188.   *Adsorption of n-Dodecylamine at the Interfaces between Water and Cupric, Nickel, and Zinc Oxides.*

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Cupric, nickel and zinc oxides adsorb dodecylamine from aqueous solution as free base, and not as dodecylammonium ions. The adsorption isotherms have been interpreted in terms of an equilibrium process since, within reasonable limits of experimental error, the equilibrium position may be reached from either side. The free-energy change on adsorption increases as more amine is adsorbed. This is attributed to interaction between the hydrocarbon chains at the interface. The order of the values of $-\Delta G$ is $CuO > NiO > ZnO$, which is consistent with the postulate that each adsorption site is associated with the near presence of a metal ion in the solid lattice, and that the amine molecule replaces water molecules at the site.

THE factors which control the adsorption of solute molecules and ions at solid–liquid interfaces are not well understood. One difficulty is that the forces responsible for the concentration of a substance at the interface may be of different kinds, depending on the nature of the solid surface and of the species adsorbed. It seems likely that in some cases the adsorption process can be regarded as being formally analogous to the formation of aggregates, or complexes, between ions or molecules in solution.[1] This implies that the heat of formation of a bond between an adsorbed molecule or ion and a metal ion held at the surface of the solid, is similar to that of the bond produced by the first step in the formation of a complex between the same molecule or ion and the solvated metal ion in solution. However, the bond strength will depend on the environment of the metal ion, which is very different in the two cases. Other factors, also, make direct comparison difficult; for instance, interaction between adsorbed molecules or ions will affect the enthalpy change, and the entropy change on adsorption may be very different from that occurring on complex formation. It is necessary, therefore, in the first instance, to test the analogy between adsorption and complex formation by choosing systems where it seems likely to hold, and to compare the behaviour on adsorption with that predicted from existing data on complex formation.

Aliphatic amines may be adsorbed at a solid surface under a variety of conditions, depending on the composition of the solid. In the case of quartz and glass, n-dodecyl-ammonium ions are adsorbed from $\sim 10^{-6}$N-solutions.[2,3] Amine in excess of a monolayer is adsorbed on glass as molecules from 10^{-5}N-solutions.[3] In these cases it is reasonable to suppose that the solid surface has replaceable hydrogen ions attached to oxygen ions bound in the solid lattice. Since the long-chain alkylammonium silicates are extremely insoluble, the adsorption of the amine from very dilute solutions is easy to understand. At low pH values, however, the competition between the alkylammonium ions and hydrogen ions results in less adsorption of amine. If adsorption of amine resembles complex formation in solution, then solids for which this is true must adsorb free amine molecules. Such solids must, obviously, contain a metal which forms a bond to nitrogen which is much stronger than the bond to the oxygen of water, where this is the liquid medium. A primary aliphatic amine should be adsorbed much more readily to a solid containing copper than to one containing nickel, and rather more readily to this than to a zinc compound. The values of $\log K_1$ for complex formation with ammonia, extrapolated to infinite dilution, at $30°$ are [4] for Cu(II) 4·01, Ni(II) 2·67, and Zn(II) 2·18. To avoid complications due to the

[1] Burkin and Halsey, *Nature*, 1961, **191**, 348.

[2] Gaudin and Bloecher, *Mining Engineering*, 1950, **187**, 499; Buckenham and Rogers, *Trans. Inst. Mining Metallurgy (London)*, 1954, **64**, 11; Burkin and Soane, *Proc. 3rd Internat. Congress of Surface Activity (Cologne)*, 1960, Vol. IV, p. 430.

[3] Halsey and Burkin, *Nature*, 1962, **193**, 1177.

[4] "Stability Constants," Part II, *Chem. Soc. Special Publ.* No. 7, 1959.

presence of other ions in the solid, this prediction has been tested for cupric, nickel, and zinc oxide. The adsorption of material used was n-dodecylamine.

