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INTERPRETATION OF MIXED WETTABILITY STATES IN RESERVOIR ROCKS

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ABSTRACT

It has recently been noted that the diffuse electrical double layers which exist at (1) the oil/brine and (2) the mineral/brine interfaces in sandstone reservoirs will in many cases be quite similar with respect to electric charge and potential. Extremely thin aqueous wetting films separating such interfaces are thus stabilized by the electrostatic repulsive force acting between the double layers. In the present paper the limits under which stable thin films can exist are examined in more detail. It is shown that there exists a lower limit to the pore size in which thin wetting films will occur and that this limiting size depends on the salinity of the brine. It is also shown that whether this limiting pore size becomes a factor in determining the wettability of the rock/brine/oil system depends on the pore size distribution curve and on the initial brine saturation of the rock. Geological factors which may come into play in establishing the initial water saturation in a given case are discussed.

INTRODUCTION

Recent studies (1-3) dealing with the nature of aqueous wetting films in the Athabasca tar sand deposit have emphasized the role of several factors which contribute to the stability of these films. The work reported in the present paper extends the physico-chemical analysis of the wetting film stability problem developed previously. This analysis is then applied to the interpretation of mixed wettability states in conventional petroleum reservoirs.

In previous work (1,2) evidence was presented which indicates that the diffuse parts of the electrical double layers at the mineral/brine and brine/oil interfaces are similar with respect to the magnitude and sign of the electric potential and the electric charge density. As first pointed out by Langmuir (4), these electric double layers give rise to osmotic forces within thin aqueous wetting films. This causes the film boundaries to mutually repel each other, and such films are thereby stabilized. It was subsequently recognized that for these thin films the effect of the osmotic or electrostatic forces is modified by the existence of both dispersion (or van der Waals) forces (5) and hydration (or adsorption) forces (6). Whereas the very short range hydration forces also stabilize aqueous wetting films, the dispersion forces tend to destabilize the films in question.

In the study reported by Hall et al (1), the effect of the hydration forces was accounted for in an approximate way by assuming that the so-called compact part of an electrical double layer was equivalent to two water molecules in thickness (about 0.55 nm). The dispersion force was neglected since the objective of the work was to obtain an estimate for the maximum thickness of the films under conditions which are appropriate to Athabasca. Zeta potential data were used to calculate the magnitude of the electrostatic repulsive force for various aqueous phase salinities. For these calculations it was assumed that the diffuse double layer (zeta) potentials were the same for the two interfaces forming the boundaries of a film.

The wetting films were also assumed to be in hydrostatic and chemical equilibrium with the bulk aqueous phase, which in turn was taken to be in equilibrium with the bulk oil phase. Thus, the brine/oil interface formed at the boundary between a wetting film and the oil phase was characterized by the same value of the brine/oil interfacial tension as the interface between the bulk aqueous and oil phases. The difference between the pressures in the two bulk phases was taken as entirely due to the capillary pressure across highly curved brine/oil interfaces. However, the difference in pressure between the aqueous films and the oil phase was modified by the repulsive force due to the electrical double layers.

On the basis of the calculations corresponding to these assumptions, it was concluded that in Athabasca the films were in the range of 5-6 nm in thickness. It was also estimated that films of this thickness corresponded to about three-fourths of the total brine saturation, taking the latter to be about

References and illustrations at end of paper.

10 percent of the total pore volume.

Takamura (2) and Takamura and Chow (3) have considered the Athabasca wetting film problem from a very similar point of view. In this work the effect of the dispersion forces was explicitly taken into account. Also, the difference in magnitude of the diffuse double layer potentials at the two boundaries of a film was considered. On the other hand, no attempt was made to treat the effect of hydration forces or to include the contribution to the film thickness of the compact parts of the two interacting double layers. It was concluded that the thickness of the films in the case of Athabasca was of the order of 10 nm. The role of such wetting films in the initiation of the process of bitumen displacement from oil sand aggregates was also discussed in some detail (3).

In the present paper the limiting conditions for the stability of thin wetting films are explicitly considered. The treatment is intended to apply to conventional oil reservoirs, as well as to tar sand deposits such as Athabasca. In particular it is shown that there exists a critical pore size such that if the wetting phase (brine) is displaced from pores smaller in size, wetting films will not be retained on the pore walls of the desaturated pore volume. It is evident that in reservoirs in which the water saturation is very low this condition will prevail for an appreciable fraction of the total pore surface area. Consequently, a state of mixed wettability can be developed in such reservoirs.

Evidence for the existence of states of mixed wettability in a large sandstone reservoir has been presented by Salathiel (7). In discussing this work and similar reports of partially oil-wet behavior in laboratory flow tests, Swanson (8) has suggested that surface roughness effects, combined with contact angle hysteresis, are important. Evidence from electrical resistivity measurements, which indicated water-wet behavior, was compared with evidence from fluid flow tests. It was postulated that roughness effects similar to those described by Morrow (9,10) produce an effectively water-wet type of fluid distribution under oil accumulation conditions. It was further postulated that this initial distribution determines the magnitude of the Archie saturation exponent, even though subsequent adsorption of crude oil components gives rise to oil-wet behavior during waterflooding.

It is clear that the stability of thin wetting films plays an important role in the oil drainage phenomena discussed by Salathiel (7) and Swanson (8) and in establishing states of mixed wettability in general. As has been suggested, the existence of a critical pore size for stable films implies that the initial or connate water saturation for a given homogeneous portion of a petroleum reservoir is a key factor in determining whether a mixed wettability condition will be developed. The value of the initial water saturation must, of course, be considered in relation to the pore size distribution for the portion of the reservoir in question. Thus, the principal objective of the physicochemical analysis of wetting film stability to be presented in this paper is the estimation of the critical pore size for the existence of stable aqueous wetting films.

In order to arrive at the critical pore size estimate, it will be necessary to consider, first, the conditions for hydrostatic equilibrium which are appropriate for thin wetting films. Next, the force versus film thickness relationships for the relevant attractive and repulsive forces will be developed. These topics are presented in the next section. In the following section the nature of the stability conditions applicable to thin films will be formulated. Estimates of film thickness and critical pore size will be presented. Finally, the estimates of the minimum or critical pore size will be discussed in relation to the existence of mixed wettability states in petroleum reservoirs.

ATTRACTIVE AND REPULSIVE FORCES IN THIN AQUEOUS FILMS

1. Conditions for Hydrostatic Equilibrium

The concept of capillary pressure is of fundamental importance in understanding the distribution of oil and brine in the pore spaces of fine-grained sandstone and carbonate rocks. The quantity referred to by this term is usually defined as the difference in pressure between two contiguous, immiscible fluid phases, as in Figure 1. This pressure difference, $P_c = P_o - P_w$, thus refers to the bulk fluid phases in the immediate proximity of the interface. Application of the fundamental principle of hydrostatics leads (11) to the well known expression which relates the capillary pressure to the interfacial tension, γ_{ow}, and to the mean curvature, $J_{ow} = (r_1^{-1}+r_2^{-1})$, of the interface,

$$P_c = \gamma_{ow}\left(\frac{1}{r_1}+\frac{1}{r_2}\right) = \gamma_{ow}J_{ow} \tag{1}$$

Application of this relationship to the analysis of the hydrostatic equilibrium within a given pore requires knowledge of the boundary condition which determines the local angle of contact, between the fluid/fluid interface and the pore wall. When stable thin films are present on the pore walls, as in Figure 1, it is clearly necessary to take the value of the contact angle to be zero. However, it must also be recognized that the pressure within a thin film is no longer simply the difference between the oil phase pressure, P_o, and the capillary pressure, $\gamma_{ow}J_{ow}$. Additional components of the microscopic stress balance within the thin aqueous film must be introduced. These are the attractive (dispersion or van der Waals) and repulsive (electrostatic and hydration) forces referred to previously. The net effect is, for stable films, repulsive in nature. Thus, denoting the <u>net</u> repulsive effect as P_F, the effective hydrostatic pressure in such a film is given by

$$P_w = P_o-(P_c)_f-P_F \tag{2}$$

This expression holds, for example, in the region AB in Figure 1. Here, $(P_c)_f$ refers to the capillary pressure across the brine/oil interface for a thin film.

