C. Hanson, Ed. (Publication TID-22800, Department of Energy, Washington, D.C., 1979).
3. Water is lost from a closed basin lake only by evaporation and not by surface or subsurface outflow.
4. W. S. Broecker, *Chemical Oceanography* (Harcourt Brace Jovanovich, New York, 1974), p. 195; D. Thurber, *Bull. Volcanol.* **28**, 1 (1965).
5. G. H. Coleman, *The Radiochemistry of Plutonium* (Publication NAS-NS-3058, National Academy of Sciences–National Research Council, Washington, D.C., 1965); R. E. Connick, in *The Actinide Elements*, G. T. Seaborg and J. J. Katz, Eds. (McGraw-Hill, New York, 1954), pp. 221–300; R. P. Larsen and R. D. Oldham, *Science* **201**, 1008 (1978).
6. T. F. Rees, J. M. Cleveland, W. C. Gottschall, *Environ. Sci. Technol.* **12**, 1085 (1978).
7. Complexing of radionuclides by organic compounds such as ethylenediaminetetracetic acid (EDTA) used in decontamination treatment has been shown to be an important additional factor in waste management [J. L. Means, D. A. Crerar, J. O. Duguid, *Science* **200**, 1477 (1978); G. de Marsily, E. Ledoux, A. Barbreau, J. Margat, *ibid.* **197**, 519 (1977)].
8. I. C. Russel, *U.S. Geol. Surv. Eighth Annu. Rep.* (1889), pp. 261–394; D. W. Scholl, R. von Huene, P. St.-Amand, J. P. Ridlon, *Geol. Soc. Am. Bull.* **78**, 583 (1967); C. M. Gilbert *et al.*, *Geol. Soc. Am. Mem. 116* (1969), p. 275.
9. Most of the stream flow has been diverted since the 1940's to the Owens Valley Aqueduct which carries drinking water to Los Angeles; as a result, the lake level has been dropping by up to 0.5 m per year.
10. G. E. Hutchinson, *A Treatise on Limnology* (Wiley, New York, 1957), vol. 1; B. F. Jones, in *Second Symposium on Salt*, J. L. Rau, Ed. (Northern Ohio Geological Society, Cleveland, 1966), vol. 1; R. M. Garrels and F. T. Mackenzie, in *Equilibrium Concepts in Natural Water Systems*, R. F. Gould, Ed. (American Chemical Society, Washington, D.C., 1967), pp. 222–242; H. J. Simpson, thesis, Columbia University (1970).
11. H. L. Volchok, *J. Geophys. Res.* **71**, 1515 (1966); A. B. Joseph, P. F. Gustafson, I. R. Russell, E. A. Schuert, H. L. Volchok, A. Tamplin, in *Radioactivity in the Marine Environment* (National Academy of Sciences, Washington, D.C., 1971), pp. 6–41.
12. E. P. Hardy, P. W. Krey, H. L. Volchok, *Nature (London)* **241**, 444 (1973).
13. A. Kaufman, R. M. Trier, W. S. Broecker, *J. Geophys. Res.* **78**, 8827 (1973).
14. The dispersed $Fe(OH)_3$ precipitate was concentrated by successive decantation of the clear supernatant from a series of containers of decreasing size (400, 80, 20 liters) until a final volume of ~ 2 liters was achieved to allow convenient transportation.
15. K. M. Wong, *Anal. Chim. Acta* **56**, 355 (1971).
16. Suspended particles in the lake water (predominantly phytoplankton during the time of our sampling) can account for only a minor fraction of the total activity of the water column. If the effective K_d for phytoplankton in Mono Lake was $\sim 10^3$, as has been measured for the organic-rich sediments in the lake, then suspended particles at a total concentration of 10 mg/liter (a reasonable upper limit for Mono Lake) would account for only 1 percent of the total plutonium in an unfiltered water sample. Living biomass in Mono Lake is generally < 1 mg/liter (this figure is based on adenosine triphosphate measurements) [D. W. Winkler, Ed., *Institute of Ecology Publication No. 12* (University of California, Davis, 1977), p. 52].
17. H. J. Simpson, C. R. Olsen, R. M. Trier, S. C. Williams, *Science* **194**, 179 (1976); C. R. Olsen, H. J. Simpson, R. F. Bopp, S. C. Williams, T.-H. Peng, B. L. Deck, *J. Sediment. Petrol.* **48**, 401 (1978); C. R. Olsen, P. E. Biscaye, H. J. Simpson, R. M. Trier, N. Kostyk, R. F. Bopp, Y.-H. Li, H. W. Feely, *Estuarine Coastal Mar. Sci.*, in press.
18. We obtained this esimate by using a concentration of $^{239,240}Pu$ in Mono Lake sediments of ~ 17 pCi/kg (dry weight), a sediment particle density of 0.4 g/cm^3, a depth of measurable plutonium of 3 cm, and a total lake sediment area of 160 km^2.
19. Fallout delivery of $^{239,240}Pu$ at Mono Lake can be roughly estimated from the rate of fallout for a station from a similar latitude (New York), multiplied by the ratio of the mean annual precipitation at Mono Lake to that of the reference station, multiplied by the total surface area of Mono Lake during the peak fallout years:

