THE STATE OF WATER ON PURE AND SILICON-ALLOYED LTI-CARBONS*

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The state of water attached to surfaces assumes an important role when, among others, these materials are placed in contact with a biological environment. This is particularly true for a low temperature isotropic (LTI) or silicon-alloyed (SLTI) carbon surface contacting blood in devices implanted into humans. Under these conditions, the adsorption of flexible macromolecules such as native proteins takes place, and the mechanism as well as the energetics of protein sorption is affected by the degree to which water is structured on those surfaces.

Microparticulate adsorbents composed of either 3% pure LTI-carbon or, 96.7% pure SLTI-carbon containing on the order of 10% by weight silicon, were obtained from discs which were prepared at the Medical Products Div., General Atomic Co. by deposition of the corresponding types of carbon on stainless steel substrates. The pulverization of both types of discs, which was carried out over extended periods of time, was performed in non-metallic equipment to avoid any contamination.

Both LTI- and the SLTI-carbon adsorbents were polydisperse particles measuring \( \leq 1\mu \) in the SEM. Specific surface area (\( \Sigma \)) determinations performed on B. E. T. multipoint N\(_2\) adsorption at -195°C gave 19.2 m\(^2\)/g for the pure LTI-carbon and 52.8 m\(^2\)/g for SLTI-carbon. In both cases, these \( \Sigma \)'s have been disproportionately greater than the specific surface area that can be estimated (viz., 10-20 m\(^2\)/g) based on the particle sizes observed and the density of the materials. This has indicated the presence of internal porosity in both types of adsorbents, which, in the case of LTI-carbon, is consistent with the established internal micromorphology of that substance.\(^1\) The value of \( \Sigma \) obtained for the SLTI-carbon, indicating of a smaller degree of porosity, is consistent with the known effects of silicon-alloying on pyrolytic carbon microstructure. To determine the pore size and shape distributions of both adsorbents, (a) the measured hysteresis between their 250°C water vapor adsorption and desorption isotherms, and (b) the pressurized mercury penetration technique\(^2\) were utilized. Analyses of these data revealed that, in both powders, their porosity is constituted by "ink-bottle" pores. The same analyses gave 27.7 and 17.8 m\(^2\)/g, respectively, for the LTI- and SLTI-carbon adsorbents as their surface areas which are exclusive of the internal surface area associated with the "ink-bottle" pores. The relatively greater degree of internal porosity in the LTI-carbon adsorbent is substantiated by the fact that its ratio between its B. E. T. surface area and "pore-free" area (3.9) is greater than that obtained for SLTI-carbon powder (3.0).

For each of the 2 microparticulate adsorbents, the 0\(^\circ\), 250 and 370°C water vapor adsorption isotherms were determined using a vacuum quartz-spring balance described elsewhere.\(^3\)

For both the LTI- and SLTI-carbon adsorbents, their 250 and 370°C heats of immersion were also determined in (a) pure water, \( h_f(SLW)_T \), and (b) a sodium acetate/HCl buffer, \( h_f(SLB)_T \), having a pH of 7.4 and an ionic strength of 0.05. These heats were measured using a custom-built, isothermal-jacketed thermistorized microcalorimeter system having a sensitivity of \( \pm 1 \times 10^{-5}\)°C when charged with 100 ml of liquid volume. Details of the design, specifications and operation of this instrument have been described elsewhere.\(^4\)

The 250 and 370°C microelectrophoretic mobilities of each of the 2 adsorbents were determined in the buffer specified above. These experiments were performed in a calibrated precision-bore glass capillary cell having a ground optical polished flat. For each adsorbent, the mobilities of an average of 12-14 particles were individually determined, after all particles > 1μ were allowed to settle out. All mobility values obtained at 370°C have been corrected to 250°C according to standard methods.

All water vapor adsorption isotherms which have been obtained at the 3 specified temperatures, are of Type II for both the microparticulate LTI- and SLTI-carbon adsorbents. Consistent with the internal porosity found in both materials, determination of their heats of water vapor adsorption in the first statistical monolayer can not be performed according to the B.E.T. method. For both adsorbents, every isotherm plotted in terms of the B.E.T. function vs. relative pressure deviates from linearity at values of \( p_T/p_T^0 \approx 0.1 \). In fact, when plotted up to \( p_T/p_T^0 = 0.3 \), the B.E.T. isotherm of SLTI-carbon appears to be parabolic.

Comparison of the water vapor adsorption and desorption isotherms of the LTI-carbon powder did not indicate hysteresis up to \( p_T^f/p_T^0 \approx 0.3 \), and those of the SLTI-carbon up to \( p_T^f/p_T^0 \approx 0.4 \). Thus, the application of standard thermodynamic functions which imply equilibrium conditions is justified in the range up to those relative pressures. Differential isosteric heats of adsorption have been computed using \( q_{st} = (RT_T^2/p_T^2 - T_1)\ln(p_1/p_2) \) where \( T_2 \) is taken as either 310, 160 or 298, 190K, with \( T_1 = 273, 190K \), and \( p_1 \) and \( p_2 \) denote the measured equilibrium pressures at the respective temperatures. With this set of \( q_{st} \) values and the computable free
energies of sorption, changes in entropy and the entropy of sorbed layers have been determined.

