Adsorptive Mechanism on Activated Carbon in the Liquid Phase. I. Free Energy Change for Adsorption of Organic Compounds from Aqueous Solution on Activated Carbon

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The adsorption isotherms, from aqueous solution onto activated carbon, have been determined for the 22 aliphatic monofunctional compounds; alcohols, carboxylic acids, ketones, ethers, esters, and aldehydes. The free energy change for the adsorption process has been calculated from the adsorption equilibrium constant at infinite dilution; a linear relationship exists between the free energy change and the number of carbon atoms in the solute. The free energy of adsorption has been divided into two contributions: the hydrocarbon and the functional group contribution. The free energy change for the adsorption process has been compared with the free energy change for the precipitation process from solution into the pure liquid solute. The free energy contribution per individual methylene group to the adsorption process shows an approximate agreement with that for the precipitation process indicating that the adsorption process of the hydrocarbon portion of the solute is analogous to the precipitation process. The free energy contribution of the functional group to the adsorption process is smaller than that for the precipitation process indicating that the functional group portion of the solute is not appreciably dehydrated in the adsorption phase.

The adsorption theory in the gas phase has been extensively investigated but not in the liquid phase. In gas phase adsorption Polanyi's potential theory[1] and its modifications[2-5] have been widely used. In the theory Polanyi considered the energy processes in transferring a molecule from the gas to the adsorbed state and concluded that the free energy change in passing from the gaseous to the saturated liquid state represents a valid criterion for the free energy change of the whole process.

In liquid phase adsorption the potential theory has been applied by Hansen and Fackler[6] to the adsorption of liquid mixtures on carbon black, and by Manes[7] *et al.* to the adsorption of solids from several solvents on activated carbon. Polanyi originally supposed that the adsorption of solid solutes from solution was analogous to the adsorption of gases with precipitation of the solid taking the place of liquefaction of the gas, *i.e.*, the adsorption process was identically equal to the reverse of the solution process. This suggests that the free energy change for the adsorption process is analogous to the reverse of the solution process.

In this study, the free energy change of the adsorption process for aliphatic monofunctional compounds has been determined and compared with the free energy change of the solution process.

Experimental

Materials. The adsorbent in all instances came from a single batch of Pittsburgh Activated Carbon (grade CAL) which was ground and sieved to yield 200×350 mesh size. After sieving, the carbon was washed with distilled water to remove all fines and dried at 110 °C. The BET surface area found from nitrogen adsorption at 77 K was 1010 m²/g. The pore volume was 0.575 ml/g, when calculated from the limiting vapor adsorption at $P/P_0 \rightarrow 1$. The experimental conditions and the pore volumes determined are listed in Table 1.

All organic compounds were purchased from commercial sources and distilled, if necessary, to a minimum purity of 99% as determined by gas chromatography. All aldehydes were used without further purification.

TABLE 1. PORE VOLUME OF THE ADSORBENT CALCULATED FROM THE LIMITING VAPOR ADSORPTION AT $P/P_0 \rightarrow 1$

Adsorbate	Temperature (K)	Pore volume (ml/g)
Nitrogen[a]	77	0.586
Methanol[b]	298	0.573
2-Butanone[b]	298	0.568
Benzene[b]	298	0.572
		Av 0.575

a) Measured with BET adsorption apparatus. b) Measured by a modification of Hirata's method.[8]

Procedure. Equilibration took place in 50-ml double stoppered flasks, which were shaken for a minimum of 14 h at 25 °C in a thermostated bath; check experiments at longer shaking times established that the shaking time sufficed for equilibration. In order to eliminate loss through evaporation, pressure filtration was chosen for removing the carbon from the solution. The concentration of solute was analysed by determining the total organic carbon in a Shimadzu Model TOC-10A analyzer. The amount of adsorbed solute (mg) on carbon (grams) was calculated from the following relation:

$$X = \frac{V \cdot \Delta C}{M} \tag{1}$$

where ΔC (mg/l) is the solute concentration decrease due to adsorption and V (l) is the volume of solution added to M (g) of carbon.

