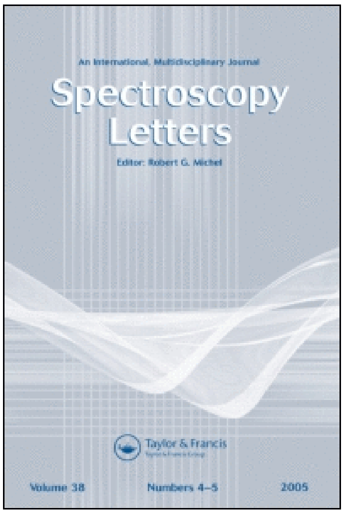

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APPLICATION OF THE POLANYI ADSORPTION POTENTIAL THEORY TO ADSORPTION PHENOLIC COMPOUNDS FROM WATER SOLUTION ONTO ACTIVATED CARBON

Key Words : Adsorption, Polanyi, Phenolic Compounds

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ABSTRACT :

Adsorbtion isotherms, from water solution onto activated carbon have been determined over a wide consantration range for phenol and some its derivetives. At the first look, it was observed that the experimental data of 3-hydroxyphenol (resorsine) agree with predicted isotherm calculated by the Hansen-Facker modification of Polanyi Adsorption Potential Theory, using only the solute refractive index and molar volume, together with characteristic curve for the carbon as determined from gas-phase adsorption data but, 4-nitrophenol isotherm agree with the theoretical isotherm after correction for its hydration and corrected experimental curves of phenol, 2,4-dinitrophenol and 2,4,6-trinitrophenol appear to be related to the theoretical isotherm by single abscissa scale factor.

INTRODUCTION :

The Polanyi Adsorption Potential Theory and modifications thereof have been widely applied to gas-phase adsorption (1-6). By contrast, application of the theory to liquid-phase adsorbtion has been used only in modified form for adsorption of binary liquids (7).

In their study of the adsorption of two dyes from a number of organic solvents, Manes and Hofer had found that the limiting adsorbate volumes (calculated on the assumption of equality of bulk and adsorbate densities) were significantly lower than for gases on the same carbon (8). They attributed these lower apperent volumes to porous packing of the adsorbates, postulating that the entire adsorption space should be accupied at saturation. Some investigator found the same effect in their investigation of a number solids from water (9,10).

This study is aimed to the adsorption of phenolic compounds from water solution. Water was chosen as the solvent because of its anomalously low energy of adsorption and the widest application of activated carbons in water solution for example to study tha water pollution problems.

THEORETICAL SECTION :

Polanyi (11) considered that just as the adsorption of gases takes place by liquefaction of the gas on the surface with the potential $\varepsilon(V)$ estimated as

$$\varepsilon(V) = RT\ln(P_s / P) \qquad (1)$$

also the adsorbtion of solid solutes take place by the prencipitation or crystallization of the solute on the surface with potential estimated as

$$\varepsilon(V) = RT\ln(C_s /C) \qquad (2)$$

where C_s and C are the saturated and equilibrium consentration respectively, and ε is the adsorbtion potential of the adsorbed pure solute.

In a later paper, Polanyi (12) considered that the adsorption a solute must be accompanied by desorption of equal volume of solvent. Equation (2) therefore becomes

$$\varepsilon_s = RT\ln C_s/C = \varepsilon_s - \varepsilon_1(Vs/Vl) \qquad (3)$$

We have here slightly changed the nomenclature by removing the symbol (V) from the potential ε , ε_s and ε_1.

Equation (3) may be written more symmetrically and succinctly as

$$\frac{\varepsilon}{V_s} = \frac{\varepsilon_s}{V_s} - \frac{\varepsilon_1}{V_1} \qquad (4)$$

provided that the potential is always regardet as pertaining to a given volume of loading (where ε_1 is the adsorption potential of the pure solvent adsorbing as a vapor and ε_{sl} is adsorption potential of pure solute being adsorbed from solution. V_s and V_1 are the molar volumes of solute and solvent). We can write equation (4) more compactly as

$$\alpha_{sl} = \alpha_s - \alpha_1 \qquad (5)$$

where each α is the corresponding ε/V. If we assume, with Polanyi that the characteristic curves for the solvent and the solute have the same functional form, expect for a constant factor in the adsorbtion potential, then the α's are directly propertional to the affinity coefficients of Dubinin (1).

