Acidity at a Liquid–Liquid Interface*

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By using porous polypropylene as a support, we have measured the
contact angle of buffered aqueous droplets on surfaces which were over half
bis(2-ethylhexyl)hydrogen phosphate, HA. From the variation of the contact
angle with the pH of the aqueous solution the degree of dissociation, α, of
HA has been evaluated as a function of pH. By defining the standard states
of the interfacial HA and its conjugate base at the 50% ionized aqueous-
organic interface, a pK_a is obtained for the interfacial acid, equal to the pH
of the aqueous solution which is in equilibrium with the 50% ionized in-
terfacial acid.

Following Katchalsky and Spitnik[14] the ratio of the activity coefficient
of the conjugate base γ_{A^-} to the activity coefficient of the acid, γ_{HA} is
equated to $[\alpha/(1-\alpha)^{(n-1)}]$ for α values near 0.5. This permits the evaluation
of the empirical parameter, n, and leads to a relation between pH and α.

$$pH = pK_a - n \log [(1-\alpha)/\alpha]$$

This relation is found to hold from $\alpha > 0.1$ to $\alpha < 0.9$, although it cannot
be valid for either $\alpha = 0.0$ or $\alpha = 1.0$.

INTRODUCTION

Bis(2-ethylhexyl)hydrogen phosphate (HA) is a widely used reagent for the ex-
traction of metal ions from aqueous solution.[1-5] The covalency changes that such ex-
tractions require often occur at the aqueous–organic interface, and require the par-
ticipation of the conjugate base of HA, A−.[6-9] However, the acid dissociation of HA
at the interface does not appear to have been studied. There is also a problem in
the economical representation of the interfacial ionization.

We have now used a technique, based on contact angle, developed by Whitesides
and coworkers, to determine the degree of dissociation.[10] We have used a scheme in-
troduced by Katchalsky and Spitnik[11] to obtain an interfacial dissociation constant

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K_a, and another parameter, n, which is a measure of the inhibition of dissociation by preexisting charged groups. The resulting pK_a, 2.85, is somewhat higher than the value, 2.3, which can be inferred for the same substance in dilute aqueous solution.[12] A value of 1.85 is obtained for n. This is reasonably consistent with Katchalsky's experience[11] combined with an estimated distance between acidic groups in the interface, 13–20 Å.[13–15] (A distance of 11Å can be estimated by assuming the HA molecules are close-packed cylinders with standard bond lengths, tetrahedral bond angles around phosphorus, and a van der Waals radius of 4.0 Å for a CH_2 group.) The Katchalsky formalism successfully represents the degree of dissociation from 0.10 to 0.90.

EXPERIMENTAL

Materials. HA was purchased from Aldrich Chemical Co. It was about 98% pure, containing about 1% each of 2-ethylhexyldihydrogen phosphate and tris(2-ethylhexyl)phosphate, as determined by the intensity and location of bands in its ^{31}P-NMR spectrum. Celgard® 2400 and 2500 were obtained from the Celenese Corp. They are porous polypropylene materials with a void volume of 37% and 45% respectively. They are both 2.5×10^{-3} cm thick. Contact angles were determined using the sessile drop method[16,17] implemented in a home-built contact angle goniometer.[17] It was equipped with an environmental chamber, in which a water-saturated environment was maintained to avoid evaporation, and a low-power telescope for observations. The appearance of the drop through the telescope is shown, and the contact angle is defined, in Figure 1.
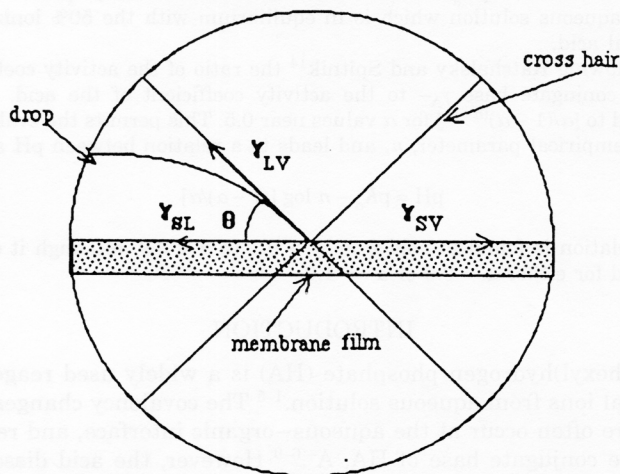

Figure 1. A sessile drop, as seen through the telescope of the goniometer. The three interfacial tensions; γ_{SL}, γ_{SV}, and γ_{LV} and the contact angle, Θ, are defined.