Results

Figures 1—6 illustrate the 25 °C adsorption isotherms for alcohols, carboxylic acids, ketones, ethers, esters, and aldehydes, from solution, onto CAL carbon. The adsorption isotherms have been approximated by the adsorption Eqs. 2 and 3:

$$\frac{C}{X} = a_0 + a_1 C \tag{2}$$

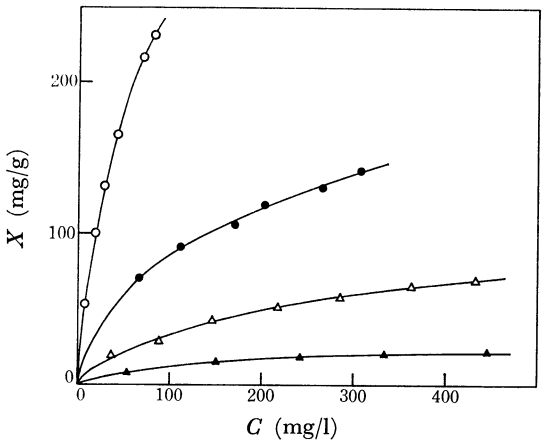

Fig. 1. Adsorption isotherms of alcohols on CAL activated carbon from aqueous solutions, 25 °C. ▲: 1-Propanol, △: 1-butanol, ●: 1-pentanol, ○: 1-hexanol.

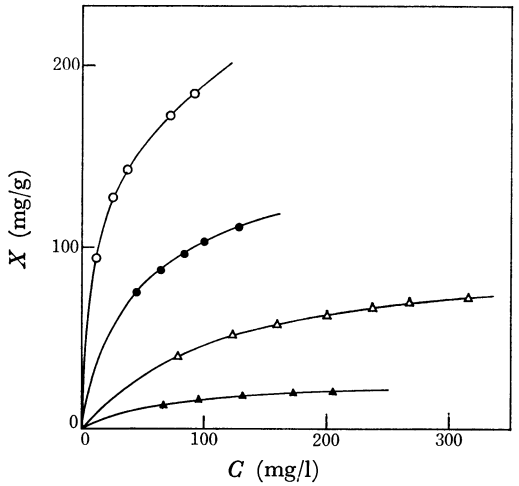

Fig. 2. Adsorption isotherms of carboxylic acids on CAL activated carbon from aqueous solutions, 25 °C. ▲: Propionic acid, △: butyric acid, ●: valeric acid, ○: hexanoic acid.

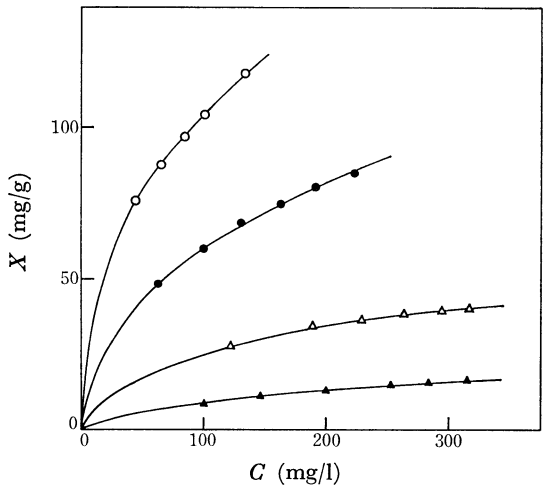

Fig. 3. Adsorption isotherms of ketones on CAL activated carbon from aqueous solutions, 25 °C. ▲: Acetone, △: 2-butanone, ●: 2-pentanone, ○: 2-hexanone.

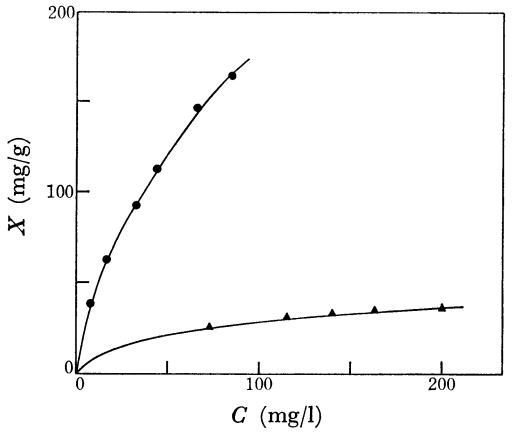

Fig. 4. Adsorption isotherms of ethers on CAL activated carbon from aqueous solutions, 25 °C. ▲: Diethyl ether, ●: dipropyl ether.

