Strong Specific Hydroxide Ion Binding at the Pristine Oil/Water and Air/Water Interfaces

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Despite claims, based largely on molecular dynamics simulations, that the surface of water at the air/water interface is acidic, with a positive charge, there is compelling experimental evidence that it is in fact basic, with a negative charge due to the specific adsorption of hydroxide ions. The oil/water interface behaves similarly. The pH dependence of the zeta potentials of oil drops has been measured by two very different techniques: on a single drop in a rotating electrophoresis cell and on about 10^{14} submicrometer drops in a 2 vol % emulsion by an electroacoustic method to give similar results with a sigmoidal pH dependence characterized by an isoelectric point at pH 2−3 and a half adsorption point about pH 5.5, or at $10^{-8.5}$ M hydroxide ion. This indicates that hydroxide ion is absorbed much more strongly than other anions. The pH dependence of a single N_2 bubble has also been measured and has the same pH dependence, independently of whether HCl or HI is used to adjust the pH. These similarities between the pH dependences of the zeta potentials of air bubbles and oil drops, as well as those reported from streaming potentials on solid inert surfaces such as Teflon, indicate that water behaves similarly, with only subtle differences, at each of these low dielectric hydrophobic surfaces, with an isoelectric point of pH 2−4. In acidic solutions at pH's below the isoelectric point, the surface is indeed positive, consistent with spectroscopic observations of the adsorption of hydrogen ions.

Introduction

A recent theoretical study purports to show that the surface of water in air is acidic, with a pH $\leq$ 4.8.[1] In fact, quite the opposite is the case: the surface is basic, due to the preferential adsorption of hydroxide ions. It has been known since 1861 that air bubbles in water are negatively charged and migrate toward the positive electrode in an electrophoresis experiment.[2] Such measurements have been refined and repeated many times, always with the same result: the bubbles are negative.[3−7] The surface of simulated water may be acidic, but the surface of real water is basic.

Oil drops in water behave similarly. Again, it has long been known that they spontaneously acquire a negative charge and migrate toward the positive electrode in a dc electrophoresis cell.[8−10] From the pH dependence of the zeta potential, it was inferred that adsorption of hydroxide ions was responsible for the negative charge.[11] By measuring the pH changes caused by the formation of an emulsion with its large surface area, it was possible to measure quantitatively the surface charge density of oils with very low solubilities in water, such as hexadecane. It corresponds to the adsorption of one hydroxide ion on every 3 nm^2 of the oil surface, nearly independent of the identity of the oil.[12]

Inert solids in contact with water are also negatively charged.[13] Streaming potential measurements on Teflon show a negative charge at neutral pH with an isoelectric point (iep) at pH 4,[14] similar to that found for the air/water and oil/water interfaces. This effect accounts for the observation of electroosmotic flow in microfluidic devices even in channels formed by polymers with no reactive charged groups.[15] The adsorption is specific to hydroxide ions. Addition of other monovalent salts results in a reduction of the zeta potential through the usual double layer compression, but the anions do not displace the adsorbed hydroxide, at least up to about 10 mM salt concentrations.[14,16,17] Multivalent ions have only a small effect on the iep of Teflon, although they do affect the zeta potential in proportion to their charge at constant ionic strength.[18]

Thus, it appears that water behaves similarly at all inert, low-dielectric hydrophobic surfaces, whether gas, liquid, or solid: specific adsorption of hydroxide ion gives them a negative charge at neutral pH which is only neutralized by addition of acid to a pH of 2−4 or less.[19] Below this isoelectric point, the interface becomes positive, presumably by the depletion of the hydroxide ion and the adsorption of protons. Surface spectroscopic techniques do show the surface enhancement of hydronium ions,[20] but this only occurs at pH's less than 2,[21] below the isoelectric point, in agreement with the macroscopic observations that such surfaces are positive. No preferential adsorption of protons is seen at pH 4−5, where the theoretical model predicts a positive surface. Although there is no spectroscopic evidence for the adsorption of hydroxide ion below pH 13,[21] the absence of a signal does not exclude the presence of the hydroxide; it may only indicate that its signal is too weak to be observed.