In contrast, the brine phase hydrostatic pressure in regions of a pore where the thin film forces can be neglected, such as CD in Figure 1, is given by

$$P_w = P_o-(P_c)_b \tag{3}$$

Here, $(P_c)_b$ denotes the capillary pressure across the brine/oil interface in the region in which the effects of the thin film interactions on the brine phase are negligible. For hydrostatic equilibrium between the thin film and the bulk brine phase, the pressure P_w, must be the same for both regions. Hence, eqs. (2) and (3) may be combined to give

$$P_F = (P_c)_b - (P_c)_f \qquad (4)$$

It follows from this expression that

$$P_F = \gamma_{ow}\{(J_{ow})_b - (J_{ow})_f\} \qquad (5)$$

Turning now to the question of an appropriate pore model, it is convenient to consider first the familiar example of a cylindrical tube. Denoting the radius of the tube as R, and the total thickness of the wetting film as t, the relevant curvatures can be written as

$$(J_{ow})_b = 2(R-t)^{-1} \qquad (6a)$$

$$(J_{ow})_f = (R-t)^{-1} \qquad (6b)$$

It follows from these expressions that the net repulsive force arising from the electrostatic, hydration, and dispersion forces within the film is given by a very simple relationship,

$$P_F = \gamma_{ow}(R-t)^{-1} \qquad (7)$$

Another familiar example of a pore model is that formed by a slot with plane parallel walls separated by the distance 2R. If, again, the film thickness is denoted by t, the curvatures for this case are given by

$$(J_{ow})_b = (R-t)^{-1} \qquad (8a)$$

$$(J_{ow})_f = 0 \qquad (8b)$$

It is seen that eq. (7) also holds for this case. Thus, in general, it can be expected that

$$P_F = \gamma_{ow}(R_{eff}-t)^{-1} \qquad (9)$$

where the effective pore size, R_{eff}, is simply related to the nominal or equivalent pore size, R_{equiv}, derived from a capillary pressure experiment.

It should be noted at this point that eq. (5) above is actually an approximation. Mohanty et al (12) have presented a detailed discussion of this relationship, pointing out that the configuration of the oil/brine interface will be somewhat perturbed from that which is assumed in writing eq. (3). This perturbation will, of course, be of most significance for the region of the interface closest to the thin film, i.e., region BC in Figure 1. It should be noted that the horizontal scale in Figure 1 is non-linear, so that the width of the thin film region is greatly exaggerated, in comparison with the radius of curvature of the fluid/fluid interface.

The correct form of eq. (3) was termed by Mohanty et al the augmented Young-LaPlace equation. Integrations of this equation for the cases of the cylindrical tube and slot with plane parallel walls were also presented. These integrated forms, although slightly different in the two cases, permit an estimation of the order of magnitude of the required corrections. For typical values of the parameters characterizing the electrostatic and dispersion forces of interest in the present context, it appears that the corrections to eq. (5) are quite negligible.

In the previous study of wetting films (1) a further approximation was introduced. The thickness of the wetting film was taken as negligible when compared to the effective pore size. Also, since the effect of the attractive forces was neglected, the net repulsive force was denoted as P_R, rather than P_F, as in the present discussion. Here, the actual repulsive force will be denoted as P_R, while the attractive force will be denoted as P_A. Thus, the net repulsive force in a stable thin aqueous film will be given by

$$P_F = P_R - P_A \qquad (10)$$

The method of calculating P_R and P_A for thin aqueous films will be outlined in the following two sections.

2. van der Waals or Dispersion Force Interactions

The attractive forces of interest in thin films are of quantum mechanical origin and are often referred to as van der Waals-London or dispersion forces. The application of the theory of these forces to colloidal and thin film behavior in general is reviewed by Mahanty and Ninham (5). Since the dispersion force between a non-polar liquid hydrocarbon phase and a mineral phase such as quartz is stronger than the dispersion force between an aqueous phase and the same solid, the effect of such forces is to destabilize a thin aqueous wetting film. The interaction force, P_A, is thus attractive in nature and when the film thickness is not too large, is given by

$$P_A = A_{qwo}/6\pi t^3 \qquad (11)$$

Here, A_{qwo} is the so-called Hamaker constant for a three-phase system: solid/aqueous film/hydrocarbon liquid. It is assumed that both of the interfaces separating the aqueous film from the adjoining bulk phases are planar and parallel.

When the film thickness, t, in eq. (11) becomes greater than about 5 nm, the force is somewhat retarded, and the magnitude of the exponent increases (5). Since the corrections for this effect are of the order of 5 percent or less for cases of interest in the present problem, the retardation effect will be neglected in the treatment given below.

Much more important uncertainties arise in estimating the value of Hamaker constant, A_{qwo}, in eq. (11). For the quartz/water/hydrocarbon system, Takamura (2) has adopted a value of $A_{qwo} = 1.0 \times 10^{-20}$J. This value was calculated from the expression

$$A_{qwo} = (A_{qq}^{1/2} - A_{ww}^{1/2})(A_{oo}^{1/2} - A_{ww}^{1/2}) \qquad (12)$$

where A_{qq}, A_{ww}, and A_{oo} are the Hamaker constants characterizing the dispersion interactions between two parallel, planar, semi-infinite portions of the same phase, separated by vacuo. The subscripts denote the solid (quartz), brine and hydrocarbon phases, respectively. The values chosen for these parameters, in units of 10^{-20}J, were $A_{qq} = 15$, $A_{ww} = 3.7$, and $A_{oo} = 6$. The A_{qq} value, however, represents a very early estimate for quartz, and it is now known (13) that a value of about 9 is more nearly correct. This would imply that the value for A_{qwo} should be about 6×10^{-21}J.

A further difficulty arises in connection with eq. (2) itself. A quite different result than that given by this equation is obtained when the ternary mixing rule derived by Israelachvili (14) is used in connection with the ternary interaction values, A_{qwq} and A_{owo}. This rule is expressed as

$$A_{qwo} = (A_{qwq} A_{owo})^{1/2} \tag{13}$$

Hough and White (13) have recently reported carefully determined values of the Hamaker constant for several types of interactions which are of interest in the present context. These data are summarized in Table I. It is seen that, depending on the alkane molecular weight, Hamaker constants varying from about 7.5 to 10.0 x 10^{-21}J may be expected for the alkane/water/quartz system. Callaghan and Baldry (15) reported a value of 3.27 x 10^{-21}J for the tetradecane/water/silica system but do not give details of their calculation. Even taking into account the expected difference in dispersion interactions between fused silica and quartz, this result is about half that predicted from the data reported by Hough and White (13).

Other factors which can be expected to introduce additional uncertainties in the estimates of the Hamaker constants for oil/brine/solid systems include temperature, the concentration and types of electrolyte in the brine, and adsorbed layers at both the oil/brine and brine/solid interfaces. In the reservoir environment the effects of pressure and of solution gas must also be considered. Unfortunately, the available theories for these effects (cf. ref. 5) are not in readily usable form. In view of these uncertainties in the value of A_{qwo}, a range of values has been used in the film stability calculations described below. This range is from 3 x 10^{-21} to 9 x 10^{-21}J. As it turns out, this range encompasses a rather significant shift in the balance between the attractive (van der Waals) and repulsive (electrostatic) forces which determine the stability of thin aqueous wetting films.

3. Repulsive Forces Resulting From Electrical Double Layers

The general features of electrical double layers were reviewed by Hall et al (1). Figure 2 is a schematic representation of the distribution and orientation of both the exchangeable cations and water molecules at a clay mineral/aqueous phase interface. As previously discussed, the layer of oriented water molecules next to the mineral surface is about twice the diameter of a water molecule in thickness (0.55 nm). This layer is known as the compact or Stern-Grahame layer and in the case of clay minerals includes more than 90 percent of the exchangeable cations. Thus, the surface charge density in the diffuse part of the double layer (the Gouy-Chapman layer) is of the order of 10 mCm^{-2}. Correspondingly, the electrical potential at the boundary between the compact and diffuse parts of the double layer is of the order of -10 mV. A relationship between the diffuse layer surface charge density, σ_d, and this value of the electric potential, ψ_d, is given by the Gouy-Chapman theory (cf. ref. 6). The appropriate expression for a 1-1 electrolyte, relating these two quantities to the electrolyte concentration, was presented previously (1). This expression will be assumed in the present work. Hence, the results will be applicable only to electrolytes of the 1-1 type, i.e., electrolytes in which all ions are monovalent. Due to the limitations of the Gouy-Chapman theory, the results are also resistricted to concentrations below about 0.5 equivalents/liter.

It was also pointed out previously (1) that with respect to the dependence of the diffuse layer potential, ψ_d, on electrolyte concentration, c, the clay mineral/brine and quartz/brine interfaces are very similar. Data for the quartz/brine interface, as reported by Gaudin and Fuerstenau (16), were used (1) to derive the following empirical relationship,

$$\sigma_d = 15.0 + 0.2\,\psi_d \tag{14}$$

Table II gives the electrical double layer parameters and the electrolyte concentrations which are consistent with eq. (14) for a temperature of 50°C. These results may be assumed to characterize the relationship between the diffuse layer potential and the electrolyte concentration for both the solid/brine and oil/brine interfaces. This assumption, of course, restricts the results to be presented below to the case of sandstone reservoirs. The diffuse electrical double layer which forms at the carbonate mineral/brine interface will not be characterized by eq. (14), since in this case the diffuse layer potential, ψ_d, will be positive in sign in the neutral pH range. In support of the premise that the potential versus concentration relationships for both the reservoir solid/brine and the oil/brine systems are similar to the quartz/brine system, various zeta potential studies were cited previously (1). It is known (17) that the zeta potential, which can be measured experimentally with relative ease, is essentially equivalent to the diffuse layer potential, ψ_d.

