

HEATS OF PREFERENTIAL SORPTION FROM LIQUID MIXTURES

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(Received August 17th, 1959)

INTRODUCTION

It is well known that adsorption of liquids on dry surfaces of solids is accompanied by the evolution of heat. Such heat effects measure the changes in surface energy of the solids and adsorbate produced in the process of adsorption.

Similar heat effects were found to take place when one liquid displaced another as an adsorbed layer on a solid, or as a sorbed liquid. Where the displacing liquid is much more strongly sorbed or adsorbed than that displaced, the heat effect is considerable even when the displacing liquid is introduced as a dilute solution in the liquid being displaced. Such displacement phenomena when applied to adsorption have been referred to in the literature as processes of preferential adsorption¹. In this paper the sorption and adsorption phenomena are both referred to under the general name of preferential sorption.

The process of preferential adsorption is of importance in the field of solid-liquid chromatography, where it forms a basis for the separations of mixtures into fractions of different chemical and physical properties¹. The type of separation achieved by a given adsorbent can be predicted on the basis of the determinations of the heat of preferential adsorption. Such predictions should be more realistic than those based on determinations of the heats of wetting of dry adsorbents by different constituents of a mixture.

This paper describes determinations of the heats of preferential sorption by a specially constructed calorimeter. The results presented illustrate application of the calorimeter to determination of the heats produced on a number of different adsorbents including an ion-exchange resin and a metal soap.

Apparatus and procedure

EXPERIMENTAL

The apparatus used is represented in Fig. 1. The apparatus has been described previously² and its prototype described in this Journal³. It consists essentially of a cell filled with an adsorbent, thermocouples placed in a direct contact with the adsorbent, and a suitable jacketing arrangement. The cell is kept at room temperature, *i.e.* $20^{\circ} \pm 2^{\circ}$. The lagging surrounding the cell is sufficient to eliminate any sudden changes of temperature inside the cell.

In the cell are placed 15 thermocouples connected in series and composed of 32 SWG copper and constantan wires. The hot junctions of the thermocouples are situated immediately above the plug and are sealed, by means of Araldite D cement, into the wall of the cell. The ends of the thermocouples are only slightly protruding