The aqueous solution for the drops was made up with 2.00 M $NaClO_4$ to provide an approximately constant ionic atmosphere and to decrease the solubility of HA in the aqueous phase; 0.01 to 0.25 M citric acid; and enough NaOH or $HClO_4$ to achieve the desired pH. To get pH values above 2.0, NaOH was added, and the pH was determined with a glass electrode

pH meter. To get pH values of 2.0 and below, $HClO_4$ was added, and the pH was equated to the negative logarithm of the $HClO_4$ concentration.

A fixed, flat surface of HA was obtained by taking it up in the pores of a porous plastic, Celgard® 2400 or 2500. An electron micrograph of the Celgard® 2500 surface is shown in Figure 2. The fraction of active area was determined by weighing micrographs like that shown, then cutting out the active areas (the striated areas) and weighing those. The fraction determined for Celgard® 2500 was 0.50, 0.51, and 0.52 in three trials giving an average of 0.51. Celgard® 2400 was similarly found to have a fractional active area of 0.55. For measurements, a strip of plastic ~ 1 × 5 cm was dipped into HA, the excess was blotted off with face tissue, then the strip of plastic was fixed to a microscope slide with adhesive tape at its two ends. The central section, on which measurements were made, rested directly on the slide. The two supports gave no detectable difference in contact angle.
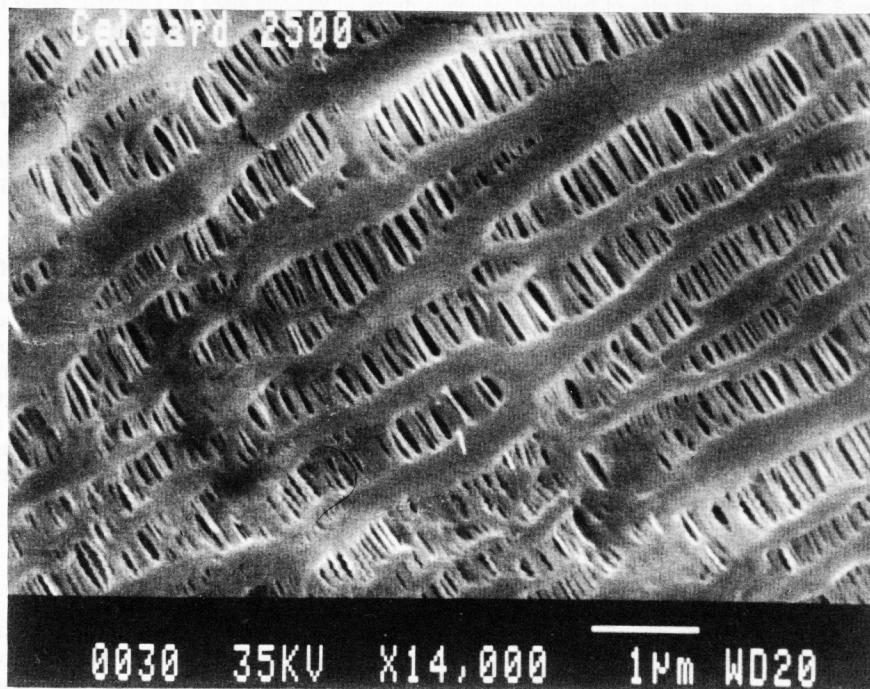

Figure 2. An electron micrograph of the surface of Celgard® 2500.

