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APPLICATION OF THE POLANYI ADSORPTION POTENTIAL THEORY TO ADSORPTION OF SURFACTANTS FROM AQUEOUS SOLUTION ON ACTIVATED CARBON[1)]

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A method, which is based on the Polanyi adsorption potential theory, is presented for estimating the adsorption isotherms of surfactants from aqueous solution onto activated carbon, from the knowledge of the critical micelle concentration, the molar volume, and a "characteristic curve" determined from a single isotherm.

The Polanyi adsorption potential theory[2)] for gases may be formulated as follows:

$$\varepsilon = RT \ln (Ps/P) \tag{1}$$

$$W = f(\varepsilon) \tag{2}$$

where ε is the adsorption potential, P the equilibrium pressure of the vapor, Ps the vapor pressure of the corresponding liquid at the equilibrium temperature T, W the volume of adsorption space. The function f represents the distribution of volume of the filled adsorption space according to adsorption potentials. Dubinin,[3),4)] Lewis,[5)] and Grant[6)] *et al.* have compared the experimental adsorption isotherms of various adsorbates with the corresponding molar volumes (V), and have found that the plots of volume adsorbed *vs.* ε/V collapsed to a single curve with considerable accuracy :

$$W = f' \ (\varepsilon/V) \tag{3}$$

In liquid phase adsorption the Polanyi potential theory[7)] has been applied by Manes[8)] *et al.* to the adsorption of solids from several solvents on activated carbon. The underlying theory may be summarized as follows.

The adsorption of solid solute takes place by the precipitation of the solute on the surface with potential estimated as :

$$\varepsilon_{sl} = RT \ln (Cs/C) \tag{4}$$

where Cs and C are the saturated and the equilibrium concentrations. The adsorption of the solute must be accompanied by the desorption of an equal volume of solvent. Equation 4 therefore becomes :

$$\varepsilon_{sl} = \varepsilon_s - \varepsilon_l(Vs/Vl) \tag{5}$$

where ε_s and ε_l are the adsorption potentials of solute and solvent adsorbing as vapor and Vs and V_l, the molar volumes of (solid) solute and solvent. We can rewrite Eq. 5 as :

$$\varepsilon_{sl}/Vs = \varepsilon_s/Vs - \varepsilon_l/V_l \tag{6}$$

Let us now consider the adsorption of surfactants from aqueous solution on activated carbon. It is obvious from Eq. 3 that ε_s/V_s is a function of W. In the case of the adsorption from water, $(\varepsilon_s/V_s - \varepsilon_l/V_l)$ is also a function of W, since ε_l/V_l is identical for each solute. Consequently, the following relation may be derived :

$$W = f^\circ(\varepsilon_{sl}/V_s) \tag{7}$$

where f° is the function of the characteristic curve.

The potential theory in liquid phase adsorption assumes that the adsorption process of solute takes place by precipitation of the solute in the adsorption phase. However, we have recently determined the free energy change of the adsorption of aliphatic monofunctional compounds from aqueous solutions and compared with the free energy change of the precipitation process of the same compound from water to pure liquid solute and the following results have been obtained[9]: 1) The free energy contribution per one methylene group to the adsorption process (–779 cal/mol) showed an approximate agreement with that of the precipitation process indicating that the adsorption process of hydrocarbon portion of solute is analogous to the precipitation process. 2) The free energy contribution of functional group to the adsorption process is smaller than that of the precipitation process indicating that the functional group portion of solute is appreciably hydrated and is present in the solution phase.

These results suggest that the pores of activated carbon are occupied by the alkyl group of the surfactant molecule provided the hydrophilic group is situated at the terminal position in the alkyl chain. Hence the filled volume of adsorption space may be expressed as :

$$W = a\cdot\overline{V}_s \tag{8}$$

where a is the amount of adsorption and $\overline{V}_s$ the molar volume of the alkyl group.

The thermodynamic behavior associated with the adsorption on activated carbon is similar to that associated with the formation of micelles, *e.g.*, the contribution of a methylene group to the free energy of micelle formation is –755 cal/mol, and the contribution of the hydrophilic group is much smaller than that of the methylene group.[10] Assuming that a surfactant molecule in adsorbed phase is energetically identical with that in the micelle phase, ε_{sl} may be expressed as :

$$\varepsilon_{sl} = RT\ln(\mathrm{CMC}/C) \tag{9}$$

Substituting Eq. 8 and 9 into Eq. 7 yields the following equation :

$$a\cdot\overline{V}_s = f^\circ(RT\ln(\mathrm{CMC}/C)/\overline{V}_s) \tag{10}$$

This equation indicates that the adsorption isotherms of various surfactants can be superimposed on a single characteristic curve represented by the function f°.