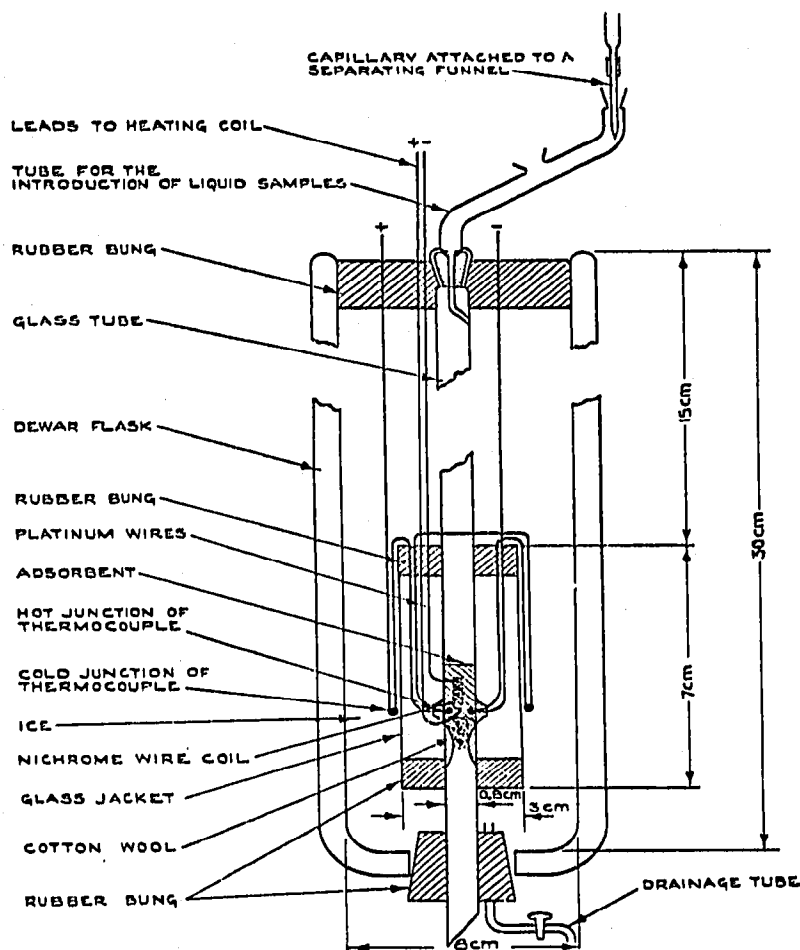


Fig. 1. Calorimeter for determination of heats of preferential sorption.

from the wall and are in direct contact with the powdered solid. The wires from the cold junctions pass out of the glass jacket through holes in the rubber bung to the outside where the cold junctions are kept at the temperature of the surrounding medium. The output from the thermocouples is fed into a potentiometric recorder of $500 \mu\text{V}$ full scale deflection. A coil of nichrome wire possessing a resistance of 10Ω is situated in the centre of the cell. The coil is used to reproduce the heat effects taking place during adsorptions, by passing through it a small current from a source of constant known voltage, for a measured length of time.

A glass tube is connected directly to the cell and extends to a special attachment which is used for introducing small quantities of the substance under examination from a micrometer syringe into a carrier liquid flowing continuously through the cell. The carrier liquid is contained in a separating funnel and its flow is regulated by a

capillary jet attached to the end of the funnel. The flow is usually between 0.3 and 0.5 ml/min.

Initially, when the carrier liquid comes into contact with the dry adsorbent in the cell, a temperature rise is produced. From this rise it is possible to obtain, if it is so desired, the heat of adsorption of the carrier liquid on the adsorbent saturated with air. After approximately 30–40 min the heat produced by wetting of the dry adsorbent is dissipated and the hot and cold junctions of the thermocouples are at the same temperature. At this point a measured amount of another liquid, or solid in solution, is introduced into the carrier liquid. As soon as the injected material reaches the adsorbent, preferential adsorption takes place with the accompanying evolution of heat.

Results

The heats of preferential sorption obtained on replacement of a carrier liquid by a more strongly adsorbed liquid are given in Fig. 2a and b; the peaks shown are scaled down to about half the size of those registered by the potentiometric recorder. Two series of determinations are presented. In one series (Fig. 2a) the heat effects are due to