Instead of expressing the relative values of the α's at some stated adsorption volume, We can consider the ratios between the α's and α_h, where α_h is the scale factor for some standart reference substance or substances, if they all have the same α, in which case We can rewrite equation (5) as

$$\frac{\alpha_{sl}}{\alpha_h} = \frac{\alpha_s}{\alpha_h} - \frac{\alpha_1}{\alpha_h} \qquad (6)$$

or

$$\gamma_{sl} = \gamma_s - \gamma_1 \qquad (7)$$

where $\gamma_{sl} = \alpha_{sl}/\alpha_h$, etc. Manes and Hofer (8) estimated the γ_{sl} values, from the refractive indices for liquids and from a table of atomic and bond refractivities for solids, without any recourse to adsorption measurements. It was assumed that adsorption potential per unit volume, α, is proportional to the polarizability per unit volume and this in turn is proportional to refractivity per unit volume P, by Lorentz-Lorenz equation

$$\frac{4}{3}\pi N_a \alpha' = \{R\} = \frac{M}{\rho}\{\frac{n^2 - 1}{n^2 + 2}\} = \frac{M}{\rho} . P \qquad (8)$$

where α' is the polarizability per molecule, $\{R\}$ is molar refraction, N_a is Avogadro's number, M is molecular weight, ρ is density and $P \equiv (n^2 - 1)/(n^2 + 2)$. We than get

$$\gamma_{sl} = \frac{P_s - P_l}{P_h} \qquad (9)$$

where P_s, P_l and P_h are the polarizability of solute, solvent and referance substances respectively. The value of P was calculated for each solute from its molecular structure and density and a table of atomic and bond refractivities (13). Heptan was picked as a standart liquid hydrocarbon.

EXPERIMENTAL SECTION :

The carbon adsorbent in all cases came from a batch of activated carbon. The surface area (B.E.T.)* of the carbon was 1140 m^2/g. The carbon was used as received, except for oven drying at 100°C for 24 hours. Distilled water was used as the solvent in all experimental works. The all chemical were purified grade and came from commercial sources.

The solublities of the adsorbates (phenol, 4-nitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol and 3-hyroxyphenol) in water at 25°C, were determined by shaking on excess of solid with water in thermostated shaker (Certomat - WR Model) bath. The concentration of solute in the saturated aqueous phase was determined by Shmadzu Model 160 UV-VIS spectrophotometer. The equilibrium concentration in the adsorption experiments were analyzed by the same method that was used to determine the solublities. The density of adsorbates were determined by a liquid displacement method at 25°C, using spectrograde benzene presaturated with solute as the displacement liquid.

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* Chemviron Granule Active Carbon CAL 12x40 mesh Ser. No. GR 31123 A, Chemviron - Chausse de Waterlov 1135, 1180 Bruxelles - Belgum

TABLE 1 : Calculated correlation curves for substances

	Phenol	4-nitrophenol	2,4-dinitrophenol	2,4,6-trinitrophenol	3-hydroxyphenol
Molacular weight (g/mole)	94.11	139.11	184.11	229.11	110.11
Density (g/cc at 25°C)	1.071	1.48	1.683	1.763	1.272
Molar volume (cc/mole)	87.87	93.99	109.39	129.95	86.565
Molar refraction (R)	27.832	35.132	42.432	49.73	29.357
$P_s = R / V$	0.317	0.374	0.388	0.383	0.339
Solublity in water (g/1 at 25°C)	8.883	1.677	0.067	1.568	381.12
$\gamma_{sl} = \frac{P_s}{P_7} - \frac{P_1}{P_7}$ (P_7=0.236 , $\frac{P_1}{P_7}$=0.280)	1.062	1.304	1.363	1.341	1.157

Calculated $\varepsilon/4.6V$ = $\varepsilon/4.6V$ (From hydrocarbon curve) X γ_{sl}

The adsorption experiments were carried out in 100 ml screw - capped erlenmeyer flasks. Into a flask were placed a weighted amount of adsorbent and 50 ml of aqueous solution of a known concentration of adsarbate. Equilibrium was achieved by shaking the flask for at least twentyfour hours with mechanical shaker, with the flasks immersed in a thermostated water bath. Than the supernatant liquid was centrifuget. The clear solution, was analyzed in the spectrophotometer.