It has been shown [5] that if a metal ion such as copper(II) is bound to an ion-exchange resin, ligands, including amines, may replace one another or water molecules in the solvation shell of the metal ion. This implies that free amine molecules interact with the metal ions. Several workers [6] have suggested that free amine molecules are adsorbed by minerals and other solids containing metal ions, but without giving proof. This was on the grounds that contact-angle measurements and the behaviour of the solids on froth flotation indicated that the amine was adsorbed at relatively high pH where the alkylammonium ion activity is low. Gaudin,[7] however, cites some similarities between results
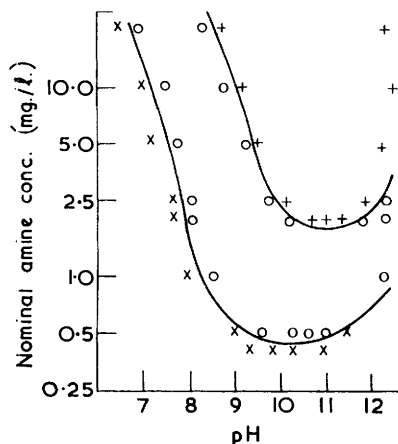

FIG. 1. Bubble pick-up diagram. Dodecylamine on CuO, experimental points: ×, no cling; ○, cling; +, pick up. Nominal amine concn. based on quantity added to the system.
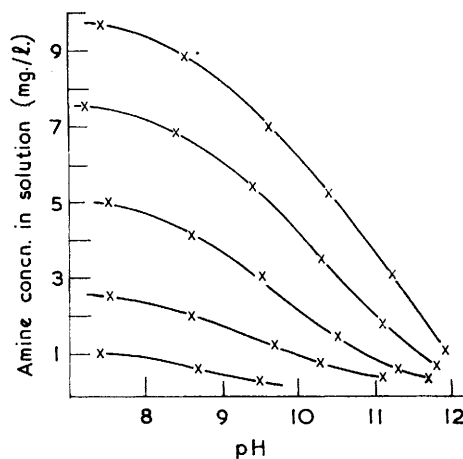
FIG. 2. Adsorption of dodecylamine to surface of glass bubble pick-up apparatus. Vol. of soln., 100 ml.; electrolyte, 10^{-3}M-NaClO$_4$. NaOH was added to solns. of amine at pH ~7·5.

for amine adsorption on metal sulphides and on quartz, and suggests that interaction of the free amine and metal ions in the solid is unlikely.

Our experiments were carried out with 10^{-3}M-sodium perchlorate which held the total ionic strength approximately constant. The amount of amine salt present was small in every case, and adjustment of pH within the limits used required little sodium hydroxide or perchloric acid. Sodium perchlorate was used because it was thought unlikely that the perchlorate ions would have a significant influence on the adsorption of amine or on the hydrogen and hydroxyl ion activities at the solid surfaces. It will be shown in another paper that the salt has little effect on the electrokinetic potentials of the solids and is not specifically adsorbed.

Dependence of Adsorption on pH.—Measurement of the quantity of the amine adsorbed by each of the three metal oxides showed that little is removed from solution at pH 8·5 and very much is adsorbed at pH 10·5. The determination of amine in solution was not sufficiently precise to permit accurate measurement of the variation in the amount adsorbed over a wide pH range and an indirect method was used to assess this (the "bubble pick-up" procedure [8]). An air-bubble, blown at the end of a narrow

[5] Helfferich, *Nature*, 1961, **189**, 1001.
[6] Arbiter, Kellog, and Taggart, Amer. Inst. Mining Metall. Engineers, Technical Publn. No. 1581, 1943; Kellog and Vasquez-Rosas, *ibid.*, No. 1906, 1945; Rey, Sitia, Raffinot, and Formanek, *Mining Engineering*, 1954, **6**, No. 4, 416.
[7] Gaudin, "Flotation," McGraw-Hill Publ. Inc., New York, 2nd edn., 1957.
[8] Cooke and Digre, *Mining Engineering*, 1949, **1**, No. 8, 299.

glass tube, was brought into contact with a bed of the solid particles, of known and similar size, under 10^{-3}M-sodium perchlorate containing dodecylamine and at a suitable pH. The tube and bubble were raised and three kinds of behaviour were possible: (1) " Pick-up: " solid particles adhered to the bubble and were not dislodged when the tube was tapped. (2) " Cling: " the particles fell away from the bubble when the tube was tapped. (3) No particles adhered to the bubble. Each experiment was carried out at a particular amine concentration, beginning at a pH at which no particles clung to the bubble. Acid or alkali was then added in stages until either the whole working range of pH had been covered or pick-up was observed. This procedure gave results which were closely reproducible by one person, and fairly well reproduced by different observers.