The values of the surface charge density, σ_d, given in Table II are applicable only to diffuse double layers which are isolated. When two such double layers are brought into proximity both electrostrictive and osmotic effects arise. The net effect is a repulsive force (6,18) tending to keep the interfaces at which the double layers are formed apart. Assuming that the double layers (which may be labelled 1 and 2) are planar and parallel, the magnitude of this net repulsive force can be calculated. For the case in which the values of the double layer potential, ψ_d, at each interface remain constant, Devereux and de Bruyn (18) have published extensive tables giving the results of such calculations. From these tables the value of the repulsive force, P_R, can be determined as a function of the distance between the interfaces, t, and the two electric potentials $(\psi_d)_1$ and $(\psi_d)_2$.

Since the interaction giving rise to the repulsive force is due to the diffuse parts of the two double layers, it is actually the distance between the two boundaries separating the diffuse and compact parts of the two double layers which is of significance. Denoting this distance by h, the total film thickness, t, will be given by

$$t = h + 4\delta \tag{15}$$

where δ is the diameter of a water molecule (0.275 nm). Thus, each boundary is taken to be a distance of 2δ from the actual phase boundary or interface separating the aqueous film from its contiguous bulk phases.

The results to be presented in the next section are based on calculations of double layer interactions in which the constant potential assumption is used. Under this assumption, a non-exact but analytical expression for the dependence of P_R on h, $(\psi_d)_1$ and $(\psi_d)_2$ has been derived by Hogg *et al* (19). This expression provides an excellent approximation to the exact results tabulated by Devereux and de Bruyn (18). It is given in the Appendix in dimensionless form. This equation enables the derivative of P_R with respect to h to be represented by an analytical expression as well. This result, also given in the Appendix, in dimensionless form, is of importance in calculating the limiting conditions for the stability of an aqueous wetting film.

MINIMUM PORE SIZE FOR WETTING FILM STABILITY

1. Calculation of Net Interaction Force

The treatment of the wetting film problem, as developed in the previous sections, dealt with an attractive interaction, due to van der Waals forces, and a repulsive interaction, due to osmotic forces arising from overlapping diffuse electrical double layers. The net force of repulsion between the plane parallel interfaces is related to the wetting film thickness, t, and to the effective pore size, R_{eff}, by eq. (9) above. Thus, eq. (9) can be rewritten, using eqs. (10) and (15), as

$$P_R - P_A = \gamma_{ow}\{R_{eff}-(h+4\delta)\}^{-1}. \tag{16}$$

This expression is given in dimensionless form in the Appendix, as is eq. (11), which gives the dependence of P_A on h.

It should be pointed out that the repulsive force, P_R, is taken to be the result of overlapping diffuse electrical double layers and does not include the effect of short-range hydration or adsorption forces. These forces are also repulsive, but are accounted for simply by assuming a constant thickness of 2δ for each compact layer. Thus, the distance, h, in eq. (16) is restricted to the range $h \geq 0$.

Calculations of the attractive and repulsive forces for various values of the film thickness, electrolyte concentration, and Hamaker constant have been carried out (20). The forces and the relevant parameters, such as film thickness, diffuse layer potential, and Hamaker constant were expressed in the dimensionless forms given in the Appendix. Calculations were restricted to the case in which the electric potentials were the same for the two interacting double layers. Plots of the dimensionless net force versus dimensionless film thickness showed that increasing electrolyte concentration and increasing values of the Hamaker constant markedly decrease the magnitude of the maximum in net force. Also indicated was the tendency of the net force to reverse in sign as the wetting film becomes thicker. This means that the net force is attractive in nature, rather than repulsive, at larger film thicknesses. In other words, there is a maximum in the film thickness beyond which the wetting films are unstable as the result of the predominance of attractive forces over repulsive forces.

In the absence of attractive forces, i.e., for zero values of the Hamaker constant, no maximum in film thickness will be encountered. Such would be the case for aqueous wetting films when the non-wetting phase is a low pressure gas, rather than oil. Under these circumstances the Hamaker constant is negative, and dispersion forces give rise to a repulsive interaction, supplementing the effect of overlapping electrical double layers.

2. Film Thickness Results

In Table III, values of the maximum film thickness for various values of the Hamaker constant are given. These results correspond to the value of the film thickness, t, for which the condition, $P_A = P_R$, is satisfied. The dependence of the maximum film thickness on the value of the Hamaker constant and on the electrolyte concentration is shown in Figure 3. It should be noted that these values of the maximum film thickness are derived without taking into account the effect of retardation on the dispersion force interaction. Somewhat larger values would be expected if corrections for this effect were introduced. However, as indicated above, such corrections are small, and the maximum film thicknesses shown in Figure 3 would not be affected in a significant way.

Also given in Table III are values of the film thickness calculated from eq. (16) for the case of R_{eff} = 5.0 um. These results are shown in Figure 4. It is seen that the effect of increasing Hamaker constant is relatively minor, even at an electrolyte concentration of 0.3 equiv./liter. As the Hamaker constant increases from 0 to 6 x 10^{-21}J, the film thickness for this concentration decreases by only 0.73 nm, i.e., less than 3 water molecules in thickness. As was pointed out above, the effect of the dispersion force interactions was neglected in previous calculations of wetting film thicknesses (1). Since the effect of these interactions is minor, the general conclusions reached previously concerning the relative amounts of film water and water in trapped configurations (pendular ring water) are unaffected.

3. Film Stability Calculations

It has been shown thermodynamically by Frenkel (21), as well as by others, that the thin wetting films under consideration here are subject to a further condition of stability, which is in addition to the condition that

$$P_F \geq 0 \text{ or } P_R \geq P_A \qquad (17)$$

This further condition can be written as

$$(\partial P_F/\partial t)_T \leq 0 \qquad (18)$$

That is, the gradient of the net force tending to separate the boundaries of a wetting film must be negative in sign. Values of the gradient of the net force as a function of film thickness, electrolyte concentration and Hamaker constant have also been calculated (20). These results indicate that negative values of the gradient of the net force are found only for a rather restricted range of film thicknesses.

It is clear that the stability condition given by eq. (18) implies that the maximum value of the net force corresponds to a state of limiting stability. From eq. (16) it follows that as the net force increases within the stable region, the corresponding value of R_{eff} must decrease, approaching a particular value as a lower limit. Since the maximum value of the force is quite sensitive to both the electrolyte concentration and to the magnitude of the Hamaker constant, it then follows that the lower limit to the effective pore size is also sensitive to these factors. Table IV gives values of the minimum pore size calculated from eq. (16) under the condition stated by eq. (18). The film thicknesses for this condition are given in Table III.

The sensitivity of the minimum effective pore size for the retention of stable wetting films to electrolyte concentration and to the magnitude of the Hamaker constant is indicated by the results shown in Table IV. Curves illustrating the trend of minimum pore size with varying concentration are plotted in Figure 5 for several values of the Hamaker constant.

It should be emphasized at this point that the film stability limit considered here refers to films retained by repulsive forces of the osmotic type, resulting from the interaction of electrical double layers. When such films are displaced, ultra-thin films may be retained. These films are held by hydration forces and are expected to be of the order of one or two water molecules in thickness, corresponding to the compact part of an electrical double layer. For reasons which will be indicated below, such ultra-thin films should not be referred to as <u>wetting</u> films, but rather as <u>hydration</u> films.

FILM STABILITY AND MIXED WETTABILITY

1. Wetting Films in Reservoir Rocks

It is usually assumed by those concerned with problems in petroleum production and exploration that the connate water saturation of reservoir rocks includes two types of water. The first of these is water in the form of thin wetting films on the pore surfaces. The second is water trapped either within a certain fraction of the individual pores which comprise the pore volume of the rock, or as pendular rings at intergrain contacts. Thus, it is implied by this assumption that all reservoir rocks are uniformly water-wet. Furthermore, it follows that the trapping of water, which is due to capillary forces, must occur primarily in the smaller pores of the system and in pendular rings with high interfacial curvatures. It is also commonly believed that the fraction of the connate water saturation which is in the form of thin films is quite small, compared to the water trapped by capillarity. These concepts, developed by early workers in the field (22-25) have achieved a time-honored status.

At the same time, the possibility that some degree of oil-wetness may occur has also been entertained by many investigators. It is a view particularly held by those who have studied the relative imbibition tendencies of native-state reservoir rocks, when alternately contacted by oil and water (26). Such work has led to the recognition that mixed-wettability systems are likely to occur in many cases (7,8).

