

## Heterogeneous Interactions of Methylamines on Porous Adsorbents. Part III. The Adsorption Characteristics of Methylamines on $\gamma$ -alumina and Types '3A' and '13X' 'Molecular Sieves'

WALTER GEORGE COOK AND ROBERT ANDERSON ROSS

Department of Chemistry, Lakehead University, Thunder Bay, Ontario

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The adsorption characteristics of mono-, di-, and trimethylamine on  $\gamma$ -alumina have been investigated and adsorption isotherms in the regions of their boiling points determined, along with isothermal calorimetric heats of adsorption up to monolayer coverage ( $\theta = 1$ ). From the initial heats of adsorption of 21.6 to 32.4 kcal/mol at  $\theta = 0.05$ , and the strong retention of the amines adsorbed at low pressures, chemisorption is considered to occur at  $\theta < 0.20$ . The maxima and minima displayed in the heat curves are discussed in terms of adsorbate-adsorbate interactions at sub-monolayer coverage levels. Adsorption isotherms for di- and tri-methylamine on Linde 'molecular sieves' '13X' and '3A' have been measured also, along with the trimethylamine heat curves for these materials.

Les caractéristiques d'adsorption des mono-, di-, et tri-méthylamines sur de l'alumine- $\gamma$  ont été étudiées de même que les isothermes d'adsorption dans la région de leur point d'ébullition ont été déterminés en même temps que les chaleurs calorimétriques isothermales d'adsorption jusqu'à un recouvrement correspondant à une couche monomoléculaire ( $\theta = 1$ ). A partir des chaleurs initiales d'adsorption qui correspondent à 21.6 jusqu'à 32.4 kcal/mol à  $\theta = 0.05$ , et de la rétention forte des amines adsorbées à basse pression, la chemisorption est prévisible pour des valeurs de  $\theta < 0.20$ . Les maxima et les minima observés dans les courbes de chaleur sont expliqués en terme d'interactions produit adsorbé - produit adsorbé à des niveaux de recouvrement inférieurs à la couche monomoléculaire. Les isothermes d'adsorption pour les di-, et tri-méthylamines sur de la sève moléculaire du type Linde '13X' et '3A', ont aussi été mesurés en même temps que les courbes de chaleur de la tri-méthylamine pour ces produits.

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### Introduction

In Parts I and II studies of the interactions of mono-, di-, and trimethylamine on silica gel and silica-alumina were reported (1, 2). The shapes of the heat curves obtained for the adsorption of these species on both materials were of particular interest as in many cases well-defined maxima and minima were observed. These phenomena were considered to arise mainly through adsorbate-adsorbate interactions. To obtain further information on the adsorption properties of the amines the work has been extended to include a study of their adsorption characteristics on  $\gamma$ -alumina and two types of synthetic zeolites, namely, Linde molecular sieves, '13X' and '3A'.

### Experimental

The techniques of measurement, sorption balance, and calorimetry have been described (3, 4) and the physical properties of the  $\gamma$ -alumina adsorbent determined. Data supplied with the  $\gamma$ -alumina (Peter Spence and Sons Ltd.) stated it to be an aluminum trihydroxide with an X-ray structure showing 97% Gibbsite and 3% Bayerite, particle size 20 to 600  $\mu$ , and BET surface area 400  $\text{m}^2/\text{g}$  after heat

treatment at 420 °C. 'Molecular sieve' pellets were obtained from Union Carbide Corporation. A crystalline potassium aluminosilicate, type 3A, and a crystalline sodium aluminosilicate, type 13X, were used.

The purification procedures used for the amine adsorbates have been specified (1, 2).

### Results

#### $\gamma$ -Alumina

In all experiments alumina samples were activated at 420 °C for 3 h in air and then outgassed at 90 °C for 1 h under a vacuum of  $10^{-5}$  Torr in the adsorption apparatus before use.

