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## Application of the Polanyi Adsorption Potential Theory to Adsorption from Solution on Activated Carbon. V. Adsorption from Water of Some Solids and Their Melts, and a Comparison of Bulk and Adsorbate Melting Points<sup>1</sup>

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Adsorption isotherms from water solution onto an activated carbon have been determined, both above and below the underwater melting points, for the following compounds: *o*-, *m*-, and *p*-nitrophenol; 2,5-dichlorophenol; coumarin; phthalide; 3,5-dichlorophenol; *p*-bromophenol; *m*-acetotoluidide; *m*-chloroacetanilide; and 2,2'-bipyridine. Of these compounds, adsorption isosteres on both sides of the underwater melting points have been determined for *o*- and *m*-nitrophenol, phthalide, and coumarin. The isotherms show distinctly higher adsorption on exceeding the melting points. The effect is ascribed to relatively inefficient packing of the solid phases into the carbon pores. The isosteres show first-order transitions at temperatures that are not detectably different from the underwater melting points and that are therefore taken as the melting points of the adsorbates. The identity of the bulk and adsorbate melting points is taken as evidence that the adsorbates are similar in their properties to the corresponding bulk phases. Except for the phenols, the adsorption isotherms of the liquids can be calculated by the previously published modified Polanyi adsorption potential theory, using gas-phase data on the same carbon, together with solute molar volumes and refractive indices. For the phenols (except *o*-nitrophenol), the theory underestimates the adsorption potential by about 20% and requires an empirical factor for each solute to account for the adsorption data.

### Introduction

There is good reason to suppose that solids should adsorb onto activated carbon from solution less strongly than the corresponding liquids because the relative inflexibility of the solid structure can make for reduced packing compatibility in fine pores. Manes and Hofer,<sup>2</sup> in applying the Polanyi adsorption potential theory<sup>3</sup> to the adsorption of two dyes from a variety of organic solvents, found the limiting adsorption volumes to be considerably lower than the common limiting volume for the adsorption of gases on the same carbon, and suggested that the discrepancy was due to packing effects. Chiou and Manes,<sup>4</sup> in a study of the adsorption of metal acetylacetonate complexes, found a similar effect. By contrast, studies by Wohleber and Manes<sup>5,6</sup> on the adsorption of organic solvents from water solution, again on the same carbon, showed the limiting adsorption volume to correspond quite closely to the gas-phase limiting volume. However, the observed differences between liquid and solid adsorbates cannot be unequivocally ascribed to the difference in state, since the adsorbates in the cited studies also differed significantly in molecular size, which could affect packing compatibility regardless of state.

We therefore decided to investigate the adsorption be-

havior, from water solution onto our activated carbon, of a series of organic compounds that melt under water and, for experimental convenience, to limit the investigation to compounds that melt in the approximate range of 30–90°. The approach was as follows: to determine the adsorption isotherms of each compound above and below the bulk melting point; to correlate the resulting data from the point of view of the Polanyi theory (*i.e.*, to plot adsorbed volume against the adsorption potential per unit volume), as in earlier articles in this series;<sup>2,4–6</sup> and to determine whether or not separate correlation curves would be required for the presumed liquid and solid adsorbates.

The investigation promised at the outset to serve two additional purposes. The first was to extend the earlier treatment<sup>5</sup> of the adsorption from water of partially miscible organic liquids to an additional series of partially miscible liquids. The second, which appeared to be even more interesting, was to use adsorption data above and below the bulk melting points to investigate the existence of an adsorbate melting point (or melting range) and possibly to compare the adsorbate and bulk melting points.

Our interest in adsorbate transition temperatures was heightened by the findings of Mattson, *et al.*,<sup>7</sup> that the adsorption of *p*-nitrophenol from water onto an activated

carbon increased anomalously on raising the temperature above 40.3°. They ascribed this anomalous increase to a reversal in sign of the heat of adsorption, which (for reasons to be given later) appeared to be highly unlikely. The fact that their reported temperature for the onset of the anomaly corresponded closely to the *underwater* melting point of their adsorbate strongly suggested that the apparent anomaly could be ascribable to adsorbate melting with a concomitant reduction of the adsorbate volume with improved packing, and led us to the expectation that such anomalies would be more widely observed.