Aqueous drops were placed on the surface with a microsyringe. If these drops are too large they will be distorted by gravity,[18] so drops ranging in size from $1 - 4 \times 10^{-3}$ cm^3 were examined at various pH values, in the presence of 0.01 M total citrate. The effect of drop size is shown in Figure 3. Each point is the average of four measurements. It was concluded that drops in this size range are free of distortion within the experimental uncertainty. Consistently, Mack has estimated a distortion of contact angle about 1° for drops of about this size.[18] All the rest of the work described in this paper was done with 1 x 10^{-3} cm^3 drops except where otherwise noted.
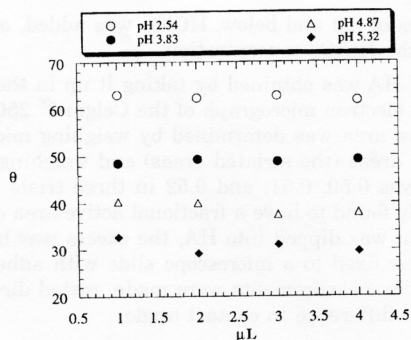
Figure 3. The contact angles of buffered aqueous drops of various sizes on Celgard® 2400 film impregnated with bis(2-ethylhexyl)hydrogen phosphate, HA. The pH values are shown.

Figure 3 suggests a probable error of about ± 2° in the contact angle measurements. This is also the result of repetitive measurements under the same conditions. This is adequate for our purposes, since the typical titration curves span a contact angle of about 20°. Nevertheless, 10 – 25 replications were averaged for each point on the titration curves, so their uncertainty is somewhat smaller.

To test for interfacial equilibrium and uniformity of the interface the contact angles of advancing and receding drops were examined. To determine the effect of an advancing interface the contact angle was determined for a drop of volume, 0.5×10^{-3} cm^3, with pH of 3.77 and total citrate of 0.01 M, on a surface of HA imbibed in Celgard® 2400. A further 0.5×10^{-3} cm^3 of the same aqueous solution was carefully added to the drop from the microsyringe, without allowing the microsyringe to touch the aqueous–organic interface. The oberseved contact angle changed by only 1°. To determine the effect of a receding interface, the microsyringe was touched to the surface of a 2.0×10^{-3} cm^3 drop, and 1.0×10^{-3} was removed. The drop and surface compositions were the same as for the advancing interface. The contact angle changed by 1.5°. Analogous measurements were also made at a pH of 1.0. The changes of contact angle with the advance or recession of the interface were even smaller. It was concluded that the surfaces are adequately uniform and the interfaces fully equilibrated.

THEORY

Nearly 190 years ago Young proposed[19] that the contact angle for a liquid drop resting on a plane surface is the result of equilibrium among three surface tensions, if the influence of gravity on the drop can be neglected. These are the surface–liquid tension, γ_{SL}, the surface-vapor tension, γ_{SV}, and liquid vapor tension, γ_{LV}. The directions of these interfacial tensions are all defined in Figure 1. Young's proposal leads to Eq. (1) for cos Θ, where the contact angle, Θ, is also defined in Figure 1.

$$\cos \Theta = (\gamma_{SV}/\gamma_{LV}) - (\gamma_{SL}/\gamma_{LV}) \tag{1}$$

In the present case the non-aqueous surface is about half HA, and half polypropylene. The HA surface is expected to be unionized at low pH, but ionized at high pH, so γ_{SL} should be pH-sensitive.[20,21] We assume that γ_{SV} and γ_{LV} are pH-insensitive.[20,21] (The assumption that γ_{LV} is pH-insensitive will be examined in the RESULTS section). We also make the following, more general assumptions, which are

originally due to Young[19] and explicated in detail by Andrade, Smith and Gregonis.[22] (a) The non-aqueous surface is smooth, planar, and not deformed during the measurement. (b) The surface is homogeneous on the scale of the drops. (c) There is no material transfer between the phases during the measurement.