The information provided by this technique was interpreted as follows. The gravitational force on a particle when the bubble was raised was opposed by the force operating at the air–water–solid line of contact. For a particular kind of particle, the latter force depended on the proportion of the solid surface covered by the hydrophobic amine. Since all particles were approximately equal in size, the lines separating the no-cling from the
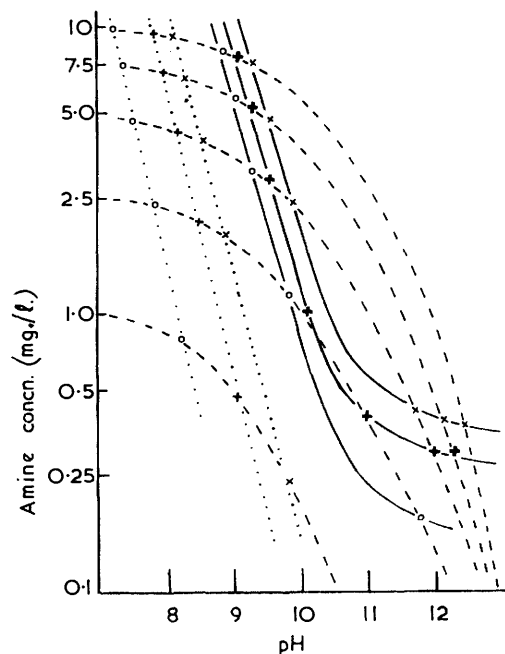

FIG. 3.   Corrected cling and pick-up curves for dodecylamine on CuO (O), NiO (+), and ZnO (×). Broken lines show actual amine concentrations in the solution at several nominal concentrations (value at pH 7). Full lines are pick-up curves for the three oxides. Dotted lines are cling curves. Shapes of the pick-up curves were determined from interpolated concentrations, not shown.

cling, and the cling from the pick-up region corresponded to coverage of particular fractions of the surface by the amine. Thus the total concentration of amine in solution necessary to give these two, unknown, fractions was obtained at a number of pH values. The results for cupric oxide are shown in Fig. 1, only those experimental results necessary to define the limits of the regions being given. The curves for nickel and zinc oxides are practically identical in shape with those for cupric oxide, but at slightly higher amine concentrations.

The shape of the curves is typical for work of this kind, and considerable doubt has existed as to the explanation of the rise in amine concentration necessary for both cling and pick-up at pH values greater than about 10·5. In the present case, and probably in many others, it is due to the fact that the total concentration of amine in solution is much lower than that calculated on the basis of the quantity of amine added. The loss of amine to the glass apparatus under the experimental conditions, but with no metal oxide present, is shown in Fig. 2. The corrected cling and pick-up curves are shown in Fig. 3 in which

the broken lines show the experimentally determined values of the amine concentration in solution in the apparatus at various nominal amine concentrations calculated from the quantity of amine added. The full lines are the pick-up curves for the three oxides, transferred from curves such as Fig. 1. Only the experimental points for pick-up at the nominal amine concentrations corresponding with the lines drawn are shown. However, the variation of solution concentration with pH for any nominal amine concentration can be interpolated accurately, and the shapes of the pick-up curves were obtained in this way. The corresponding curves for " cling " are also drawn.

The results for the three oxides are curves which correspond precisely in shape to lines of constant concentration of free dodecylamine as the pH is changed. The critical concentrations of free amine in the solution are:

	CuO	NiO	ZnO
Concn. $(10^{-7}M)$ for pick-up	7·3	11·8	19·0
Concn. $(10^{-8}M)$ for cling	1·1	8·1	16·2

The values were obtained from the curves by using $K_B = 4·3 \times 10^{-4}$ for n-dodecylamine.[9]

The results given above are taken as proving that free amine molecules, not dodecylammonium ions, are adsorbed by cupric, nickel, and zinc oxide from 10^{-3}N-sodium perchlorate solution. However, similar results obtained [10] in the goethite (Fe_2O_3,H_2O)–dodecylamine system by a different, although analogous, experimental procedure have been interpreted as showing that dodecylammonium ions were adsorbed by the solid. This deduction was based on equations derived in an argument justifying the theory that adsorption at a solid–liquid interface invariably occurs by an ion exchange process.[11] These equations imply that incipient flotation, or pick-up, should occur under conditions such that $[C_{12}H_{25}\cdot NH_3^+]/[H^+] =$ Constant. That is, if the alkylammonium ion is adsorbed by exchange with a hydrogen ion on the solid surface, the pick-up curve follows a curve

Experimental data on adsorption isotherms; c is the total amine concentration (mg./l.) in the solution in equilibrium with the metal oxide, or apparatus, which has adsorbed amine corresponding to a loss of concentration Δc in the solution. Volume of solution used in each experiment, 50 c.c.; wt. of oxide, 1 g.