Our findings have been largely in accord with expectations. The adsorption isotherms of a series of 11 compounds, which were selected only on the basis of their melting points and stability, all show significantly lower adsorption below the adsorbate melting points, both on a mass and volume basis. The abrupt increase in adsorption that was reported by Mattson, *et al.*, for *p*-nitrophenol on exceeding the underwater melting point appears to be a general phenomenon for compounds that melt underwater. The limiting adsorbate volumes for the presumed liquid adsorbates are quite close to the values found by Wohleber and Manes<sup>5</sup> for liquids of lower molecular weight, which indicates that molecular size has not yet become a factor in the packing of liquid molecules into the adsorption space. The treatment of Wohleber and Manes<sup>5</sup> for predicting the adsorption of partially miscible liquids from water solution applies to the liquid adsorbates that were here studied, with the exception that the abscissa scale factors calculated for most of the phenols are somewhat below the experimental values. In addition, the adsorbate melting points appear to be true first-order transitions, and the transition temperatures that have been determined for four compounds have in no case been significantly different from the bulk underwater melting points. We take this as suggesting that the adsorbates resemble the bulk phases.

### Theoretical

The theory is given in the preceding articles in this series.<sup>2,4,5</sup>

### Experimental Section

The activated carbon (Pittsburgh Activated Carbon Division, Calgon Corp., CAL grade activated carbon), apparatus, and experimental techniques were the same as described in previous articles in this series,<sup>2,4-6</sup> except that the high temperature solutions were allowed to settle out for several hours at equilibrium temperatures and the almost clear supernatant solutions were rapidly decanted before final filtration. All solutions were analyzed (after appropriate dilution where necessary) in a Cary 14 (ultra-violet) spectrophotometer. Distilled water was the solvent throughout.

All of the organic compounds were purchased from commercial sources and recrystallized, if necessary, to a minimum purity of 99% as determined by comparison of the molar absorptivities with values from the literature.<sup>8</sup> All compounds used in the determination of the isosteres were recrystallized.

The solubilities ( $c_s$ ) of the solid solutes at 25° (except for 3,5-dichlorophenol at 22°) and at above-melting temperatures were determined by saturation of water solutions in the shaker bath, followed by spectrophotometric analysis. The densities of the solid solutes were either taken from the literature or determined by a float-and-sink method

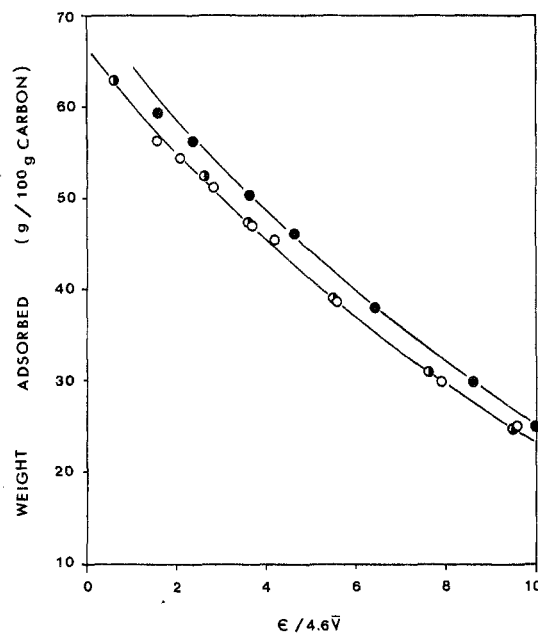


Figure 1. Weight of adsorbed *p*-nitrophenol as a function of  $\epsilon/4.6\bar{V}$  ( $= (T/\bar{V}) \log c_s/c$ ) at 42 (●), 25 (○), and 42–25° (◐).

on individual crystals. Densities of the corresponding pure molten solutes above their melting points were determined to within  $\pm 2\%$  by simply weighing measured volumes of the melts; these values were used to convert the weights of liquid adsorbates to volumes. No temperature correction was made for the densities of liquids with underwater melting points well below the normal melting points. The molar volumes,  $\bar{V}$ , later used in calculating  $\epsilon/4.6\bar{V}$  in all cases refer to the molar volumes of the liquid adsorbates.

