

Adsorption from Binary Liquid Mixtures: Some Effects of Ash in Commercial Charcoal.

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Commercial coconut-shell charcoals contain ash which may react with, or be dissolved by, organic liquids. This interferes with the measurement of physical adsorption from mixtures containing such liquids. Adsorption of the corresponding vapours may also be affected. Three simple ways of removing ash from these charcoals are examined. The effect of progressive removal of ash on adsorption from mixtures of benzene and acetic acid is considered in detail.

MOST commercial charcoals contain significant amounts of inorganic material, usually referred to as ash. This has rarely been regarded as important in the study of vapour-phase (physical) adsorption, but may interfere in experiments on adsorption from solutions. The point has long been realised for adsorption of electrolytes, as the components of the ash are themselves electrolytes, but little attention has been paid to effects obtained with solutions of non-electrolytes, or of substances such as acetic acid, which are adsorbed in non-ionised form by a charcoal surface, though they react as electrolytes with inorganic materials and in aqueous solution (Kipling, *J.*, 1948, 1483). In each of the last two cases, dissolution of ash may seriously alter the results of titrimetric or refractometric analysis of solutions, in which the observed changes in concentration are normally taken to be due to physical adsorption only.

A most important warning occurs in a paper by Garner and Kingman (*Trans. Faraday Soc.*, 1929, **25**, 24), who showed that very careful removal of ash from Norite charcoal was needed before interferometric analysis gave reliable results in adsorption from aqueous solutions of alcohols. Innes and Rowley (*J. Phys. Colloid Chem.*, 1947, **51**, 1172) found that methyl alcohol extracted sodium and potassium chlorides from their charcoal, and Blackburn and Kipling found that both acetone and acetic acid extracted ash from coconut-shell charcoal (*J.*, 1954, 3819; 1955, 1493). An example of interference with vapour-phase studies is given by Coolidge (*J. Amer. Chem. Soc.*, 1927, **49**, 708) who found that sulphur dioxide was permanently adsorbed by alkaline ash.

These effects can be avoided by the use of ashless sugar charcoals. It is, however, interesting to examine how easily ash can be removed from commercial charcoals, and how far industrial practice is likely to be affected if they are used untreated. We have therefore examined a commercial coconut-shell charcoal (*a*) as received, (*b*) after Soxhlet extraction with distilled water, (*c*) after extraction with acetic acid, followed by washing with distilled water, and (*d*) after extraction with hydrofluoric acid by Korver's method (*Chem. Weekblad*, 1950, **46**, 301), again followed by washing with distilled water. As we became aware of the last method after most of the work had been concluded we have done only a little work on charcoal (*d*). The method is interesting in requiring no more than that the charcoal be allowed to stand under aqueous hydrofluoric acid for a few days at room temperature.

The amounts of ash 1, 2, 3, and 4 from the four charcoals *a*, *b*, *c*, and *d* were respectively 4.3, 3.1, 1.7, and 0.2%.

Ash 1 was a coarse, greenish powder which strongly attacked the glaze of the porcelain crucible in which the ashing was carried out. Ashes 2, 3, and 4 were fine, straw-coloured powders, which did not attack the glaze. In relation to the reported composition of charcoal ash (*e.g.*, Long and Sykes, *J. Chim. phys.*, 1950, **47**, 361, cf. figures for uncarbonised nutshell given by Tendolkar and Thakoor, *J. Sci. Ind. Res., India*, 1952, **11**, B, 501) it seems that water extracts mainly the compounds of the alkali metals, that acetic acid further extracts those of the alkaline-earth metals and iron, and that cold hydrofluoric acid extracts most of the remainder.

The effects of the three extractions on adsorption from solution have been examined in relation to the system benzene-acetic acid. This system has already been studied by Kipling and Tester (*J.*, 1952, 4123) who thought that the results were being affected by the presence of ash. Fig. 1 shows that the untreated charcoal has a significant effect on the refractive index of the acetic acid alone. This clearly affects refractometric analysis of mixtures even though the ash has no effect on benzene. The effect becomes the more

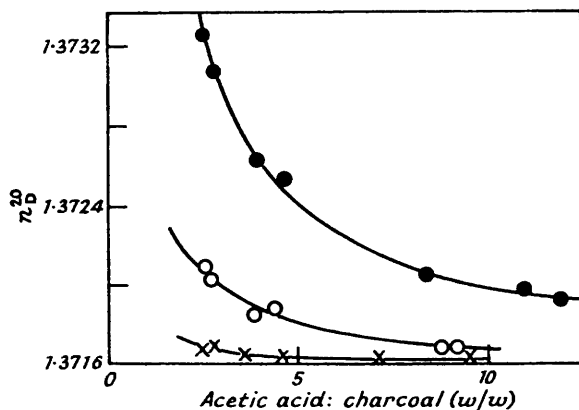


FIG. 1. Effect of charcoals on the refractive index of acetic acid.