It is of interest to note that an elementary argument (1), leads to the conclusion that stable wetting films are <u>not</u> retained on <u>convex</u> surfaces of sand or other mineral grains. This argument is based solely on the concept that a capillary pressure must be associated with each and every curved fluid/fluid interface in the system. Thus, if such films do exist on convex grain surfaces, an additional stabilizing force must be introduced. Such a force is that due to double layer repulsion. Also, sandstone surface area data (27,28) indicate that the resulting films must be relatively thin, i.e., 5 nm or less. Otherwise, the contribution to the overall connate water saturation which is due to the presence of the films would necessarily be quite significant, amounting to as much as 25 percent of the pore volume for films of 30 nm in thickness.

If, on the other hand, films of only 0.5 nm thickness, corresponding to two monolayers of water molecules, are retained, a further question arises. This is whether such thin films can still inhibit the adsorption of polar constituents from the oil phase. It has been recently demonstrated (29,30) that the asphaltene or heavy ends fraction of crude oil is strongly adsorbed by clay minerals, at least at low relative humidities. It seems quite likely, in view of this work, that adsorption of this kind would <u>not</u> be entirely blocked by a water film which was only two molecules in thickness. The local wettability, as defined by a local or "microscopic" contact angle, would then be altered to a very significant degree. Thus, even if some of the water, initially present in the form of films one or two molecules thick, was retained, a definite wettability change would occur as the result of heavy ends co-adsorption. This conclusion is consistent with the generally held concept that asphaltenes are involved in establishing the <u>in situ</u> wettability of reservoirs (32).

2. Stability of Wetting Films in Relation to Pore Size

In the context just discussed, it is clear that the stability of thin aqueous wetting films, such as have been considered above, is of critical importance in determining the nature and distribution of the wetting character of pore surfaces. This stability, in turn, is definitely a function of the effective pore radius for the smallest pores which remain in a saturated state for a given stage of the capillary desaturation process. Thus, as brine is removed from a water-wet rock by the invasion of crude oil, the displacement of brine takes place in successively smaller and smaller pores. At the same time, the wetting films retained on the walls of individual pores after desaturation become thinner and thinner. Eventually, a critical size is reached, corresponding to the stability limit for the existence of films of this type.

As indicated in Figure 5, this minimum effective pore size is probably of the order of 0.5 um. When this pore size is reached, the films remaining on the walls of all previously desaturated pores are no longer stable. That is to say, the water in these films, unless completely isolated and without access to smaller pores, will suddenly be displaced. This occurs at the saturation corresponding to the critical or minimum effective pore size. Some of these water films will no doubt be isolated and therefore retained. Hence, the total surface area of the desaturated pores will be partly covered by isolated wetting films and partly depleted with respect to such films. In the area not covered by wetting films, ultra-thin films (about 0.5 nm in thickness) will at first be retained by hydration forces. However, as indicated above, such films are not expected to inhibit fully the adsorption of highly polar heavy ends from the oil phase. This will result in what is clearly a state of mixed wettability.

The role of dispersion forces in establishing such states of mixed wettability can now be assessed in more detailed terms. These molecular forces provide the macroscopic driving force for converting films of about 5 nm in thickness to ultra-thin films, of about 0.5 nm in thickness. This driving force comes into play only after the process of capillary desaturation has proceeded a considerable way towards completion, i.e., only after all pores down to an effective radius of about 0.5 um have been desaturated. The final stage of converting water-wet pore surfaces to an oil-wet condition then follows, after the wetting films have been displaced. This stage, as already discussed, involves the adsorption of petroleum heavy ends, i.e., asphaltenes, on surfaces for which the film thickness has already been reduced to the order of 0.5 nm.

As pointed out by Czarnecka and Gillott (31), the exact nature of the interaction forces which are responsible for the final stage of wettability alteration has not yet been established. Interactions of the acid-base type may be involved. The role of this type of interaction at solid/fluid interfaces has recently been reviewed (33). The mechanism of contact charge transfer has also been discussed recently (34).

3. Connate Water Saturation in Relation to Pore Size Distribution

In order to determine, in the case of a particular reservoir, whether the processes just described may have occurred, a method of determining the wettability *in situ* would clearly be desirable. In lieu of this, a simple comparison can be made between the connate water saturation and the saturation required to exceed the critical or minimum pore radius as defined by the film stability criterion. If the connate water saturation in a given zone of a reservoir (measured by some independent technique) is less than the saturation corresponding to the critical radius, the zone in question will have been at least partly depleted of the wetting films normally present on the pore surfaces. Hence, the zone will be in a mixed wettability state. The relative permeability and capillary pressure characteristics of such a zone, during resaturation with water, will then be affected to a very significant degree.

Many reservoirs are known to have a quite low connate water saturation (35). This important reservoir parameter is, however, rarely compared directly with data given by the pore size distribution curve. In order to test the concept that a comparison of this kind can provide an indicator of wettability behavior, the case of the Pembina Cardium reservoir in Alberta was studied. For this reservoir, high values of the residual oil saturation, together with connate water saturations of the order of 10 percent (35,36) are believed to be indicative of some degree of oil-wet behavior. Pore size distribution data, as obtained by the mercury injection technique, have also been reported (37). A typical pore size distribution curve obtained by this technique is shown in Figure 6. The gas permeability for this particular core plug was 30 md, while the porosity was 23 percent. These data are close to the field-wide averages for Pembina. Saturation values corresponding to different equivalent pore sizes for this sample are also shown.

It is seen from Figure 6 that, for this particular sample, as much as 37 percent of the pore volume corresponds to pores for which the equivalent pore entry radius is less than 0.75 um. Since the typical pore shape in the smaller pore size range is more nearly slit-shaped than cylindrical (38), the effective pore radius would probably be more nearly 0.35 to 0.4 um. The electrolyte concentration of the formation brine in Pembina is estimated to be about 0.2 equivalents/liter (39). Assuming that the Hamaker constant in this case is not less than 3×10^{-21} J, the curves shown in Figure 5 indicate that the smallest values of the critical effective radius which can then be expected are also in the range of 0.35 to 0.4 um. Thus, it would be necessary for the connate water saturation to be of the order of 37 percent or more if the limiting condition for stable wetting films is to be satisfied. Clearly, an average connate water saturation of about 10 percent is insufficient to meet this requirement. In this case, therefore, it appears that reservoir wettability is predicted by a comparison between the connate water saturation and the saturation required to fill all pores smaller than the critical size for stable films.

4. Role of Geological Processes in Establishing Connate Water Saturation and Mixed Wettability States

An apparent difficulty in associating low connate water saturations with partially oil-wet pore surfaces relates to the nature of the flow processes by which the saturation of the aqueous phase decreases as oil initially enters a reservoir. As pointed out by Muskat (25), flow processes of both the imbibition and drainage types must be involved, if it is assumed that all pore surfaces are water-wet and remain so throughout the overall process of oil accumulation. Under this assumption, imbibition is thought to occur in the lower part of the oil/water transition zone. If, however, pore surfaces become oil-wet at some stage of the drainage process, it would appear that any further drainage of the aqueous phase would not take place. Also, imbibition would not take place in the lower part of the transition zone. From this point of view, then, the observation of very low connate water saturations for a particular reservoir would not necessarily be indicative of oil-wet pore surfaces, but rather of water-wet surfaces.

This line of reasoning does not, however, introduce a serious difficulty when it is realized that the mechanism of wetting-film instability should not convert all pore surfaces to an oil-wet type of behavior when the critical pore radius is reached. As pointed out, it may be expected that only part of the total pore surface area is affected, and the resulting situation is therefore best described as a mixed wettability condition. Film flow processes involving both oil and brine can then take place, as is suggested by the work of Salathiel (7), and Swanson (8). Counter-current flows of this type are in fact easier to visualize than simultaneous drainage and imbibition processes when these take place under uniform wettability conditions.

It thus appears that pore surfaces covered by ultra-thin films, formed as the result of the wetting film instability mechanism, are likely to be converted to an oil-wet condition. This requires, as was suggested above, the adsorption or co-adsorption of asphaltenes or other heavy ends from the crude oil. In the case of Pembina, a detailed study has been published of the asphaltene and resin content of the produced oil from various parts of the field (40). It appears from the high concentrations found for the resin fraction of the crude oil in this reservoir, that the adsorption of resins, as well as of asphaltenes, may be involved. The close connection between the solubility characteristics of these fractions has been emphasized by Koots and Speight (41).

Other factors which play a role in the desaturation process under oil accumulation conditions in the case of Pembina should be mentioned at this point. Natural fractures resulting from regional uplift and erosional unloading are well-documented (42). Specific features of the stratification observed in the Cardium formation have recently been reviewed and re-interpreted (43). Evidence for a significant degree of overpressuring has been noted (44), and depth-porosity relationships discussed in relation to various diagenetic processes (45). All of these geological factors are likely to exert some degree of specific control over the process by which a state of mixed wettability has developed in Pembina. The physico-chemical analysis of wetting film stability, such as has been developed above, should thus be applied to a particular reservoir, only when it provides an integral and consistent feature of the geological model of the reservoir.

CONCLUSIONS

1. Insights as to the nature of mixed wettability states in petroleum reservoirs can be derived from a physico-chemical analysis of attractive and repulsive forces arising in thin aqueous wetting films.