RESULT AND DISCUSSION :

Table 1 lists molecular weight, density, molar volume, molar refractivity and soliblity of adsorbates and that how calculated their abscissa scale factor (γ_{sl}) and $\varepsilon/4,6V$ values. Theoretical correlation curves were calculated by taking space points from the gas-phase hydrocarbon correlation curve (3) and multiplying the values of $\varepsilon/4.6V$ by a calculated abscissa scale factor for each solute. These scale factors were in turn calculated by use of the molar reflactivities of the solutes and the γ_1 value of 0.280 for water as reparted by Wohleber and Manes (14)

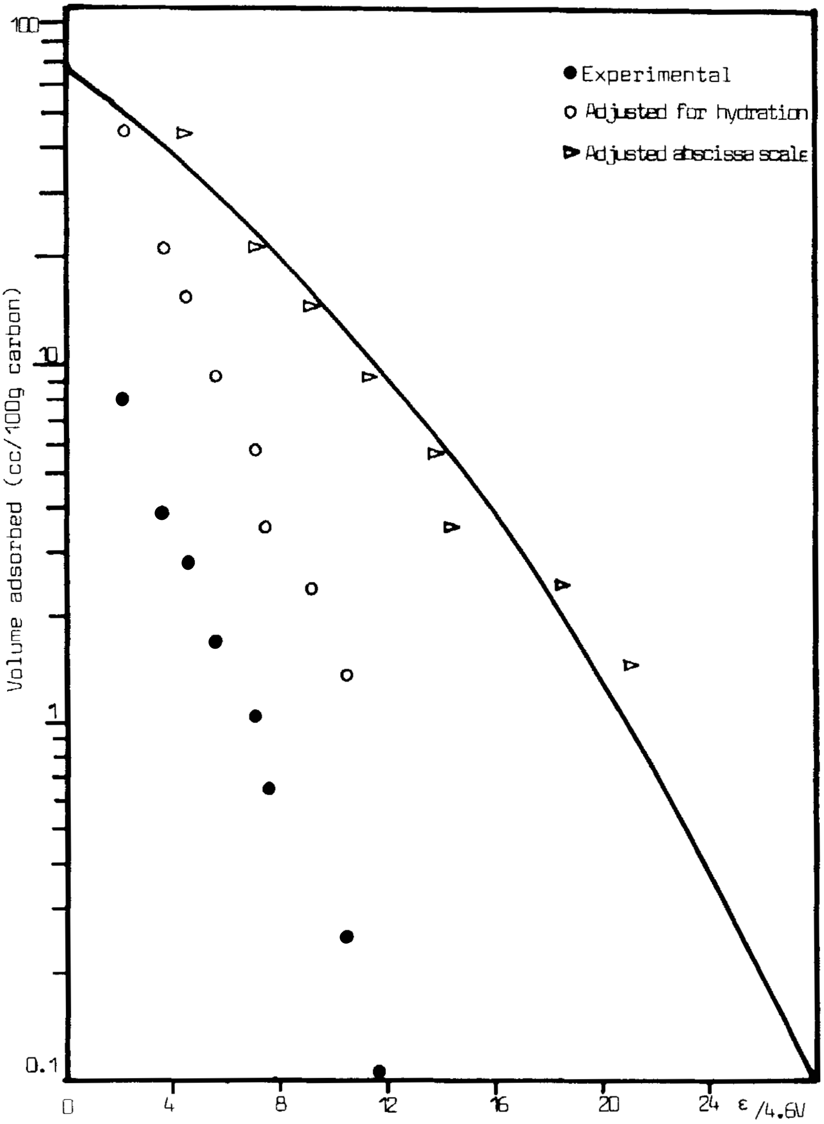

Fig. 1. Volume of phenol adsorbed, plotted as a function of adsorption potential. Solid curve is calculated for phenol from hydrocarbon curve.