The solubilities and densities for each solid and liquid compound at the below-melting and above-melting temperatures are included in Table IV.<sup>9</sup>

In order to show that the observed lower adsorption of solid adsorbates is a true equilibrium effect, the reversibility of six solid-phase adsorption isotherms was tested by first equilibrating the solutions above the melting point for the regular 16 hr, followed by cooling and re-equilibration. No hysteresis was observed. Underwater melting points were readily determined as the stationary temperatures on cooling mixtures of the melts with water. Refractive indices of the melts were determined in an Abbé-type refractometer with heated prisms. The data are included in Table III.<sup>9</sup>

### Results and Discussion

The adsorption isotherm data are all given in Table I,<sup>9</sup> as weight loading (g/100 g of carbon) *vs.* equilibrium concentration (g/l.). The adsorption isostere data are given in Table II,<sup>9</sup> as equilibrium concentration *vs.* temperature, for loadings as specified; because of the low equilibrium concentrations, the loading on the carbon does not change significantly with changing equilibrium concentration. Figures 1 and 2 show the adsorption isotherm data plotted as weight loading *vs.*  $(T/\bar{V}) \log c_s/c$  ( $= \epsilon/4.6\bar{V}$ ), where  $\epsilon$  is the adsorption potential, for *p*-nitrophenol and for phthalide, where  $c$  and  $c_s$  are the respective equilibrium and saturation concentrations. This type of plot has been chosen to show the increase in mass loading for a given relative concentration on raising the temperature above the underwater melting point. All of the determined isotherms

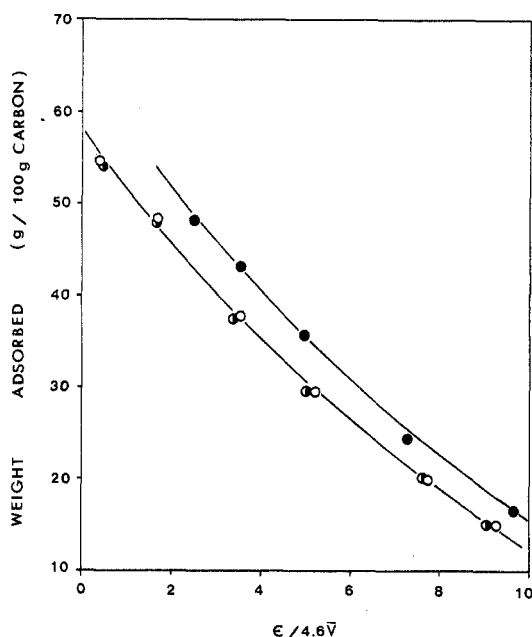


Figure 2. Weight of adsorbed phthalide as a function of  $\epsilon/4.6\bar{V}$  at 63 (●), 25 (○), and 63–25° (◐).

show the same effect. We show the plot of *p*-nitrophenol to confirm the experimental findings of Mattson, *et al.*,<sup>7</sup> and the plot of phthalide to show the typical behavior of the nonphenols. Similar plots, which have been omitted to save space, may be readily constructed from the data of Tables I and IV.

Figures 3 and 4 show the data for nitrophenol and for phthalide, this time plotted as correlation curves, *i.e.*, as plots of the log of the adsorbed volume *vs.*  $\epsilon/4.6\bar{V}$ , the factor of 1/4.6 being retained for conformity with the notation of earlier publications. In Figure 4, the solid line through the points for the adsorption of solid is simply the best fit through the points; however, the dotted line through the liquid adsorption points is the theoretical curve calculated by the Wohleber–Manes<sup>6</sup> method for correlating the adsorption of partially miscible liquids. This line is essentially the gas-phase hydrocarbon correlation line for the carbon, as determined from gas-phase adsorption (a similar correlation line could have been drawn from the results of Wohleber and Manes on the adsorption of one of their partially miscible liquids from water solution), with an abscissa scale factor calculated from the molar volume, the refractive index, and an empirical scale factor determined by Wohleber and Manes for the adsorption of water. In the calculation of this line there are no adjustable parameters, and its fit to the data illustrates the extent to which the corresponding adsorption isotherms could have been calculated from theory. In Figure 3 the dotted line is again the theoretical line as calculated in Figure 4, and it may be seen to be not nearly as good a fit to the data. The lack of fit appears to be due to the abscissa scale factor; the alternately dotted and dashed line is the same as the dashed line, except for application of an empirical scale factor, which is apparently necessary to fit the data for all of the phenols studied, with the exception of *o*-nitrophenol. Again, Figure 3 is typical for the phenols (with the exception just noted), and Figure 4 is typical for all of the others. Table III<sup>9</sup> includes the theoretical and experimental scale factors ( $\gamma_{sl}$ ) required to bring the points for liquid-phase adsorption into the kind

