

Hydrogen-bonding and Adsorption of Dicarboxylic Acids by Alumina

By E. H. M. Wright

Adsorption of succinic acid and adipic acid by the alumina trihydrate, Alcoa C730, from aqueous solution has been studied. The results could be satisfactorily interpreted in terms of a parallel orientation of acid molecules on the adsorbent surface, but the acid molecules seem to be associated with some water molecules in the adsorbed phase. The acid molecules in the adsorbed phase are thus linked by hydrogen-bonding intermolecularly with other acid molecules or with adjacent water molecules, and not with surface hydroxyl groups as is the case with monocarboxylic acids.

In adsorption from organic solutions, stearic acid is adsorbed with the major axis of the molecule perpendicular to the surfaces of various forms of alumina.^{1,2} The molecules are adsorbed at specific sites, and for the alumina trihydrate, Alcoa C730, there was complete coverage of the surface by perpendicularly oriented acid molecules.¹ Evidence was discussed to show that the acid molecules were adsorbed by hydrogen-bonding between the carboxylic groups of the acid and the surface oxide and hydroxyl groups.¹ The process of adsorption thus involved initial breaking of hydrogen bonds between adjacent acid molecules, followed by formation of new surface-hydrogen bonds.

In the work now described, an examination is made of the part played by hydrogen-bonding in the adsorption of two dicarboxylic acids by Alcoa C730.

EXPERIMENTAL

The nature of the adsorbent, Alcoa C730, was previously described.¹ The purification and criteria of purity of the acids were also described,³ as were the methods⁴ for adsorption from solution at 20°. The systems adipic acid-water (over the whole concentration range of solubility) and succinic acid-water (over a limited concentration range) were analysed titrimetrically.

RESULTS AND DISCUSSION

The composite isotherms^{5,6} of surface excess of acid ($w_0 \cdot \Delta c/m$) plotted against concentration are shown in

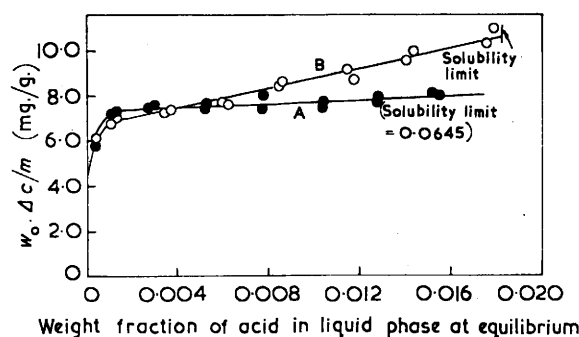


FIGURE 1 Adsorption by Alcoa C730 from aqueous solutions of (A) succinic acid and (B) adipic acid at 20°

Figure 1, and the individual isotherms⁵ in Figures 2 and 3. For the purpose of calculating individual iso-

* Nitrogen surface area of Alcoa C730 = 21.8 m.²/g. Effective parallel-orientation molecular areas for the acids are: succinic acid, 36.5 Å², adipic acid, 47.9 Å².

¹ J. J. Kipling and E. H. M. Wright, *J. Chem. Soc.*, 1964, 3535.

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therms, the assumption was made that the acid molecules are oriented with major axes parallel to the adsorbent surface, so that the monolayer value, $(w_1^s)_m$ for succinic acid is 11.73 mg./g. of adsorbent, and for

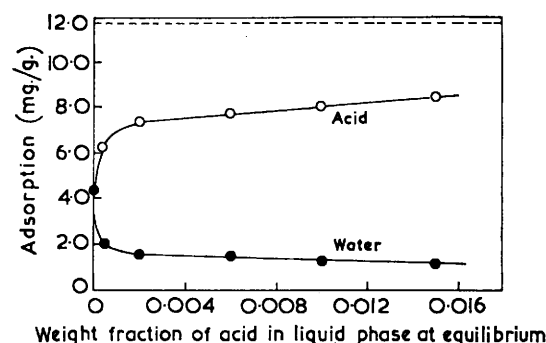


FIGURE 2 Individual isotherms for the adsorption on Alcoa C730 from aqueous solutions of succinic acid; the broken line indicates the monolayer level for the acid

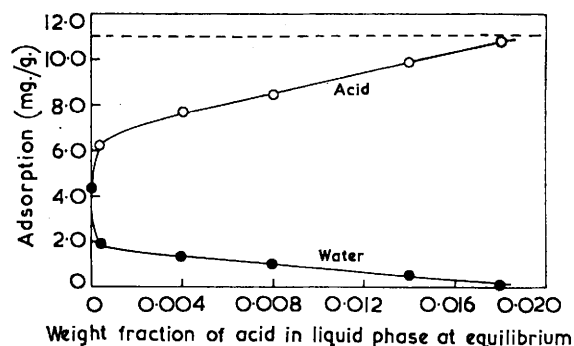


FIGURE 3 Individual isotherms for the adsorption on Alcoa C730 from aqueous solutions of adipic acid; the broken line indicates the monolayer level for the acid

adipic acid, 11.05 mg./g. of adsorbent.* Because of the low concentration ranges of the systems, the values of w_1^s , the true adsorption of the acids, do not, and cannot be expected to, differ significantly⁷ from those of

² A. S. Russell and C. N. Cochran, *Ind. Eng. Chem.*, 1950, **42**, 1332.

³ E. H. M. Wright, preceding Paper.

⁴ A. Blackburn, J. J. Kipling, and D. A. Tester, *J. Chem. Soc.*, 1957, 2373; A. Blackburn and J. J. Kipling, *J. Chem. Soc.*, 1954, 3819.

⁵ E. H. M. Wright, *Trans. Faraday Soc.*, 1964, **60**, 1814.

⁶ J. J. Kipling and E. H. M. Wright, *Trans. Faraday Soc.*, 1959, **55**, 1185.

⁷ J. J. Kipling and E. H. M. Wright, *J. Chem. Soc.*, 1962, 855.

$w_0 \cdot \Delta c/m$ at the same concentration, so that for these systems it does not matter very much what orientations are assumed in estimating the monolayer values of the acids in order to calculate individual isotherms.

It is significant that the $(w_1^s)_m$ values for the acids are about one-fifth of what would be expected if the acids were oriented perpendicular to the surface of the adsorbent. On the other hand, a parallel orientation of the acid molecules on the adsorbent surface would mean that the maximum adsorption of adipic acid corresponds to about 98% surface coverage by the acid, and that of succinic acid at the same concentration would be about 72%; at all concentrations the adsorption of adipic acid (measured as the fraction of surface covered) is greater than that of succinic acid. These observations are consistent with a parallel orientation of acid molecules on adsorption, with the adsorbed phase containing some water molecules, the amount of water decreasing with increasing bulk concentration of acid.

The nature of the aqueous solutions of the dicarboxylic acids is not fully understood, but there is little doubt that the acid molecules are linked with water molecules in infinite chains by hydrogen-bonding. It appears that the process involving a tendency for the acid molecules to be linked in infinite chains by hydrogen-bonding (as in the solid state), and to be adsorbed on the Alcoa C730 surface parallel to the surface, is more favourable than that which involves perpendicular orientation of acid molecules on the surface. Hence, the dicarboxylic acids do not behave in the same way as the fatty acids adsorbed on alumina.^{1,2} It may be noted that the dicarboxylic acids adsorbed on carbon blacks from organic solutions assume a parallel orientation as well on such surfaces,³ thus showing the same behaviour on these adsorbents as the fatty acids.⁷

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