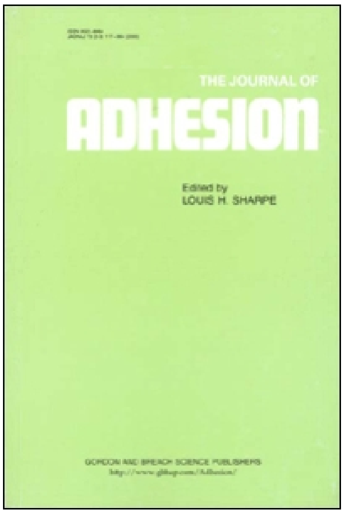

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Influence of the pH of Water on its Electron-Accepticity and Donicity

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Influence of the pH of Water on its Electron-Accepticity and Donicity

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By means of contact angle measurements on dry layers of electrostatically neutral dextran with pure water (pH 6.1), water acidified with HCl (to pH 1.94) and water made alkaline with NaOH (to pH 12.8), it could be shown that there was essentially no change as a function of pH in the ratio of γ^+/γ^- *of water as compared with the aqueous acid and alkaline solutions. (Here* γ^+ *is the Lewis acid parameter of the polar surface tension component of water and* γ^- *is its Lewis base parameter). In contrast, with contact angles measured with the same liquids on negatively charged clean glass, a significant decrease in contact angle was observed with water at pH 12.8, which was caused by the fact that at this alkaline pH an increase in surface hydrophilicity took place. This is because surfaces that have a given surface electrical potential at neutral pH generally acquire an even higher surface potential under more alkaline conditions which, concomitantly, also gives rise to an increase in surface hydrophilicity, and thus to lower contact angles with water.*

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We gratefully acknowledge the role played by Mr. Arno Hefers, Research Assistant, Texas Transportation Institute, Texas A & M University, College Station, Texas 77843, who queried by e-mail on 29 April 2004: “Do you know if anyone has determined surface energy components (LW, Acid and Base) for water at different pH levels?” As we did not believe that anyone had done that so far, we tried it and hope that the present paper furnishes an answer.

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Finally, contact angles with acid water, pure water, and alkaline water, deposited on hydrophobic Parafilm surfaces, were exactly the same.

Keywords: pH of water; Contact angles of water drops; Surface tension of water; Lewis acid parameter of surface tension; Lewis base parameter of surface tension

1. INTRODUCTION

It is known that the surface tension components (γ^{LW} and γ^{AB}) of liquid water change relatively little as its temperature increases [1, 2]. However, also as its temperature increases, the parameters making up γ^{AB} [2, 3]:

$$\gamma^{AB} = 2\sqrt{\gamma^{+}\gamma^{-}} \tag{1}$$

(where γ^{+} is the electron-acceptor or Lewis acid parameter and γ^{-} the electron-donor or Lewis base parameter of γ^{AB}), increase from $\gamma^{+}/\gamma^{-} = 1.0$ at 20°C, to $\gamma^{+}/\gamma^{-} = 1.75$ at 38°C [2], indicating that for water, γ^{+}/γ^{-} increases considerably with an increase in temperature.

It is, however, unknown if the γ^{+}/γ^{-} ratio of water changes as a function of pH. It should be noted that even though γ^{+} is the Lewis acid and γ^{-} the Lewis base surface tension parameter, the meaning of the terms acid and base in the Lewis system [4] is not necessarily interchangeable with those that one expresses as conventional pH values.