n_D^{20} for pure acetic acid : 1.3716

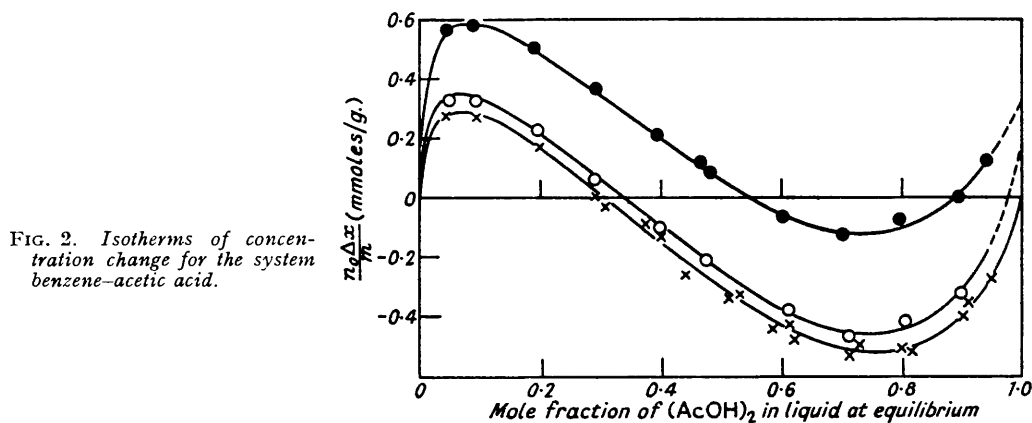


FIG. 2. Isotherms of concentration change for the system benzene-acetic acid.

For all Figs., ● = charcoal (a); ○ = charcoal (b); × = charcoal (c); □ = charcoal (d)

serious the higher the ratio of charcoal to acid. It is largely eliminated by washing the charcoal with water and almost completely eliminated by washing with acetic acid.

The effect on the isotherm of concentration change for this system is shown in Fig. 2. The position of the isotherm clearly depends on the amount of ash left in the charcoal. This has been emphasised in Fig. 2 by the use of a high ratio of charcoal to liquid for the untreated charcoal (about 1 g. of charcoal to 4 g. of liquid). The isotherm therefore differs from that published by Kipling and Tester in which the ratio was about 1 g. of charcoal to 20 g. of liquid. By contrast, there is only a small separation between the isotherms for the charcoals extracted with water and acetic acid respectively.

The two upper curves in Fig. 2 show two points of intersection with the concentration axis (*i.e.*, two points of zero selectivity). All previous experience shows that physical adsorption from such systems can give rise only to S- or U-shaped curves (one or no point of intersection), showing zero change in concentration when adsorption takes place from each pure component. The third curve is normal in this respect. It is clear that the extra point of intersection shown by the first two curves arises from the added effect of interaction between acetic acid and ash. The effect of ash in this respect vitiates several reported studies of liquid-phase adsorption, *e.g.*, that on the system toluene-acetic acid (Kane and Jatkar, *J. Indian Inst. Sci.*, 1938, **21**, A, 331); the isotherms, besides showing

FIG. 3.
(a) Adsorption of benzene vapour.
(b) Adsorption of pyridine vapour.

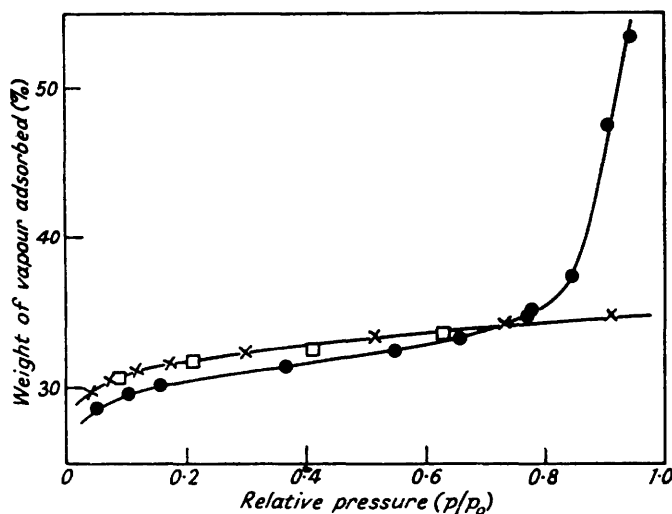
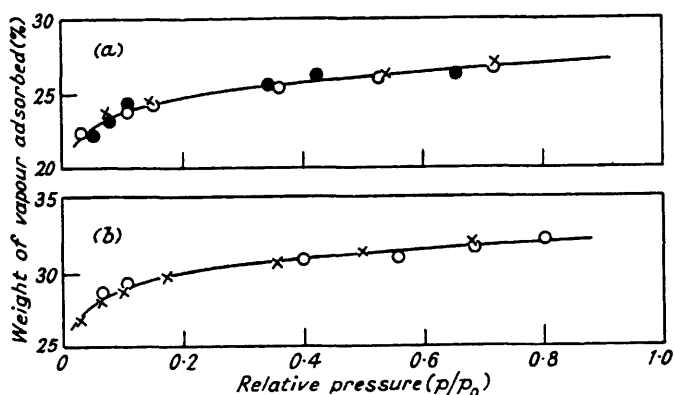