The complete adsorption-desorption isotherm for monomethylamine on  $\gamma$ -alumina at 266 °K is shown in Fig. 1, curve B. Equilibrium times were 45 min up to  $p/p_0 = 0.50$  and 4 h above this pressure. The heat curve for monomethylamine adsorption on  $\gamma$ -alumina at 266 °K is shown in Fig. 3, curve B.

Figure 1 curve A shows the adsorption-desorption isotherm determined for dimethylamine on  $\gamma$ -alumina at 280 °K and Fig. 3 shows the heat curve C for this system. The corresponding data

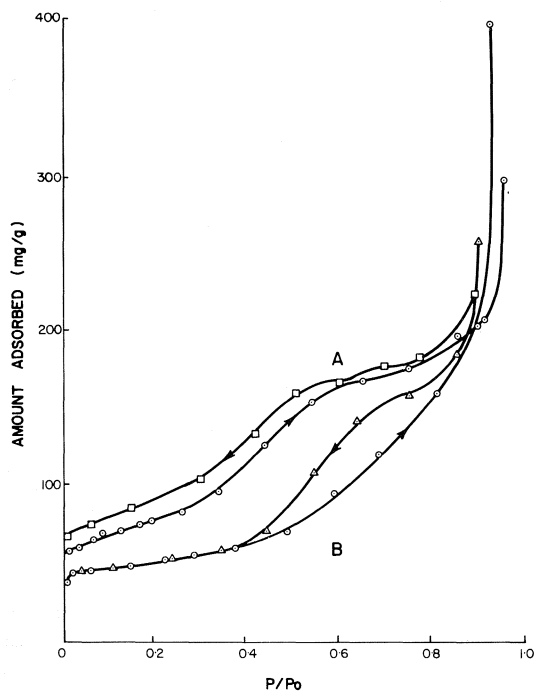


FIG. 1. Adsorption-desorption isotherms for *A*, dimethylamine at 280 °K and *B*, monomethylamine at 266 °K on  $\gamma$ -alumina.

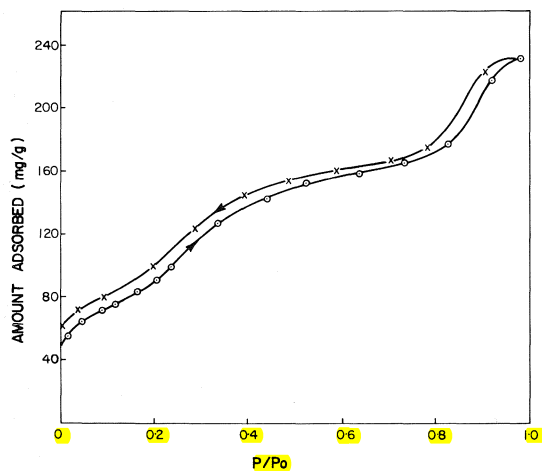


FIG. 2. Adsorption-desorption isotherm for trimethylamine at 276 °K on  $\gamma$ -alumina.

for trimethylamine adsorption at 276 °K are shown in Figs. 2 and 3, curves *A*.

The monolayer coverage values for mono-, di-, and tri-methylamine on  $\gamma$ -alumina were determined from BET plots to be 40.7, 65.0, and 72.7 mg/g, respectively, at the isotherm temperatures shown.

