in cyclohexane 1.3%, 1.05; 4.8%, 1.19; 27%, 4.5; in cetane 22%, 8. These increases in viscosity are negligible compared to those produced by the hydroxylaurate.¹⁰

(5) W. W. Harple, S. E. Wiberly and W. H. Bauer, *Anal. Chem.*, **24**, 635 (1952).

(6) The difficulty of obtaining really pure compounds of this class may be judged by the following per cent. deviations from theoretical values for some recent preparations: triacetate,⁷ Al_2O_3 : +5%; tripropionate,⁷ Al_2O_3 : +10%; trilaurate,⁴ Al_2O_3 : +20%; *s*-butoxy dilaurate,⁸ L: -24 to -36%; *s*-butoxy stearate,⁸ St: 0 to -14%; cresoxy dilaurate,⁸ L: -15 to -30%; dihydroxymonolaurate,⁸ Al_2O_3 : -20 to +6%.

(7) G. C. Hood and A. J. Ihde, *THIS JOURNAL*, **72**, 2094 (1950).

(8) C. G. McGee, *ibid.*, **71**, 278 (1949).

(9) J. Timmermans and L. Gillo, *Rozniki Chem.*, **18**, 812 (1938); K. J. Mysels, *J. Phys. Colloid Chem.*, **51**, 708 (1947).

(10) K. J. Mysels, *J. Colloid Sci.*, **2**, 375 (1947); H. Sheffer, *Can. J. Research*, **B26**, 481 (1948); V. R. Gray and A. E. Alexander, *J. Phys. Colloid Chem.*, **53**, 9 (1949).

The passage of moist air through hydrocarbon solutions caused the hydrolysis of only about one-half the chlorine present. Most of the remainder was removed during lyophilization of the hydrolyzed solution. During the hydrolysis of solutions, even of those containing 27% of the compound, we never observed any bulk gelation. Occasional small fragments of gel appeared but always redispersed. The viscosity of the solutions (as measured by the rate of rise of air bubbles) increased to about double the original value in early stages of hydrolysis and then decreased. This behavior is contrary to that observed by Condit¹¹ who studied a chlorine-containing product¹² of reaction of naphthalenic acid with aluminum chloride and that reported for alcoxy and cresoxy soaps.^{3,13}

(11) D. H. Condit, U. S. Patent 2,321,463 (1943).

(12) D. H. Condit, private communication.

(13) T. S. McRoberts and J. H. Shulman, *Proc. Royal Soc. (London)*, **A200**, 136 (1949).

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The Magnetic Susceptibility of Adsorbed Paramagnetic Salts¹

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The only systematic study of the magnetic susceptibilities of adsorbed salts is that of Bhatnagar, Mathur and Kapur² who reported that salts of iron, cobalt, nickel and manganese lost their paramagnetism when adsorbed on charcoal, but not when adsorbed on silica gel. This behavior might be explained by postulating the formation of a covalent complex between the ion and the surface of the charcoal; the magnetic moments would then correspond to the diamagnetic, or weakly paramagnetic covalent complexes, rather than the strongly paramagnetic ionic complexes, in each case. However, the charcoal they used was itself paramagnetic so there is some question concerning the interpretation of their observations. Since data of this type should provide fundamental knowledge concerning the nature of the adsorption of ions we have reinvestigated this problem using adsorbents free of paramagnetic impurities.

Experimental

Apparatus.—Magnetic susceptibilities were measured by the Gouy method using a semi-micro balance. The electromagnet was constructed in the shop of the Chemistry Department; the rectangular yoke is built up from 2" × 8" mild steel bars with 4.5" diam. pole pieces located centrally. The coils are each wound with 1440 turns of No. 8 d.c.c. magnet wire and double turns of wire are separated by spacers to allow the circulation of cooling oil through the windings. Current is supplied by a 7.5-kw. motor generator set and is controlled both by resistances in series with the windings and by varying the field resistance of the generator. Interchangeable pole pieces of various types are provided and the pole gap can be continuously varied. The field was calibrated after each change of pole gap using both 29.20% nickel chloride solution and distilled water as standards.³ The iron was demagnetized between runs by rapidly reversing a continuously diminishing direct current through the windings. The glass susceptibility tubes were each divided by a septum and showed no change in weight with field strength. Measurements were always made at

(1) This work was performed under contract NRO57232, Nonr-02300 with the Office of Naval Research.

(2) S. S. Bhatnagar, K. N. Mathur and P. L. Kapur, *Ind. J. Phys.*, **3**, 53 (1928).

(3) P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943.

five field strengths, varying from 8,000 to 13,500 gauss, and the arithmetic mean of the values was used.

Method.—A weighed amount of adsorbent (about 7 g.) was agitated for about an hour with 10 ml. of a standard solution of the paramagnetic salt, the mixture filtered through sintered glass, the adsorbent washed several times with water, dried in an oven (110° for charcoal and 140° for silica gel) for two hours and transferred to the susceptibility tube for measurement. The filtrate and washings were combined and analyzed, the amount of salt adsorbed being determined by difference. The susceptibility of the pure adsorbent was determined in a separate experiment. When ferrous (or ferric) salts were studied the drying was carried out in an inert atmosphere and special analyses were made to determine whether any oxidation (or reduction) had occurred in handling.

Analytical methods used were as follows: (a) ferrous iron was determined by titration with cerate, (b) ferric ion was reduced in a silver reductor and the ferrous ion titrated with cerate, (c) nickel was determined gravimetrically with dimethylglyoxime, (d) cobalt was titrated potentiometrically with ferricyanide in ammonium citrate-ammonium hydroxide solution, (e) manganese ion was titrated potentiometrically with permanganate in a neutral pyrophosphate solution.