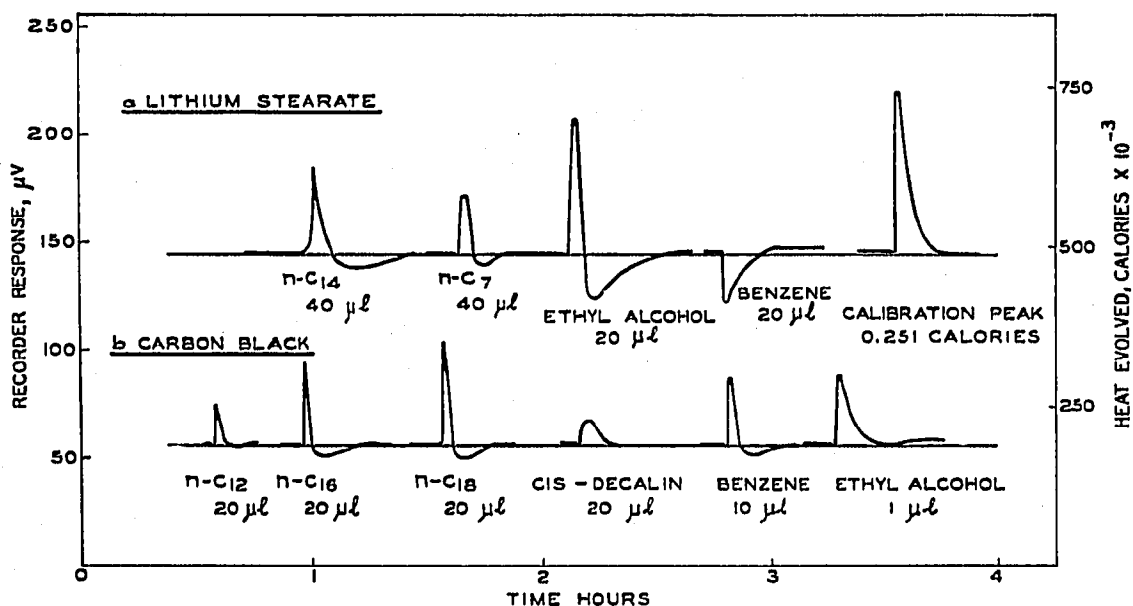


Fig. 2. Heats of preferential sorption registered by a recording potentiometer.

preferential sorption of liquids on lithium stearate from benzene which was the carrier liquid. The benzene peak in Fig. 2a was produced by replacement of *n*-heptane by benzene. In the preferential adsorption on carbon black (Fig. 2b), the heat effects are due to replacement of *n*-heptane from the adsorbent.

In both series the carrier liquid was flowing through the adsorbents at the rate of 0.4 ml/min.

In Figs. 3 and 4 the heats produced by the preferential sorption by the two solids

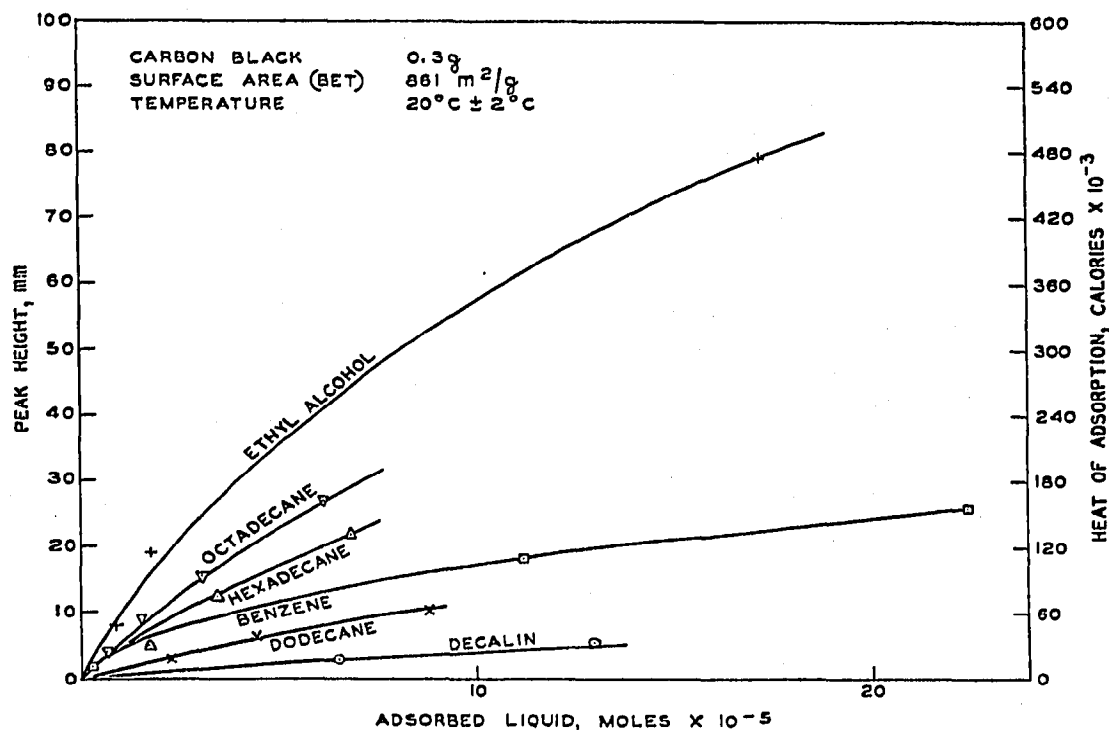


Fig. 3. Heats of preferential adsorption from *n*-heptane on carbon black.

