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A MODEL FOR THE FREE ENERGY OF ADSORPTION ON LOW ENERGY SURFACES.

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ABSTRACT

In constructing a generalized thermodynamics for the fluid-vapor-solid equilibrium in poorly wetted systems the specific free energy of adsorption at saturation vapor pressure is a basic and elusive term. If the adsorbed phase is modeled as a two dimensional gas, systems for which a complete spectrum of data is available can serve as an empirical basis for constructing and testing adsorption-contact angle relationships. From the extension of such relationship other often inassessible terms can be estimated. Such a construct is reported here and extended to the estimation of the excess adsorption entropy at saturation vapor pressure in non-wetting systems

INTRODUCTION

Vapor phase interaction with solid surfaces can be characterized, not only in terms of adsorption features, but in terms of the bulk (condensed vapor) fluid interaction with the solid. This characterization is particularly effective when the vapor-solid and liquid-solid interaction energies are small. In such cases we refer to the solid as a low energy surface and recognize this circumstance by the non-spreading character of the liquid-solid interaction. A drop of fluid placed on the surface in the presence of vapor at saturation pressure retains a semblence of its fluid form and exits as a spherical segment, perhaps gravitationally distorted if it is a large drop, on the surface. The fluid geometry can be described in terms of the angle of contact(θ) with the surface measured through the liquid phase.

The thermodynamics of such systems is well developed.[1] We define the adhesion energy (ψ) as the energy required to separate the bulk fluid from the solid leaving an adsorbed film on the solid which is characteristic of the vapor solid interaction at saturation pressure. This adhesion energy is equivalent to the energy of immersion ($\varepsilon_{Sl}{}^\circ$) of the solid with such as preformed film present. We measure this energetic quantity directly as a heat of immersion ($h^\circ{}_{i(sv)}$) since PV terms are negligible. The negative sign is a calorimetric convention. If the same solid were immersed in the absence of any presorbed film, the difference in immersion heats would represent the adsorbed film energy,

$$[h_{i(s)}-h^\circ{}_{i(sv)}] = \Delta\lambda = \pi^\circ - T\frac{d\pi^\circ}{dT}. \qquad (1)$$

The notation follows convention which was established in other contexts. The term π° is the (excess) adsorption free energy at saturation pressure of the adsorbate vapor. The adhesion energy then is

$$\psi = -h^\circ{}_{i(s_u)} = -h_{i(s)} - \pi^\circ + T\,\frac{d\pi^\circ}{dT}. \tag{2}$$

The adsorption free energy is accessible, in principle, from conventional adsorption techniques which provide an adsorbed quantity (Γ moles/m^2) vs P when measurements (effectively) extend to saturation pressure (P°) of the vapor

$$\pi^\circ = RT \int_0^{P^\circ} \frac{\Gamma}{p}\, dp. \tag{3}$$

The implied qualification "in principle" derives from that feature of both immersion heat and adsorption measurements which requires that the sample be of reasonably high surface area (approximately 1 m^2/gm). This, in turn, requires that the sample be particulate and, unfortunately, leads to Kelvin condensation at points of particle contact (or near contact) which confuses both measurement at relative pressures (p/p°) above about 0.6. Such bulk fluid condensation is irrelevent to, but many times larger than, the adsorbed quantity of interest.

If the only interest resided in adhesion energies, these are available through precise contact angle studies[2,3]

$$\psi = u_{LV}\cos\theta - T\gamma_{LV}\,\frac{d\,\cos\theta}{dT} \tag{4}$$

where u_{LV} is the bulk fluid (excess) surface energy ($\gamma_{LV} - T\,d\gamma_{LV}/dT$). Again, convention dictates the use of surface tension (γ_{LV}) as an experimentally accessible quantity for the thermodynamically preferred and numerically equal free surface energy of the liquid-vapor interface. Such measurements provide, together with the uncomplicated $h_{i(s)}$ term, both the adhesion energy and the adsorption energy. While these terms alone are useful in questions relating to wetting, they do not permit resolution of the π° and $d\pi^\circ/dT$ terms separately. Both terms are of large importance in arriving at an understanding of the nature of the adsorbed film on low energy surfaces. This film appears to have unusual properties.