Materials.—Eimer and Amend Co. C.P. charcoal was treated with concd. sulfuric acid to remove materials which reduced cerate, washed several times with water and dried at 110° for two hours. Silica gel from Davison Chemical Co. was used directly and showed no change in susceptibility after treatment with water and redrying at 140° for two hours. Both adsorbents were shown to be reasonably free of ferromagnetic impurities by the small change in susceptibility observed with varying field strength.

Results.—The gram susceptibilities of the adsorbed salts were calculated by the additivity rule from the observed gram susceptibilities of the mixtures, the analytical data and the susceptibility of the pure adsorbent. In each case measurements were made on several samples treated in various ways, and the values so obtained were averaged. The mean values of the gram atomic susceptibilities of the adsorbed paramagnetic metal atoms are shown in Table I along with the corresponding magnetic moments, in Bohr magnetons, calculated on the assumption that the molecular field constant Δ is zero. The range of magnetic moments commonly observed for the ion in solution or in simple salts is given for comparison, and an average value of the amount of metal ion adsorbed is shown for each ion studied. The diamagnetism of the anions has been neglected. The probable error in χ_A for the adsorbed salt is about 15% so the magnetic moments are, in general, reliable to only about ± 0.4 ; this precision is adequate for the purpose of the present work.

In a separate series of experiments it was shown that the charcoal used was a good adsorbent for base, a poor adsorbent for acids and, when equilibrated with a neutral salt solution (KCl), hydrogen ion was liberated from the charcoal but no change in the chloride ion concentration occurred. This indicates that the charcoal is a low-tempera-

ture air-activated material which behaves as though it were a cation exchanger.¹

Discussion

The paramagnetic cations studied here evidently do not lose their paramagnetism when adsorbed on sugar charcoal or on silica gel. This is in qualitative agreement with the results of Bhatnagar, *et al.*,² for silica gel but is contrary to their findings in the case of charcoal. Since their charcoals were strongly paramagnetic and so must have contained paramagnetic (and possibly ferromagnetic) impurities, it seems possible that the losses in paramagnetism they observed resulted from desorption of impurities in the charcoal.

The magnetic moments observed here for the adsorbed ions are within the normal range of values observed for the corresponding ion in solution or in a simple salt,³ with the exception of adsorbed ferrous and ferric ions. The origin of the discrepancies for these ions are not known but may be associated with the formation of surface oxides or hydroxides of iron. Since, in every case, the covalent complexes of the ions have much smaller magnetic moments (or are diamagnetic),⁵ we conclude that the ions are held on the surface by essentially ionic bonds. This would be expected for cations adsorbed on silica gel since they presumably displace hydrogen ions from acidic hydroxyl groups on the silica gel surface. A similar ion-exchange mechanism for the adsorption of cations on charcoals which have been activated in air at low temperatures (<600°) has been postulated.⁴ The charcoal surface would thus be covered by a surface oxide characterized by acidic hydroxyl groups which could exchange hydrogen ions with the cations in solution and the ions so adsorbed would be held by an essentially ionic bond to an oxygen atom of the surface.⁶⁻⁸ Our results are in agreement with this hypothesis.

Acknowledgment.—We are indebted to the Office of Naval Research for support of this work.

(4) See, for example, B. Steenberg, "Adsorption and Exchange of Ions on Activated Charcoal," Almquist and Wiksells, Uppsala, 1944.

(5) L. Pauling, "Nature of the Chemical Bond," Second Ed., Cornell University Press, Ithaca, N. Y., 1940.

(6) H. L. Bennister and A. King, *J. Chem. Soc.*, 991 (1938).

(7) J. Wilson and T. R. Bolam, *J. Colloid Sci.*, 5, 550 (1950).

(8) S. Weller and T. F. Young, *THIS JOURNAL*, 70, 4155 (1948).

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TABLE I

THE MAGNETIC SUSCEPTIBILITIES AND MAGNETIC MOMENTS OF ADSORBED IONS

Adsorbent	Adsorbate	Amount adsorbed ^a	χ_A , c.g.s. units $\times 10^{-6}$	$\mu_{\text{eff.}}$, adsorbed salt	$\mu_{\text{eff.}}$, typical salts
Charcoal	NiCl ₂	4.5	3,930	3.08	2.9-3.4
Charcoal	CoCl ₂	4.6	10,100	4.96	4.4-5.2
Charcoal	CoSO ₄	2.0	10,470	5.05	4.4-5.2
Charcoal	MnSO ₄	4.5	15,450	6.13	5.2-5.96
Charcoal	FeSO ₄	1.8	13,400	5.69	5.0-5.5
Charcoal	Fe ₂ (SO ₄) ₃	2.6	16,750	6.24	5.4-6.0
Charcoal	None	...	-0.462 ^c
Silica gel	NiCl ₂	7.2	4,660	3.32	2.9-3.4
Silica gel	FeSO ₄	0.7	10,110	4.93	5.0-5.5
Silica gel	Fe ₂ (SO ₄) ₃	2.5	8,400	4.50	5.4-6.0
Silica gel	None	...	-0.317 ^c

^a Milligrams of metal per gram of adsorbent. ^b See ref. 3, pp. 79 and 99. ^c Gram susceptibility.

Some Nitrogen Derivatives of Dibenzothiophene

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It has been shown that 3-acetylaminodibenzothiophene and 3-acetylaminodibenzothiophene-5-oxide are carcinogenic to rats.² For this reason N-substituted derivatives of 3-aminodibenzothiophene have been prepared. The isomeric 2-substituted derivatives have also been synthesized for comparison.

(1) Cancer Research Laboratory, University of Florida, Gainesville, Fla.

(2) E. C. Miller, J. A. Miller, R. B. Sandin and R. K. Brown, *Cancer Research*, 9, 504 (1949).