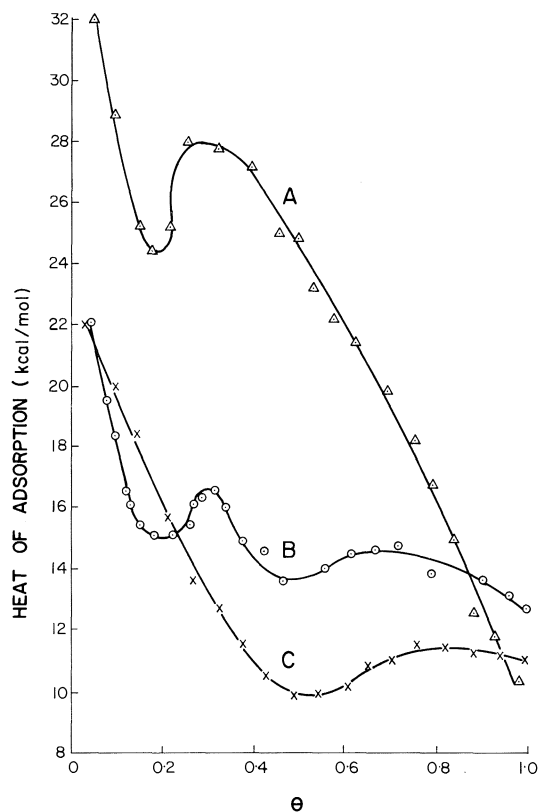


FIG. 3. Variation of isothermal calorimetric heats of adsorption with  $\theta$  (fraction of surface covered) for *A*, trimethylamine at 276 °K, *B*, monomethylamine at 266 °K and *C*, dimethylamine at 280 °K on  $\gamma$ -alumina.

#### 'Molecular Sieves'

The adsorption isotherms determined for dimethylamine adsorption on 'molecular sieves' '3A' and '13X' at 280 °K are shown in Figs. 4 and 5, curves *A*. Both materials had been activated in air at 316 °C (5) for 3 h and outgassed at 90 °C under a vacuum of  $10^{-5}$  Torr for 1 h. In experiments with the '3A' 'molecular sieve', equilibrium was taken to be established when no measurable adsorption was detected over a 1 h period. This basis was used as an arbitrary standard since only on prolonged exposure of the 'molecular sieve' to the amine for 24 h was a further small uptake observed. The experimental error involved by adopting this procedure was estimated to be less than 0.5%. Equilibrium times for the '13X' molecular sieve were 30 min below  $p/p_0 = 0.90$  and 60 min at the highest pressures. Desorption times were consistently 60 min over the entire pressure range.

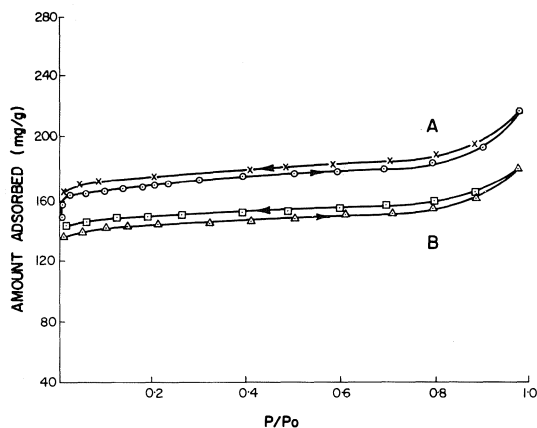


FIG. 4. Adsorption-desorption isotherms for *A*, dimethylamine at 280 °K and *B*, trimethylamine at 276 °K on 'molecular sieve' '13X'.

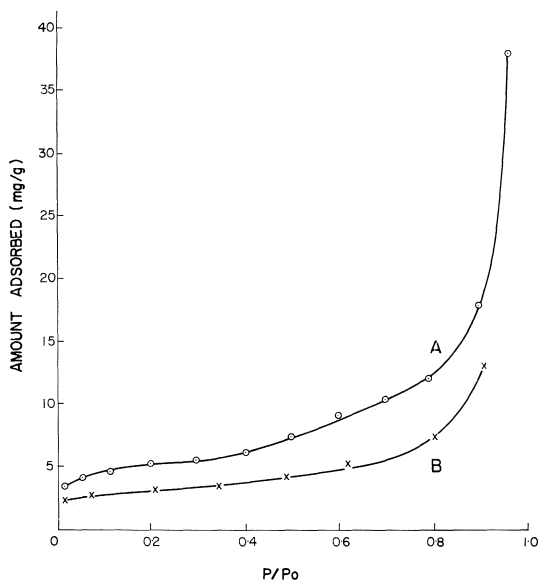


FIG. 5. Adsorption isotherms for *A*, dimethylamine at 280 °K and *B*, trimethylamine at 276 °K on 'molecular sieve' '3A'.