Furthermore, the measurement of a change (if any) in the γ^{+}/γ^{-} value of water as a function of pH is not as simple a matter as one might initially assume. For instance the contact angles measured with drops of water of different pH values on electrically charged and/or on amphoteric surfaces vary widely. This does not occur, however, because at different pH values the γ^{+}/γ^{-} ratio of water changes, but because when such electrically charged surfaces are exposed to water of different pHs, the ζ-potentials of such surfaces change. A number of examples of this phenomenon can be found in the literature. On amphoteric surfaces the highest water contact angle (i.e., the greatest hydrophobicity) is found with drops of water of a pH corresponding to the point of zero charge of the amphoteric substratum [5]. Water contact angles on layers of dissolved protein are highest with water drops of the pH of the isoelectric point of the protein (i.e., where the protein's surface is at its most hydrophobic) [2, 6]. Water contact angles measured on phosphatidyl serine and on phosphatidylic acid vesicle membranes (both negatively charged) reach the highest values with drops of water of a pH of 2 or less (indicating greater hydrophobicity), where the absolute values of the ζ-potentials of these phospholipid membranes are at their lowest [7]. These examples, however, are mainly if not solely manifestations of the influence of the pH of the water of the drops on the surface properties of the condensed-phase substrata upon which these contact angles were measured, so that these results do not allow one to arrive at any conclusions regarding the influence (if any) on the γ^+/γ^- ratio of the water of these drops as a function of their pH.

To investigate whether the pH of drops of water has an influence on the γ^+/γ^- of the water of these drops, this should be done with a substratum that is electrostatically neutral and at the same time hydrophilic, e.g., a monopolar, electron-donating solid. One such material is the linear polysaccharide, dextran, which is a polymer of maltose [which is itself a dimer of glucose (also called dextrose)]. Its ζ-potential has been measured at neutral pH and ionic strength $\mu = 0.015$ and was found to be $-0.5\,\text{mV}$, with a Beckman Model H Tiselius electrophoresis device, with schlieren optics [8]. For all practical purposes, a ζ-potential of $-0.5\,\text{mV}$ is negligibly small and may be considered zero. It was therefore decided to measure contact angles with drops of water at different pH values, on dried layers of dextran, deposited on glass microscope slides. As a control, contact angles were also measured on untreated clean glass microscope slides. Finally, to ascertain whether the pH of water as a contact angle liquid has any influence on hydrophobic surfaces, contact angles with acid, neutral, and alkaline water were also measured on surfaces of long-chain paraffins, in the guise of Parafilm sheets (American National Can, Greenwich, CT, USA). To obviate any complications engendered by undesirable interactions between the solid substrata and added anions or cations, the use of buffers was avoided.

2. EXPERIMENTAL

A 10% (w/v) solution of dextran (Mw 100,000–200,000, ICN Pharmaceuticals, Cleveland, OH, USA) in reverse osmosis (RO) treated water was deposited on ($1'' \times 3''$) clean glass microscope slides (Fisher). The glass slides covered with the 10% dextran solution in RO water were air-dried for 24 h. And then stored in a glass vacuum desiccator until use. After drying the surfaces of the dextran-coated slides were extremely smooth, as judged by their mirror-like specular reflection, which indicates that any roughness is of a dimension that is smaller than the wavelength-range of visible light.

Uncoated (precleaned) microscope slides (Fisher) were used as is. The RO-purified water used had a resistivity of 2,000,000 Ohm cm and a pH of 6.1. With drops of ~0.1 M HCl, RO water was acidified to pH 1.94 (with a resistivity of 260 Ohm cm) and with drops of ~0.1 M NaOH, RO water was made basic, to pH 12.8 (with a resistivity of 100 Ohm cm).

All contact angle measurements were done at 20°C, ±1° in a constant temperature laboratory in the Department of Geology. A Gaertner (Chicago, IL) instrument was used, with a 10× telescope provided with crosshairs and an ocular rim divided into 360 degrees. The telescope was mounted on an optical bench with an X-Y-Z movable track. To administer the contact angle liquids Teflon micrometer syringes (Gillmont, VWR International, West Chester, PA, USA) were used, with a Teflon piston in a glass housing and a removable injection needle fitting onto the tip of the glass housing. The syringe was solidly clamped on a support stand. The slides on which the contact angles were measured were placed on a vertically movable jack [9]. For each set of measurements 22–24 observations were made and the results averaged. The results obtained with the drops of acid, close-to-neutral (RO) and alkaline water on glass and dextran are shown in Table 1; for Parafilm, the results are shown in Table 2.