In order to verify experimentally the validity of Eq. 10, the adsorption isotherms of the sodium alkyl sulfonates with carbon number 3 – 13 were measured at 40°C. The adsorbent was Pittsburgh Activated Carbon (grade CAL), which was ground and sieved to yield 200 x 350 mesh size. The BET surface area found from nitrogen adsorption at 77 K was 1010 m^2/g. The pore volume was 0.575 ml/g, when calculated from the limiting vapor adsorption at $P/P_0 \rightarrow 1$.[9]

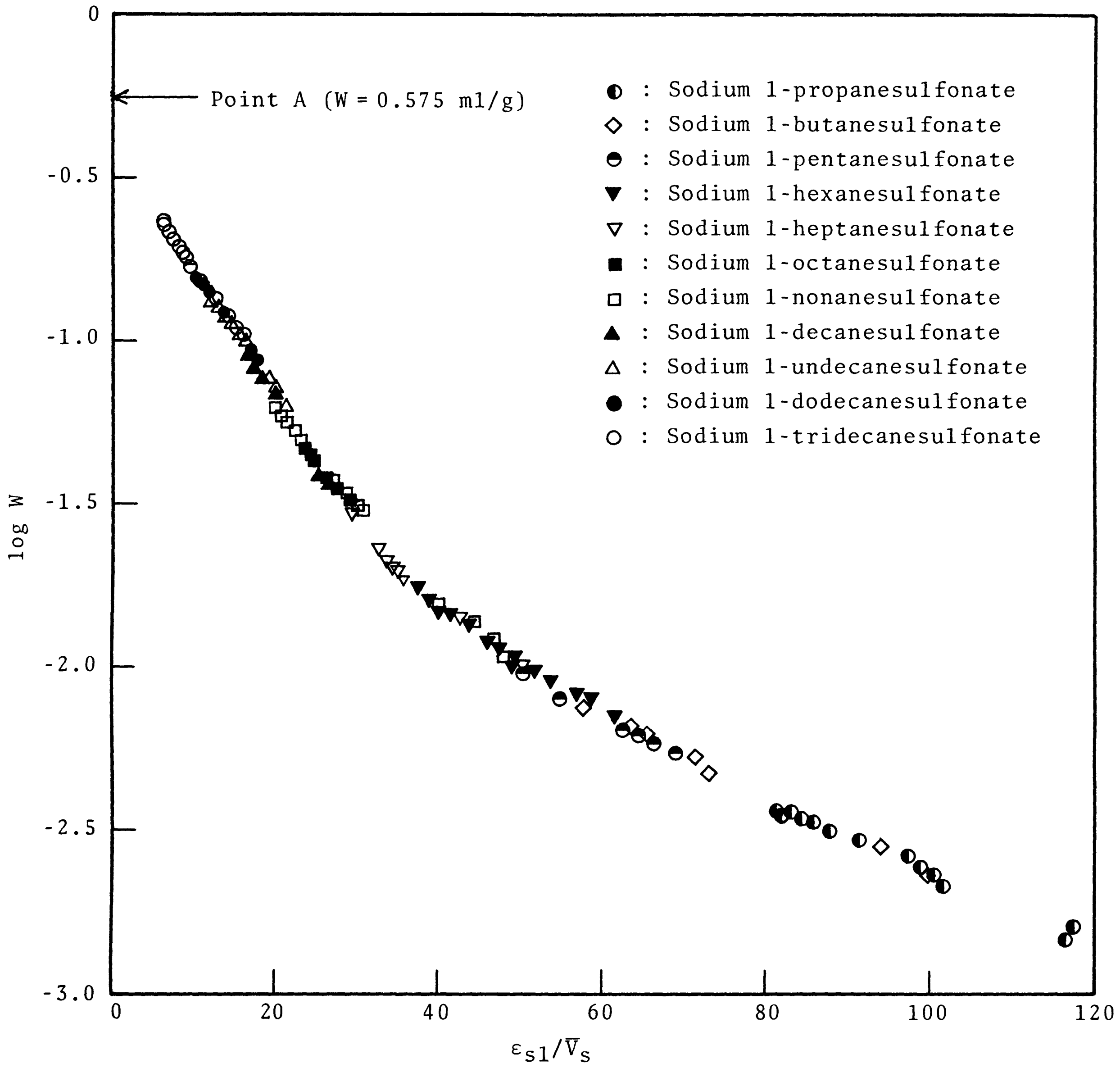

Fig. 1. Adsorption isotherms of sodium alkyl sulfonates from aqueous solutions on CAL activated carbon, 40°C.

For sodium alkyl sulfonates the following relation exists between the critical micelle concentration (CMC) at 40°C and the carbon number (N) :11)

$$\log \mathrm{CMC} = 1.59 - 0.294\,N \qquad (11)$$

The CMC of lower alkyl sulfonates was calculated from Eq. 11 on the assumption that these surfactants form the micelles.

In order to estimate the molar volume of the alkyl group, the molar volume per one methylene group and methyl group have been determined from the molar volume of pentane – decane ($-CH_2-$: 16.0 ml/mol, $-CH_3$: 33.9 ml/mol). By the use of the values, the molar volume of the saturated linear alkyl group may be approximated by the following equation :

$$\overline{V}_S = 16.0\,N + 17.9 \qquad (12)$$

The adsorption data for these surfactants were correlated by Eq. 10 and the plots of log W *vs.* $\varepsilon_{sl}/\overline{V}_S$ were illustrated in Fig. 1.

It can be seen from Fig. 1 that all isotherms are superimposed on a single characteristic curve. The extrapolated value of the curve at $\varepsilon_{sl}/\overline{V}_S = 0$ represents the limiting volume of the adsorption space and is equal to the value of pore volume calculated from vapor adsorption (W = 0.575 ml/g at Point A). These results indicate that the adsorption isotherms of sodium alkyl sulfonates can be expressed by Eq. 10 derived from the Polanyi adsorption theory. The function f° reflects the porous structure of the given activated carbon only and does not depend on adsorbate. If the function f° for a given activated carbon is determined from a single isotherm of a surfactant, the adsorption isotherms for other surfactants can be calculated from Eq. 10 and the known values of CMC and $\overline{V}_S$. These relations may be also applicable to the other adsorbent-adsorbate systems in which hydrophobic interactions are the dominant component of adsorption interaction.

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