Chemistry of the Crude Oil/Brine Interface

Jill S. Buckley
New Mexico Petroleum Recovery Research Center
New Mexico Institute of Mining and Technology

Introduction

Interfacial properties of crude oils are complex and not well understood. Interfacial tensions and contact angles can depend not only on the specific oil and solid, but on brine composition and on the length of time that the various phases are in contact before a measurement is made. The molecular species responsible for interfacial activity are not a chemically distinct and separable class, but they do have in common some polar functionality that imparts the observed interfacial properties. The effects of various polar functional groups on oil/brine interfacial properties are considered as a step toward interpretation of the more complex interactions involved in the wetting phenomena observed for ensembles of crude oil, brine, and rock.

There is ample evidence of the influence of interfacially active species at oil/brine interfaces. Any model of the crude oil/brine interface must be consistent with observations that include:

♦ IFTs between crude oils and brines are lower than IFT values for paraffinic or aromatic refined oils. They are highest near neutral pH and can fall to very low values at low or high pH.
♦ Electrophoretic mobility measurements of oil droplets emulsified in brine show the presence of both negatively and positively charged species. Isoelectric points (IEP) are usually between pH 3 and 7.
♦ Rigid interfacial films are sometimes observed at oil/brine interfaces, especially when the area of the interface is decreased.

Carboxylic acids and basic nitrogen compounds are likely candidates for surface active components of crude oils. The acid/base and interfacial properties of these polar constituents are reviewed. The extent to which aqueous dissociation parameters can be applied to describe dissociation reactions at an oil/water or solid/water interface is evaluated. Crude oil/brine interfacial properties resulting from acid/base dissociation reactions are demonstrated.

Interfacial Properties of Organic Acids and Bases

Electrophoresis demonstrates that crude oil interfaces are positively charged at low pH and negatively charged at high pH, as shown in Fig. 1 for Moutray crude oil. This behavior is consistent with dissociation of organic acids and basic compounds at the oil/brine interface (Buckley et al., 1989; Dubey and Doe, 1993). The Ionizable Site Group (ISG) model (Healy and White, 1978; Takamura and Chow, 1985) has been applied to reproduce the observed zeta potentials of charged oil droplets suspended in brine (Buckley et al., 1989).
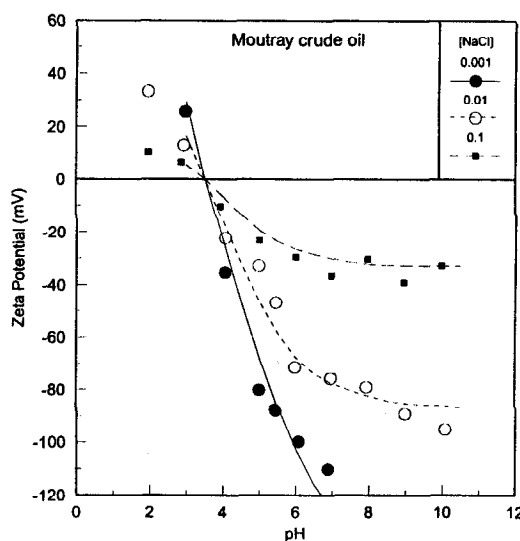

Figure 1: Zeta potentials of emulsions of Moutray crude oil in brines of varying pH and ionic strength (after Buckley et al., 1989).

The ISG Model

The concentrations of ions near a charged surface (or interface) are described by the Poisson-Boltzmann equation. Surface charge density, bulk concentrations of the ions in solution, their valence and sign, and distance from the charged interface are all important variables. For a surface with ionizable sites, the surface charge density depends, in turn, on the surface concentrations of some of the ions in solution. In the case of dissociation of acidic and basic species, the hydrogen ion concentration at the surface $[H^+]_s$ shifts

the position of equilibrium and thus the surface charge. If the densities and dissociation constants of the ionizable sites are known, conditions that satisfy both the dissociation equations and the Poisson-Boltzmann relationship can be found.