From the RO water contact angles, plus contact angles measured with diiodomethane (DIM) and with glycerol (GLY), the surface properties were determined [1, 3] for the clean glass as well as for the dextran-coated slides. These surface properties were:

$$\text{Glass: } \gamma^{LW} = 45.2,\ \gamma^{+} = 0.5,\ \gamma^{-} = 63.7\,\text{mJ/m}^2$$

($\theta_{DIM} = 45.2°$; $\theta_{GLY} = 27.8°$; $\theta_W = 10.5°$ [cf. Table 1]). Its ζ-potential from earlier measurements was -53 mV [10].

$$\text{Dried dextran: } \gamma^{LW} = 42.8,\ \gamma^{+} = 1.1 \text{ and } \gamma^{-} = 35.2\,\text{mJ/m}^2$$

($\theta_{DIM} = 33.3°$; $\theta_{GLY} = 35.6°$; $\theta_W = 35.8°$) [cf. Table 1]. Its ζ-potential from earlier measurements was a virtually negligible -0.5 mV [8].

$$\text{Parafilm: } \gamma^{LW} = 26.4,\ \gamma^{+} = 0 \text{ and } \gamma^{-} = 0.8\,\text{mJ/m}^2$$

($\theta_{DIM} = 63.8°$; $\theta_{GLY} = 96°$; $\theta_W = 102.5°$) [cf. Table 2]. The equations needed, as well as their use for deriving the γ^{LW}, γ^{+}, and γ^{-} values from the contact angles obtained from the three above-mentioned contact angle liquids can be found in refs. [2, 3, 11].

From these data the degree of hydrophilicity of both hydrophobic surfaces can also be expressed in terms of the free energy of interaction between two such surfaces, immersed in water, at closest approach, i.e., as ΔG_{1w1}, where positive values denote hydrophilicity [12].

TABLE 1 Contact Angles with Drops of Water at Different pH Values on Clean Glass Slides and on Dried Dextran Films

pH	Glass[a]			Dextran[b]		
1.94	9.7° ± 3.04° 1 sd	$P = 0.35$		34.8° ± 3.00° 1 sd	$P = 0.276$	
6.1[c]	10.5° ± 2.06° 1 sd	$P = 0$	$P^d = 0.0002$	35.8° ± 3.35° 1 sd	$P = 0.19$	$P = 0.016$
12.8	6.8° ± 1.91° 1 sd			36.7° ± 2.52° 1 sd		

[a] Precleaned glass microscope slides, Fisher

[b] Dextran (Mw 100,000–200,000; ICN Pharmaceuticals, Cleveland, OH, USA), deposited on glass microscope slides, air-dried and kept in a vacuum desiccator

[c] Reverse osmosis purified water, as is

[d] $P = 0.0002$: This signifies that there is one chance out of 5,000 that the difference between a water contact angle of 9.7° (at pH = 1.94) obtained on glass, and a water contact angle of 6.8° (at pH = 12.8) could have occurred by chance.

TABLE 2 Contact Angles with Drops of Water at Different pH Values, on Hydrophobic Parafilm

pH	Contact angle		
1.94	102.63° ± 1.87°	$P^b = 0.92$	$P^b = 0.74$
6.1[a]	102.5° ± 1.39°	$P^b = 0.87$	
12.0	102.25° ± 2.69°		

[a]RO water, as is; [b]For the definition of P, see note d of Table 1. All three P values shown in Table 2 indicate that the (very slight) differences between any of these three (averaged) contact angles are insignificant.

For clean glass, $\Delta G_{1w1} = +42.5\,\text{mJ/m}^2$ and for dried dextran, $\Delta G_{1w1} = +7.1\,\text{mJ/m}^2$. Thus, clean glass, with a strongly positive ΔG_{1w1} value is very hydrophilic, and the dried dextran is also, albeit somewhat more modestly, still definitely hydrophilic.