The physically adsorbed film on all solids is usually assumed to approach multilayer character and, at adsorption pressures approaching saturation vapor pressure, approach the bulk liquid in character. This "multilayer" adsorption model is the basis for the BET method of surface area measurement which is normally and correctly applied to Type II isotherms. The model is also assumed to apply to Type III isotherms. Although here the monolayer is not complete during early stages of adsorption, the apparent adsorption does approach the equivalent of many layers at pressures approaching saturation vapor pressure.

In recent years there has been a general acceptance of the thesis that such an adsorbed film cannot be present when the bulk fluid exhibits a finite contact angle.[4] Esoteric arguments aside, the proposition that a fluid will not spread on itself is patently unacceptable. We now recognize that the adsorption isotherm is not realistically representing adsorption at high relative pressures but condensation in all cases. This is often a trivial difficulty on high energy (Type II isotherm) systems, but always an insurmountable problem on low energy (Type III isotherm) systems.

Resolution of this problem has been approached from all obvious directions. Calculation[5] of the condensed quantity for idealized particle geometries and packing arrangements shows that condensed fluid in a quantity consistent with adsorption observations is a reality at pressures approaching P°. However such calculations cannot replicate the random size and packing feature of an experimental system and cannot presume to provide condensation correction to within the fraction of monolayer coverage required. Avoidance of the condensation problem has proved difficult. For certain adsorbents, stacked plates can provide a sufficient surface area to mass ratio for conventional gravimetric adsorption studies while minimizing (but not eliminating) points of contact. The single[6] such study which has been accomplished seems to confirm that adsorption near P° is not unbounded but definitely finite with π° values approaching zero for the higher contact angle systems. Indirect methods[7,8,9] of measuring adsorbed film density using flat plates or their equivalent are unfortunately sensitive to the smallest presence of high energy hetero-geneities and produce unrealistically high π° values. Direct calculation[10,11,12,13] of π° values using assumed molecule interaction constants can provide only order of magnitude arguments. At present the empirical evaluation of adsorption energy parameters by fitting an adsorption model to the condensation-free region of the adsorption isotherm appears to be the most fruitful approach. Assuming that the model is realistic, extrapolation to P° produces the desired information.

The present state of adsorption theory suggests that the most appropriate model for adsorption on both high and low energy surfaces is the Hill-de Boer two-dimensional van der Waals gas[14] accompanied by successive condensations to produce multilayer adsorption on high energy surfaces and submonolayer adsorption on low energy surfaces. The model has not proved to be particularly effective in a computational sense for the general high energy surface since it requires an exceptionally high degree of energetic homogeneity. When such stringent criteria are met the predicted features of the model are observed.[15] On low energy surfaces the range of energetic variation is also reduced to produce effective homogeneity with only isolated sites of high interaction energy to be treated. Isotherm features associated with such sites permit reasonable correction to be constructed based on early (unconfused) stages of adsorption.[16,17,18]

As indicated by Eqn 2, the construction of an internally consistent thermodynamic framework in which all related observations on low energy surfaces can be accomodated is inhibited by our inability to experimentally resolve the adsorption features of the problem, in particular π° and $d\pi^\circ/dT$ values. It is, perhaps, because of this inability to set down a totally acceptable framework that the conceptual advantages of cataloging all thermodynamic features of interactions on low energy surfaces into a single fluid-variable substrate format have not been explored. Data are normally obtained in the opposite context, i.e. the format of various vapor and fluid interactions on a single substrate. The wealth of such data, generated over decades of study, has produced few thermodynamically valid generalizations. We hope to illustrate the potential of the variable substrate format by producing estimates of the $d\pi^\circ/dT$ term relying on model calculations. Sign and order of magnitude are at present unknown.