FIG. 4. Adsorption of acetic acid vapour.

more than one point of intersection, varied with the ratio of charcoal to liquid used, and it was admitted that the charcoal contained much ash. Similarly the isotherms obtained by Dobine (*Compt. rend.*, 1941, **212**, 156) for the system acetic acid-water show a concentration change at 100% acetic acid; this again was almost certainly due to dissolution of ash.

A related effect is found in the adsorption of vapours. Figs. 3a and b, showing the adsorption of benzene and of pyridine, suggest that the extraction processes do not significantly alter the surface area of the charcoal. Furthermore, the ash appears to be indifferent to benzene (which would be expected) and the water-insoluble ash is indifferent also to pyridine, which, as a base, could react with acidic or amphoteric ash. It may be assumed that the highly basic water-soluble ash will not react with pyridine. By contrast, the ash has a profound effect on adsorption of acetic acid, particularly at high

relative pressures (Fig. 4). On the treated charcoals, the isotherms are of the Langmuir type usually found for adsorption of organic substances on this charcoal.

In Fig. 5 we present the individual isotherms for adsorption from mixtures, both vapour and liquid, of benzene and acetic acid. These are of the general shape given by Kipling and Tester, but are now corrected for the effect of ash. It has been assumed that the acetic acid is adsorbed essentially in the form of dimeric molecules (cf. Blackburn and Kipling, *loc. cit.*, 1955).

Finally, we have found that charcoal extracted with hydrofluoric acid gave the same isotherm for adsorption from acetic acid-water mixtures as charcoal extracted with acetic acid (Blackburn and Kipling, *loc. cit.*).

We conclude that the ash present in this type of charcoal may interfere with adsorption from aqueous and other mixtures capable of dissolving inorganic salts, especially those of the alkali metals, and also mixtures involving acids, as the ash is basic. The ash does not interfere with adsorption involving bases, or with substances in which the ash is insoluble.

The ash can be removed in three stages. Korver's method gives the most satisfactory results for a simple method, though more elaborate treatment can reduce the ash content still further (Long and Sykes, *loc. cit.*). On the other hand, simple Soxhlet extraction with water gives results which may be adequate for many purposes [Reyerson (*Ind. Eng. Chem.*, 1925, 17, 1114) showed that Soxhlet extraction removes most of the inorganic

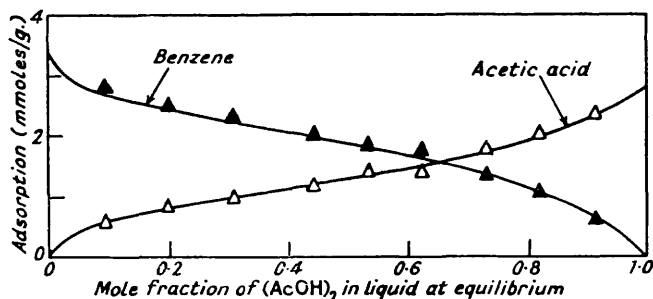


FIG. 5. Individual isotherms for adsorption from the system benzene-acetic acid.

Points: vapour-phase results;

▲ = benzene.

△ = acetic acid.

Curves: calculated from liquid-phase results.

matter from the coconut-shell before carbonisation]. This might also be a useful method of producing relatively ash-free charcoals, but in practice the shell is often available commercially only in carbonised form.

EXPERIMENTAL

The coconut-shell charcoal and the methods of determining isotherms have been described previously (Kipling and Tester, *loc. cit.*; Blackburn and Kipling, *loc. cit.*).

Extractions were carried out with (i) distilled water, (ii) purified glacial acetic acid, (iii) "AnalaR" hydrofluoric acid (40%). For the last extraction Polythene bottles were used rather than the waxed beakers described by Korver. This modification has also been used by Frey (*Proc. Roy. Soc.*, 1955, A, 228, 510).

The charcoal samples were ashed in porcelain crucibles heated in an electric furnace to not above 700°, to avoid the loss of the more volatile components of the ash which is reported to occur at higher temperatures (Tendolkar and Thakoor, *loc. cit.*). The figures quoted are the means of several determinations.

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