2. The dependence of the attractive (van der Waals) forces on film thickness can be expressed by an inverse third power relationship. The Hamaker constant characterizing attractive interaction is estimated to be in the range of 3 to 9 x 10^{-21} J.

3. Repulsive interactions in wetting films arise from osmotic forces associated with the diffuse electrical double layers at the boundaries between such films and the adjoining bulk phases. The case of constant diffuse layer potentials was assumed. The dependence of the interaction force on electrolyte concentration follows from the experimentally observed dependence of the zeta potential on concentration, for solid/brine and oil/brine systems.

4. Limits to the stability of thin wetting films arise from the requirements that (a) the net interaction force is always repulsive, and (b) the derivative of the net force with respect to film thickness is negative. These requirements correspond to upper and lower limits, respectively, on the thickness of wetting films. It is estimated that stable wetting films range from 2 to 6 nm in thickness.

5. The existence of a lower limit to the thickness of a wetting film can be shown to imply a minimum effective pore size for which such films are stable. It is found that for electrolyte concentrations less than about 0.1 equivalents/liter, the minimum pore size for film stability falls in the range of 0.2 to 0.8 um, depending on the magnitude of the Hamaker constant. For electrolyte concentrations greater than 0.1 equiv./l, the minimum pore size increases sharply for values of the Hamaker constant greater than about 6 x 10^{-21} J.

6. Estimated values of the minimum pore size for film stability can be used, in conjunction with pore size distribution data and values of the connate water saturation, to predict when the in situ wettability of a petroleum reservoir is likely to be of the mixed wettability type.

7. The physico-chemical analysis of wetting film stability should be applied only within the context of a general geological model for a particular reservoir.

TABLE OF NOMENCLATURE

Fundamental Constants

e = electronic charge, 1.602189×10^{-19} C

k_B = Boltzmann constant, $1.380662 \times 10^{-23} J \cdot K^{-1}$

N_A = Avogadro number, $6.022045 \times 10^{23} mol^{-1}$

ε_o = permittivity of vacuum, $8.854188 \times 10^{-12} F \cdot m^{-1}$

Physical Variables

A = Hamaker constant characterizing dispersion force interaction

c = electrolyte concentration

h = distance between interacting plane parallel electrical double layers (as measured between outer Helmholtz planes)

H = scale factor for pore size

J = mean curvature of fluid/fluid interface

n = number of carbon atoms in alkane molecule

P = fluid pressure or thin film interaction force per unit area

r = radius of curvature of fluid/fluid interface

R = pore size

t = thickness of aqueous wetting film

T = absolute temperature

x = dimensionless distance between double layers

y = dimensionless diffuse double layer potential

z = dimensionless thin film interaction force per unit area

α = dimensionless Hamaker constant

γ = fluid/fluid interfacial tension

δ = diameter of water molecule

ε = dielectric permittivity

λ_D = characteristic distance for isolated electrical double layer

ξ = dimensionless thickness of compact parts of two interacting electrical double layers

ρ = dimensionless pore size

σ = surface charge density characterizing electrical double layer

ψ = electric potential characterizing electrical double layer

Subscripts

A = attractive force

b = interface between bulk fluid phases

c = capillary property associated with interface

d = diffuse part of electrical double layer

f = interface between thin aqueous film and oil phase

o = oil phase

s = solid SiO_2 phase (quartz)

r = relative to vacuum

R = repulsive force

w = aqueous phase or aqueous film

disp = dispersion interaction

eff = effective

equiv = nominal or equivalent

elec = osmotic interaction

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APPENDIX A - FORCE VERSUS FILM THICKNESS RELATIONSHIPS IN DIMENSIONLESS FORM

The Debye screening distance, λ_D, is a measure of the thickness of isolated double layers. It is given by the expression,

$$\lambda_D = \{(\varepsilon_r \varepsilon_o k_B T)/(2e^2 N_A)\}^{1/2} c^{-1/2} \qquad \text{(A1)}$$

The various parameters in eq. (A1) are defined in the Table of Nomenclature, and values of λ_D for several concentrations are shown in Table II. The dimensionless distance between the interacting diffuse double layers is then defined as

$$x = t/\lambda_D \qquad \text{(A2a)}$$

and the dimensionless diffuse layer potentials as

$$y_i = -e(\psi_d)_i/k_B T \quad (i = 1,2) \qquad \text{(A2b)}$$

The corresponding dimensionless attractive and repulsive forces are next defined as

$$z_{disp} = P_A/cN_A k_B T \qquad \text{(A3a)}$$

$$z_{elec} = P_R/cN_A k_B T \qquad \text{(A3b)}$$

The dimensionless form of eq. (16) can now be written as

$$z_{elec} - z_{disp} = \{\rho-(\lambda_D/H)(x+\xi)\}^{-1} \qquad \text{(A4)}$$

where

$$\rho = R_{eff}/H \qquad \text{(A5a)}$$

$$\xi = 4\delta/\lambda_D \qquad \text{(A5b)}$$

and the scale factor, H, is given by

$$H = \gamma_{ow}/cN_A k_B T \qquad \text{(A5c)}$$

A dimensionless Hamaker constant is next defined as

$$\alpha = A_{owo}/6\pi c N_A k_B T \lambda_D^3 \qquad \text{(A6)}$$

so that eq. (11) gives the following expressions for z_{disp} and the gradient of z_{disp},

$$z_{disp} = \alpha(x + \xi)^{-3} \qquad \text{(A7a)}$$

$$dz_{disp}/dx = -3\alpha(x + \xi)^{-4} \qquad \text{(A7b)}$$

Values of α and of the scale factor H as functions of the electrolyte concentration are also given in Table II. The values of α correspond to $A_{owo} = 5 \times 10^{-21}$ J.

The expressions for z_{elec} and the gradient of z_{elec} used in this work are equivalent to those derived by Hogg et al (22). These expressions are

$$z_{elec} = \frac{2y_1 y_2}{\sinh^2 x} \{\cosh x - \frac{1}{2}(\frac{y_1}{y_2} + \frac{y_2}{y_1})\} \qquad \text{(A8a)}$$

$$dz_{elec}/dx = \frac{2}{\sinh x} \{y_1 y_2 - z_{elec} \cosh x\} \qquad \text{(A8b)}$$

Note that the stability limit defined by the condition

$$dz_{elec}/dx = dz_{disp}/dx \qquad \text{(A9a)}$$

corresponds to a value of the dimensionless pore size, ρ, such that

$$d\rho/dx = \lambda_D/H \qquad \text{(A9b)}$$

Since H >> λ_D, this condition may be approximated by

$$d\rho/dx \simeq 0 \qquad \text{(A10)}$$

However, it is seen that the minimum pore size for stable films is not precisely the same as the minimum in the relationship between R_{eff} and t, as defined by eq. (16).

TABLE I

HAMAKER CONSTANTS FOR VARIOUS SELF AND TERNARY INTERACTIONS IN ALKANE/WATER/QUARTZ SYSTEMS [a]

Interaction	A, 10^{-20}J	Interaction	A, 10^{-20}J
O-O, $n^b = 6$	4.07	Q-W-O, $n^b = 6$	0.782^c
O-O, n = 8	4.50	Q-W-O, n = 8	0.835
O-O, n = 10	4.82	Q-W-O, n = 10	0.886
O-O, n = 16	5.23	Q-W-O, n = 16	0.958
W-W	3.70		
Q-Q	8.83		

a From ref. 13.

b n = number of carbon atoms in alkane molecule.

c Values calculated from eq. (13).

TABLE II

RELATIONSHIP OF DIFFUSE DOUBLE LAYER PARAMETERS TO ELECTROLYTE CONCENTRATION [a]

$y = -e\psi_d/k_BT$	$-\psi_d$ mV	σ_d mCm^{-2}	c, equiv./l	λ_D, nm	H, µm	α for $A = 6 \times 10^{-21}$J
0.4	11.14	12.77	0.3025	0.5434	0.03076	2.4412
0.5	13.92	12.22	0.1758	0.7128	0.05294	1.8608
0.6	16.71	11.66	0.1102	0.9004	0.08446	1.4732
0.7	19.49	11.10	0.0726	1.1091	0.12815	1.1960
0.8	22.28	10.54	0.0495	1.3428	0.18785	0.9879

a Based on Gouy-Chapman theory, eq. (1) of ref. (1), and empirical approximation, eq. (14). T = 323°K; $\varepsilon_r = 69.9$; $\gamma_{ow} = 25.0$ $mN \cdot m^{-1}$. The symbols used are given in the Table of Nomenclature.