$$1.8 \text{ mCi/km}^2 \times \frac{25 \text{ cm}}{100 \text{ cm}} \times 200 \text{ km}^2 = 90 \text{ mCi}$$

Integrated fallout of $^{239,240}Pu$ to 1978 at New York, N.Y., has been estimated to be 1.8 mCi/km^2 (H.L. Volchok, personal communication), based on a production ratio of $^{239,240}Pu$ to ^{90}Sr of 0.017 from weapons testing [J. H. Harley, in *Proceedings of the Environmental Plutonium Symposium* (Publication LA-4756, Los Alamos National Laboratory, Los Alamos, N.M., 1971), pp. 13–19] and the history of ^{90}Sr deposition in New York.
20. Financial support was provided by Department of Energy contract EY 2529. Contribution No. 2895 from Lamont-Doherty Geological Observatory of Columbia University. We thank B. Seal and others associated with the Sierra Nevada Aquatic Research Laboratory of the University of California for their help during our field sampling.

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An Interface Phase Transition: Complete to Partial Wetting

Abstract. *When two fluid phases are near a critical point, one of them will be excluded from contact with any third phase that happens to be present by a wetting film of the other critical phase. A simple and quite general strategy that may be used to induce a phase transition from complete wetting of the third phase to incomplete wetting is to add a new component to the fluid phases chosen to drive the two phases away from their critical point. This strategy is illustrated for methanol-cyclohexane mixtures.*

The observation that the contact angle (that is, the dihedral angle subtended by a fluid phase along a line contact with two other phases) may be either zero or nonzero dates back at least to Young (*1*). More recently, Butler found evidence from surface tension measurements for two transitions from nonzero to zero contact angle in the mercury-water-benzene system; however, his contact angle measurements failed to confirm the expected transitions (*2*). In this report we present unambiguous evidence for a phase transition from zero to nonzero contact angle in methanol-cyclohexane-water mixtures. The circumstances under which the contact angle changes from zero to nonzero values supports a group of phenomenological ideas that have been discussed under the title "critical point wetting" (*3*). These ideas relate wetting phenomena to the proximity of critical lines in fluid mixtures; thus they can be used in a wide variety of situations as a guide for locating transitions from zero contact angle (complete wetting) to nonzero contact angle (incomplete wetting). Such a guide will facilitate detailed study of the wetting transition itself and may assist in the control of wetting for technological purposes. We will first briefly review the argument that complete wetting must occur near critical points. This will motivate our measurements on fluid mixtures. Finally, we will comment on some remaining problems.

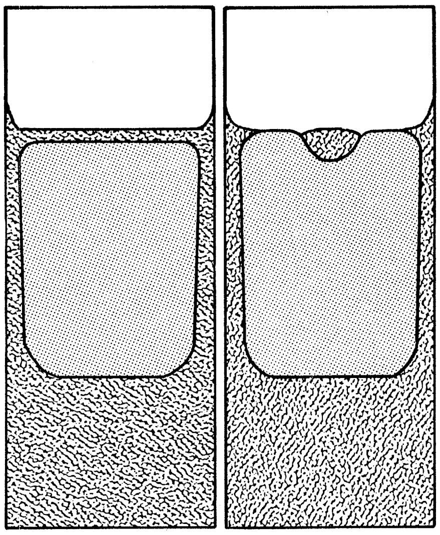

Fig. 1. Sketch of cuvettes containing two liquid phases and vapor. (Left) The lower (CH_3OH-rich) phase intrudes between the middle (C_6H_{12}-rich) phase and the cuvette wall. The lower phase also intrudes between the middle phase and the vapor. (Right) Water has been added to the solution. The lower phase still intrudes between the cuvette wall and the middle phase. The lower phase no longer intrudes between the middle phase and the vapor. Instead, there is a line of three-fluid phase contact near the cuvette wall and a line of three-fluid phase contact surrounding a lenticular drop of the lower phase suspended at the vapor interface.