Apparatus		Cupric oxide		Nickel oxide		Zinc oxide	
c	Δc	c	Δc	c	Δc	c	Δc
2·67	0·24	1·72	0·28	1·67	0·23	2·33	0·16
3·55	0·26	2·60	0·34	3·34	0·47	3·90	0·33
4·58	0·32	3·26	0·74	3·43	0·41	4·51	0·47
5·31	0·40	3·91	1·01	4·03	0·68	5·17	0·76
5·35	0·36	4·52	1·30	4·68	1·03	5·77	1·15
5·52	0·30	5·77	2·25	5·22	1·32	6·21	1·67
5·71	0·56	5·61	2·17	5·83	1·79	6·86	2·24
6·14	0·75	6·01	2·72	6·02	1·69	7·45	3·05
6·61	1·00	6·72	3·24	6·27	2·19	7·58	2·72
6·86	0·76	7·36	3·50	6·77	2·73	8·04	3·47
7·48	1·25	7·93	3·71	7·21	2·53	8·75	4·35
8·92	1·48	8·21	3·98	7·36	3·16		
10·05	1·59	9·01	4·62	8·10	3·75		
11·91	2·65	9·35	5·20				

corresponding to constant free-amine concentration as the pH is changed. The argument is open to several objections which are not relevant here, but the following points are important. (1) It is found, as pointed out above, that the pick-up curve for quartz and dodecylamine follows a curve of constant dodecylammonium ion concentration. In this case it is reasonable to suppose that the ion is adsorbed at the surface. (2) The results for goethite refer to nominal amine concentrations only. Since the work was carried out in

[9] Hoerr, McCorkle, and Ralston, *J. Amer. Chem. Soc.*, 1943, **65**, 328.
[10] Iwasaki, Cooke, and Colombo, U.S. Bureau of Mines, Report of Investigations, 1960, No. 5593.
[11] Cook and Nixon, *J. Phys. Colloid Chem.*, 1950, **54**, 445; Last and Cook, *J. Phys. Chem.* 1952 **56**, 637.

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glass apparatus, corrections are necessary over much of the pH range used. Such corrections would probably explain also a number of puzzling results obtained [10] with trimethyldodecylammonium chloride. There seems no reason to alter the conclusion that amine molecules, not ions, are adsorbed by the three metal oxides studied by us.

Adsorption Isotherms.—Adsorption isotherms of n-dodecylamine on cupric, nickel, and zinc oxide were measured at 31° from 10^{-3}M-sodium perchlorate at pH 9·5. The particles of the oxides were prepared by sintering fine powders and grinding the lumps. The amount of amine adsorbed by the apparatus in the absence of metal oxide was measured and subtracted from the amount adsorbed with the oxide present. A certain latitude is possible in deriving the adsorption isotherms of the oxides by difference and the experimental values are given, therefore, in the annexed Table. By taking smoothed curves, the quantity of amine adsorbed by 1 g. of each of the oxides at any aribitrarily chosen
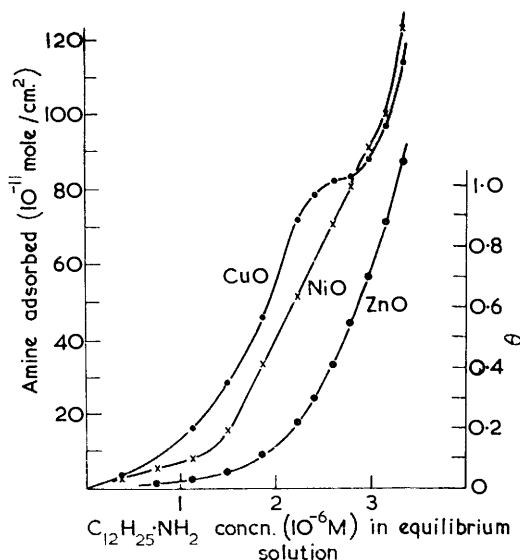

FIG. 4.   Adsorption isotherms: n-dodecyl-amine on CuO, NiO, and ZnO.

equilibrium concentration of total amine in solution may be obtained. The discussion of the adsorption isotherms is based on these values, shown in Fig. 4.