In order to relate the contact angle to the degree of interfacial dissociation it is assumed that HA presents to the aqueous phase the maximum number of functional groups that its size and shape will allow, in both the ionized and unionized states, and that this number does not change on ionization. Finally γ_{SL} is assumed to be the weighted sum of the contributions of the various groups present in the surface; the weighting factors being the fractional areas presented by each type of group to the aqueous drop. In the present case there are three kinds of groups present in the nonaqueous surface; the polypropylene support, with fractional area, A_C; the ionized A^-, with fractional area, A_I'; and the unionized HA, with fractional area, A_U'. This gives Eq. (2) for γ_{SL}.

$$\gamma_{SL} = A_C\gamma_C + A_I'\gamma_I + A_I'\gamma_U \tag{2}$$

For convenience A_I and A_U are now defined by Eq. (3) and (4), so that they represent the fractions of the phosphate surface which is ionized and unionized, respectively, and their sum is unity.

$$A_I = A_I'/(A_I' + A_U') \tag{3}$$

$$A_U = A_U'/(A_I' + A_U') \tag{4}$$

Substitution in Eq. (2) gives Eq. (5) for γ_{SL} and substitution of this expression into Eq. (1) gives Eq. (6), where the pH-independent quantities, C_1 and C_2, are defined in Eqs. (7) and (8).

$$\gamma_{SL} = A_C\gamma_C + (A_I\gamma_I + A_U\gamma_U)(A_I' + A_U') \tag{5}$$

$$\cos\Theta = C_1 - C_2[A_I(\gamma_I - \gamma_U) + \gamma_U] \tag{6}$$

$$C_1 = (\gamma_{SV}/\gamma_{LV}) - (A_C\gamma_C/\gamma_{LV}) \tag{7}$$

$$C_2 = (A_I' + A_U')/\gamma_{LV} \tag{8}$$

In the low pH limit A_I is zero, while it is unity in the high pH limit. These equations permit the evaluation of γ_U and γ_I from $\cos\Theta_U$ and $\cos\Theta_I$, the low and high pH limits of $\cos\Theta$ respectively.

$$\gamma_U = (C_1 - \cos\Theta_U)/C_2 \tag{9}$$

$$\gamma_I = (C_1 - \cos\Theta_I)/C_2 \tag{10}$$

When these values are substituted in Eq. (6) a relation among cos Θ, A_I, and the limiting values of cos Θ, Eq. (11), is obtained.

$$\cos \Theta = A_I \cos \Theta_I + (1 - A_I) \cos \Theta_U \qquad (11)$$

It seems reasonable to identify A_I with α, the degree of ionization of the interfacial phosphate groups.[20,21] If this is done, and Eq. (11) is rearranged, an explicit expression for α in terms measurable quantities is obtained, Eq. (12).

$$\alpha = (\cos \Theta - \cos \Theta_U)/(\cos \Theta_I - \cos \Theta_U) \qquad (12)$$

The same expression is obtained if the HA spreads out over the whole polymer surface. In that case Θ_U is simply the contact angle at the HA–water interface, but, since it is a measured quantity, the reasult is unchanged. Whitesides has also obtained the same result for the contact angle on an acid-derivatized, partially ionized, polymer surface.[20,21]

For dissociation of an acid in solution, α is related to the pH and the acid dissociation constant, K_a, by Eq. (13).

$$pH = pK_a - \log [(1 - \alpha)/\alpha] + \log [(\gamma_{A^-})/\gamma_{HA}] \qquad (13)$$

Equation (13) should also apply to an interfacial dissociation provided that standard states are appropriately chosen. The pH is measured in the bulk aqueous phase, so the conventional standard state is used for H^+; an ideal, 1.0 molal solution. The A^- and HA that are of interest are those at the interface. Also, it is a practical convenience to chose standard states so that $pK_a = pH$ when $\alpha = 0.5$, as it does for simple acids in solution. Therefore, the standard state for HA is chosen as interfacial HA in a half-neutralized interface. For A^- the standard state is correspondingly chosen as interfacial A^- in a half neutralized interface. These choices make γ_{A^-}/γ_{HA} unity and $K_a = pH$ at $\alpha = 0.5$.