To argue that complete wetting must occur near critical points we consider two fluid phases, α and β, in equilibrium somewhere near their critical point. The α and β phases may be partially miscible liquids [such as mixtures of methanol (CH_3OH) and cyclohexane (C_6H_{12})] below a consolute or critical temperature (T_c); alternatively, α may be a liquid and β may be a vapor. In either case, the surface tension between the α and β phases, $\sigma_{\alpha\beta}$, approaches zero at the $\alpha\beta$ critical point as $(T_c - T)^\mu$, where μ is known from experiment (*4, 5*) and theory (*6*) to be about 1.3. When a third, noncritical fluid phase, γ, is present (such as a vapor over the liquids), one must consider two additional surface tensions, $\sigma_{\alpha\gamma}$ and $\sigma_{\beta\gamma}$. As the α and β phases approach their critical point, we expect both $\sigma_{\alpha\gamma}$ and $\sigma_{\beta\gamma}$

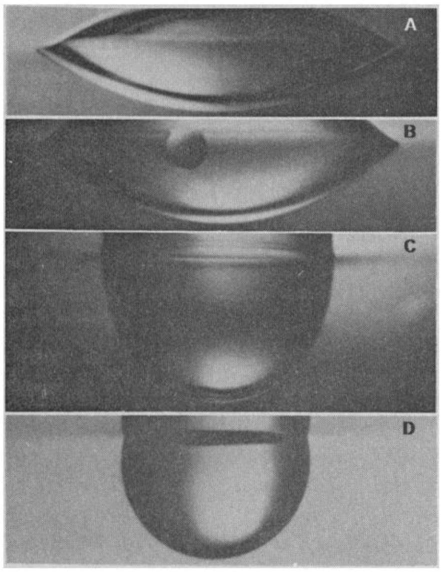

Fig. 2. Suspended lenticular drops (and reflections) photographed from 3° below the liquid-vapor interface. The mole fraction of water (X_{H_2O}) and the largest dimension of each drop are approximately as follows: (A) 0.024, 9 mm; (B) 0.027, 7 mm; (C) 0.080, 5 mm; and (D) 0.2, 1 mm.

to approach some value σ_c. Because the γ phase is not critical, it is plausible that the T dependences of $\sigma_{\alpha\gamma}$ and $\sigma_{\beta\gamma}$ reflect the T dependence of the compositions (or densities) of the α and β phases. Thus we expect $\sigma_{\alpha\gamma} - \sigma_c$ and $\sigma_{\beta\gamma} - \sigma_c$ to vary as $(T_c - T)^\beta$, where β is in the range 0.3 to 0.4. If, at some temperature, the three fluid phases meet at a nonzero contact angle, the balance of surface forces implies $|\sigma_{\alpha\gamma} - \sigma_{\beta\gamma}| < \sigma_{\alpha\beta}$. As one approaches T_c, this inequality will become an equality at some finite T before the critical point, because the exponent (μ) governing the decrease in $\sigma_{\alpha\beta}$ is larger than the exponent (β) governing the decrease in $|\sigma_{\alpha\gamma} - \sigma_{\beta\gamma}|$. As the inequality approaches the equality, the contact angle tends to zero and one of the critical phases forms a film between the third phase and the other critical phase. For example, if $\sigma_{\beta\gamma} > \sigma_{\alpha\gamma}$, the β-γ surface is replaced by a thin film of α separating β from γ. The β-γ surface has undergone the surface analog of a classical first-order transition. Because the σ's represent free energies per unit area, exactly at the transition $\sigma_{\beta\gamma} = \sigma_{\alpha\beta} + \sigma_{\alpha\gamma}$ and the $\beta = \gamma$ surface has two configurations of equal free energy. One of these is an intruding α-layer.