Within the relative pressure range specified above, each of the isosteric heat curves of LTI-carbon power absorbers which were activated either at 25°C or 37°C, display 2 peaks as a function of surface coverage. The first peak is quite sharp, and is centered at a coverage of 2 x 10^{13} molec/cm², with a maximum heat of adsorption that is about 5.5 Kcal/mole greater than Q (~10.6 Kcal/mole), the latent heat of condensation of water vapor. The second peak which is flatter but more broad, is centered at 2.5 x 10^{14} molec/cm², with a maximum ~1.5 Kcal/mole > Q. The peaks indicate the presence of 2 types of heterogeneous (viz., non-carbon) active sites on the LTI-carbon surface, which are capable of binding water in an ordered state. In the domain of these peaks, the differential and integral entropies of water sorbed onto LTI-carbon are significantly below the entropy value of bulk liquid water at the corresponding temperatures. At surface coverages > 4 x 10^{14} molec/cm², qₜ rapidly approaches the value of Q indicating the absence of interaction between water and the LTI-carbon surface.

The microcalorimetrically-determined 25°C and 37°C heats of immersion of the LTI-carbon powder into pure water are, respectively, -66.7 ± 4.7 erg/cm², and -62.6 ± 4.7 erg/cm², which are statistically indistinguishable indicating no temperature-dependence. As compared to Graphon, which is a graphitized carbon black with a comparable B.E.T. N₂ surface area of 95.0 m²/g and an h₁(SLW)₂₅₀ = -32.4 ± 4.0 erg/cm²,[5] the LTI-carbon surface is more polar. After conversion into the appropriate units, the integral of the qₜ function of LTI-carbon corresponds to about 85% of the measured heat of immersion values of that adsorbent. In view of the fact that qₜ and h₁(SLW) have been determined by entirely different methods, the correspondence is satisfactory.

The 25°C and 37°C electrophoretic mobilities of LTI-carbon particles are uₑ(25°C) = 1.63 ± 0.17 and uₑ(37°C corr. to 25°C) = -1.45 ± 0.24 μm·sec⁻¹·V⁻¹·cm⁻¹. Since prior to these measurements all particles > 1μ were allowed to settle, the mean radius of those whose mobility has been determined, a ~ 2.5 x 10⁻⁵ cm. It can be shown that, in the buffer used, the thickness of the Debye-Hückel double layer, 1/K ~ 12.5 x 10⁻⁸ cm indicating that the ionic atmosphere surrounding these particles << a. This justifies application of the Helmholtz-Smoluchowski equation to compute the charge density of LTI-carbon particles, σ = 1.1 μCoul/cm² which converts to 6.9 x 10¹² sites/cm². Taking that water vapor interacts with all potential binding sites regardless of whether these are on the particle surface or inside of "ink-bottle" pores, but charged sites outside of these pores can not contribute to electrophoretic mobility, the ratio between 2 x 10¹³ cm⁻², the surface number density of active sites binding water with the relatively greatest energy, and the computed charged site density given above is 2.9. This value compares favorably with 3.9, which is the ratio between the total B.E.T. and "pore-free" surface areas noted earlier for LTI-carbon. Based on these data, it can be assumed that the sites on the LTI-carbon surface, which are binding water with energies equal to that of an H-bond and induce the negative charge of those particles, are of the carboxylic acid type.

The differential isosteric heat curves of water vapor sorption on the SLTI-carbon powder which was activated at either 25°C or 37°C, also display 2 peaks. The first of these is centered at a coverage ~ 5 x 10¹³ molec/cm² with a maximum energy of about 3.5 Kcal/mole > Q; and the second at ~ 2 x 10¹⁴ molec/cm² with 2 Kcal/mole in excess of Q. At coverages > 5 x 10¹⁴ molec/cm², qₜ falls below the value of Q, and the integral entropy of sorbed water becomes greater than that of the bulk liquid at corresponding temperatures. This indicates that, except for a relatively low surface number density of hydrophobic sites, the rest of an SLTI-carbon surface is "hydrophobic" as compared to that of pure LTI-carbon. This is substantiated by the fact that both heat of immersion values of SLTI-carbon into pure water, h₁(SLW)₁₂₅₀ = 51.4 ± 3.50 and h₁(SLW)₁₃₇₀ = 52.5 ± 3.54 erg/cm², are smaller than those of pure LTI-carbon.

Since the state of silicon atoms in LTI-carbon has not been clarified, only the following information can be derived about the type of functional groups present on SLTI-carbon surfaces. The absence of temperature-dependence in the h₁(SLW)¹'s of SLTI-carbon implies that the mechanism of water attachment to the binding sites of this surface could be similar to that exhibited by the active sites of pure LTI-carbon. However, the calorimetrically-determined difference, h₁(SLB)¹ - h₁(SLW)¹ measures the energy of attachment of Na⁺ counterions from the buffer to the adsorbent particles. For the SLTI-carbon, these differences are ~ -8.9 and ~ -13.2 erg/cm² at 25°C and 37°C, respectively, whereas for LTI-carbon they are greater, by a factor ~ 2, viz., ~ -16.8 and ~ -25.1 erg/cm² at the corresponding temperatures. The electrophoretic mobilities of SLTI-carbon particles are uₑ(25°) = -1.46 ± 0.2 and uₑ(37° corr. to 25°) = -1.58 ± 0.15 μm·sec⁻¹·V⁻¹·cm⁻¹, which are statistically indistinguishable from those of pure LTI-carbon particles, indicating approximately equal charge densities. In this case, the smaller values of h₁(SLB)¹ - h₁(SLW)¹ obtained for the Na⁺ binding of SLTI-carbon, imply smaller binding energies per site which, in turn, suggests that the type of its functional groups may not be identical to those on the pure LTI-carbon. This is corroborated by the fact that the heats of sorption of native human γ-(7S)-globulin which have been microcalorimetrically measured as presented in a companion paper,[6] are smaller on the SLTI surface under identical conditions.

REFERENCES