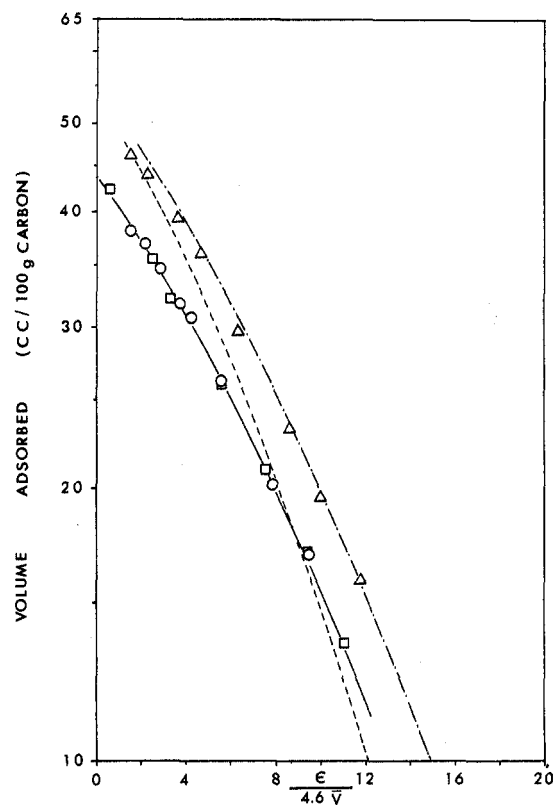


Figure 3. Correlation curves (volume adsorbed *vs.*  $\epsilon/4.6\bar{V}$ ) for *p*-nitrophenol at 42 (Δ), 25 (○), and 42–25° (□): (---) theoretical curve, no adjustable parameters; (-·-) theoretical curve empirical scale factor (theoretical factor  $\times 1.2$ ); (—) best fit through low-temperature data.

of coincidence that is illustrated in Figures 3 and 4. It should be pointed out that in calculating the adsorbate molar volumes in the ordinates in Figures 3 and 4 we have used the liquid densities to correlate the data above the melting point and the solid densities below the melting point. This could in itself have produced a separation between the correlation curves for liquid and solid, even in the absence of any real packing effects. Figures 1 and 2, and the similar figures that may be drawn from the data of Table I, demonstrate that the presumed packing effect is not merely an artifact of the calculation method. Finally, the low-temperature points of Figures 1–4 contain a number of points representing preequilibration above the melting point and demonstrate the reversibility of the low-temperature isotherms.

Figures 5 and 6 are isostere plots of  $\log c$  *vs.*  $1/T$  for *o*-nitrophenol, *m*-nitrophenol, phthalide, and coumarin. The intersection of the lines of different slope, or the sawtooth discontinuity between the lines, is taken as locating or bracketing the transition temperature, or adsorbate melting point, which can be localized from the data to about  $\pm 1^\circ$ . The bulk underwater melting points are given in Table III. The estimated transition temperatures for all four isosteres were identical with the corresponding underwater melting points.

We now consider the results exemplified by Figures 1–4. These results first show quite clearly that there is a clear demarcation between the correlation curves, on a mass basis or on a volume basis, for adsorption above and below some fixed temperature for each solute, and that this transition temperature is at least in the region of the underwater melting point. If the temperature is increased

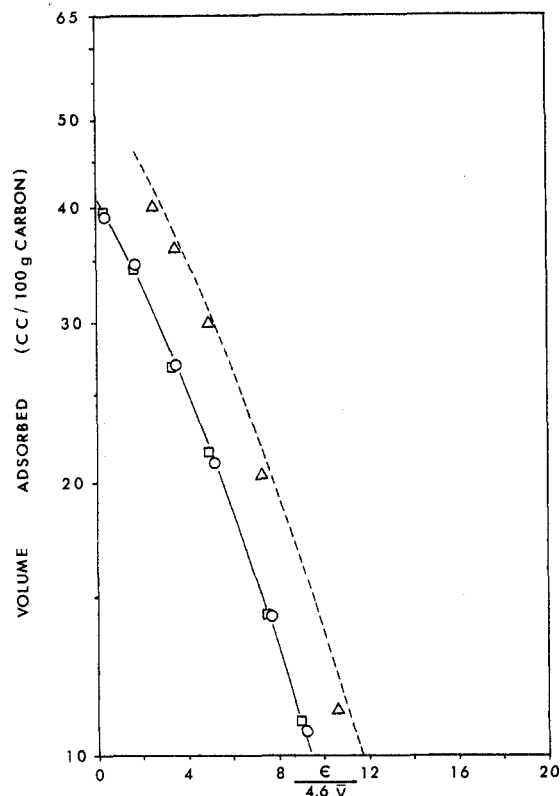


Figure 4. Correlation curves (volume adsorbed vs.  $\epsilon/4.6V$ ) for phthalide at 63° ( $\Delta$ ), 25° (O), and 63–25° ( $\square$ ): (---) theoretical correlation curve with no adjustable parameters; (—) best fit to the low-temperature data.