This argument suggests a simple strategy for locating a phase transition from complete to incomplete wetting of any desired third phase. Start with any two fluid phases sufficiently near their critical (or consolute) point that complete wetting of the chosen third phase occurs. Then take the two fluids away from their critical point by changing T or by adding another component. We have followed exactly this strategy, with mixtures of CH_3OH and C_6H_{12} playing the roles of the critical α and β phases and air saturated with CH_3OH-C_6H_{12} vapor acting as the third phase.

The two coexisting phases of CH_3OH-C_6H_{12} mixtures have been very well studied near ambient conditions, perhaps because of the ready availability of the pure components and the occurrence of a T_c near 46°C. The literature contains measurements of the coexisting densities (*7*), indices of refraction (*8*), coexisting compositions (*9*), capillary constant associated with the critical surface tension (*4*), and shifts in phase equilibria upon the addition of various third components (*9*–*11*).

At ambient conditions the CH_3OH-rich phase completely wets glass, quartz, and air saturated with vapor whereas the C_6H_{12}-rich phase completely wets Teflon and similar materials. The consequences of this are sketched on the left side of Fig. 1. When the denser, CH_3OH-rich phase is present in bulk at the bottom of a glass cuvette, it forms a thin wetting layer which separates the C_6H_{12}-rich phase from the glass and from the vapor. At the vapor interface, this wetting layer is macroscopically thick; it may be partially dislodged if one taps the cuvette (*12*). We have used ellipsometry to verify that this wetting layer has the composition of the CH_3OH-rich phase (*13*). By the addition of a dye (such as naphthol green or bromophenol blue), which dissolves preferentially in CH_3OH, the layer can be made strikingly visible.

We attempted to find transition from complete wetting to incomplete wetting at the vapor interface by cooling the mixture, thus taking it away from its T_c. The mixture began to freeze before we encountered any wetting transition. On the other hand, raising the T_c by adding water to this mixture did induce such a transition at ambient T (22°C). Somewhat after the transition, the cuvette looked like the sketch on the right in Fig. 1. An interface between the air (saturated with vapor) and the C_6H_{12}-rich phase has now appeared. Because the CH_3OH-rich and C_6H_{12}-rich phases have nearly the same density, it is easy to suspend a CH_3OH-rich drop up to several millimeters in diameter at the vapor interface. In most cases, vigorous shaking of the cuvette will lead to the formation of such drops. These drops can be photographed through the sides of the cuvette if the camera is placed to view the air-liquid interface from below. A sequence of such photographs with increasing water concentration is shown in Fig. 2, A through D. Each photograph shows a drop, along with its reflected image in the air-liquid interface. In some instances a much smaller drop of C_6H_{12}-rich phase may be formed inside a large CH_3OH-rich drop (Fig. 2B). It is clear from Fig. 2 that the interior dihedral angle of the CH_3OH-rich drop, θ, increases from a very small value to an angle greater than 90° as more water is added. In Fig. 3, we have plotted cos θ as a function of the mole fraction X of water added to the CH_3OH-C_6H_{12} mixture. (These data at 22°C are for a mixture of five parts C_6H_{12} to one part CH_3OH, by volume.) The value of θ was measured directly from photographs such as those in Fig. 2. The graph (Fig. 3) provides unambiguous evidence that a transition from complete to incomplete wetting occurs at $X = 0.020$. The hatched area in Fig. 3 indicates that we were never able to obtain a suspended CH_3OH drop with $X \leq 0.020$. All droplets provided by agitation completely merged into the CH_3OH film right up to and including the composition marked by the large circle. Figure 3 also shows the discontinuity in the compositional derivative of θ and thus confirms, within the resolution of these measurements, the first-order nature of the surface phase transition.

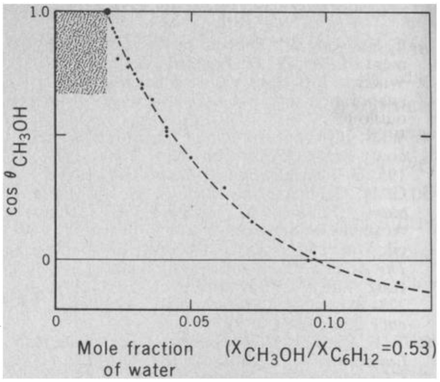

Fig. 3. Cosine of the dihedral angle of the CH_3OH-rich phase (θ) in contact with the C_6H_{12}-rich phase and the vapor phase as a function of the mole fraction of water in the solution.