An isoelectric point of pH 4 or lower implies that the hydroxide ion is adsorbed at the surface at least 10^6 times more favorably than the proton. This 10^6 ratio for $[OH^-]_{surf}/[OH^-]_{bulk}$ is larger than the 10^4 enhancement recently reported for polarizable anions such as iodide at the air/water interface.[22]

In view of this large hydroxide ion effect, and because of the importance of understanding the properties of water at hydrophobic surfaces, it is desirable to verify the above observations and conclusions with as many different techniques

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as possible. Here, we report the comparison of the pH dependence of the zeta potential of oil-in-water drops by two very different techniques. The spinning cell ZetaMeter enables measurements of the dc electrophoretic mobility of a single drop of millimeter diameter.[4] The ZetaProbe obtains the zeta potential from the high frequency dynamic mobility of a relatively concentrated emulsion of about 10^{14} submicrometer drops in a 100 mL sample. In the emulsion experiments, the iep can only be approached because coalescence of the surfactant-free oil drops would occur if there were no remaining charge to provide electrostatic stabilization. The single drop experiments of course do not suffer from this limitation. Finally, the ZetaMeter is used to measure the pH dependence of the zeta potential of a single bubble for comparison with the oil drop. (The dynamic mobility of bubbles is as yet an unexplored phenomenon.)

Experimental Section

Materials. The oils octane, decane, dodecane, benzene, and nitrobenzene were from Aldrich with a purity grade up to 99% and were purified three times with alumina and silica columns to eradicate contamination, especially of surfactant species such as carboxylic acids, confirmed by GC-MS analysis. Hexadecane (Aldrich 99%) was purified by five passages through a column of basic alumina. Water was purified by a Millipore milli-Q 185 E system to give a resistivity of 18.2 MΩ cm. The pH was adjusted with solutions of NaOH and HCl.

Methods. For the single drop measurements, the spinning cell was coated as described previously,[4] then cleaned by soaking with a 10% solution of nitric acid for 48 h, and then abundantly rinsed with pure water. Contamination by CO_2 was avoided by bubbling nitrogen and keeping the sample out of contact with atmospheric air. The zeta potentials were calculated from the measured electrophoretic mobility with the expression of Sherwood, as described previously, from an average of 10−20 separate measurements.[4] At the lower pH values, Fe electrodes separated by frits from the aqueous solution were used to avoid formation of gas bubbles.

The 2 vol % surfactant-free hexadecane-in-water emulsions were prepared at pH 9 in the absence of added salt with the technique previously described[12] and then titrated to pH 3 in the measurement cell of the ZetaProbe. This instrument (Colloidal Dynamics Inc., Warwick, RI) uses the electroacoustic effect to obtain the zeta potential, without acquiring the full dynamic mobility spectrum that also enables determination of the droplet size. Each data point can hence be obtained more rapidly over 1−2 min, to reduce the effects of any emulsion droplet coalescence. Background corrections were made to data below pH 5 with solutions of NaCl and HCl to match the conductivity and pH.