Surface-area Determination.—Two methods were used to estimate the surface area per unit mass of the three oxides, based one on krypton adsorption and the other on particle measurement by an optical microscope. A third method was possible for cupric oxide, since the adsorption curve for dodecylamine showed a well-defined plateau. If this is assumed to correspond to the formation of a complete monolayer of amine on the surface, the surface area of the solid can be calculated by using 20·5 Å ^{2} as the area of an adsorbed amine molecule. The results (cm.^{2}/g.) obtained were:

	Krypton adsorption	Amine adsorption	Particle measurement	Surface area taken
CuO	1690	748	221	748
NiO	7900		206	(685)
ZnO	990		304	990

Particle measurements were made by a comparison graticule. Sufficient numbers of particles were examined to give an accuracy of $\pm 5\%$ in the value of the mean diameter in each case. The results were: CuO, 42 μ; NiO, 39 μ; ZnO, 35 μ. The surface areas were calculated on the basis of spheres of the mean projected area.

The krypton-adsorption method seems to be suitable for the determination of relatively small surface areas, and the individual measurements showed no irregularities or abnormal

features. The results it gave with cupric and nickel oxide are, however, very large when compared with the measured particle sizes. For non-porous solids the increase in surface area due to irregular shape and surface roughness usually gives a value about three times that calculated from the size measured, on the assumption that the particles are smooth spheres. Samples of the three oxides were mounted in resin and polished, finally with diamond dust, and examined microscopically. The nickel oxide particles were somewhat porous and, particularly at their edges, there was evidence that the very small grains had sintered together at the points of contact, leaving voids. This was also true for the cupric oxide, but to a smaller extent. The zinc oxide particles, however, appeared to be non-porous. These observations were consistent with the behaviour of the materials on sintering. Zinc oxide is appreciably volatile so that crystallisation occurred from the gas phase. Cupric oxide sintered fairly readily but no melting or vaporisation occurred, so adhesion between grains took place by a solid-state reaction which did not fill the voids in the time available. Nickel oxide was very difficult to sinter, so that interaction between grains was slow even at the points of contact.

Since the grains of nickel oxide were very small the spaces between them in the compressed block must have been small. The surface area of the sintered particles was, therefore, measured by using propane adsorption. The experiments were carried out by Mr. R. Hughes and we thank Mr. D. Bryant for assistance and advice. The limits of the surface area were 3280 and 3650 cm.^{2}/g. Thus the larger gas molecules were not able to occupy some of the surface available to krypton.

The values of the surface area of the oxides relevant for adsorption of dodecylamine from aqueous solution were chosen as follows. For zinc oxide, 990 cm.^{2}/g., since this behaves as a non-porous solid. For cupric oxide, 748 cm.^{2}/g., as the information required is the fraction of the adsorption sites available to amine which are occupied in equilibrium with solutions containing various concentrations of amine. The ratios of these areas to those calculated from particle-size measurements are 3·25 and 3·39, respectively. Thus in the case of cupric oxide the space between the grains sintered together was not available to the amine, which is reasonable since the holes were almost certainly too small to admit water under the experimental condtions. The shapes of the particles obtained by grinding the sintered oxides were similar in each case and it was assumed that for nickel oxide the relevant surface area would be 3·32 times that calculated from particle-size measurement, giving a value 685 cm.^{2}/g.. The probable error in this figure would not affect the conclusions drawn in this paper. The value is also supported by the slight discontinuity in the adsorption isotherm for the amine on this oxide, mentioned below.

Interpretation of Adsorption Isotherms.—The adsorption curves, expressed in terms of amine adsorbed per cm.^{2}, are shown in Fig. 4. The value of K_B for n-dodecylamine [9] is $4·3 \times 10^{-4}$, so that at pH 9·5 the ratio ions : base is 13·5 : 1. There is some indication of discontinuity in the curve for nickel oxide at a value of the fraction of the surface covered by amine, θ, slightly greater than unity. This could possibly be due to experimental error but is more likely to indicate completion of the monolayer. In the latter case the estimated value of the surface area per unit mass is supported.

The Freundlich isotherm, $\theta = kc^n$, is followed by the results for zinc oxide at $\theta = 0$—1, for nickel oxide at $\theta = 0·2$—0·5, and for copper oxide at $\theta = 0·2$—0·7. The values of the constants are:

	CuO	NiO	ZnO
log k	12·23	18·43	21·93
n	2·17	3·29	4·00

The Langmuir adsorption isotherm is obeyed between the following values of θ: copper oxide 0·1—0·3; nickel oxide 0·1—0·3; zinc oxide 0·2—0·3 (Fig. 5). In the case of zinc oxide the deviation below $\theta = 0·2$ is slight and probably due to experimental error. With more than one third of the solid surface occupied by amine molecules it is clear that some,

at least, of the assumptions on which the Langmuir isotherm is based are not valid for these systems. It seems likely that interaction of adsorbed amine molecules will occur at quite low values of θ, since each molecule can occupy far more than 20·5 Å ^{2} when not close packed on the surface.