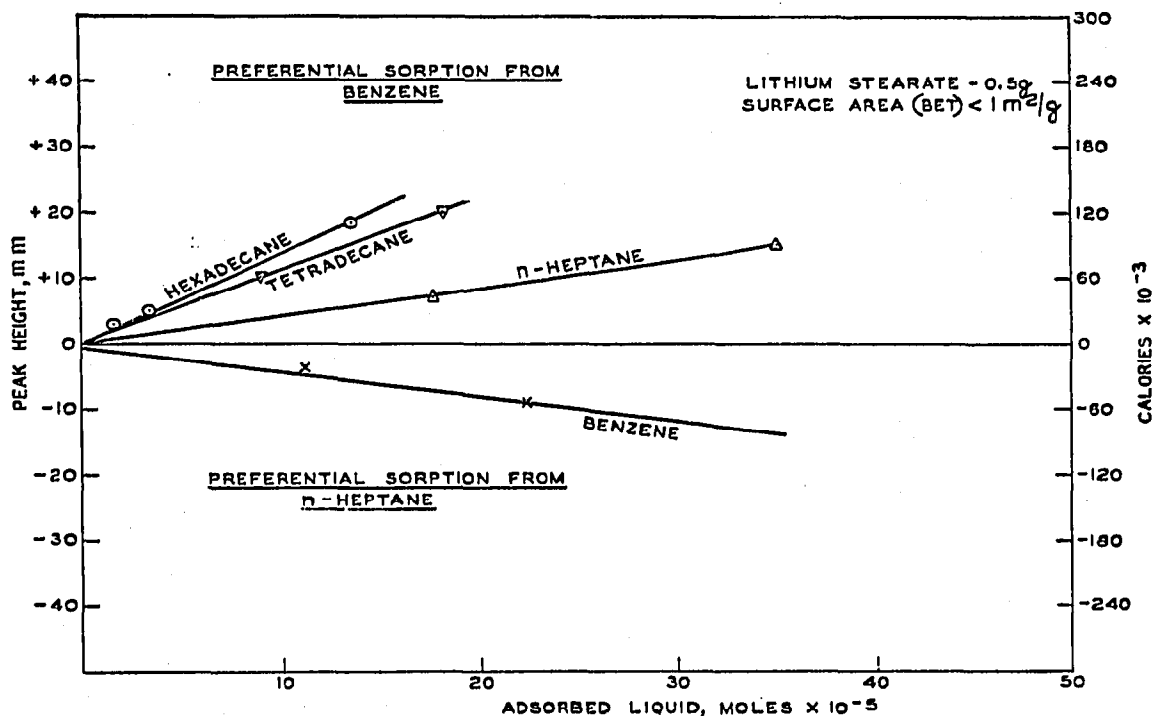


Fig. 4. Heats of preferential sorption on lithium stearate.

are plotted against the increasing amounts of liquids preferentially sorbed. The same relationships are shown in Figs. 5 and 6 for adsorptions on silica gel, and sorption on Zeocarb 225 (cation exchange resin) respectively.

DISCUSSION AND CONCLUSIONS

The nature of the apparatus used in this work was such that the sorptions taking place were dynamic in character, *i.e.* the sorption that occurred was immediately followed by a desorption process, which usually, although not exclusively, produced a measurable heat effect opposite to that occurring in the adsorption process.

The heat effects produced by preferential adsorption have been studied under conditions in which the amount of the displacing liquid is insufficient to form a monomolecular layer on the available surface. All of the adsorbents used had surface areas in excess of $100 \text{ m}^2/\text{g}$. For paraffinic molecules lying flat on such a surface, and occupying about 10 \AA^2 per carbon atom, 100 m^2 of surface would accommodate 10^{21} such carbon atoms, equivalent to about 24 mg of hydrocarbon. For straight-chain organic molecules of molecular weight of 100 adsorbed end-on, and each occupying 16 \AA^2 , 100 m^2 of surface would accommodate about 100 mg. The quantities of displacing liquids used in this work were in the range 0.2 to 70 mg per gram of adsorbent and thus in general were insufficient to provide a monomolecular layer over these high surface area materials. On the other hand, one solid used (lithium stearate) had a surface area of less than $1 \text{ m}^2/\text{g}$, which would be covered by less than 1 mg of adsorbate. Considerable heat effects obtained for this material indicate that mainly sorption processes take place, whereby the molecules of liquids enter into the crystalline lattice of the solid. On another solid of surface area less than $1 \text{ m}^2/\text{g}$ (a cation exchange resin in the acid form, Zeocarb 225) the heat of the exchange process with metal chlorides was examined, but at much lower concentrations, so that all the hydrogen ions available were not exchanged.