Results

The first set of measurements was to determine whether the single-drop technique in the spinning cell gave the same results as obtained previously from the dynamic mobility with the electroacoustic method, that is, that the zeta potential at pH 9 was essentially independent of the alkali metal counterion.[16] This test was not trivial, for the spinning cell measurements of the zeta potentials of gas bubbles did show some dependence on the alkali metal counterion, with the zeta potential at 10^{-3} M LiCl about 10 mV smaller than that with the same concentration of CsCl.[23] The results are shown in Figure 1. While there is a small difference in the same direction between LiCl and CsCl at greater than 10^{-4} M concentrations, the zeta potentials are essentially the same within the experimental error of ±3 mV,
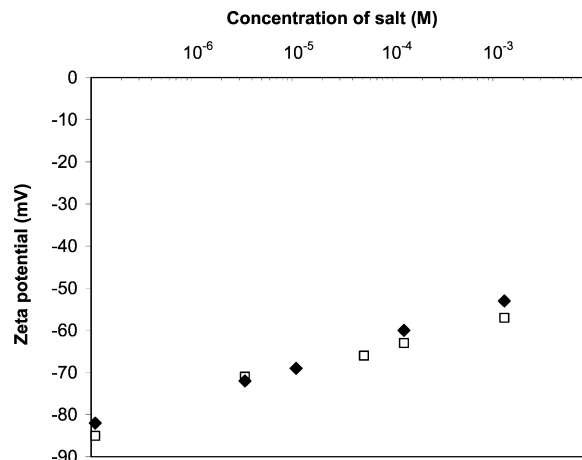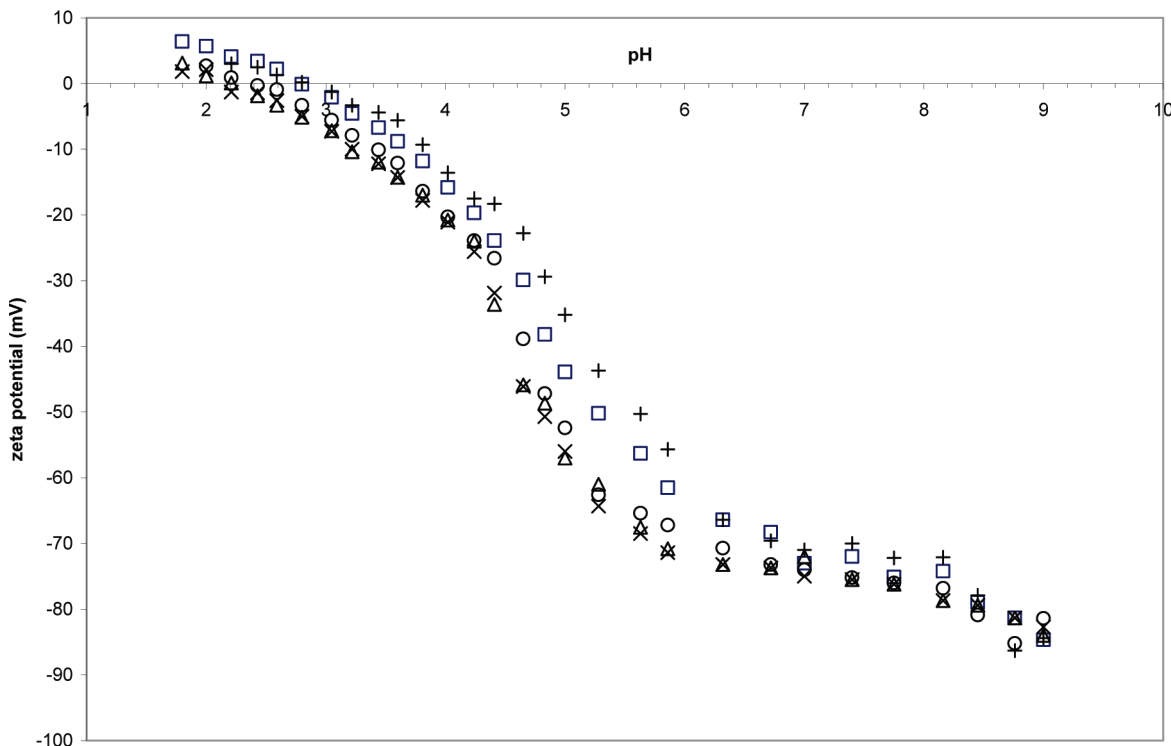

Figure 1. Zeta potentials of hexadecane droplets as a function of MCl concentration in 10 μM MOH with M = Li (◆) or Cs (□).

consistent with the electroacoustic results. This remains a surprising result, as a large fraction of the surface charge is compensated by counterion condensation, yet the identity of the counterion has little effect on the zeta potential.[12] We infer in addition that, although they are very similar, there are some subtle differences between the oil/water and air/water interfaces.

The second set of measurements was of the pH dependence of the zeta potentials of single drops of various oils. The results are shown in Figure 2. The overall shape of the pH dependence is the same for the five oils examined, despite the significant difference between the polar and polarizable oils such as nitrobenzene and benzene and the alkane oils hexane, octane, and decane. There is a systematic trend for the more soluble oils to have a less negative zeta potential than the not-so-soluble oils. This has been observed previously, although the difference reported there was much larger than that observed here.[24] We have reported further on this effect elsewhere.[25] The pH dependence displays a sigmoidal shape, with isoelectric points between pH 2 and 3, much lower than the estimate of pH 4 that would be made by extrapolation from the data around pH 5. Above pH 7, the zeta potential becomes even more negative as hydroxide ions are added to the solution to increase the pH.