DISCUSSION

Equations 1, 3 and 4 make the requirements of a model treatment clear. The basic requirement, which can only be approached empirically, is a relationship between some adsorption feature and contact angle. Although π° is a feature of substantial thermodynamic concern, the more fundamental quantity is the adsorption coverage at saturation pressure which we define as Ω° (monolayers). This term, which leads to π° through Eqn 3, can be approached directly in terms of the theoretical isotherm and relates directly to the major feature of adsorption on low energy surfaces, i.e. that a condensed monolayer is a practical precondition for higher layer adsorption. The absence, at relative pressures significantly below $P/P^\circ = 1$, of a condensed monolayer follows as a practical precondition for a finite contact angle system.

The absence of condensation of the two-dimensional (2-d) gas which is presumed to exist throughout the isotherm can be regarded as either 1) a relatively ideal 2-d gas resulting from a force field so weak that the adsorbed phase density does not meet condensation requirements at pressures below P°, or 2) the adsorbed phase is post critical and condensation is not a feature. At present we can only note that insufficient theoretical attention has been addressed to such systems to resolve the most probable feature and that any present choice must depend on observable features derived from the isotherm form when condensation-free parameters are obtained and extrapolated to saturation pressure. Such isotherm forms suggest that the two-dimensional phase is post critical.[16] We therefore choose to accept some feature of the critical phase density as a limiting adsorption feature at P° which differentiates between spreading and non-spreading in the bulk fluid interaction. An adsorbed phase density of 0.33 monolayers is widely accepted and theoretically tenable for the critical phase density.[12]

Another key feature of any adsorption model is the heat of adsorption. At present, for low interaction energy systems only some half dozen values derived from heat immersion data in precision calorimeters[19,20,21] can be regarded as adequate in addition to two values obtained from direct adsorption calorimetry.[22] These data can only suggest an acceptable range. As Eqn 1 suggests, a zero value for $\Delta\lambda$ could reflect only that $d\pi°/dT$ is non zero positive.

With these remarks, we define the model framework as follows:

1. for a fluid of specified energetics, i.e., surface free energy $\pi°$, temperature derivative of surface free energy $d\pi°/dT$ and heat of vaporization (Q_V), the adsorption and wetting properties are defined by the adsorbed quantity $\Omega°$ (monolayers adsorbed at P°) and by the equilibrium contact angle θ_e and that a general interrelationship holds for the two quantities on all surfaces,

2. that the limiting coverage for low contact angle systems is given by the two-dimensional critical phase density, i.e.,

$$\lim_{\theta \to 0} \Omega° = \Omega/3$$

and that the limiting value for high contact angle sytems is

$$\lim_{\theta \to 180°} \Omega° = 0,$$

also that surface coverge by the adsorbed phase is related to the conventional adsorption isotherm, $\Gamma = \Gamma(P)_T$, through b, the area (m^2) occupied by 1 mole of adsorbate in close packed geometry and that b is independent of detailed substrate structure.

3. that low energy surfaces may be regarded as energetically uniform and that, for the low limiting coverage values characteristic of vapor interactions with such systems, the heat of adsorption is constant,

4. that the adsorption process is described by the Hill-de Boer Equation,

$$P/P° = \frac{1}{K}\frac{\Theta}{1 - \Theta} \exp \frac{\Theta}{1 - \Theta} - \frac{2a2\Omega}{RTb_2} \qquad (5)$$

$$K = B \exp(-Q/RT).$$

The isotherm form expressed by Eq. 5 can be integrated to provide, where $b = b_2$

$$\pi^\circ = \frac{kT}{b} \frac{\Omega}{1 - \Omega^\circ} . \qquad (6)$$

The relationship between Ω° and Θ_e must be consistent with known values of π° for vapors adsorbed on solids where the fluid-solid contact angle is finite and known. On intuitive grounds we assume an exponential decrease in Ω° with Θ such that

$$\Theta^\circ = \frac{\Omega(\mathrm{lim})}{1 - \alpha} \exp(\beta\Theta - \alpha) \qquad (7)$$

where α is a normalization factor and $\Omega(\mathrm{lim})$ is the assumed limiting coverage above which two-dimensional condensation and higher layer adsorption occurs together with spreading of the bulk fluid.