Treatment of Adsorption as a Chemical Equilibrium.—It is necessary to show that the equilibrium adsorption positions may be reached from either side. This is difficult to achieve experimentally with sufficient accuracy, but the following results were obtained.

Equilibrium was reached by the standard experimental procedure, the total weight of the vessel, oxide, and solution being known. Samples of the solution were taken for amine determination. About one-third of the solution was then removed and the vesse and contents were weighed. Electrolyte containing no amine was added to give
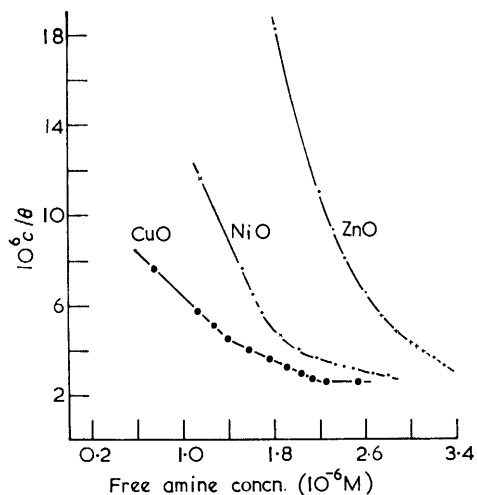

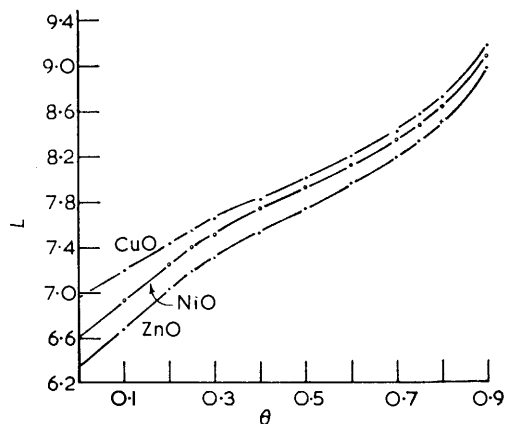FIG. 5. Langmuir isotherms: n-dodecyl-
amine on CuO, NiO, and ZnO.

FIG. 6. Variation of L with surface cover-
age of n-dodecylamine on CuO, NiO,
and ZnO.

approximately the original quantity of solution. The vessel was replaced in the constant-temperature bath and the pH adjusted to 9·50 after 30 minutes and subsequently until it remained constant. The amine content of the solution was then determined:

	CuO	NiO	ZnO
Amine present in original soln. (mg.)	0·281	0·313	0·343
,, removed (mg.)	0·112	0·183	0·132
,, present in new soln. (mg.)	0·209	0·188	0·265
,, expected in new soln. (mg.)	0·215	0·202	0·275
Theoretical removal from solid (%)	87	81	84

The lowest line of this table gives the proportion of the amine which should be desorbed from the solid surface by the dilution of the solution, which is found experimentally in the diluted solution. In view of the experimental errors involved, and in particular the need to use a glass electrode in the solution several times, it is concluded that the adsorption may reasonably be regarded as a reversible equilibrium. This may be represented as

$$C_{12}H_{25} \cdot NH_2 + M \rightleftharpoons C_{12}H_{25} \cdot NH_2M$$

where M is an adsorption site on the solid surface.

If activities are assumed to equal concentrations, the equilibrium constant K_1 may be taken as $\theta/c(1 - \theta)$, where c is the concentration of free amine in the solution. If free-energy changes are calculated from the individual values of K_1, it is found that the values

of $L = -2 \cdot 303 \, \boldsymbol{R}T \log K_1$ increase with increasing values of θ (Fig. 6). This is contrary to the usual situation, where L decreases as the adsorption sites with greater affinity for the adsorbed molecules are successively filled. The increase of L as more amine is adsorbed may be attributed to the reaction between the hydrocarbon chains when amine molecules are removed from the very dilute aqueous solution and concentrated on the solid surface.