Since a substance injected into the carrier liquid is diluted by the liquid surrounding the adsorbent in the cell, a possibility was considered of the heats of solution forming a part of the total heat effect obtained. For this purpose the cell of the calorimeter was filled with a coarse sand (surface area $< 1 \text{ m}^2/\text{g}$ by N_2 adsorption) having no sorptive properties. Various liquids were injected into *n*-heptane flowing through the sand and heat effects measured. No heat effect was obtained for the injections of *n*-hexadecane, and a positive heat of 0.03 cal obtained for an injection of $45 \cdot 10^{-5}$ moles of benzene. That heat effect was considerably smaller than the heats of preferential sorption determined in the present work, which were at least 10 times higher for a similar amount of benzene adsorbed.

A possibility was also considered that some of the heat effects obtained on adsorption of *n*-heptane or benzene on lithium stearate may be due to the soap dissolving in these liquids. This was checked by passing 50 ml of *n*-heptane and benzene through 1 g of the soap placed in the cell of the calorimeter at the rate of 0.4 ml/min, and filtering and evaporating the collected liquids. The residue was

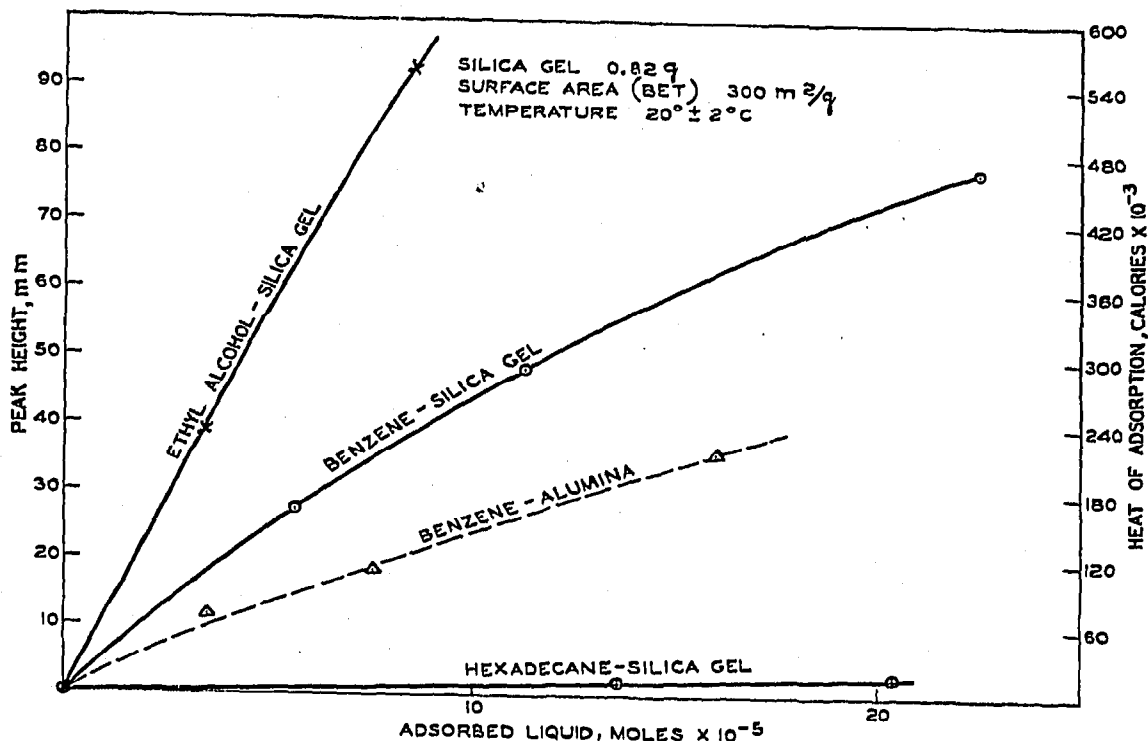


Fig. 5. Heats of preferential adsorption from *n*-heptane on silica gel and aluminium oxide.