As indicated above and in the introduction there is very little data which include estimates of π°, net heats of adsorption and contact angle terms. We choose to use the Whalen and Wade data[19,20,21] since it is complete, although it is not entirely consistent with the variety of other data. We select empirical β values for Eqn 7 then on the basis that $\pi^\circ < 3\mathrm{x}10^{-3}$ joules m^{-2} for $\Omega = 12^\circ$, $1/b = 3\mathrm{x}10^{-6}$ mole m^{-2} (hexane) and $\pi^\circ < 1.7\mathrm{x}10$ joules m^{-2} for $\Omega = 26^\circ$, $1/b = 1.5\mathrm{x}10^{-6}$ mole m^{-2} (octane).

Fig. 1 reflects π° values obtained for several choices of the empirical parameter B, with the hexane data. Data points[19] representing π° values for hexane and octane are superimposed for comparison. The $\beta = -0.02$ curve is consistent with the hexane data. For larger molecules π° will be decreased proportionately making the $\beta = -0.02$ curve an acceptable fit for both data points. Other estimates of π° obtained from van der Waals parameter curve fit are in reasonable agreement when those data relating to markedly heterogenous surfaces are rejected[16].

For the low converages considered, the lateral interaction energy term in Eq. 5 may be neglected giving, at saturation pressure

$$K = \frac{1 - \Omega^\circ}{\Omega^\circ} \exp - \frac{\Omega}{1 - \Omega^\circ} \qquad (8)$$

for each Ω° and therefore for each Ω. Providing that a reasonable assumption can be made for Q_0, the heat of adsorption associated with a substrate on which the fluid just spreads, (Eq. 1) will provide Q_Ω. A number of cases have been considered for $Q_0 = \eta Q_v$, where Q_v is the heat of vaporization and η assumes values ranging from 1.05 to 1.5 in accord with adsorption experience.[18,21]

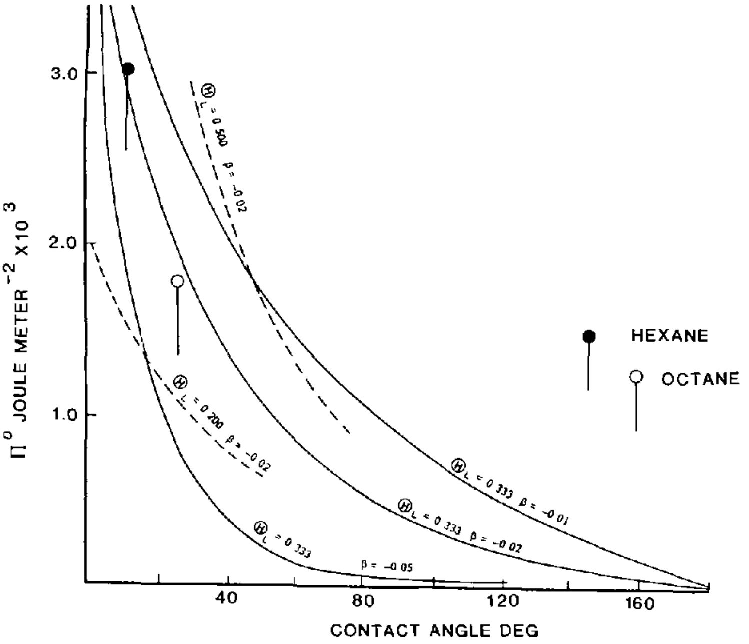

Fig.1. Spreading pressures vs contact angle via Eq 6 for several choices of Eq 7 parameters. Data points from Ref 18.