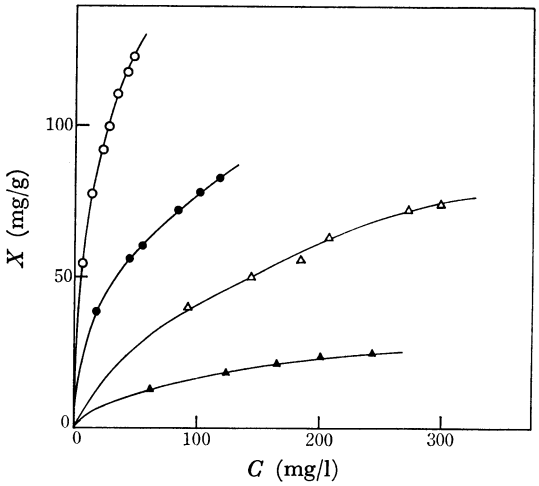

Fig. 5. Adsorption isotherms of esters on CAL activated carbon from aqueous solutions, 25 °C. ▲: Methyl acetate, △: ethyl acetate, ●: propyl acetate ○: butyl acetate.

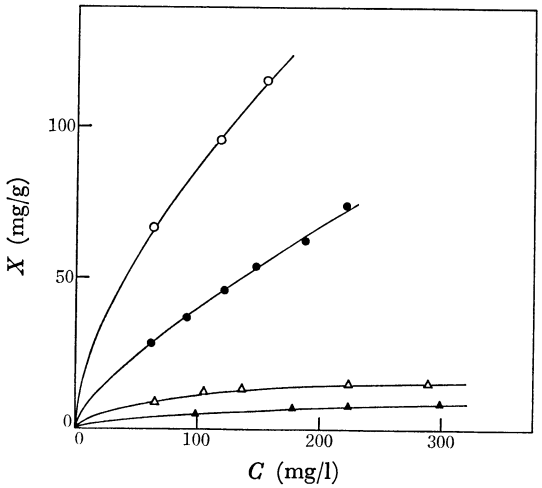

Fig. 6. Adsorption isotherms of aldehydes on CAL activated carbons from aqueous solutions, 25 °C. ▲: Acetaldehyde, △: propionaldehyde, ●: butyraldehyde, ○: valeraldehyde.

Table 2. Adsorption parameters of various organic compounds on CAL activated carbon from aqueous solutions (25 °C)

Compound	$b_2 \times 10^5$	b_1	b_0	α	a_1	a_0
[Alcohols]						
1-Propanol	−2.24	0.0407	5.43	0.184	0.0292	6.17
1-Butanol	−1.49	0.0167	1.48	0.680	0.0148	1.21
1-Pentanol	−0.794	0.00801	0.443	2.25	0.00539	0.609
1-Hexanol	−0.729	0.00356	0.110	9.08	0.00301	0.116
[Carboxylic acids]						
Propionic acid	11.7	0.00526	4.35	0.230	0.0342	2.84
Butyric acid	0.469	0.00870	1.24	0.813	0.0103	1.13
Valeric acid	−0.545	0.00770	0.260	3.84	0.00692	0.285
Hexanoic acid	−1.06	0.00569	0.0621	16.1	0.00480	0.0735
[Ketones]						
Acetone	−3.31	0.0448	7.96	0.125	0.0316	9.14
2-Butanone	1.63	0.0114	2.78	0.361	0.0180	2.20
2-Pentanone	−0.652	0.0100	0.719	1.39	0.00845	0.795
2-Hexanone	−2.01	0.00974	0.195	5.13	0.00652	0.306
[Ethers]						
Diethyl ether	2.77	0.0133	1.83	0.548	0.0203	1.43
Dipropyl ether	−3.39	0.00719	0.145	6.91	0.00531	0.152
[Esters]						
Methyl acetate	2.84	0.0196	3.65	0.274	0.0276	3.20
Ethyl acetate	−1.71	0.0148	1.10	0.913	0.00895	1.51
Propyl acetate	−3.02	0.0136	0.236	4.24	0.0103	0.295
Butyl acetate	−4.44	0.00892	0.0633	15.7	0.00711	0.0740
[Aldehydes]						
Acetaldehyde	2.84	0.0424	17.8	0.0561	0.0538	16.8
Propionaldehyde	13.3	0.00674	6.63	0.151	0.0445	4.70
Butyraldehyde	−2.44	0.0119	1.56	0.641	0.00577	1.89
Valeraldehyde	−2.64	0.00995	0.413	2.41	0.00465	0.646

$$\frac{C}{X} = b_0 + b_1 C + b_2 C^2 \tag{3}$$

where C is the equilibrium concentration; X is the amount of adsorption at C; a_0, a_1, b_0, b_1, and b_2 are constants. The results of regression analysis using Eq. 2 or Eq. 3 are presented in Table 2.