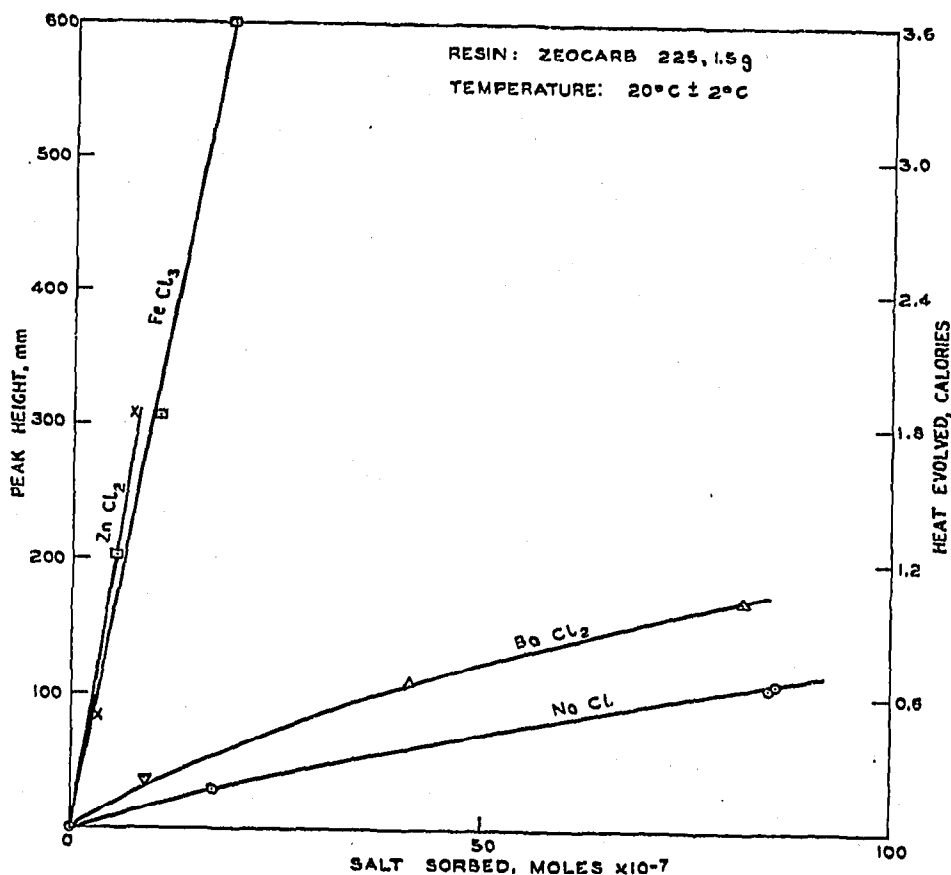


Fig. 6. Heats of preferential sorption of metal chlorides from water-ethyl alcohol solution on cation exchange resin in acid form.

found to be less than 1 mg. It was concluded therefore that no solution of lithium stearate took place in the experiments described, and the heat effects were due entirely to sorption.

In the process of sorption, the heat effect is due to a change in free energy of the solute which exchanges the environment of the solvent for that of the solid surface of the adsorbent^{4, 5}.

Let us consider a solution of substance A in solvent B and assume that the total number of moles present in the solution is $m_A + m_B$.

When this solution is placed in contact with a solid adsorbent saturated with solvent B, adsorption of A occurs only if it is accompanied by a decrease of free energy.

If p moles of A are adsorbed and r moles of B desorbed from the solid, the total number of moles remaining in the solution after the process will be $m_A - p + m_B + r$.