For Parafilm on the other hand, $\Delta G_{1w1} = -84.4\,\text{mJ/m}^2$, indicating pronounced hydrophobicity. For the definition and calculation of ΔG_{1w1}, which defines the degree of hydrophilicity when $\Delta G_{1w1} > 0$ and the degree of hydrophobicity when $\Delta G_{1w1} < 0$, see [12].

3. RESULTS AND DISCUSSION

From the results obtained with contact angles of water at different pHs it can be seen (Table 1) that there is no significant difference in the contact angles between those found with RO water, of pH 6.1 and with acid water of pH 1.94, measured on clean glass. On the other hand the decrease in contact angle found with water at the alkaline pH of 12.8 compared with drops of water at both acid and close to neutral pH values is quite significant, with P-values of 0.0002 and 0.0000..., respectively. This shows that the strongly alkaline pH caused a large increase in the ζ-potential of the glass, with a concomitant increase in the γ^- of glass and thus also in its hydrophilicity [1, 11].

On surfaces of dried dextran, however, the pH of the water drops has very little influence on their contact angles (see also Table 1). The small differences in contact angle between RO water (pH 6.1) and acidified water (pH 1.94), as well as between RO water and alkaline water (pH 12.8) are not significant. The still small but modestly significant difference between contact angles found on layers of dried dextran with water drops at the two extremes of pH (1.94 and 12.8) may be disregarded on account of the fact that water containing some HCl slightly decreases in surface tension, while water containing some

NaOH increases in surface tension [13]. This is because HCl itself has a lower surface tension than water (γ_{w}) while NaOH has a higher surface tension than water, so that admixture of HCl lowers γ_{w} and the addition of NaOH increases it [13]. At the rather low concentrations of HCl and NaOH used to reach the desired acidity and alkalinity, respectively, these effects are too small to distinguish them to a significant degree from the contact angles on dried dextran obtained with pure water, but they are just significant enough to show a difference between the contact angles obtained at the two extremes of pH 1.94 and 12.8 used in these experiments. However, these (still small) differences between the contact angles obtained with drops of water containing HCl and those containing NaOH are most likely not due to differences in the γ^{+}/γ^{-} ratios of these aqueous solutions, but rather a consequence of the fact that HCl has a lower free energy of cohesion than water (and thus a lower surface tension) and of the fact that NaOH has a higher free energy of cohesion than water (and thus a higher surface tension) [13]. These differences are therefore not related to the electron-acceptor/electron-donor parameter ratios (γ^{+}/γ^{-}) of these solutions, but only to their γ^{LW} and γ^{AB} values, of which the latter are function of their electron-acceptor-electron-donor parameter products ($\gamma^{+}\cdot\gamma^{-}$) [2, 3]; see equation 1.

Finally, the averaged contact angles with drops of the same acid water, pure (close to neutral) and alkaline water, as used on the glass and dried dextran surfaces, when measured on Parafilm were all essentially the same, i.e., between 102.6° and 102.3° (cf. Table 2). This shows that water contact angles on a virtually non-polar, hydrophobic surface are not influenced by the pH of the water. It should, however, be noted that at the 36° level contact angle differences of the order of one degree correspond to cos θ differences that are about 1.63 times smaller than with contact angles at the 100° level. Thus, the small difference in γ_{w} at pH 1.96 versus pH 12.8 which were just noticeable on dextran surfaces, were unlikely to be discernible among the large contact angles measured on Parafilm.

4. CONCLUSION

As the slight difference between contact angles on dried dextran found with water at pH 1.94 and water at pH 12.8 can be mainly ascribed to other factors than to differences in the γ^{+}/γ^{-} ratios of the diluted aqueous HCl and NaOH solutions, it may be concluded from the contact angles on dried surfaces of hydrophilic dextran with drops of water at different pHs, that changes in the pH of water cause no substantial deviations of its Lewis acidity or basicity, especially at pH values no more than three or four pH points removed from pH 7. The virtually identical water contact angles at acid, neutral, and alkaline pH, measured on Parafilm, show that the electron-accepticity and donicity of water also remain unchanged when in contact with a hydrophobic surface.

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