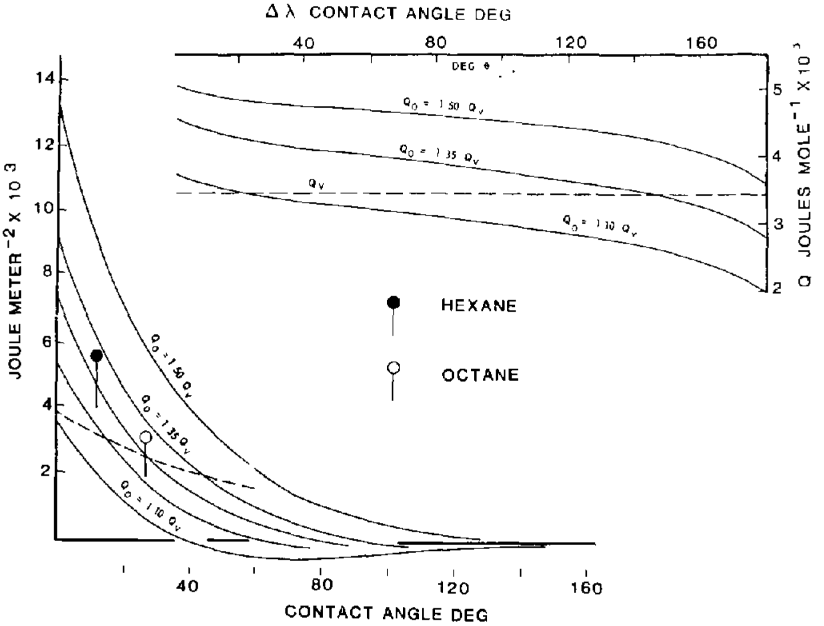

Fig. 2. a) Limiting heat of adsorption vs contact angle via Eqn 8 for hexane with Q_V=3.34 x10^3joule mole^{-1}, b) $\Delta\lambda$ via Eqn 9 vs contact angle for various limiting heats of adsorption. Solid lines with 1/b = 3x10^{-6}mole m^{-2} (hexane) dashed line with 1/b = 1.5x10^{-6}mole m^{-2}(octane). Data points from Ref. 19.

Figure 2-a demonstrates the Q_Ω relationship for several cases within the suggested framework, $\beta = -0.02$. Where,

$$-(h_{i(s)} - h_{i(sv)}) = \Gamma^{\circ}(Q_\Omega - Q_v) = \Delta\lambda \qquad (9)$$

a comparison with previously reported data points can be effected (Figure 2-b). The data are presented for a particular molecular area, again comparable to that of hexane. The dashed line is for $Q_0 = 1.35$ using the octane constants. It can be concluded that $1.10 < \eta < 1.35$ for hydrocarbon-like molecules on low energy solids.