Thus the concentration of A in mole fractions in the solution decreases from

$$\frac{m_A}{m_A + m_B} = X \quad \text{to} \quad \frac{m_A - p}{m_A + m_B - p + r} = Xe$$

and that of B increases from

$$\frac{m_B}{m_A + m_B} = Y \quad \text{to} \quad \frac{m_B + r}{m_A + m_B - p + r} = Ye$$

where X , Y and Xe , Ye are the mole fractions of A and B in the solution before adsorption and at equilibrium after adsorption, respectively. Thus the adsorption and desorption processes continue until equilibrium concentrations of A and B, given by Xe and Ye respectively, are reached.

The total change in free energy of the system is composed of four main factors, *i.e.* those due to adsorption of A, desorption of B, decrease in concentration of A in the solution and increase in concentration of B in the solution. If the energy of the surface covered by solvent B is represented by $rS_B\gamma_B$ and that covered by solute A by $pS_A\gamma_A$, where S_A and S_B are the areas covered by one mole of the adsorbates, γ_A and γ_B are the surface tensions of the adsorbent covered with molecules A and B respectively, the change in free energy of the surface on the preferential adsorption is $pS_A\gamma_A - rS_B\gamma_B$.

The changes of free energy accompanying the decrease and increase in concentration of A and B in the solution can be represented by:

$$pRT \ln \frac{Xe}{X} \quad \text{and} \quad rRT \ln \frac{Ye}{Y}$$

respectively where $Xe < X$ and $Ye > Y$.

Thus the total change in free energy during the process of preferential adsorption is:

$$\Delta F = pS_A\gamma_A - rS_B\gamma_B + pRT \ln \frac{Xe}{X} + rRT \ln \frac{Ye}{Y} \quad (1)$$

where R is the gas constant and T the absolute temperature.

The heat change in the process is given by the Gibbs-Helmholtz equation:

$$\Delta F = \Delta H - T\Delta S \quad (2)$$

where ΔH = heat change during adsorption

ΔF = free energy change during adsorption

ΔS = entropy change during adsorption.

Usually the heat change is approximately equal to the change in free energy. In some cases however, the entropy change may be appreciable. In particular, this effect may be appreciable if the adsorbed molecules change the configuration they had in solution⁵.

The heat $-\Delta H$ lost by the system during the process of preferential adsorption is given by eqn. (3) obtained by combining eqns. (1) and (2).

$$-\Delta H = -\left(pS_{A\gamma_A} - rS_{B\gamma_B} + pRT \ln \frac{Xe}{X} + rRT \ln \frac{Ye}{Y}\right) - T\Delta S \quad (3)$$

For many adsorptions the difference between the first two factors of the free energy term is so large that the other factors are negligible in comparison. An example of this is the preferential adsorption of ethyl alcohol from solution in *n*-heptane on silica gel (Fig. 5). Thus, 0.270 cal of heat are evolved on adsorption of $4 \cdot 10^{-5}$ moles of the alcohol and the heat of dilution of the same amount of alcohol in *n*-heptane is only 0.020 cal.

According to theoretical predictions of DE BOER⁷ it may be possible for sorption to occur with an endothermic heat effect, when the entropy change is sufficiently large and positive to allow ΔF in eqn. (2) to have a negative value in spite of the positive value of ΔH . The preferential sorption of benzene from *n*-heptane on lithium stearate (Fig. 2a) may be a case in point. It may be added here that the heats of sorption of dry lithium stearate by *n*-heptane and benzene are both positive, but the heat for *n*-heptane is greater (3.00 cal/g) than that given by benzene (1.90 cal/g).

In liquid-solid chromatography the separation of constituents of a mixture may be influenced by all the factors on the right hand side of eqn. (3). The attempts to grade the eluting power of solvents on the basis of the heat of complete wetting of dry adsorbents⁸ may be misleading if the pattern of adsorption of a substance, when preferential adsorption takes place, is different from the adsorption of the pure substance. The difference in question is one between the energy changes corresponding to terms $pS_{A\gamma_A}$ and ΔF given in eqn. (1). Thus, in general, it is considered that the determination of the heats of preferential sorption can predict the sequence of adsorption better than the determination of the heats of adsorption of dry adsorbents.