In the third set of measurements, the dynamic mobility of the electroacoustic effect was used to determine if the sigmoidal shape of the pH dependence of the zeta potentials shown in Figure 2 occurred with an emulsion as well as with the single drops. In previous studies with the electroacoustic technique, the pH titrations were terminated at pH 5 to avoid coalescence of the emulsion droplets with low charge.[12] Extrapolation then led to the estimation of an isoelectric point of about pH 4, similar to that found with streaming potential measurements on Teflon surfaces.[14] The ZetaProbe allows more rapid measurements of just the zeta potential so that a lower pH can be reached before coalescence occurs. The results with a hexadecane emulsion are shown in Figure 3 and display the same sigmoidal shape as observed with the single drops.

The data can be fitted as an acid−base titration curve with $\zeta = \zeta_s K/([H^+]^n + K)$, where ζ_s is the high pH saturated zeta potential (-78 ± 2 mV), K the acid−base equilibrium constant ($(1.1 \pm 0.3) \times 10^{-3}$), and $n = 0.54 \pm 0.3$. In a normal titration curve with $n = 1$, the pH changes from 10 to 90% over two pH units. In the present case, this transition requires almost four decades increase in hydroxide ion concentration. This is typical of adsorption onto a polyelectrolyte, where interactions occur between the adsorbed species, requiring higher concentrations

Figure 2. pH dependence of the zeta potentials of single oil drops of nitrobenzene (+), benzene (□), octane (○), decane (△), and dodecane (×).
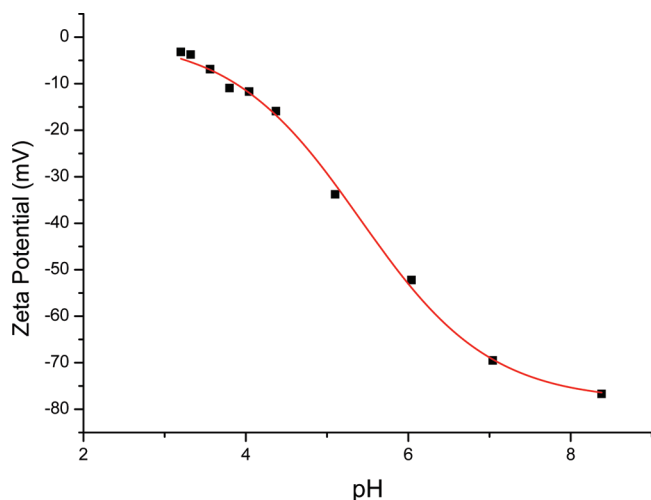
Figure 3. ZetaProbe measurement of pH dependence of the zeta potential of 2 vol % hexadecane emulsion with the pH reduced by addition of HCl.

to effect complete adsorption. The half titration pH calculated from n and K is pH 5.5, or pOH 8.5. Interpreting the curve as reflecting the adsorption of hydroxide ions at the interface, this implies an adsorption equilibrium constant of $10^{8.5}$. While this sigmoidal titration curve is an incomplete description, ignoring the presence of the isoelectric point, it does give a satisfactory description of the pH dependence of the zeta potential at higher pH's. A more comprehensive theoretical treatment is presented elsewhere.[26]

In the fourth set of measurements, the pH dependence of the zeta potential of a single bubble was measured with the spinning cell technique. A similar sigmoidal curve was obtained, with an iep of pH 2.5. This is in contrast to the iep of pH 4 reported by Takahashi measured with a rising bubble method[7] but in agreement with earlier measurements of Li and Somasundaran[5]

who found negative zeta potentials above pH 2.5. We have no explanation for the discrepancy with Takahashi's results, except to note that near the iep the small zeta potentials lead to large experimental errors with all of the techniques.

Both HCl and HI were used to adjust the pH from 7 to 1; both acids gave the same pH dependence of the zeta potential, indicating that other anions do not compete with hydroxide ion at the air/water interface in determining the zeta potential.