TABLE III

THICKNESS OF WETTING FILMS AS A FUNCTION OF HAMAKER CONSTANT AND ELECTROLYTE CONCENTRATION

c, equiv./l	t_{max}, nm, for values of A in 10^{-21} J			
	A = 0	A = 3	A = 6	A = 9
0.3025	-	3.98	3.29	2.73
0.1102	-	7.40	6.32	5.53
0.0495	-	12.04	10.77	9.96

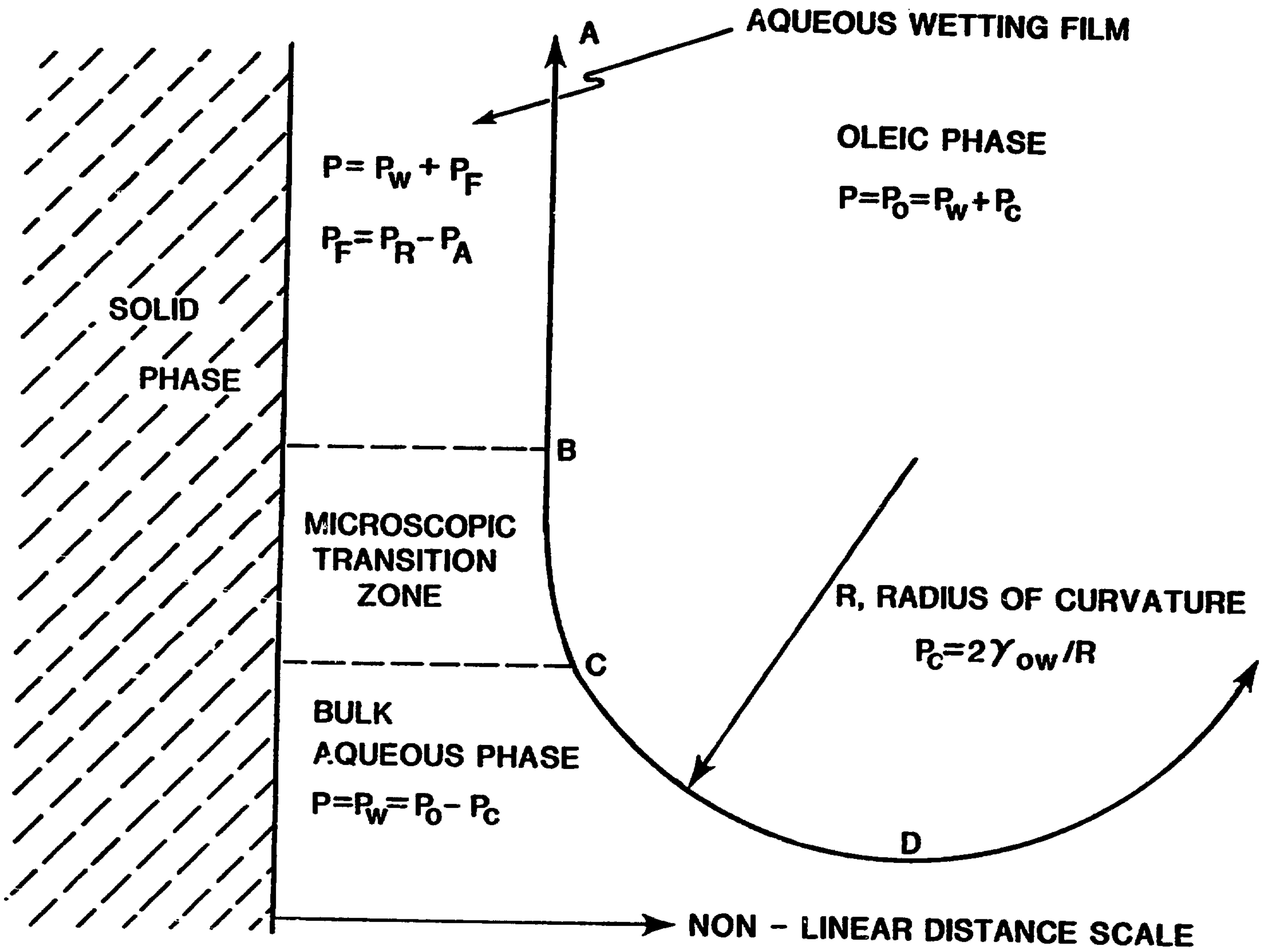
c, equiv./l	t, nm, for R = 5 um and values of A in 10^{-21} J			
	A = 0	A = 3	A = 6	A = 9
0.3025	3.61	3.25	2.88	2.42
0.1102	5.10	4.87	4.63	4.37
0.0495	6.71	6.58	6.45	6.31

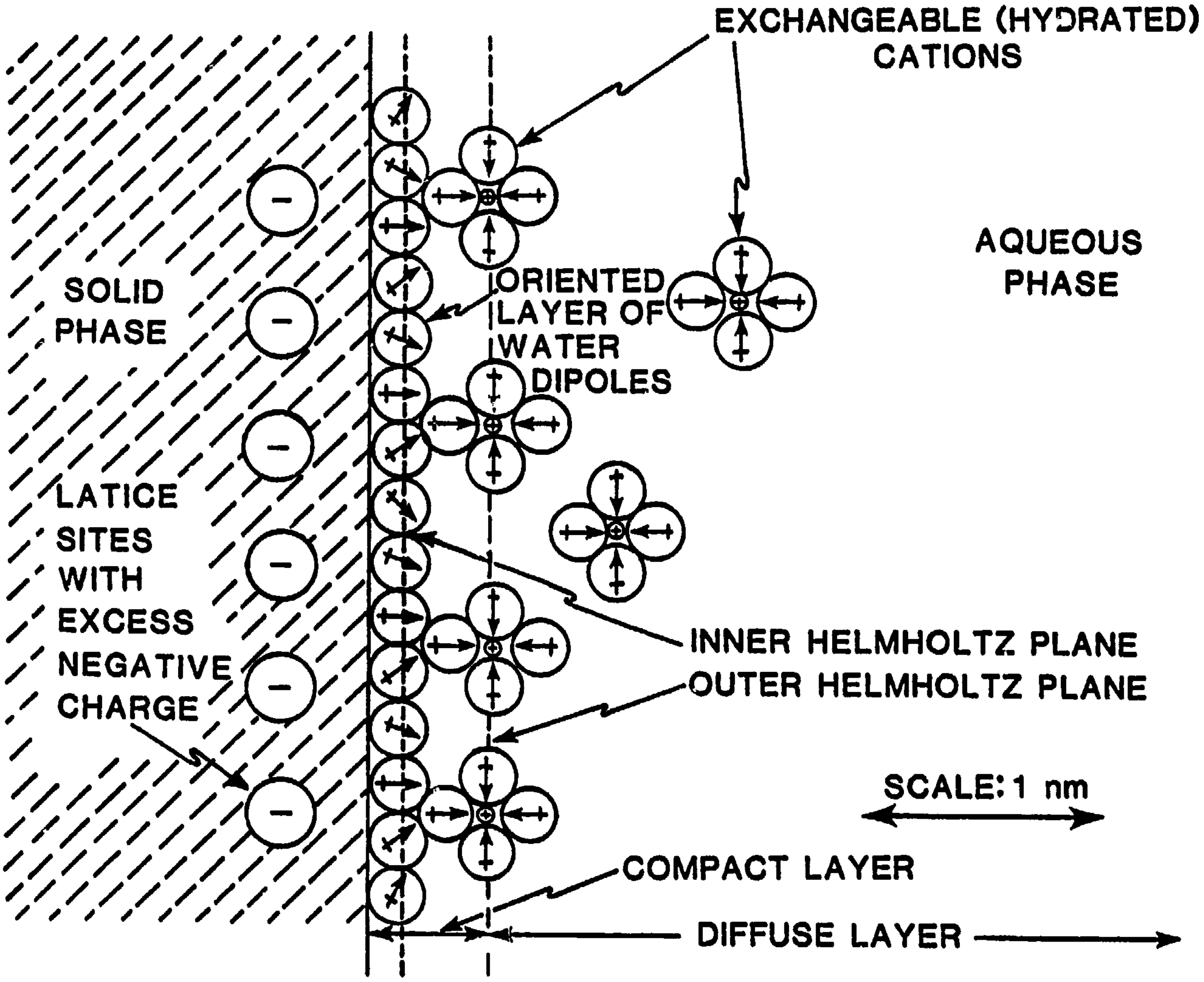
c, equiv./l	t_{min}, nm, for values of A in 10^{-21} J			
	A = 0	A = 3	A = 6	A = 9
0.3025	1.10	1.56	1.80	2.02
0.1102	1.10	1.86	2.15	2.37
0.0495	1.10	2.19	2.52	2.77