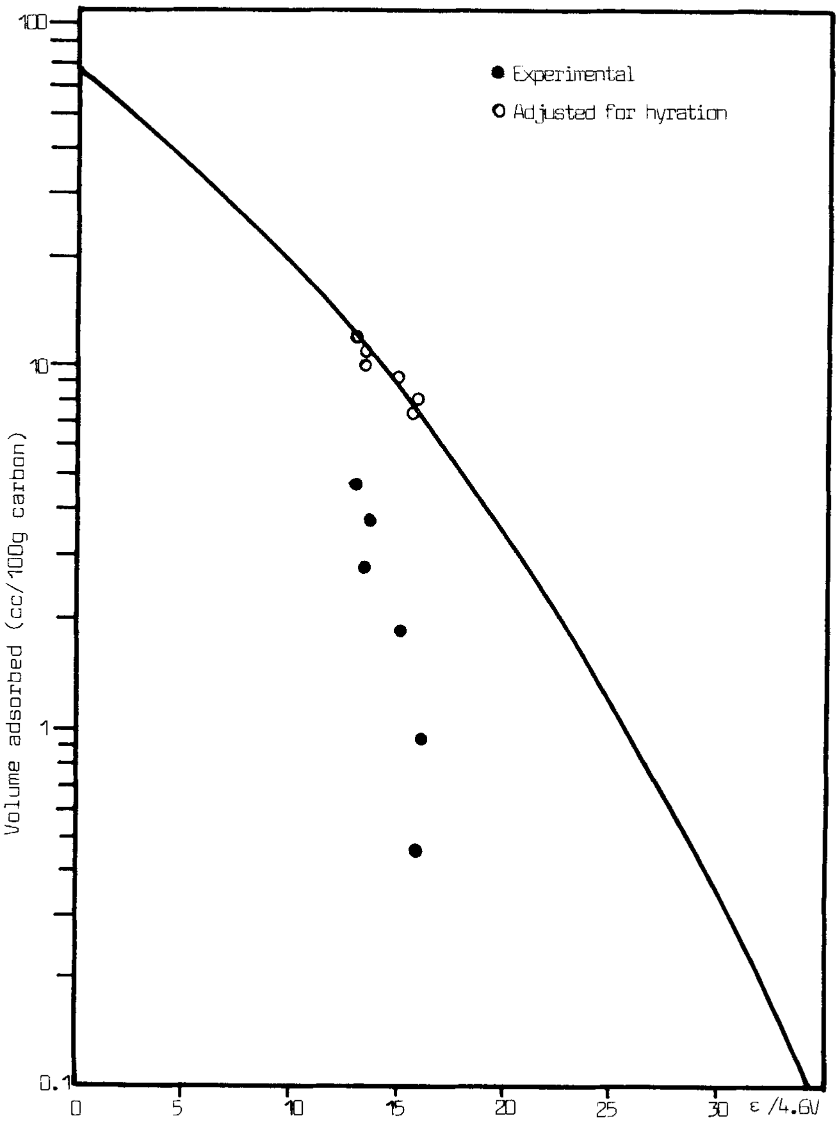

Fig. 2. Volume of 4-nitrophenol adsorbed, plotted as a function of adsorption potential. Solid curve is calculated for 4-nitrophenol from hydrocarbon curve.