The variation of L with θ is linear if $\theta < 0 \cdot 3$ and extrapolation to $\theta = 0$ gives the following values (kcal. mole^{-1}):

	CuO	NiO	ZnO
L	6·96	6·62	6·34

When the Langmuir adsorption isotherm is obeyed, L is usually taken as ΔG. In the case of complex formation between ammonia and the hydrated Cu^{2+}, Ni^{2+} and Zn^{2+} ions the values of ΔG are 5·56, 3·70, and 3·02 kcal. mole^{-1}, respectively. No comparative data are available for alkylamines with these metals.

It is clear that the prediction that dodecylamine should be adsorbed most strongly on cupric oxide and least strongly on zinc oxide, is fulfilled. The difference between the three oxides is less than that expected, but this can be accounted for by the interaction of adsorbed amine molecules which is shown to occur. It would be particularly interesting to know the entropy change on adsorption at different values of θ. Calorimetric measurements of the heats of adsorption are, therefore, being carried out.

EXPERIMENTAL

Materials.—Cupric oxide. " AnalaR " cupric oxide was compressed into pellets and kept at $1005° \pm 5°$ for 3 hr. Microscopic examination of the sintered product (m. p. 1064°) showed it to consist of a mass of small crystals, with estimated size 100—150 μ, very firmly bound together. An X-ray powder photograph showed the solid to be tenorite.

Zinc oxide. The m. p. is about 1975° but the oxide is appreciably volatile above 1000°. Pure oxide, as supplied for pigment, was compressed and kept in a closed vessel at 1370° for 60 hr. The product was hard and had no tendency to form very fine particles during grinding or agitation in water.

Nickel oxide. The m. p. is about 1960° and the oxygen pressure at this temperature is about 10^{-2} atm. Pure nickel oxide (supplied by the Mond Nickel Co.) was compressed to give pellets of sufficient strength to support themselves in the event of breakage of the alumina crucible. The oxide was kept for 1 hr. in an induction furnace at about 1800—1900°. The temperature was uncertain because of local variations. The product appeared crystalline, and had considerable bulk strength. The outer layer, which had been in contact with the crucible, was broken off and rejected.

Each oxide was ground in an agate pestle and mortar. The required size-fractions were separated by sieving. Material used for bubble pick-up tests was of 72—100 mesh B.S.S. size and just before use was roasted at about 1000°, washed with dilute hydrochloric acid and with distilled water, and stored in closed bottles under distilled water from which dissolved gases had been expelled by boiling.

Oxides used for adsorption experiments were fractions which passed a 200 mesh B.S.S. screen (74 μ holes). The particles smaller than 40 μ were then removed by sedimentation in water. Samples of the 74—40 μ particles of each oxide were obtained from the bulk of the material by careful sampling.

n-Dodecylamine. The radioactive amine was prepared by using potassium cyanide containing carbon-14, of activity 1 mc per 0·232 g. of the 98% pure solid. n-Undecyl alcohol was examined by gas-chromatography and reported to be pure, with no detectable homologues. The bromide was prepared from the alcohol, phosphorus, and bromine in the usual way. Equivalent quantities of potassium cyanide and undecyl bromide were refluxed in anhydrous methanol (5 c.c.) for 12 hr. Methanol was then removed, finally *in vacuo*, and the nitrile was transferred to a separating funnel with the aid of toluene. Butan-1-ol (1·17 g.) was added and the mixture cautiously run into a suspension of sodium metal (0·37 g.) as droplets in boiling toluene (6 c.c.). When reaction appeared to have ceased, the walls of the

apparatus were washed with toluene (2 c.c.), a little butanol (0·2 c.c.) was added, and boiling was continued for about 15 min. After cooling, water was added to remove the excess of sodium, and the toluene layer was separated. Toluene and butanol were then removed, finally *in vacuo*. Benzene was added to the residue and the solution filtered. Benzene, saturated with hydrogen chloride, was added, and after storage at 5° overnight the n-dodecyl-amine hydrochloride was filtered off. It was recrystallised again from benzene containing hydrogen chloride and washed 4 times with 2,2,4-trimethylpentane.

A pilot preparation had previously been carried out in the same conditions. Some of the dodecylamine hydrochloride was added to a little aqueous sodium hydroxide, and the water was allowed to evaporate. The residue was boiled with benzene, the extract was dried (NaOH) and evaporated, finally *in vacuo*, and the dodecylamine examined by gas-chromatography. Only water and carbon dioxide were present as detectable impurities, not undecyl alcohol or bromide, cyanide, or butanol. No evidence has been found for the presence of secondary amines.