As can be seen in Fig. 2a and b, the positive heat effects are in most cases followed by negative heats. The latter heats are due to the desorption of material preferentially adsorbed when its concentration in the solution is below the equilibrium value Xe . Depending on this value, the negative heats are more or less marked. Thus, when ethyl alcohol is injected into a stream of benzene flowing through powdered lithium

stearate, preferential sorption of ethyl alcohol takes place from benzene solution, the process continuing so long as the concentration of ethyl alcohol in the solution surrounding the adsorbent is above its equilibrium concentration X_e . When the concentration of ethyl alcohol in the solution becomes less than X_e , it is desorbed from lithium stearate, the process being accompanied by the absorption of heat.

If the value X_e is very low, the desorption process may be very slow, and the absorption of heat occurring then is not indicated by the apparatus. Very small values of such negative heat effects characterize substances which are adsorbed very strongly from solution, *i.e.* substances for which the factor $\rho S_A \gamma_A$ is considerably greater than $\nu S_B \gamma_B$. An example of this type of adsorption is furnished by preferential adsorption of ethyl alcohol on carbon black from *n*-heptane solution (Fig. 2b).

Most of the curves given in Figs. 3 to 6 show clearly that the heats of preferential adsorption and sorption decrease as the amount of substances adsorbed increases. This effect is very similar to that exhibited by the heats of adsorption of liquid and gaseous substances on solid surfaces⁹.

It is concluded that the solid surfaces studied in this work are not uniform in character and consequently the heat evolved when the first molecules of a substance are adsorbed is higher (when expressed as a differential heat of adsorption) than that produced when the surface is partly saturated with the absorbate.

It may be expected therefore that when a small amount of a substance is absorbed on the same weight of identical adsorbents possessing different surface areas, the solid with the greatest surface area would give the highest heat of preferential sorption. This has been in fact found for silica gel where the adsorption of 20 μ l of benzene from solution in *n*-heptane on the gel possessing the area of 700 m²/g gives a heat effect of 0.570 cal, whereas the same amount of benzene adsorbed on the gel with a surface area of 300 m²/g gives 0.450 cal.

The heat effects shown in Fig. 6 correspond to the process of sorption involving strong ionic forces. When the metal chlorides come into contact with the resin in its acid form, a reaction sets in, whereby a metal salt of the resin is produced together with a corresponding amount of hydrochloric acid. The heat effect is mainly the result of the differences in the heat produced on the formation of the resin-metal complex and that absorbed in the decomposition of the chloride with the subsequent formation of hydrochloric acid and its solution in the water-alcohol mixture used as the carrier liquid.

It is interesting to note that the differential heats of preferential sorption that can be obtained from the curves shown in Fig. 6 decrease continuously, which is similar to the trend exhibited by the preferential adsorption.

It is inferred from the results shown in Figs. 3 and 5, for processes in which the entropy change is negligible, that if mixtures of the substances studied (*e.g.* *n*-heptane-benzene, benzene-ethyl alcohol, etc.) were passed through columns filled with the respective adsorbents, the separations achieved would be predicted by the order of the heats of preferential sorption, the substance with a lower heat being the first to emerge from the column.

ACKNOWLEDGEMENTS

The author wishes to acknowledge helpful assistance from Mr. J. R. LODWICK, Dr. J. N. HARESNAPÉ and Mr. S. R. PETHRICK, and to thank the Chairman and Directors of the British Petroleum Company Limited for permission to publish this paper.

SUMMARY

The construction and applications of an inexpensive calorimeter suitable for the determination of heats of preferential sorption from liquid mixtures on solid surfaces is described. The calorimeter is very sensitive and is capable of detecting the heat effects as low as 0.001 cal/g.

The application of the calorimeter is illustrated by determinations of the heats of sorption for a number of liquids dissolved in *n*-heptane and benzene on solid adsorbents such as carbon black, silica gel, alumina, lithium stearate and Zeocarb 225 (a cation exchange resin).

The significance of the results is discussed with special reference to the theory of solid-liquid chromatography.

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