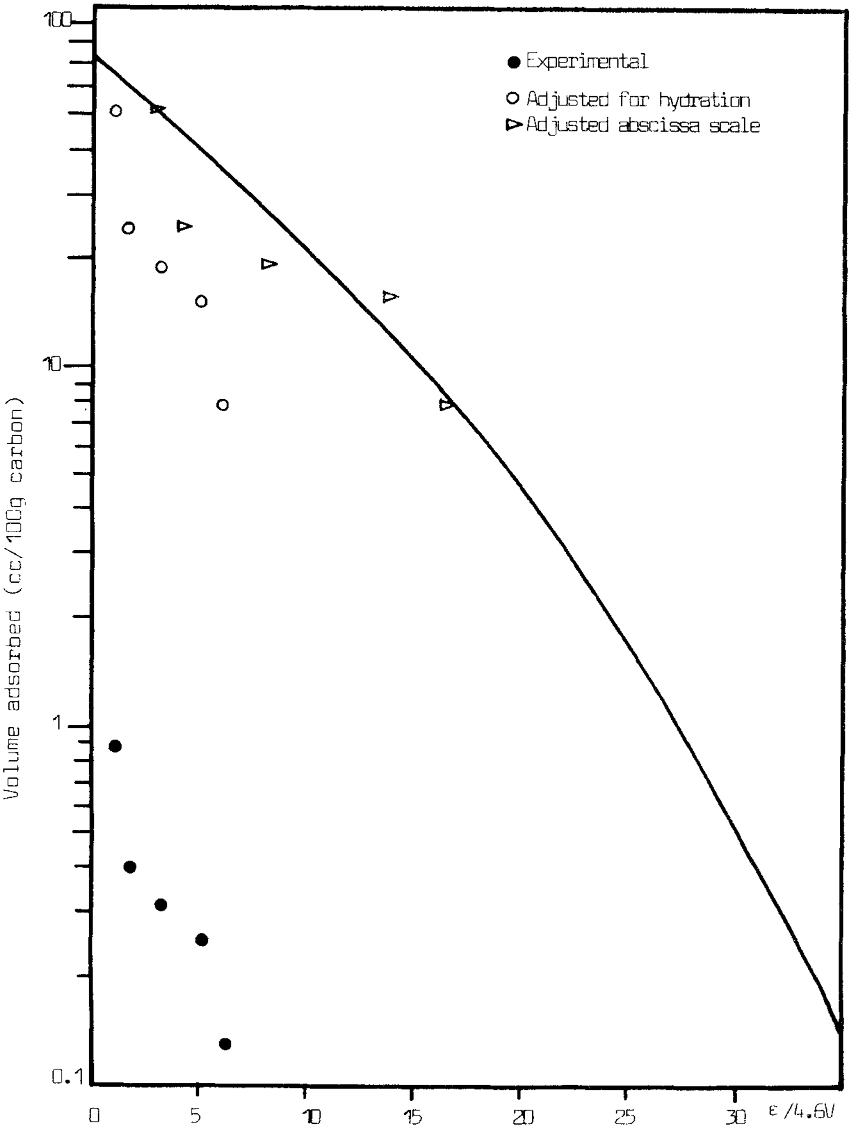

Fig. 3. Volume of 2,4-dinitrophenol adsorbed, plotted as a function of adsorption potential. Solid curve is culculated for 2,4-dinitrophenol from hydrocarbon curve.