from below to above the transition temperature over a reasonably narrow range, there will be either a reduction in relative concentration at constant loading, or else an increased loading at constant relative concentration. This is the effect that was reported by Mattson, *et al.*,<sup>7</sup> for the adsorption of *p*-nitrophenol on increasing the temperature above 40.3°, and it appears to apply generally to solutes that melt underwater. Mattson, *et al.*, interpreted their observation in terms of steadily increasing adsorption with increasing temperature rather than in terms of a discontinuity, and this interpretation led them to account for their observation on the basis of a reversal of the sign of the heat of adsorption. Since the entropy change on adsorption from dilute solution is negative, it must follow, as pointed out by Brunauer<sup>10</sup> for gas adsorption, that the adsorption must be exothermic, since an endothermic adsorption would be endergonic. The explanation in terms of a reversal of the sign of the heat of adsorption is therefore unacceptable on thermodynamic grounds. If however, we analyze the data from the point of view of the Polanyi theory, we immediately recognize the discontinuity between the two correlation curves (which could otherwise easily be mistaken for a region of increasing adsorption with increasing temperature). We shall see, as a matter of fact (Figures 5 and 6), that on either side of the discontinuity the adsorption continues to decrease continuously in normal fashion with increasing temperature, and that the enthalpy of adsorption is normally exothermic on both sides of the transition temperature. Finally, the demarcation between what we may now presume to be the adsorption of liquid and of solid now allows us to determine with some accuracy the temperature of the transition and to

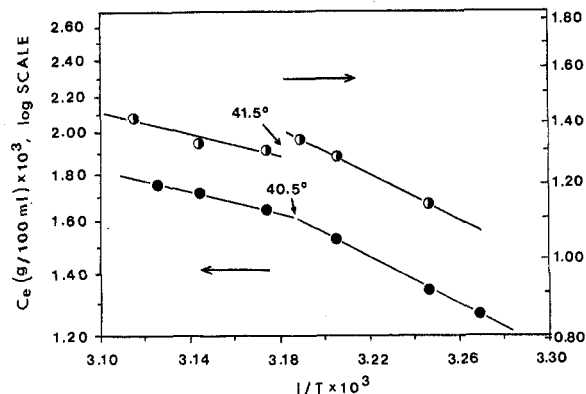


Figure 5. Adsorption isosteres for *o*-nitrophenol (●, right scale) and *m*-nitrophenol (●, left scale). Indicated numbers are estimated transition temperatures.

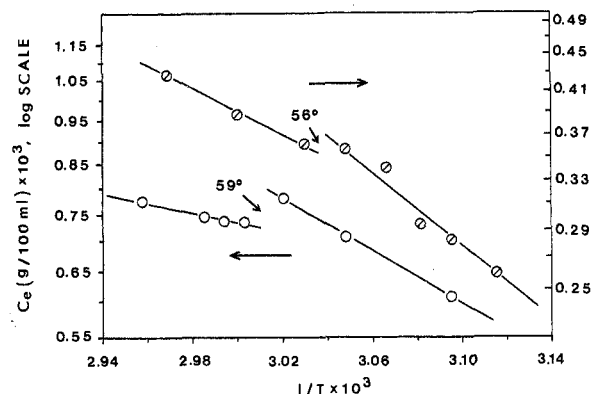


Figure 6. Adsorption isosteres for coumarin (○, right scale) and phthalide (○, left scale). Indicated numbers are estimated transition temperatures.

see how close it comes to the underwater melting point. This will be discussed later.

Consider now the magnitudes of the limiting adsorption volumes. As illustrated in Figures 3 and 4, the limiting volumes for the liquid-phase correlation curves are comparable to the corresponding volumes found by Wohleber and Manes<sup>6</sup> in the adsorption of some (room-temperature) organic liquids, which volumes were in turn comparable to limiting volumes for gas-phase adsorption on the same carbon. The present results indicate the absence of any major packing anomalies in the liquid phase for the somewhat larger adsorbate molecules of this investigation.