Trimethylamine adsorption isotherms at 276 °K on 'molecular sieves' '13X' and '3A', (Figs. 4 and 5), were of the same general form as the corresponding dimethylamine isotherms. The heat curves for trimethylamine on these materials are shown in Fig. 6.

### Discussion

The adsorption of all amines on  $\gamma$ -alumina was initially strong, particularly in the region  $p/p_0 < 0.02$ . Samples of alumina equilibrated at 266

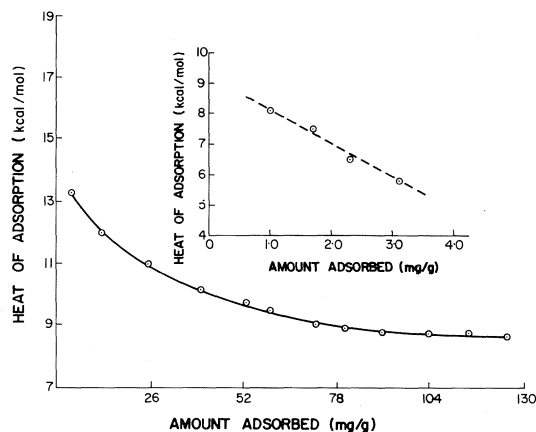
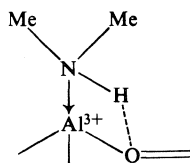


FIG. 6. Variation of isothermal calorimetric heats of adsorption with amount adsorbed for trimethylamine at 280 °K on 'molecular sieve' '13X' and 'molecular sieve' '3A' (inset).

°K in mono-methylamine vapor,  $p/p_0 = 0.90$ , when evacuated to  $10^{-5}$  Torr for 1 h at this temperature retained 22.7 mg/g of the amine which corresponds to 55.7% of the monolayer coverage amount. On raising the temperature to 353 °K, the alumina still held 9.3% of the monolayer amount after being evacuated to  $10^{-5}$  Torr for 1 h. This region of surface coverage therefore, is considered to involve strong adsorption which may involve chemisorption (6).

The adsorption isotherms of the amines on alumina show marked increases in the amounts adsorbed, after monolayer completion, beginning at  $p/p_0 = 0.50, 0.30$  and  $0.25$  for mono-, di-, and trimethylamine, respectively. With mono- and dimethylamine, the amount adsorbed increased asymptotically above  $p/p_0 = 0.90$  while trimethylamine adsorption showed a sharp increase between  $p/p_0 = 0.83$  and  $0.99$ . These effects are probably linked to the distribution of pore sizes of this adsorbent, which were determined (7) from low temperature nitrogen isotherms by the method of Cranston and Inkley (8), and which range from 20 to 300 Å in diameter with maxima occurring at 30 and 230 Å. The very steep increase in adsorption found for mono- and dimethylamine may be due to condensation of these adsorbates in the 230 Å diameter pores of the alumina. An analogous effect has been reported for the adsorption of methylamines on a "macroporous" silica gel which also showed a maximum in its pore size distribution in the range 200 to 230 Å diameter (1, 2).