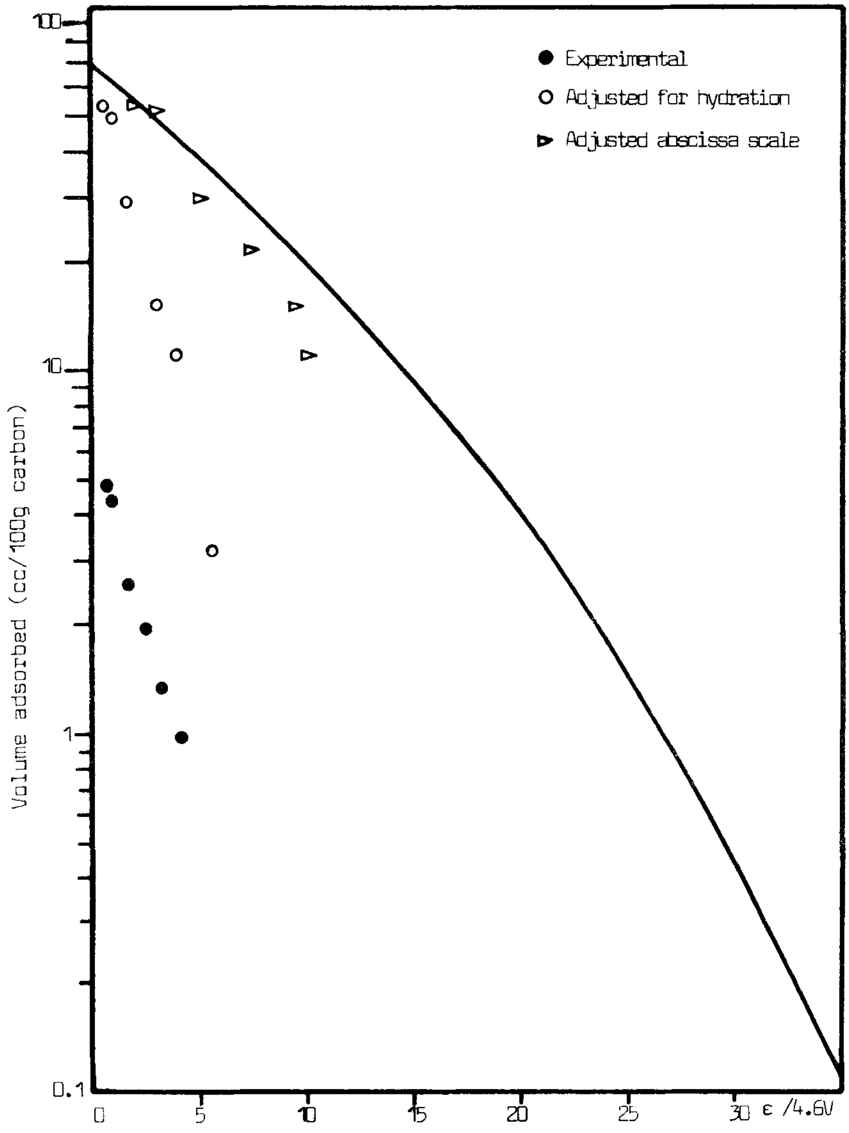

Fig. 4. Volume of 2,4,6-trinitrophenol adsorbed, plotted as a function of adsorption potential. Solid curve is calculated for 2,4,6-trinitrophenol from hydrocarbon curve