The contact angle we have measured, θ, is most sensitive to the rapidly changing (critical) surface tension between the CH_3OH-rich and C_6H_{12}-rich phases. In rough experiments we have determined that this tension changes from less than 0.2 mN/m (dynes per centimeter) in the absence of water to 4.8 mN/m when $X = 0.10$. At the complete wetting-incomplete wetting transition ($X = 0.020$), this tension is roughly 1.2 mN/m. These measured tensions and the location of the complete wetting-incomplete wetting

ting transition are not sensitive to small changes in T. This insensitivity is expected. By the time enough water has been added to the CH_3OH-C_6H_{12} mixture to induce the wetting transition at the air-liquid interface, the T_c of the two liquid phases has been raised to about 75°C (*11*). Then small fluctuations in ambient T will not significantly change the "distance" from the critical line.

We have observed several other transitions from complete to incomplete wetting starting with CH_3OH-C_6H_{12} mixtures. As water is added, the CH_3OH-rich phase will cease to wet glass completely. Instead of raising T_c by adding water, we have also raised it by adding NaOH or NaI; as we expected, complete wetting of the fluid-air interface by the CH_3OH-rich phase ceased. After the addition of sufficient water to cause dewetting at the vapor interface, the addition of acetone, which is known to lower T_c (*10*), restores wetting. Wetting and dewetting of the glass walls of the cuvette were also observed.

Our experiments leave open an important issue. Two recent phenomenological descriptions of the first-order phase transition from complete to partial wetting have been given (*3, 14*). In one description (*3*), the transition we have observed is merely the end point of a manifold of interface phase transitions. If this description is correct, a study of, for example, the interface between the vapor and a C_6H_{12}-rich liquid should reveal discontinuous transitions from low to high adsorption of CH_3OH accompanied by discontinuities in the first derivatives of the tension of this interface. These phenomena are predicted to occur at saturated vapor pressure along a surface in the space of three thermodynamic variables: temperature and mole fractions of water and CH_3OH. This surface is anchored at the line of three-phase coexistence, which happens to pass through the point: $T = 22°C$, $X_{H_2O} = 0.020$, $X_{CH_3OH}/X_{C_6H_{12}} = 0.53$. Experimental observations of the predicted manifold of interface transitions in the absence of three coexisting phases would be most interesting.

M. R. MOLDOVER
Thermophysics Division,
National Bureau of Standards,
Washington, D.C. 20234
JOHN W. CAHN
Metal Science and Standards Division,
National Bureau of Standards

References and Notes

1. T. Young, *Philos. Trans.* **95**, 65 (1805).
2. E. B. Butler, *J. Phys. Chem.* **67**, 1419 (1963).
3. J. W. Cahn, *J. Chem. Phys.* **66**, 3667 (1977).
4. C. Warren and W. W. Webb, *ibid.* **50**, 3694 (1969).
5. W. Rathjen and J. Straub, in *Proceedings of the Seventh Symposium on Thermophysical Properties*, A. Cezairliyan, Ed. (American Society of Mechanical Engineers, New York, 1978), p. 839.
6. S. Fisk and B. Widom, *J. Chem. Phys.* **50**, 3219 (1969).
7. A. N. Campbell and S. C. Anand, *Can. J. Chem.* **50**, 1109 (1972).
8. D. T. Jacobs *et al.*, *Chem. Phys.* **20**, 219 (1977).
9. E. L. Eckfeldt and W. W. Lucasse, *J. Phys. Chem.* **47**, 164 (1947).
10. V. E. Leibnitz, H.-G. Konnecke, S. Niese, *J. Prakt. Chem.* **4**, 278 (1957); E. R. Washburn and H. C. Spencer, *J. Am. Chem. Soc.* **56**, 361 (1934); A. N. Campbell and S. C. Anand, *Can. J. Chem.* **50**, 479 (1972).
11. D. C. Jones and S. Amstell, *J. Chem. Soc.* **1930**, 1316 (1930).
12. R. B. Heady, thesis, Massachusetts Institute of Technology (1969); ——— and J. W. Cahn, *J. Chem. Phys.* **58**, 896 (1973).
13. R. E. Dehl of the Polymer Science and Standards Division of the National Bureau of Standards assisted with these measurements.
14. B. Widom, in *Statistical Mechanics and Statistical Methods in Theory and Application*, U. Landman, Ed. (Plenum, New York, 1977), p. 33. This report does not consider the question of whether the complete-to-partial wetting transition is the end point of a manifold of interface transitions. If this question were considered, the same conclusions as were presented in (*3*) may well have been reached.
15. We thank B. Stephenson for stimulating comments and experimental assistance; Dr. R. Dehl for advising us concerning ellipsometry; J. Gallagher and L. Ketron who assisted with the photography; and Prof. B. Widom who made numerous helpful suggestions. This work has been supported in part by the NASA Lewis Research Center under contract C-62861.