The initially-high heats of adsorption of the amines on alumina, Fig. 3, are compatible with the suggestion that chemisorption is involved at low surface coverages,  $\theta < 0.2$ . These heats, from 21.6 to 32.4 kcal/mol, probably arise through a chemisorptive process which may involve donation of the lone pair electrons of the amine nitrogen atom to empty  $sp^3$  hybrid orbitals of surface aluminum ions (9). In this connection it is worth noting that nuclear magnetic resonance studies of the adsorption of monomethylamine on  $\gamma$ -alumina indicate that the hydrogens of the amino group are more restricted than the methyl hydrogens (10). Other modes of adsorption have been suggested for ammonia on  $\gamma$ -alumina, including adsorption on surface oxygen species with the formation of amide ions (11), and also adsorption through coordination of the nitrogen atom to a surface aluminum ion with concurrent hydrogen bonding to surface oxide ions (11). The absence of strong Brønsted acidity on alumina has been deduced from both pyridine (12) and ammonia adsorption studies (11). Thus the adsorption of methylamines may not only involve interaction between amine-nitrogen electrons and surface aluminum ions but also simultaneous hydrogen bonding of amino hydrogens to surface oxide species. Thus for dimethylamine



amine adsorption through interactions with surface hydroxyl groups and oxide ions may also occur.

The heats of adsorption on alumina for monomethylamine (Fig. 3, curve *B*) and trimethylamine (Fig. 3, curve *A*) fall to a minimum at  $\theta = 0.20$  and  $0.17$ , respectively, and then rise to a maximum at  $\theta = 0.30$  and  $0.28$ , respectively. The magnitude of these rises was 1.5 kcal/mol for monomethylamine and 3.6 kcal/mol for trimethylamine. This effect may result from lateral interactions between amine molecules which have been adsorbed at pressures corresponding to the minimum value of the heat curve in close proximity to amine molecules adsorbed earlier. Similar increases in the heat of adsorption to those displayed at low surface coverages with mono- and trimethylamine have been reported for ammonia adsorption on alumina (13).

The dimethylamine heats of adsorption on alumina do not show the rise which might be expected by analogy to occur at approximately  $\theta = 0.29$ . However, a noticeable similarity between the heat curves for mono- and dimethylamine is the occurrence of the minimum at  $\theta = 0.50$  and  $0.48$ , respectively. This fraction of monolayer coverage may correspond to the occupation of the "most active" adsorption sites by these adsorbates. Following these minima both curves show a gradual rise to a maximum at  $\theta = 0.70$  and  $0.81$  and then a slight decrease to monolayer coverage. The increase in the heat of adsorption in this region is probably due to van der Waals interactions (14) amongst the adsorbed molecules while the subsequent decrease may occur as a result of repulsion between the partially-formed layer of polarized adsorbed molecules and molecules adsorbing subsequently in close proximity as the monolayer nears completion.

After the maximum shown at about  $\theta = 0.28$  in the heat of adsorption of trimethylamine on alumina (Fig. 3), the heat evolved falls almost linearly from 28.0 to 9.9 kcal/mol at monolayer completion. The absence of a minimum at approximately  $\theta = 0.5$  in this curve is difficult to explain but it may be that the large trimethylamine molecule, cross-sectional area about  $30 \text{ \AA}^2$  (1, 2), interacts with closely-adsorbed molecules over the entire range of surface coverage from from  $\theta = 0.30$  to monolayer completion. This suggestion does not exclude any decrease in the heat of adsorption which would be expected to occur through surface heterogeneity.

The adsorption isotherms of di- and trimethylamine on 'molecular sieve' '13X', Fig. 4, are of the Langmuirian type. The effective pore diameter of this material is  $10 \text{ \AA}$  (5) and these isotherms indicate that the internal cavities are almost filled by the amines at  $p/p_0 = 0.01$  with little increase in adsorption below  $p/p_0 = 0.70$ . Between these pressures, the increase in amount adsorbed for dimethylamine was 17.0 and 13.0 mg/g for trimethylamine. Above  $p/p_0 = 0.70$  both isotherms showed a considerably greater increase in the adsorbed amount, 37.0 mg/g for dimethylamine and 27.0 mg/g for trimethylamine while hysteresis occurred on desorption of both adsorbates over the entire pressure range.