For phosphate groups packed together at the interface, as for a polyacid, both γ_{A^-} and γ_{HA} can be expected to depart from unity because of nearby, dissociated, charged phosphate groups. That is, A^- already present in the interface will make it harder to introduce a probe A^- and easier to introduce a probe HA into the interface. Thus, γ_{A^-}/γ_{HA} should be less than unity for $\alpha < 0.5$ and greater than unity for $\alpha > 0.5$. A convenient form with some flexibility is given in Eq. (14).

$$\gamma_{A^-} / \gamma_{HA} = [\alpha / (1 - \alpha)]^{(n - 1)} \qquad (14)$$

The quantity, $\alpha/(1 - \alpha)$ is 1.0 for $\alpha = 0.5$, which defines the standard states of HA and A^-. For this value of α the ratio of activity coefficients must be 1.0, and it is, regardless of the value of n. As α becomes greater than 0.5 it is expected that the ratio, γ_{A^-}/γ_{HA} should become greater than 1.0. Conversely, as α becomes less than 0.5, γ_{A^-}/γ_{HA} should become smaller. For any value of $n > 1.0$ Eq. (14) has the proper behavior. The larger the value of n, the more sensitive is the ratio to changes in α. The spacing between functional groups in the interface must have a strong influence on n. If that spacing were infinite, n would be 1.0 and the system would be ideal

for all values of α. Equation (14) will clearly fail in the limits, since it gives infinity for γ_{A^-}/γ_{HA} at $\alpha = 1.0$ and zero at $\alpha = 0.0$. The real activity coefficient ratio can be expected to go to large but finite and small but non-zero values, respectively. However, these limits are not of much interest, as methods for determining α generally do not work well for very large or very small values, in any event.

Replacement of γ_{A^-}/γ_{HA} in Eq. (13) with its equivalent from Eq. (14) leads to Eq. (15). This equation was first suggested, for polyacids,

$$pH = pK_a - n \log[(1 - \alpha)/\alpha] \tag{15}$$

by Katchalsky ans Spitnik.[11] Although the choice of standard states and the definition of n only make Eq. (15) derivable for α values approching 0.5, it may, empirically, have broader validity, and, in the present case, it does.

RESULTS

Figure 4 shows typical contact angles at various pH values on polyethylene, untreated Celgard® 2400, and Celgard® 2400 treated with HA. The aqueous solutions all contained 2.0 M $NaClO_4$, 0.01 M citric acid/sodium citrate buffer, and were made up as described in the experimental section. These results show that Θ is only sensitive to pH when an ionizable substance makes up part of the interface, as anticipated. They support the assumption, made in the theoretical section, that γ_{LV} is pH-insensitive. The contact angle on the mixed air–hydrocarbon surface is not significantly different from that on the pure hydrocarbon.
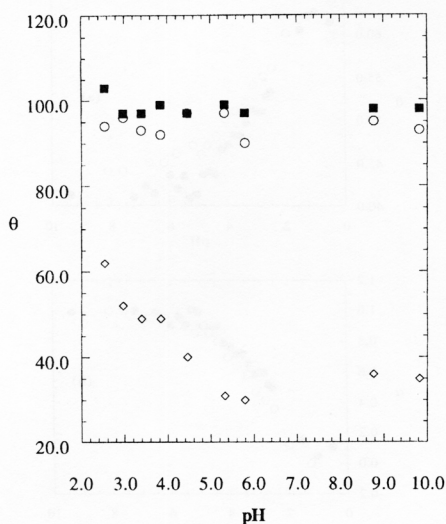

Figure 4. Contact angles of 1 μL buffered aqueous drops on various surface: o is polyethylene; ■ is unmodified Celgard® 2400; ◊ is Celgard® 2400 impregnated with HA. The contact angles and polyethylene and untreated Celgard® 2400 are similar. The contact angles on Celgard® 2400 with HA are lower, and only these vary systematically with pH.

   To determine the interfacial acidity of HA, contact angles were determined at various pH values on HA treated Celgard®. The aqueous solutions contained $0.01 - 0.25$ M citric acid, 2.0 M $HClO_4$, and enough NaOH (or, for very low pH values, $HClO_4$) to produce the desired pH. Figure 5 shows Θ and α as a function of pH for Celgard® 2400 and 2500, with drops containing 0.01 M citric acid. Figure 6 shows Θ and α for drops containing various citric acid concentrations, using Celgard® 2400. Figure 7 shows the fit of the α values to Eq. (15).