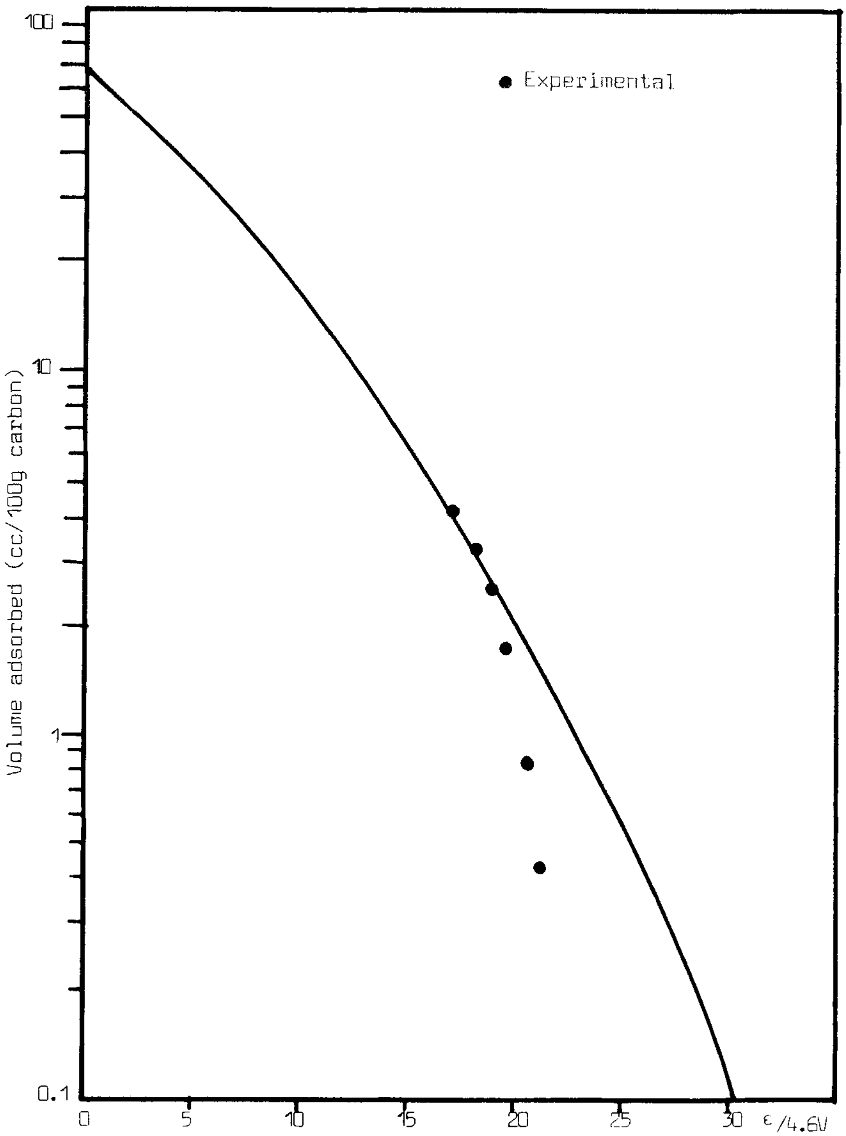

Fig. 5. Volume of 3-hydroxyphenol adsorbet, plotted as a function of adsorption potentiol. Solid curve is calculated for 3-hydroxyphenol from hydrocarbon curve

Figures 1 - 5 give a comparison between the calculated and experimental values for the correlation curve points, they relate the liquid-phase adsorption data to gas-phase adsorption on the same carbon. 3-hydroxyphenol does fit theory quite well, because of its experimental points come close to the theoretical calculation as seen in figur 5. Deviations from theoretical curve at low loadings, probably are a result of its ionization and hydrogen binding capacity. As shown from figures 1, 2, 3 and 4 the theoretical calculation does not come close to the experimental points for these copound. One may postulate that the adsorbate is hyrated and therefore the adsorption space is filled to the same volume as before, but partially with hydration water. The correction for assumed hydration is made graphically by adding a fixed logarithm to the ordinate of experimental line, i.e., raising it until it coincides with the theoretical line at the limiting volume.The above adjusment for hydration succesfully brings the adjusted experimental points for 4-nitrophenol into reasonable coincidence with the theoretical line as seen in fig. 2. This result can be explained by its well packinable structure.

Application of the ordinate scale factor did not suffice in any case to bring the data into coincidence with the theoretical curve. It is noticed that after above adjusment for hydration, the adjusted experimental curves now appear to be related to the theoretical curves by a single abscissa scale factor. Following the procedure of Manes and Hofer (9) the adjusted experimental curve points were multiplied by a single scale factor, arbitrarily chosen to give maximum fit. As seen in fi. 1, 3 and 4, phenol, 2,4-dinitrophenol and 2,4,6-trinitro phenol adsorption isotherms agree with theoretical isotherms (derived from gas-phase adsorption) after correction for hydration and applying a single abscissa scale factor. Lack of fit to the theoretical curve for unadjusted data appears to be due to complications arising from solution chemistry.

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REFERENCES

1. Dubinin, M.M., Chem. Rev., 60:235 (1960)
2. Lewis, W. K., Gilliland, E.R., Chertow, B. and Cadogan, W.P., Ind. Eng. Chem., 42:1319 (1950)
3. Grant, R.J., Manes, M. and Smith, S.B., A. I. Ch. E. J. 8:430 (1962)
4. Grant, R.J. and Manes, M., Ind.Eng. Chem. Fundamentals,3:221 (1964)
5. Grant, R.J. and Manes, M., Ibit, 5:490 (1966)
6. Manes, M., In Activated carbon adsorbtion of organics from the aqueous phase, Vol. 1, ed. by I.H.Suffet and M.J.Guire, pp. 43-64 Ann Arbor, MI, Ann Arbor Science Publishers, 1980
7. Hansen, R.S. and Fackler, M.V., J. Phys. Chem., 57:634 (1953)
8. Manes, M. and Hofer, L.J.E., J.Phys. Chem., 73:584 (1969)
9. Rosene, M.R., Özcan, M. and Manes, M.,J. Phys. Chem., 80:2586 (1976)
10. Rosene, M.R. and Manes, M., J. Phys. Chem., 80:953 (1976)
11. Polanyi, M.,Verh. Deut. Physik. Ges., 16:1012 (1914) ; 18:55 (1916) Z. Elecktrochem., 26:370 (1920)
12. Polanyi, M., Z. Physik., 2:111 (1920)
13. Lange, N.A. (ed.), Handbook of Chemistry, 10 ed., pp.1391, McGraw Hill, New York, 1961
14. Wohleber, D.A. and Manes, M., J. Phys. Chem. 75:61 (1971)

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