The adsorbability (α) of solute at infinite dilution has been defined as follows:

$$\alpha \equiv \lim_{C \to 0} \frac{X}{C} \tag{4}$$

In order to determine the adsorbability, C/X has been plotted against C from the data of Figs. 1—6 and the result for butyl acetate shown in Fig. 7. The intercept of the adsorption isotherm gives the value of α. It is evident from Fig. 7 that the experimental data more closely approximates to Eq. 3 than to Eq. 2 and consequently the value of α has been taken from Eq. 3. The values of α ($1/b_0$) are presented in Table 2.

Equation 2 is of Langmuir type:

$$\frac{C}{X} = \frac{1}{aX_m} + \frac{C}{X_m} \tag{5}$$

where X_m is the amount of adsorption at saturation

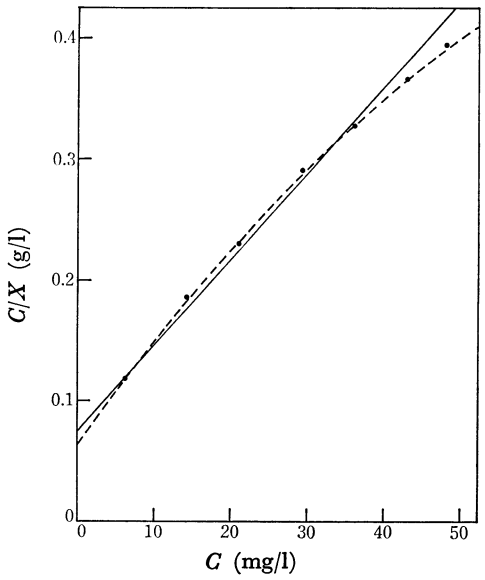

Fig. 7. Adsorption isotherm of butyl acetate on CAL activated carbon from aqueous solution, 25 °C. ●: Experimental, ——: best fitting model Eq. 2, ----: best fitting model Eq. 3.

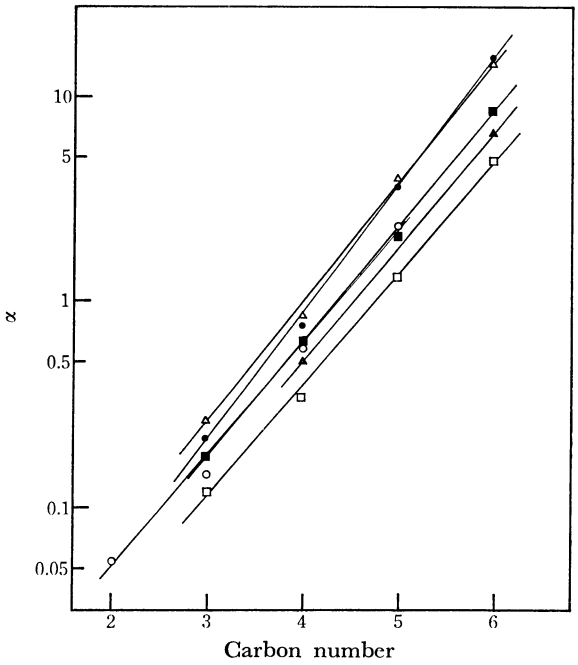

Fig. 8. Relationship between adsorption constant α and carbon atom number N. ○: Aldehydes, ●: carboxylic acids, △: esters, ▲: ethers, □: ketones, ■: alcohols.

and a is a constant. The value of α calculated by Eq. 2 is identical with X_m $(=1/a_0)$. As can be seen from Table 2, there is little difference between $1/b_0$ and $1/a_0$.

Figure 8 illustrates the relationship between log α and the number of carbon atoms in the solute. It can be seen from Fig. 8 that for a homologous series the following relation exists:

$$\log \alpha = \beta N + \gamma \tag{6}$$

where N is the number of carbon atoms and β and γ are constants. This demonstrates that Traube's rule[9] is valid in the adsorption of the homologous paraffin chain solutes.