In order to determine if the increased adsorption of di- and trimethylamine on 'molecular sieve' '13X' above  $p/p_0 = 0.70$  could be explained by adsorption in surface discontinuities in the

pellets of the material, corresponding isotherms were determined on 'molecular sieve' '3A'. Since the effective pore diameter of this zeolite is 3 Å (5), the adsorption of di- and trimethylamine would be limited to the external surface. In both isotherms, Fig. 5, a distinct rise in the amount adsorbed took place at high pressures which seems to confirm that the final increase in adsorption on both molecular sieves did arise through intercalation and condensation of the adsorbates in the fissures and cracks in the surfaces of the pellets.

The heat of adsorption of trimethylamine on 'molecular sieve' '13X' is shown in Fig. 6. The curve falls smoothly from 13.3 kcal/mol at 5.2 mg/g adsorbed to 8.8 kcal/mol at 91.0 mg/g adsorbed and then remains constant. (It should be noted that the heats of adsorption for the 'molecular sieves' have been plotted against the amount of amine adsorbed since the basic assumptions of surface area determination do not hold for these materials (15).) A similarly-shaped heat of adsorption curve has been reported (16) for ammonia adsorption on synthetic Na faujasite. The '13X' 'molecular sieve' does not appear to contain any strong acidic adsorption sites as the initial heat evolved on trimethylamine adsorption is much lower than that observed with trimethylamine adsorption on alumina, silica-alumina or silica gel. The heats evolved on these materials were 32.4, 21.4, and 21.0 kcal/mol, respectively, at  $\theta = 0.05$  (2). The fact that no irregularities are displayed in the '13X' heat curve may imply that a degree of surface heterogeneity is a factor in giving rise to increases in

the heat of adsorption at low surface coverages on  $\gamma$ -alumina and the other siliceous adsorbents.

An attempt was made to estimate the heat evolved on trimethylamine adsorption on 'molecular sieve' '3A', Fig. 6 (inset). Extrapolation of the dotted line in this Figure gives a value of approximately 9.5 kcal/mol for initial adsorption compared with 14.0 kcal/mol for 'molecular sieve' '13X'.

1. W. G. COOK and R. A. ROSS. *Can. J. Chem.* **50**, 1666 (1972).
2. W. G. COOK and R. A. ROSS. *Can. J. Chem.* **50**, 2451 (1972).
3. R. A. ROSS and A. H. TAYLOR. *Proc. Brit. Ceram. Soc.* **5**, 167 (1965).
4. E. ROBINSON and R. A. ROSS. *J. Chem. Soc. (A)*, 2521 (1969).
5. Union Carbide molecular sieves for selective adsorption. British Drug Houses. 1967. Section 5.
6. C. CLARKE-MONKS, B. ELLIS, and K. ROWAN. *J. Colloid. Int. Sci.* **32**, 628 (1970).
7. S. BRUNAUER, P. H. EMMETT, and E. TELLER. *J. Am. Chem. Soc.* **60**, 309 (1938).
8. R. W. CRANSTON and F. A. INKLEY. *Adv. Catal.* **9**, 143 (1957).
9. M. L. HAIR. *Infrared spectroscopy in surface chemistry*. Edward Arnold, London. 1967. p. 146.
10. K. HIROTA, K. FUEKI, and T. SAKAI. *Bull. Chem. Soc. Jap.* **35**, 1545 (1962).
11. J. B. PERI. *J. Phys. Chem.* **69**, 220 (1965).
12. E. P. PARRY. *J. Catal.* **2**, 371 (1963).
13. V. KERVORKIAN and R. O. STEINER. *J. Phys. Chem.* **67**, 545 (1962).
14. J. H. DE BOER. *The dynamical character of adsorption*. 2nd ed. Oxford University Press, London. 1968. p. 157.
15. M. M. DUBININ. *J. Colloid Int. Sci.* **23**, 487 (1967).
16. L. H. LITTLE. *Infrared spectra of adsorbed species*. Academic Press Inc., New York. 1966. p. 276.