Discussion

A remarkable aspect of the present results is the concordance between the two very disparate techniques used. In the spinning cell ZetaMeter, a single drop of about a millimeter diameter is observed by dc electrophoresis. In the ZetaProbe, a 2 vol % emulsion dispersion containing about 10^{14} 0.2−0.4 μm droplets in a 100 mL sample is measured with the MHz dynamic mobility effect. However, the results are in almost quantitative agreement, providing strong confidence in the validity of both methods, and indicating that impurities are not the cause of the observed effects.[27]

An extraordinary feature of the hydroxide ion adsorption is its total specificity. The very good fit of the adsorption curve shown in Figure 3 implies that it describes a single adsorption process from pH 3 to 8. We have shown previously by pH-stat measurements that the negative zeta potentials at pH 7−9 can be ascribed to hydroxide ion adsorption.[12] The present results allow this inference to be extended to pH 3. This means that even at 10^{-11} M (pH 3) hydroxide ion is adsorbed preferentially over 10^{-3} M chloride ion arising from the acid used to adjust the pH. Furthermore, the observations on nitrogen gas bubbles illustrated in Figure 4 indicate that replacement of the chloride ion by iodide has no effect on the zeta potentials in acidic solutions from pH 7 to pH 1, despite spectroscopic evidence for the (weak) adsorption of iodide at the air/water interface.[22]

The similarities in the pH dependence of the oil drops and air bubble are consistent with the view expressed in the

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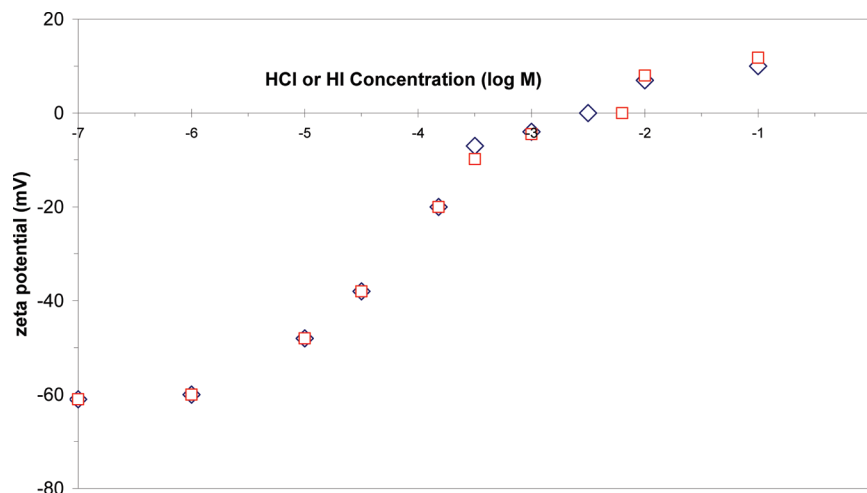
Figure 4. Dependence of the zeta potential of a single nitrogen bubble with the pH adjusted by addition of HCl (○) or HI (□).
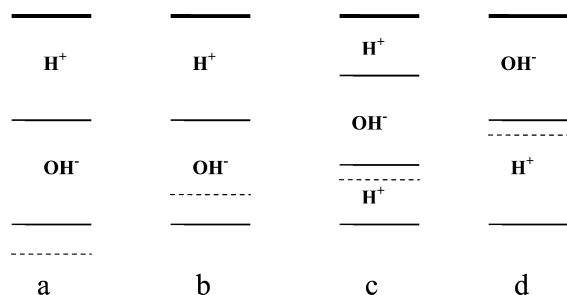
Figure 5. Alternative dispositions of excess protons and hydroxide ions in the double layer.

Introduction that water behaves similarly at both hydrophobic surfaces, with only minor differences. This allows inferences from the behavior of oil drops to be applied to the description of the air/water interface as well. One of these is that the air/water surface is not positive at near neutral pH's. There is no experimental evidence for a positive interface at pH's above the iep. The molecular dynamics simulations of Jungwirth et al. appear to miss some essential aspect of the physics.[1] These authors have suggested that protons might indeed be adsorbed preferentially at the surface and then covered by a layer of hydroxide to generate the negative charge observed in the zeta potential measurements (Figure 5a).[28] However, because of electroneutrality, in the double layer [H$^+$] = [OH$^-$], so if the shear plane indicated by the dashed line is outside of the double layer the zeta potential would be zero, and if it is anywhere inside of the double layer the zeta potential would be positive (Figure 5b), both contrary to experiment. The only way to have protons at the surface and a negative zeta potential is to postulate a triple layer: some protons near the surface and also in the diffuse layer, with hydroxide ions in between (Figure 5c). The simpler model of Figure 5d, with hydroxide at the surface and protons in the diffuse layer, is preferred until there is some experimental evidence to the contrary.