For a thermodynamic study of adsorption from solution, it is necessary to determine the standard free energy change ΔG°. Alexander and Johnson[10] calculated ΔG° by the following equation:

$$\Delta G^\circ = -RT \ln\left(\frac{\Gamma}{tC_{\text{bulk}}}\right) \tag{7}$$

where Γ is the surface excess per unit area and t the thickness of the adsorbed layer. In this equation it is assumed that the adsorbed molecules behave ideally. Fu and Bartell[11] showed that the activity coefficient of the adsorbate on the solid greatly differed from unity, and proposed that the equilibrium constant K for the process (8) should be obtained from the limiting slope of the adsorption isotherms at zero concentration, in which the adsorbates behave ideally:

$$\text{Solute in solution} \rightleftharpoons \text{Solute in adsorption phase.} \tag{8}$$

In order to determine K, it is necessary to convert the amount of adsorption into concentration and for this purpose, the volume of the adsorption phase must be determined. Bartell[12] *et al.* used the product of the surface area of the adsorbent and the thickness of the adsorbed layer as the volume. In the case of high-porous adsorbents such as activated carbon, however, the adsorption process may be regarded as pore filling rather than monolayer coverage[13] and consequently the pore volume has been adopted as the volume of the adsorption phase. It has been assumed that the pore volume is equal to the volume calculated from the limiting vapor adsorption at $P/P_0 \rightarrow 1$, and that every pore contributes in the same manner to the adsorption of adsorbate. It may be seen from Table 1 that the volume is almost independent of the nature of vapor. Hence an average of the values obtained from four vapors has been adopted as the volume of CAL carbon (0.575 ml/g). After the volume of adsorption phase (V) has been obtained, K and ΔG° may be calculated from the following equation:

$$K = \alpha/V \tag{9}$$

$$\Delta G^\circ = -RT \ln K. \tag{10}$$

By substituting for K from Eq. 9 into Eq. 10 and for log α from Eq. 6 into Eq. 10, it may be shown that at a certain temperature:

$$\begin{aligned}\Delta G^\circ &= -RT(\ln \alpha - \ln V) \\ &= -2.303RT(\beta N + \gamma - \log V) \\ &= \beta_0 N + \gamma_0\end{aligned} \tag{11}$$

where β_0 and γ_0 are constants. The constants and the correlation coefficients calculated by regression analysis are given in Table 3. The overall statistics are excellent with an average correlation coefficient of 0.9990. The constant β_0 corresponds to the standard free energy change per individual methylene group ($\Delta G^\circ_{\text{C}}$) and γ_0 to the functional group contribution for ΔG°. Therefore, assuming that the hydrocarbon and functional portions contribute independently to the standard free energy change for monofunctional aliphatic compounds, it follows that:

$$\Delta G^\circ = \Delta G^\circ_{\text{HY}} + \Delta G^\circ_{\text{FG}}. \tag{12}$$

For the compounds examined in this study, $\Delta G^\circ_{\text{HY}}$ may be expressed by the following equation:

$$\Delta G^\circ_{\text{HY}} = \Delta G^\circ_{\text{C}} \cdot N = \beta_0 \cdot N \tag{13}$$

As seen from Table 3, $\Delta G^\circ_{\text{C}}$ and $\Delta G^\circ_{\text{FG}}$ give similar values for all functional groups (the averages are -779 cal/mol and -1060 cal/mol, respectively).

Table 3. Results of regression analysis using Eq. 11

Compound	$-\beta_0$	$-\gamma_0$	Correlation coefficient r
Alcohols	764	1120	0.9996
Carboxylic acids	848	969	0.9993
Ketones	740	925	0.9987
Ethers	755	1040	1.0000
Esters	811	1190	0.9991
Aldehydes	755	1140	0.9974

Discussion

The free energy change for the solution process has been calculated by Amidon[14,15] *et al.* The molecular surface area for 158 aliphatic hydrocarbons, olefins, alcohols, ethers, ketones, aldehydes, esters, and fatty

Table 4. Free energy contribution per one methylene group to the solution process

Compound	$\Delta G^{\circ}_{C,sol}$ (cal/mol)
Alcohols	798
Carboxylic acids	759
Ketones/Aldehydes	807
Ethers	872
Esters	720
	Av 791

acids were computed and correlated with the aqueous solubilities. For monofunctional aliphatic compounds the total surface area (*TSA*) may be divided into two contributions, namely the hydrocarbon (*HYSA*) and functional group (*FGSA*) contributions.