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How Electric Fields Modify Alkane Solubility in Lipid Bilayers

Abstract. *The planar lipid bilayer membrane is assumed to be in osmotic equilibrium with the surrounding Plateau-Gibbs border (annulus) and entrapped microlenses. An electric field applied across the membrane raises the chemical potential of the alkane in the bilayer, causing it to shift from the bilayer to the annulus and microlenses. This shift results in a decrease in thickness.*

Accurate description of bulk solution properties in molecular terms is a longstanding problem of physical chemistry. The problem is a difficult one because little is known about the behavior of solutions in volumes of molecular dimensions. Much could be learned if a "slice" of a solution a few molecules thick could be isolated and scrutinized. While this is not possible in a literal sense, the black lipid film formed in aqueous media (*1*) is an excellent approximation to such a slice in that it is two molecules thick and may have dissolved in it alkane or related molecules. The black lipid film, or planar lipid bilayer membrane, forms spontaneously in the manner of soap films when a solution (~ 1 percent) of surface active lipid in an alkane solvent is spread across an aperture separating two aqueous phases. The resulting film consists of a lipid bilayer saturated with alkane surrounded by a Plateau-Gibbs border (annulus) of the bulk solution. Bulk solution is also dispersed as microscopic lenses within the bilayer. The optical reflectance of the bilayer is very small and hence the films are "black."

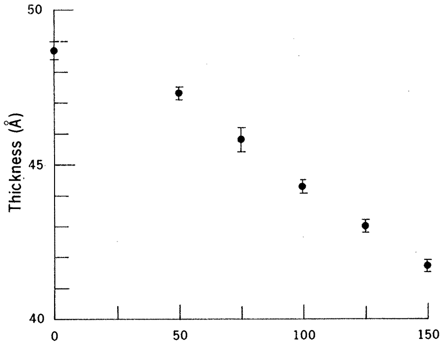

Fig. 1. Thickness of black lipid bilayer membranes as a function of applied potential. The bilayers were formed at 20°C from GMO and *n*-decane (10 mg/ml) in 0.1*M* NaCl solutions. Thickness (δ_B) is calculated from measurements of specific geometric capacitance C_g (Table 1) as described in (*19*).

I report here a mechanism for the modification of the solubility of alkanes in the bilayer by applied electric fields. The mechanism leads to a better understanding of the relation between the gross behavior of a solution and the solution's microscopic properties. Understanding the behavior of alkane-in-bilayer solutions is of particular importance in membrane biology, since biomembranes are essentially "two-dimensional solutions" consisting of hydrophobic proteins dissolved in a bilayer [reviewed in (*2*)].

Electric fields cause large decreases in the thickness of black lipid bilayer membranes (*3-5*). An example of this effect for bilayers formed from glyceryl monooleate (GMO) and *n*-decane is shown in Fig. 1. The thickness change apparently results from a shift of the alkane from the bilayer into the annulus and microlenses (*5*). The shift is generally attributed (*3-5*) to an electrostrictive pressure rise (P_V, dynes per square centimeter) in the bilayer given by

$$P_V = \left(\frac{\epsilon_0 \epsilon_B}{2\delta_B^2} V^2\right) \times 10^7 \qquad (1)$$

where $\epsilon_0 = 8.85 \times 10^{-14}$ farads per centimeter, ϵ_B is the dielectric coefficient of