The reduction in limiting adsorption volume in going from liquid to solid is not exactly constant from compound to compound, but averages to about a 15% reduction relative to the liquid phase. This reduction is interpreted as reflecting relatively inefficient packing of solid crystallites in the adsorption space, the volume of which is assumed to be constant. The limiting volumes observed here are higher than was observed by Manes and Hofer<sup>2</sup> in the adsorption of their two dyes. However, they were of larger molecular size than the compounds studied here, which suggests, as one might expect, that packing inefficiencies in the solid phase increase with increasing molecular size. In the present work the packing effect is clearly distinguishable from molecular sieving, since we compare the solid and liquid phases of the same substances.

We should note in passing that the adsorbate volumes for the liquid phases have been calculated on the assump-

tion that the densities of the liquids are not significantly different at the underwater melting points from their values at the pure melting points where they were determined. Moreover, we have made no correction for the volume of dissolved water in the adsorbed liquid phase. The water content of the bulk liquid phase may be estimated to be about 1% by weight for each 4–5° depression of the melting point. In all cases but two (*p*- and *m*-nitrophenol) the water content was estimated as not more than 5% in the bulk phase; it was therefore neglected in making the calculations.

Before leaving Figures 3 and 4, let us consider their implications for the prediction of adsorption isotherms from water solution. Figure 4 illustrates the extent to which the adsorption data of all of the nonphenolic compounds here investigated could be accounted for by the treatment by Wohleber and Manes<sup>6</sup> of the adsorption of partially miscible liquids. Again we emphasize that there are no adjustable parameters in the calculation of the theoretical curve in Figure 4. The fit of the theoretical curve is not as good in Figure 3, which again is illustrative of our results with phenols (except for *o*-nitrophenol, which is not anomalous). In Figure 3 the Polanyi theory applies, in that one can fit the experimental data with the correlation curve for the carbon that was derived from gas-phase adsorption. However, the calculation of Wohleber and Manes<sup>6</sup> (based on the earlier article by Manes and Hofer<sup>2</sup>) underestimates the abscissa scale factor by about 20%. Anomalous strong adsorption of phenols has been reported, for example by Radke and Prausnitz,<sup>11</sup> who ascribed it to specific interaction of phenols with the carbon surface. It is interesting that *o*-nitrophenol, which is intramolecularly hydrogen bonded, does not show the typical anomalous behavior (from our point of view) of phenols, and it is tempting to associate the anomalous behavior of phenols with intermolecular hydrogen bonding. However, we should expect hydrogen bonding effects of phenols to be swamped out in water solution.

We now consider the determination of the adsorbate melting points and their implication for the state of the adsorbates. Figures 5 and 6 show the transition temperatures to be equal to the underwater melting points within the precision of the measurement, which is about 1°. The plots show discontinuities in the adsorption amounts as well as in the slopes, *i.e.*, there is a sawtooth intersection at the transition temperature. This sawtooth is of course consistent with the existence of separate correlation curves for the liquid and solid adsorbates; it is ascribed to the increase in adsorption potential at the adsorbate–solution interface (Polanyi model) as the newly formed melt shrinks into the adsorption space. The fact that adsorption does not detectably change the transition temperature is in keeping with the Polanyi model, in which the adsorbed and bulk phases have essentially the same properties. Moreover, the similarity in properties implied for the bulk and adsorbed phases is for coverages less than one average monolayer. For example, for *o*-nitrophenol, with an estimated surface area of 52 Å<sup>2</sup> (assumed flat con-

figuration; measured from a molecular model), an average monolayer for our carbon of 1140 m<sup>2</sup>/g is approximately 50 g/100 g of carbon. Since the other adsorbates have approximately the same densities, one may estimate the range of coverages in the isosteres at from 60% (*o*-nitrophenol) to approximately 30% (phthalide) of a monolayer, which were the lowest coverages at which we could measure equilibrium concentrations with sufficient accuracy for isostere plots.

## Conclusions

(1) For all 11 compounds studied, exceeding the underwater melting point results in a sharp increase in the adsorption from water solution onto activated carbon. The effect is ascribed to less efficient packing of the solid in the adsorption space.

(2) Adsorption isosteres on four compounds have shown the existence of adsorbate transitions at temperatures that are not detectably different from the bulk underwater melting points, and that may be considered as adsorbate melting points. The identity of bulk and adsorbate melting points suggests similarity between the bulk and adsorbate phases.

(3) Adsorption above the melting point can be accounted for by a modified Polanyi adsorption potential theory. No adjustable parameters are needed for the nonphenolic compounds and *o*-nitrophenol; an abscissa scale factor about 20% higher than the theoretical factor is needed to account for the adsorption of the phenolic compounds studied.

**Supplementary Material Available.** Tables I–IV will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JPC-74-622.

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