$$TSA = HYSA + FGSA \quad (14)$$

Assuming that the hydrocarbon and functional group portions contribute independently, the following generalized equation is suggested for use in solubility correlations:

$$\log S = \Theta_1 \cdot HYSA + \Theta_2 \cdot FGSA + \Theta_3 \cdot IFG + \Theta_0 \quad (15)$$

where S is the aqueous solubility, Θ_0 is the intercept, and *IFG* is the functional group index (zero for hydrocarbons and unity for a monofunctional compound). From the coefficients for the *HYSA* term in Eq. 15, the free energy contribution per individual methylene group to the solution process ($\Delta G^{\circ}_{C,sol}$) may be calculated (assuming 31.8 Å^2 as the area per CH_2 group). The value of $\Delta G^{\circ}_{C,sol}$ for each homologous series is shown in Table 4. The average $\Delta G^{\circ}_{C,sol}$ value is 791 cal/mol and shows approximate agreement with the value of $-\Delta G^{\circ}_{C,ad}$ (779 cal/mol) obtained from the adsorption of the same homologous series on CAL carbon from aqueous solutions. This suggests that the adsorption process of the hydrocarbon portion of solute is analogous to the precipitation process from the aqueous solution into the pure liquid solute, and that the solute in the adsorption phase is in the liquid form. The Polanyi adsorption potential theory is also based on the concept that the adsorption process is identical to the precipitation process.

For the six groups of compounds included in Table 4 the general tendency is that the more polar compounds give smaller methylene group hydrophobic effects. On the other hand, Table 3 indicates that the more hydrophobic compounds have smaller hydrophobic effects caused by the methylene group. This may be due to the different effect of a methylene unit on the solute-solute interaction between the adsorption phase and the pure liquid solute phase.

The free energy contribution of the functional group to the solution process ($\Delta G^{\circ}_{FG,sol}$) may be calculated from the *FGSA* and *IFG* terms in Eq. 15. The hydroxyl group contributes −3.81 kcal/mol to the free energy of solution for the addition of a hydroxyl group to a normal hydrocarbon in the 1-position.[14] The values of $\Delta G^{\circ}_{FG,sol}$ for other functional groups are similar in magnitude to that for the hydroxyl group.[15] The free energy contribution of the functional group to the adsorption process ($\Delta G^{\circ}_{FG,ad}$) is on average −1.06 kcal/mol for the six groups of compounds in Table 3, suggesting that the adsorption of the functional group portion of the solute differs from the precipitation process. There are, however, certain factors that influence the value of $\Delta G^{\circ}_{FG,ad}$. The first is the volume of the adsorption phase. The volume of the adsorption phase in liquid phase may differ from that in the gas phase. Assuming that the volume is half the value in Table 1, the value of $\Delta G^{\circ}_{FG,ad}$ decreases from −1.06 kcal/mol to −1.47 kcal/mol. Therefore, the influence of this factor on the value of $\Delta G^{\circ}_{FG,ad}$ would not be very large.

Table 5. Free energy contribution of functional groups to the adsorption process

Compound	Functional group	Number of methyl groups	γ_1 (cal/mol)	γ_2 (cal/mol)
Alcohols	-OH	1	230	230
Carboxylic acids	-COOH	1	381	−467
Ketones	>CO	2	1775	1035
Ethers	-O-	2	1660	1660
Esters	-COOR	2	1510	699
Aldehydes	-CHO	1	210	−545

The second factor is the validity of extrapolation of the linear relationship in Eq. 11. The estimation of $\Delta G^{\circ}_{FG,ad}$ from the intercept is based on the assumption that every carbon atom in a solute compound makes the same contribution to the free energy as one methylene group. It has, however, frequently been noted that a methyl group and a methylene unit make different contributions:[16–18] the contribution to the free energy of solution for a methyl group is greater by approximately 1.35 kcal/mol than that for a methylene group.[14] The value of γ_0 in Table 3 has been corrected on the basis that the adsorption process on hydrocarbons is identical with the precipitation process, the value of the corrected γ_0 being given in the fourth column of Table 5. A similar correction must be made for the carbon atom in the functional group. The value of γ_1 does not contain the free energy contribution of the carbon atom in the functional group and it is difficult to estimate this contribution. The free energy contribution of the functional group containing the carbon atom is given in the fifth column of Table 5.