   To evaluate α from a measured contact angle using Eq. (12), values of $\cos \Theta_I$ and $\cos \Theta_U$ are required. Figure 5 and 6 show that Θ_I can be evaluated by inspection, from high pH measurement, since limiting values are reached. It is not possible to evaluate Θ_U in the same way, because limiting values cannot be reached without using unacceptably large concentrations of mineral acid. Fortunately, the limiting value of Θ_U appears to be the same for Celgard® 2400 and 2500, and for all concentrations of citric acid. We have, therefore, combined the results obtained with 0.01 M citric acid using Celgard® 2400 and 2500, and treated Θ_U, K_a, and n as adjustable parameters. Using Eqs. (11) and (15), and subjective estimates of Θ_U and K_a, n was varied systematically so as to minimize the sum of the squares of the discrepancies between calculated and observed values of $\cos \Theta$. Then n was fixed and K_a was optimized in the same way; then Θ_U. This process was repeated, cyclically, until further repetition did not reduce the sum of the squares of the discrepancies. The overall fit of the 0.01 M citric acid results to Eq. (15) is shown in Figure 7. The best values of pK_a and n are $2.85 \pm .09$ and $1.85 \pm .30$, respectively. The cited uncertainties take into account the coupling of the parameter values.[23,24].
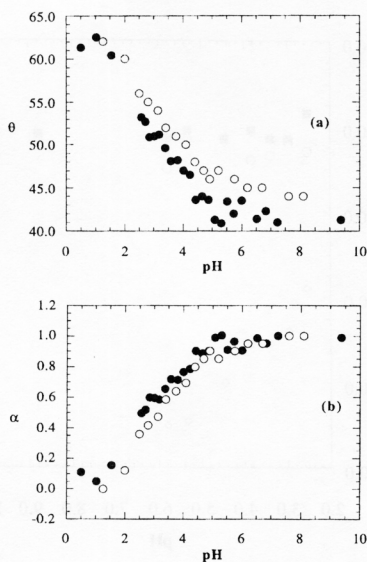

Figure 5. Contact angles (a) and degrees of dissociation (b) as a function of pH for buffered aqueous drops on Celgard® 2400 (•) and 2500 (o) impregnated with HA. The citrate buffer concentration was 0.01 M in all cases. To calculate α, Θ_I was taken as 41.5° for Celgard® 2400 and 44.0° for 2500.

    The best value of $\cos \Theta_U$, $0.464 \pm .002$, was used, along with the subjective values
of Θ_I (given in the captions of Figs. 5 and 6) in Eq. (12), to calculate the α values
shown in Figs. 5b and 6b. The value of Θ_I is somewhat different for Calgard® 2400
than for Celgard® 2500, and strongly dependent on the buffer concentration. How-
ever, the calculated α values are nearly independent of the support and the buffer
concentration. It is not clear why Θ_I depends so strongly on the buffer concentration,
but this problem does not jeopardize our results, since it disappears when α values
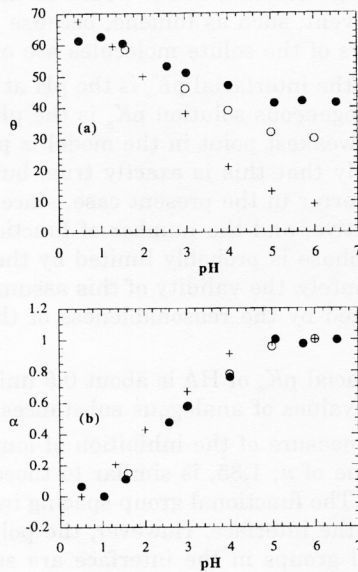are calculated.