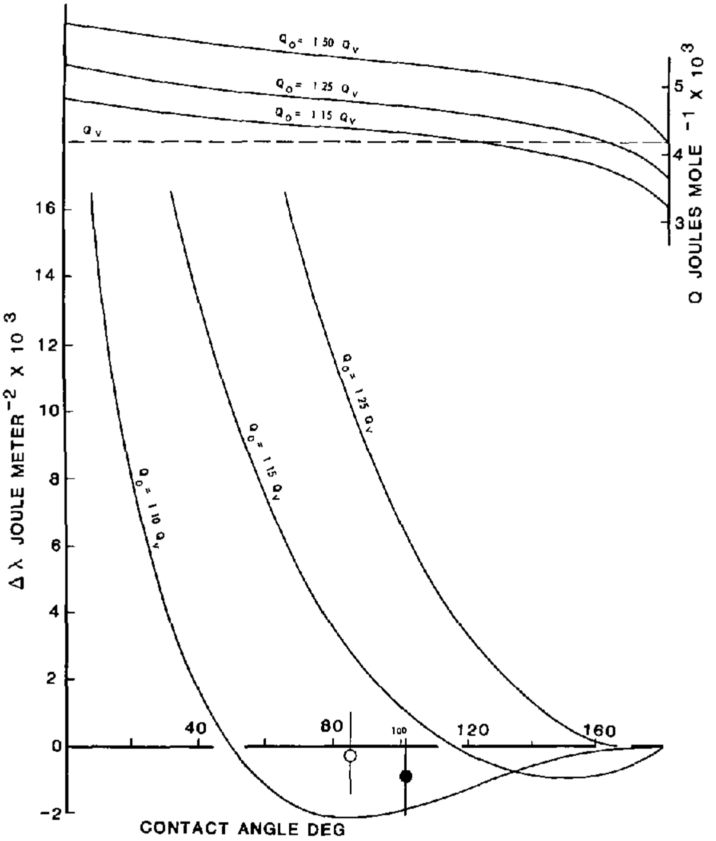

Fig. 3 a) Limiting heat of adsorption vs contact $\Delta\lambda$ angle via Eq 8 with $Q_v = 41.8\text{x}10^3$ joule mole^{-1}, b) via Eq 9 vs contact angle for various limiting heats of adsorption with $1/b = 16.6\text{x}10^{-6}$ mol m^{-2}. Data points from Ref. 20, 21.

Figure 3 illustrates the extension of this treatment to an adsorbate having a molecular cross section for adsorption and a heat of vaporization comparable to that of water $1/b = 17\times10^{-6}$mole m^{-2}, Q_v = 41.8 kjoule mole^{-1}). The only available data (water on teflon, Ω = 104° and water on spheron, Ω=85°) are for high contact angle systems where experimental difficulties attend the measurement of the low immersion heats, however, assuming that Ω(lim) has been realistically chosen, $1.10 < \eta < 1.15$, consistent with the above limits.

The relationships are summarized in Figure 4 which demonstrate π°_Θ and Q_Θ values for water-like systems.

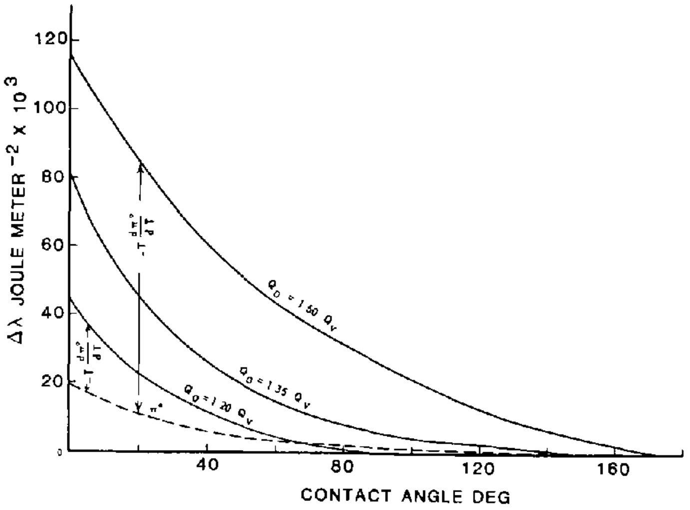

Fig. 4. General illustration of π°, $\Delta\lambda$ and $d\pi^\circ/dT$ relationships based on Fig. 3 parameters.

Where:

$$\frac{-d\pi^\circ}{dT} = \frac{\Gamma^\circ_\Theta(Q_\Theta - Q_V) - \pi^\circ_\Theta}{T}, \qquad (10)$$

typical values of $d\pi^\circ/dT$ are shown in Figs. 5 and 6. Such data have not been obtained by experiment and, in view of the order of magnitude indicated and the condensation related uncertainty in the adsorption isotherm, will not be accessible by experimental means.