Measurement of Adsorption of Amine. It was essential to use a vessel which adsorbed relatively little amine compared with the amount adsorbed by the compound being studied. In addition, the shape of its adsorption isotherm should be similar to that of the oxides. These requirements severely restricted the choice of materials of construction, as also did the need to clean the apparatus and yet have a reproducible surface. The most satisfactory vessel found was a crucible of pure nickel, with capacity 70 c.c. This was oxidised by heating and cooling it in air several times. After cleaning in acid, the oxide layer was re-formed. Samples of liquid were removed by means of a small nickel-silver spoon, oxidised in the same way. This was also used for stirring. Cleaning of crucible and spoon was also carried out at times by heating, to oxidise adsorbed amine. pH was measured by a glass electrode, care being taken to ensure that adsorption of amine on it did not occur to such an extent as to produce incorrect readings. A silk thread dipped into the solution, the other end being in a beaker of distilled water, in which a calomel electrode was placed.

The adsorption due to the apparatus itself was determined as follows. The vessel and spoon were washed in water, heated to redness, and cooled, water being sprayed on to the out-side of the crucible. Water (50 c.c.) was placed in the crucible, and known volumes of standard sodium perchlorate and dodecylammonium chloride solutions were added to give 10^{-3}M-sodium perchlorate and the required amine concentration. The pH was adjusted by adding sodium hydroxide, and the solution was set aside for 15 min. About 1 c.c. of the solution was removed for determination of dodecylamine and weighed in the vessel used in the liquid scintillation counter. More amine was added to the crucible, and reagents were added to give the correct volume, pH, and perchlorate concentration.

Adsorption due to metal oxide was measured by placing 1·000 g. of the compound in the crucible before heating it. The procedure was as in the blank experiments except that, before the sample of solution was taken, stirring was stopped so that all the oxide settled to the bottom. The results given in the Table were obtained from a number of runs with each oxide. It was undesirable to use more than two or three amine concentrations per run because of evaporation and errors involved in adjustment of reagent concentrations.

Determination of Dodecylamine.—The radioactivity due to the amine was measured by using a liquid scintillation counter (Ekco type N612) and an automatic scaler (Ekco type N530 E). The sample of liquid containing the amine was placed in the counting-dish and weighed. The water was allowed to evaporate very slowly, its temperature not rising above 30°. When the material was dry, toluene (20 c.c.) was added to the dish and the mixture was kept overnight to allow the amine to dissolve. To this product was added a solution (10 c.c.) containing 2,5-diphenyloxazole and 2,2'-*p*-phenylenedi-(5-phenyloxazole) (8 g. and 0·36 g., respectively, per l. of toluene). The dish was placed in the counting-chamber and left for a few minutes before counting.

Primary standard solutions of the amine were prepared by dissolving a few mg. of the hydrochloride in toluene. The salt for both standard and stock solutions was weighed on to small pieces of platinum foil which were placed in the solvent. Aqueous solutions of the amine were stable if strongly acid, but a slow decrease in concentration was invariably observed, particularly in the more concentrated solutions.

The effects of the traces of the reagents other than dodecylamine present in the counting dishes, on the counting rate recorded for radioactive amine, were examined. Sodium hydroxide,

hydrochloric acid, sodium perchlorate, traces of water, and non-radioactive dodecylamine had no effect on the background or on the rate of slightly, or highly active solutions.

Liquid Scintillation Counting.—Non-reproducible results were obtained when the counter was used in the laboratory, because of temperature variations during the day. The counter and scaler were, therefore, used in a thermostatically controlled room at $4.5° \pm 1°$. The instruments required a minimum warming-up period of 4 hr.; at least 10 hr. were allowed. Three minutes was sufficient time for the phosphorescence of the solutions, due to exposure to light, to decay to a negligible level.

Operating conditions, giving suitable sensitivity and stability, were: gain 250; bias 12 v; high voltage 1150 v. Counting times were chosen to give an accuracy of $\pm 5\%$ in every case, with use of curves based on the equation:

$$T \text{ (min.)} = (100/V_s)^2/Rb \left[\sqrt{r} - 1\right]^2),$$

where V_s is the percent r.m.s. error, $r = Rt/Rb$, and $Rt = (Rs + Rb)$. In many cases the time used gave an accuracy of better than $\pm 2\%$. Counts were repeated when necessary.