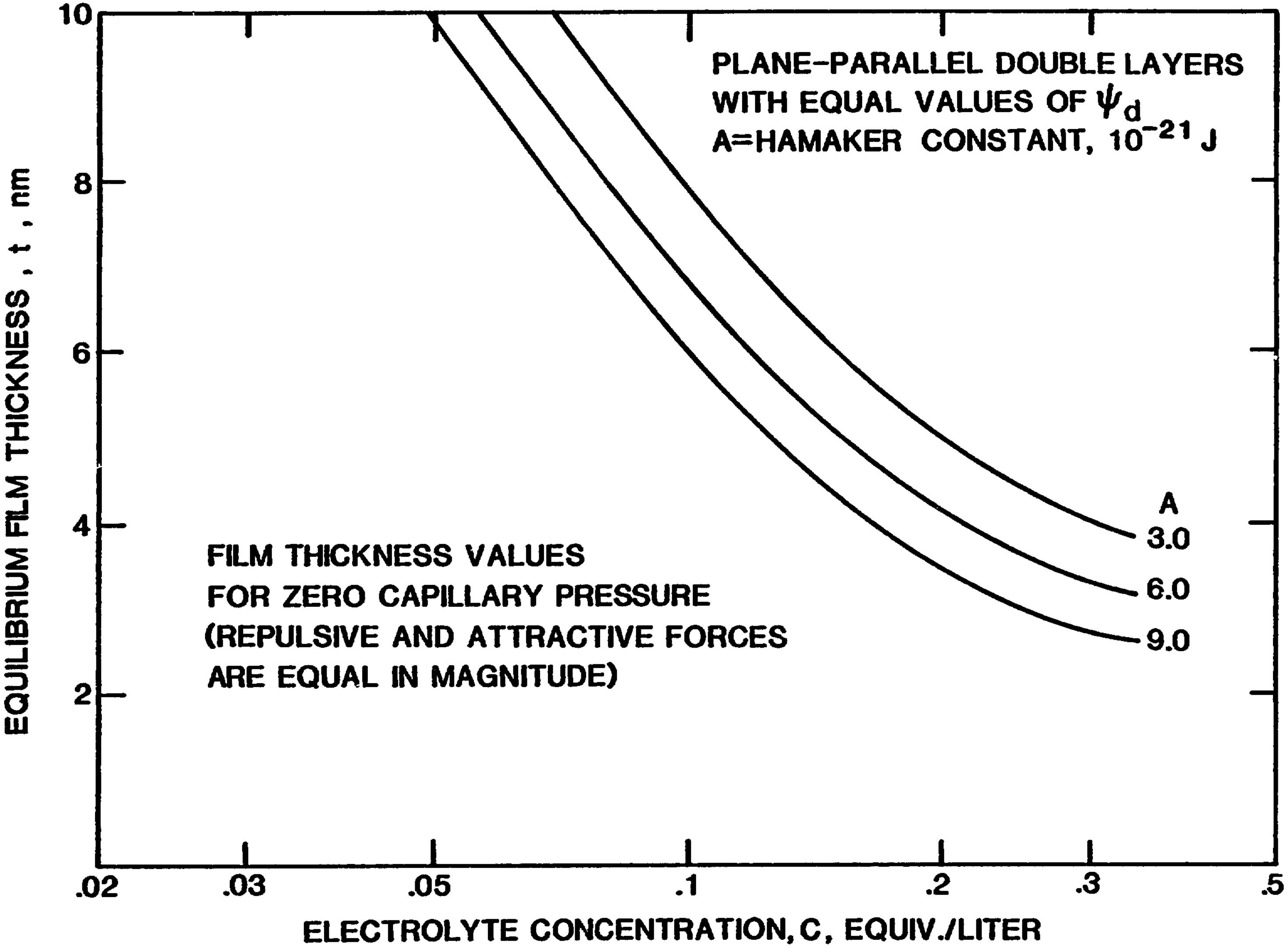
TABLE IV

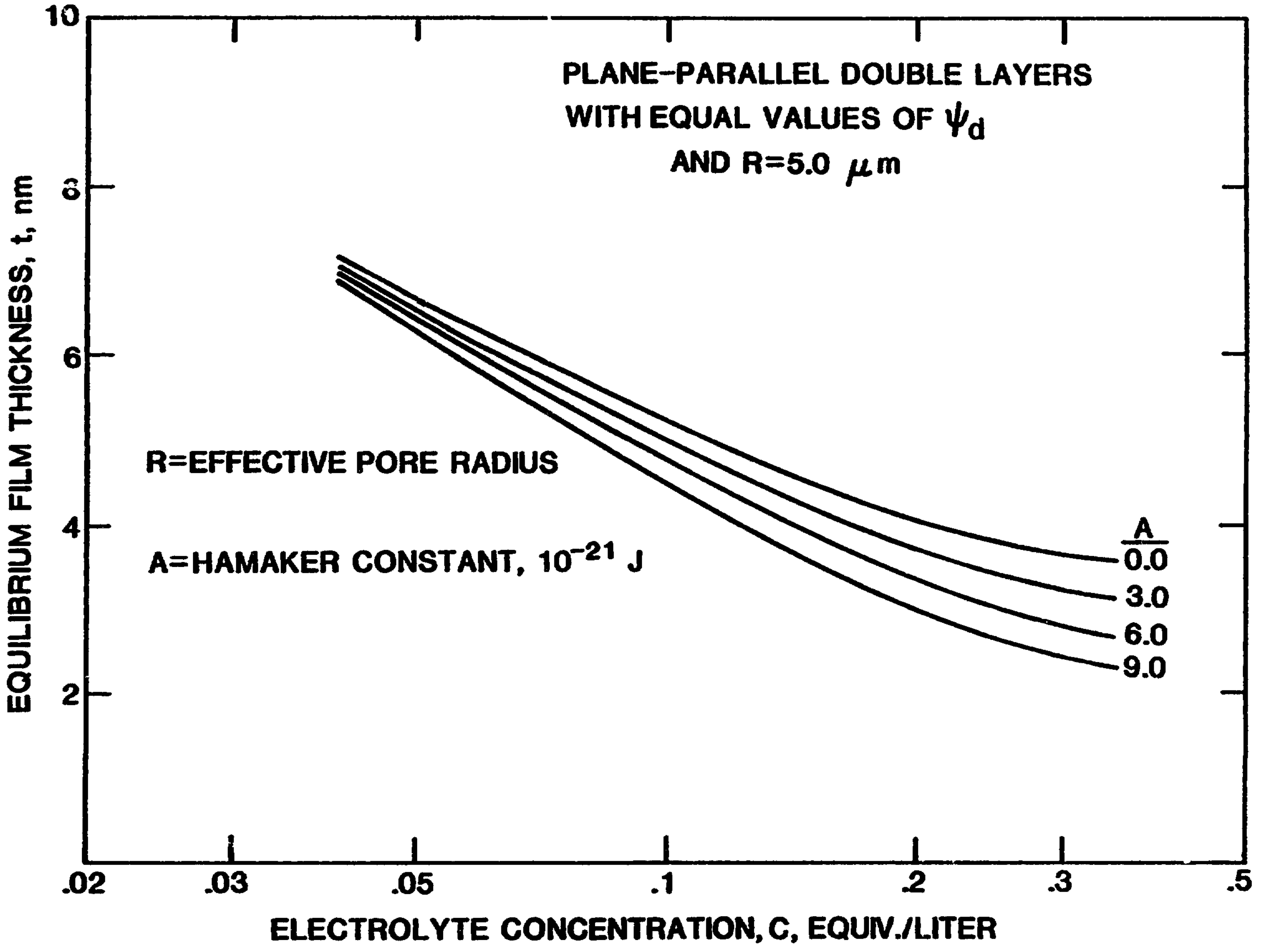
MINIMUM PORE SIZE FOR STABLE WETTING FILMS AS A FUNCTION OF HAMAKER CONSTANT AND ELECTROLYTE CONCENTRATION

c, equiv./l	R_{min}, um for Values of A in 10^{-21} J			
	A = 0	A = 3	A = 6	A = 9
0.3025	0.193	0.373	0.747	2.420
0.1102	0.236	0.387	0.555	0.800
0.0495	0.295	0.438	0.554	0.684