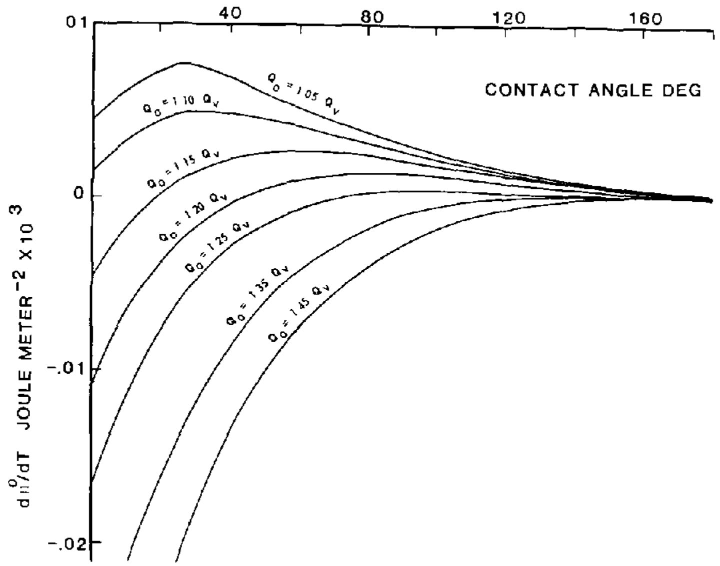

Fig. 5. dπ°/dT for various net heat of adsorption values vs contact angle for hydrocarbons.

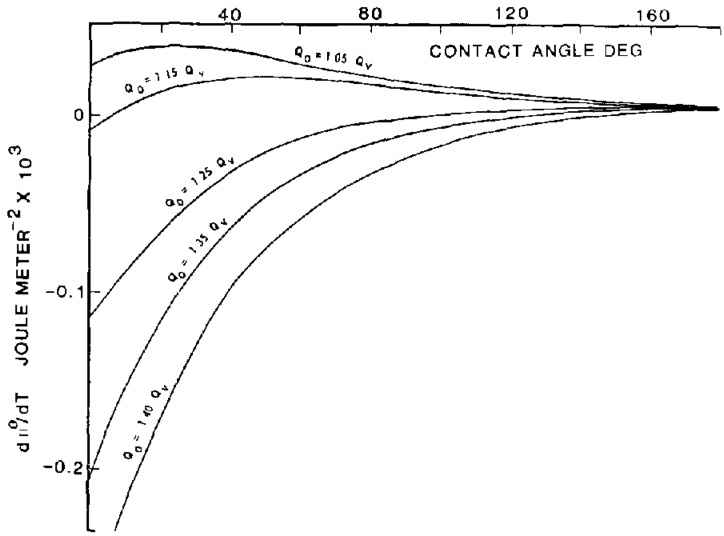

Fig. 6. dπ°/dT for varous net heat of adsorption values vs contact angle i water.

CONCLUSIONS

Given the model limitations, extended discussion of the results does not seem warranted but the general conclusions seem important. Confining attention to the most reasonable range of Q_0 curves in Figures 6 and 7, it appears that $d\pi°/dT$ is negative over the $0° < \Omega < 90°$ contact angle region and otherwise effectively zero. In magnitude the term could be as large as -1.5×10^{-5} joule m^{-2} for $\Omega \rightarrow 0$. If so, then $T\ (d\pi°/dT)$ at room temperature and in the range of maximum contact angle interest $0 < \Omega < 30°$ could be of order -4.5×10^{-3} joule m^{-2} to order -10^{-3}joule m^{-2}. Such values are of the same order as $\pi°$ if the estimates obtained from immersion heats[18] are accepted. Over the range of adsorption heats suggested by the Figure 3 data, $d\pi°/dT$ for water should be positive and of order 5×10^{-5}joule m^{-2} in the range of contact angle $20° < \theta < 90°$. Values of $\pi°$ are generally expected to be about one order of magnitude higher for water so that the magnitude of $T(d\pi°/dT)$ is, again, probably of the same order as $\pi°$ over the range of greatest contact angle concern.

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