These results resolve some ambiguities in the explanation of the enigmatic Jones−Ray effect recently discussed by Petersen and Saykally.[22] These authors used second harmonic generation (SHG) spectroscopy to examine the adsorption of anions at the air/water interface. Their measurements were made under a N$_2$ atmosphere, so presumably at pH 6−7, at which pH the surface is nearly saturated with hydroxide ions. From our surface charge measurements on the oil/water interface, this corresponds to one hydroxide about every 3 nm^2; by analogy, a similar charge density is expected at the air/water interface. In contrast, the anion adsorption measured by the SHG experiments is much less dense, corresponding to an anion every 100−2500 nm^2. This explains why the zeta potential is essentially independent of the identity of the anion:[12] the surface charge is created by the hydroxide ions and the weaker adsorption of other co-ions contributes little to the total charge.

The Jones−Ray effect describes a minimum in the surface tension of water at low electrolyte concentrations of about 1 mM, before the well-known increase at higher concentrations due to depletion of ions from the surface region. Karraker and Radke[29] offered an explanation for this effect which postulated an adsorbed layer of hydroxide ions at the air/water interface inferred from the pH dependence of the disjoining pressure of thin films. Their surface charge density was quite low, however, with one hydroxide ion every 65 nm^2, because it was based on the diffuse layer charge, and not on the surface charge. We have shown that most of the surface charge is compensated by counterion condensation inside of the shear plane.[12]

Manciu and Ruckenstein[30] also provide an explanation of the Jones−Ray effect by postulating a strong adsorption of hydroxide ions at the interface. Their equilibrium constant of 10^{-10} M corresponds to half adsorption at pH 4, an order of magnitude stronger than reported above at pH ∼5.5. Again, the density of the calculated surface charge is low, about one OH$^-$ every 200 nm^2. In their model, the Jones−Ray effect arises from the attraction of cations to this surface charge.

Petersen and Saykally[22] resile from this explanation in favor of adsorption of anions, partly in the mistaken belief in the flawed theoretical models that indicate that protons are favored at the surface. As described in the Introduction, and elsewhere,[31] there is no experimental evidence for this. Indeed, as they recognize, their own results with hydroiodic acid,[20] which display a much weaker effect than do sodium and potassium iodide, are consistent with the surface hydroxide hypothesis.

In summary, all of the available evidence is consistent with the interpretation that the surface of water in contact with a low-dielectric constant interface (air or oil or inert solid) acquires a spontaneous negative charge from the strong specific adsorption of hydroxide ion. Most of the negative charge is compensated by counterion condensation, leaving a lower diffuse layer charge that creates the negative zeta potentials observed by electrophoretic, streaming potential, and disjoining pressure measurements. The Jones−Ray effect describes the effect of cations replacing protons in the double layer on addition of dilute (mM) electrolyte solutions. Only below the isoelectric points

of pH 2−4 (depending on the surface) does the interface become positive through neutralization of the hydroxide ions and adsorption of protons. The surface layer of hydroxide ions creates a positive surface potential, as was recognized years ago,[32] despite some recent theoretical models that lead to the opposite sign.[33,34]

There remains the question of why the hydroxide ion is so strongly adsorbed to the interface of low-dielectric hydrophobic substances. Many authors have called for such an explanation, or speculated about one. Indeed, Petersen and Saykally recently described it as "an unknown specific adsorption mechanism".[35] A comprehensive explanation has now been provided.[26] It is based on the known experimental facts that electrolytes reduce the dielectric constant of water and that hydroxide ion has a particularly large effect. The endothermic suppression of dipole fluctuations with the surrounding bulk water is minimized if the hydroxide ion approaches the low dielectric interface. This force can account quantitatively for the pH dependence of the zeta potentials shown in Figures 3 and 4 and all of the other experimental observations of hydrophobic interfaces of near neutral water at low ionic strengths.

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