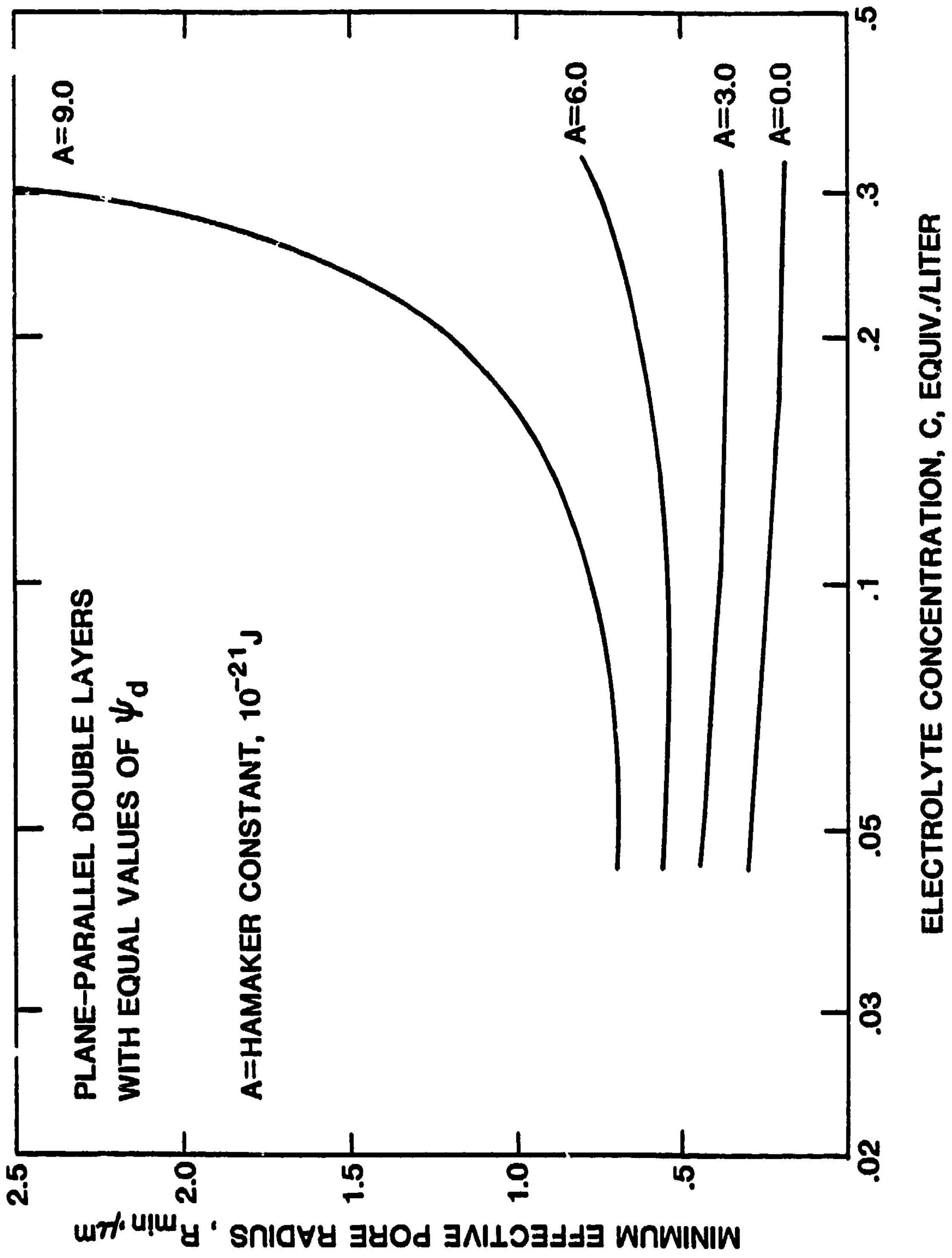

AQUEOUS WETTING FILM
A
OLEIC PHASE
$P=P_o=P_w+P_c$
$P=P_w+P_F$
$P_F=P_R-P_A$
SOLID
PHASE
B
MICROSCOPIC
TRANSITION
ZONE
R, RADIUS OF CURVATURE
$P_c=2\gamma_{ow}/R$
C
BULK
AQUEOUS PHASE
$P=P_w=P_o-P_c$
D
NON - LINEAR DISTANCE SCALE


EXCHANGEABLE (HYDRATED) CATIONS
AQUEOUS PHASE
SOLID PHASE
ORIENTED LAYER OF WATER DIPOLES
LATICE SITES WITH EXCESS NEGATIVE CHARGE
INNER HELMHOLTZ PLANE
OUTER HELMHOLTZ PLANE
SCALE: 1 nm
COMPACT LAYER
DIFFUSE LAYER

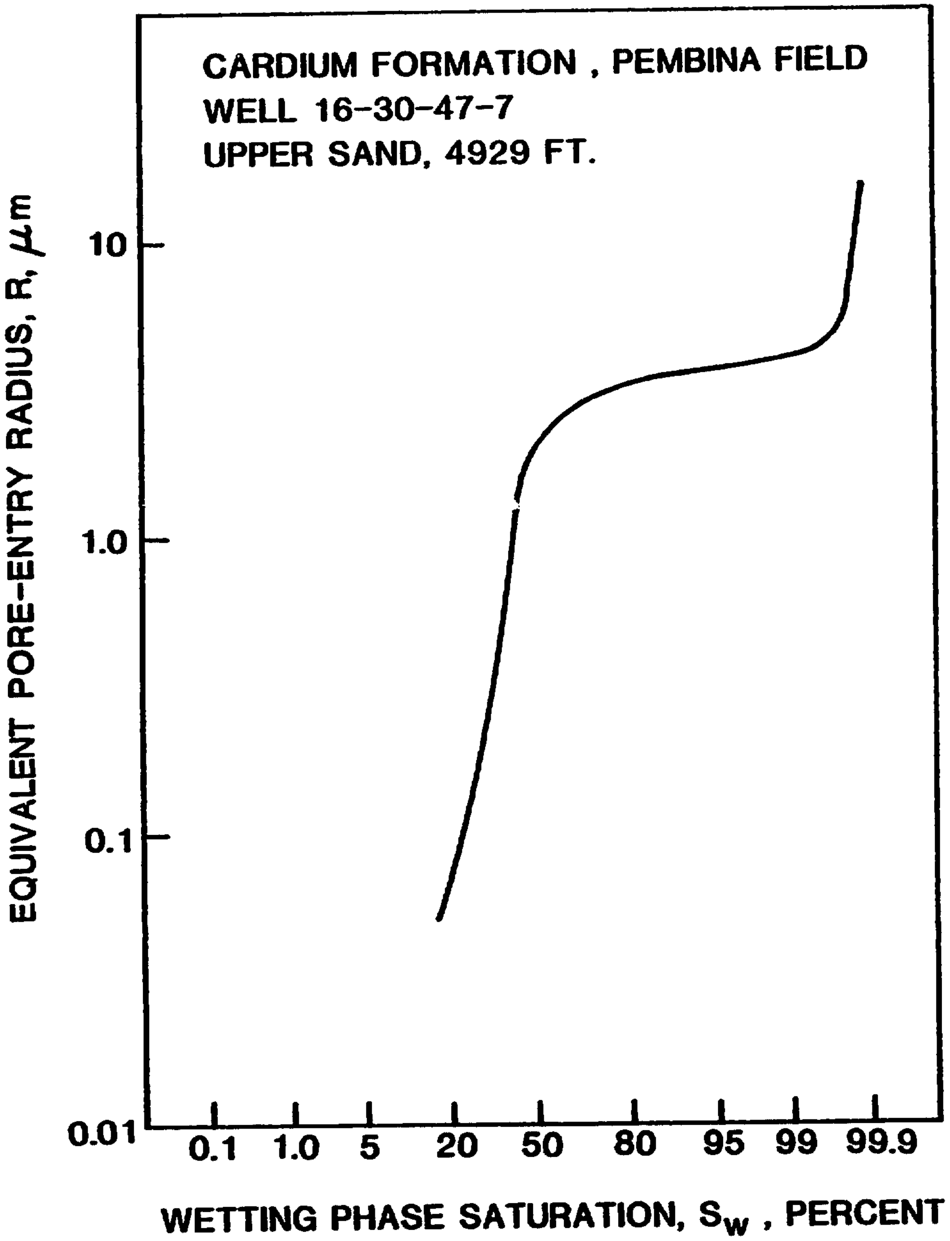

PLANE-PARALLEL DOUBLE LAYERS
WITH EQUAL VALUES OF ψ_d
A=HAMAKER CONSTANT, 10^{-21} J
FILM THICKNESS VALUES
FOR ZERO CAPILLARY PRESSURE
(REPULSIVE AND ATTRACTIVE FORCES
ARE EQUAL IN MAGNITUDE)
A
3.0
6.0
9.0
EQUILIBRIUM FILM THICKNESS , t , nm
10
8
6
4
2
.02
.03
.05
.1
.2
.3
.5
ELECTROLYTE CONCENTRATION, C, EQUIV./LITER


PLANE–PARALLEL DOUBLE LAYERS
WITH EQUAL VALUES OF ψ_d
AND R=5.0 μm
R=EFFECTIVE PORE RADIUS
A=HAMAKER CONSTANT, 10^{-21} J
A
0.0
3.0
6.0
9.0
EQUILIBRIUM FILM THICKNESS, t, nm
10
8
6
4
2
.02
.03
.05
.1
.2
.3
.5
ELECTROLYTE CONCENTRATION, C, EQUIV./LITER

4


PLANE-PARALLEL DOUBLE LAYERS
WITH EQUAL VALUES OF ψ_d
A=HAMAKER CONSTANT, 10^{-21} J
A=9.0
A=6.0
A=3.0
A=0.0
MINIMUM EFFECTIVE PORE RADIUS, R_{min}, µm
2.5
2.0
1.5
1.0
.5
ELECTROLYTE CONCENTRATION, C, EQUIV./LITER
.02
.03
.05
.1
.2
.3
.5

5



Sw, PERCENT	R, μm
20	.066
30	.24
40	1.06
50	2.07