Figure 6. Contact angles (a) and degrees of dissociation (b) as a function of pH for various ci-
trate buffer concentrations. The surface was Celgard® 2400 impregnated with HA. • is for 0.01 M
buffer. ○ is for 0.05 M buffer. + is for 0.25 M buffer. In calculating α, Θ_I was taken as 41.5°
for 0.01 M buffer, 30.0° for 0.05 M buffer, and 9.0° for 0.25 M buffer.
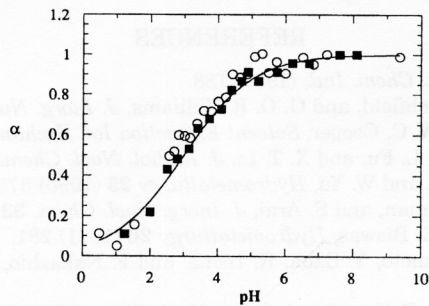

Figure 7. The fit of Eq. (15) to measured degrees of dissociation. $pK_a = 2.85$ and $n = 1.85$ were
used. ○ represent α values obtained with Celgard® 2400 and ■ represent values obtained with
2500. The buffer concentration was 0.01 M throughout.

DISCUSSION

It is clear from the derivation given above that interfacial pK_a values like those described in this paper are not entirely comparable to homogeneous solution pK_a values. Equilibrium constants depend on the standard states chosen for the participating species. Homogeneous solution equilibrium constants refer to standard states in which there are no solute–solute interactions.[25] In contrast, the interface of interest is completely occupied by ionized or unionized acid. We have enforced this condition in the present case by using neat HA, but it would be likely even if the acid were dissolved in a nonpolar solvent, such as toluene, because the acid is surface active. Thus, the nearest neighbors of the solute molecules are other solute molecules.

If our model is correct, the interfacial pK_a is the pH at which the interfacial acid is half ionized, as the homogeneous solution pK_a is the pH at which the acid in solution is half ionized. The weakest point in the model is probably the identification of α with A_I. It is not likely that this is exactly true, but we think that it is also unlikely to be seriously in error in the present case, since both the ionized and unionized acid are surface active, and the number of functional groups which can be presented to the aqueous phase is probably limited by the bulk of the hydrophobic part of the molecule. Ultimately, the validity of this assumption, and the rest of our model will have to be judged by the reasonableness of the pK_a values to which it leads.

Numerically, the interfacial pK_a of HA is about 0.5 units more positive than the homogeneous solution pK_a values of analogous substances.[12]

The parameter n is a measure of the inhibition of ionization by nearby ionized functional groups. Our value of n, 1.85, is similar to those obtained by Katchalsky and Spitnik for polyacids.[11] The functional group spacing in the polyacids is probably closer than the spacing in the interface. However, the polyacids are approximately linear, while the functional groups in the interface are surrounded by other functional groups in two dimensions.

Overall, we believe that the present results are reasonable.

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SAŽETAK

Kiselost na granici tekućih faza

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Koristeći podlogu od poroznog polipropilena, mjeren je kontaktni kut puferiranih vodenih kapljica na površinama koje su sadržavale kiselinu (HA) bis(2-etilheksil)hidrogen fosfat (preko polovice ukupnog sadržaja). Na osnovi ovisnosti kontaktnog kuta o pH vodene otopine, izračunan je stupanj disocijacije, α, kiseline HA, kao funkcija pH. Definiranjem standardnih stanja za kiselinu HA u međufazi i za njezinu konjugiranu bazu na 50% ioniziranoj granici između vodene i organske tekuće faze, određen je pK_a kiseline u međufazi koji je jednak pH, one vodene otopine koja je u ravnoteži sa 50% ioniziranom kiselinom u međufazi. Omjer koeficijenata aktiviteta konjugirane baze, γ_A, i kiseline, γ_{HA}, izjednačen je s potencijom $[\alpha/(1-\alpha)]^{(n-1)}$ za α vrijednosti oko 0.5, prema Katchalskom i Spitniku.[11] To omogućava određivanje empirijskog parametra n i upućuje na odnos između pH i α:

$$pH = pK_a - n \, \log[(1 - \alpha)/\alpha]$$

Nađeno je da taj odnos vrijedi u rasponu $0.1 < \alpha < 0.9$, iako ne može vrijediti za $\alpha = 0$ i $\alpha = 1$.