The third factor is the effect of the surface oxygen complex of activated carbon on adsorption.[19–21] The dominant component of the driving force for adsorption is the dispersion component of the Van der Waals forces. However, the polarizing component of the Van der Waals forces also contributes to adsorption for polar or polarizable substances. Consequently it is assumed that the value of γ_2 for carboxylic acids and aldehydes is smaller than that of other functional groups due to these polar effects. Aldehydes may be converted in part to carboxylic acids by oxidation in aqueous solution.

It is necessary to take into further consideration other factors in order to exactly estimate the free energy contribution of the functional group. However, in

view of these three main factors, the following conclusions may be derived. The free energy contribution of the functional group to the adsorption process is smaller than the free energy contribution of the functional group to the precipitation process, *i.e.*, the functional group of the solute molecule in the adsorption phase is appreciably hydrated.

The functional groups of alcohols, carboxylic acids, and aldehydes suffer little dehydration and be present in the solution phase, since the functional groups are situated at terminal positions in the alkyl chain. On the other hand, the functional groups of ketones, ethers, and esters would be more dehydrated and be present in the pores of the activated carbon, since the functional groups are situated between the alkyl chains.

The potential theory in liquid phase adsorption assumes that the adsorption of solute take place by precipitation of the solute in the adsorption phase. From the present investigation, however, it has become apparent that the adsorption of solute takes place by precipitation of the hydrocarbon portion of the solute and that the functional group portion of the solute is not appreciably dehydrated in the adsorption phase.

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References

1) M. Polanyi, *Verh. Deut. Phys. Ges.*, **16**, 1012 (1914); **18**, 55 (1916); *Z. Electrochem.*, **26**, 370 (1920); *Z. Phys.*, **2**, 111 (1920).
2) M. M. Dubinin, *Chem. Rev.*, **60**, 235 (1960).
3) M. M. Dubinin, E. D. Zaverina, and L. V. Radushkevich, *Zh. Fiz. Khim.*, **21**, 1351 (1947).
4) L. V. Radushkevich, *Zh. Fiz. Khim.*, **23**, 1410 (1949).
5) M. M. Dubinin and V. A. Astakhov, *Adv. Chem. Ser.*, **102**, 69 (1970).
6) R. S. Hansen and W. V. Fackler, *J. Phys. Chem.*, **57**, 634 (1953).
7) a) M. Manes and L. J. E. Hofer, *J. Phys. Chem.*, **73**, 584 (1969); b) D. A. Wohleber and M. Manes, *ibid.*, **75**, 61 (1971); c) D. A. Wohleber and M. Manes, *ibid.*, **75**, 3720 (1971).
8) M. Hirata, T. Kiryu, A. Omi, and Y. Sugiyama, *Kagaku Kogaku*, **24**, 572 (1960).
9) I. Traube, *Ann.*, **265**, 27 (1891).
10) A. E. Alexander and P. Johnson, "Colloid Science," Clarendon, Oxford (1949), Vol. 1.
11) Y. Fu, R. S. Hansen, and F. E. Bartell, *J. Phys. Colloid Chem.*, **52**, 374 (1948); **53**, 1141 (1949).
12) F. E. Bartell, T. L. Thomas, and Y. Fu, *J. Phys. Chem.*, **55**, 1456 (1951).
13) K. S. W. Sing, *Ber. Bunsenges. Phys. Chem.*, **79**, 724 (1975).
14) G. L. Amidon, S. H. Yalkowsky, and S. Leung, *J. Pharm. Sci.*, **63**, 1858 (1974).
15) G. L. Amidon, S. H. Yalkowsky, S. T. Anik, and S. C. Valvani, *J. Phys. Chem.*, **79**, 2239 (1975).
16) R. Aveyard and R. W. Mitchell, *Trans. Faraday Soc.*, **66**, 37 (1970).
17) P. Molyneux, C. T. Rhodes, and J. Swarbrick, *Trans. Faraday Soc.*, **61**, 1043 (1965).
18) G. Nemethy, I. Z. Steinberg, and H. A. Scheraga, *Biopolymers*, **1**, 43 (1963).
19) P. H. Emmett, *Chem. Rev.*, **43**, 69 (1948).
20) J. J. Kipling, *Quart. Rev.*, **10**, 1 (1956).
21) M. M. Dubinin and E. D. Zaverina, *Zh. Fiz. Khim.*, **23**, 469 (1949).