In the case of a crude oil/brine interface, densities and dissociation constants of ionizable sites are not known a priori. Instead these parameters can be chosen to fit existing data on interfacial properties. The validity of the curve fitting procedure can be tested for data from interfaces with known ionizable compounds (either acidic or basic) and shown to lead to physically reasonable values for both the density of sites and their dissociation constants.
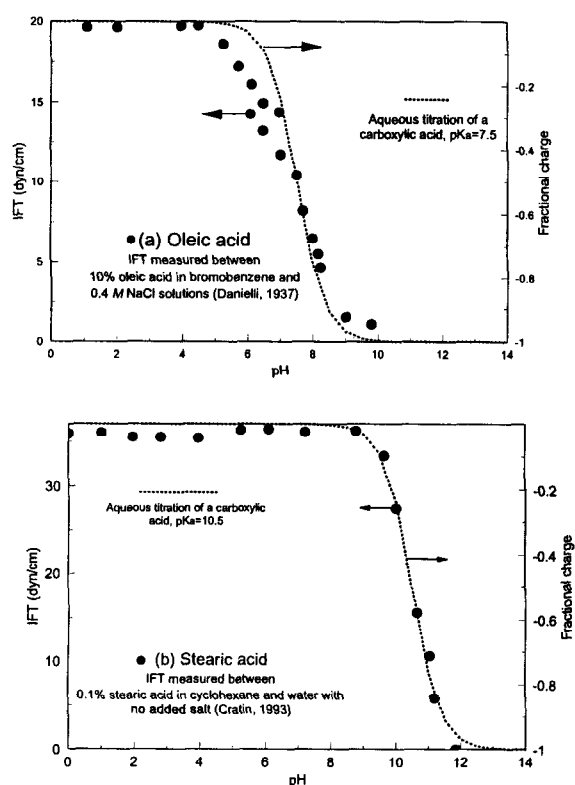

Figure 3: Calculated surface charge for hypothetical surfaces with ionizable sites. Surface charge depends on the site density, pK_a of those ionizable sites, aqueous phase pH, and ionic strength.

titration curves, but the apparent pK_a is shifted to higher pH values than would be expected for water-soluble carboxylic acids ($pK_a \leq 5$). The similarities in shape between IFT and titration curves strongly suggest that IFT reduction is related to an increasing extent of ionization, but observed differences in pH dependence in different buffers could not be satisfactorily explained (Hartridge and Peters, 1922;

Figure 2: The IFT between solutions of oil-soluble carboxylic acids and varying pH aqueous solutions is shown on the left axes. On the right are calculations of the charged fraction of the hypothetical weak acids with titration curves that roughly match the IFT vs pH curves for: (a) oleic acid and (b) stearic acid.

Tests of the ISG Model with Known Compounds

IFTs measured between oil solutions of water-insoluble fatty acids and aqueous solutions of varying pH have been reported, showing that IFT decreases with increasing pH (two examples are shown in Figs. 2a and b). The IFT vs. pH curves mimic acid/base
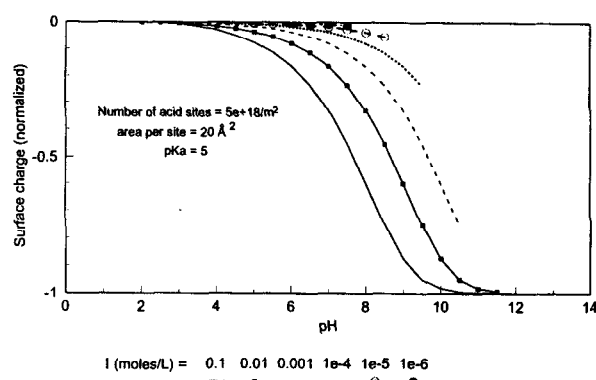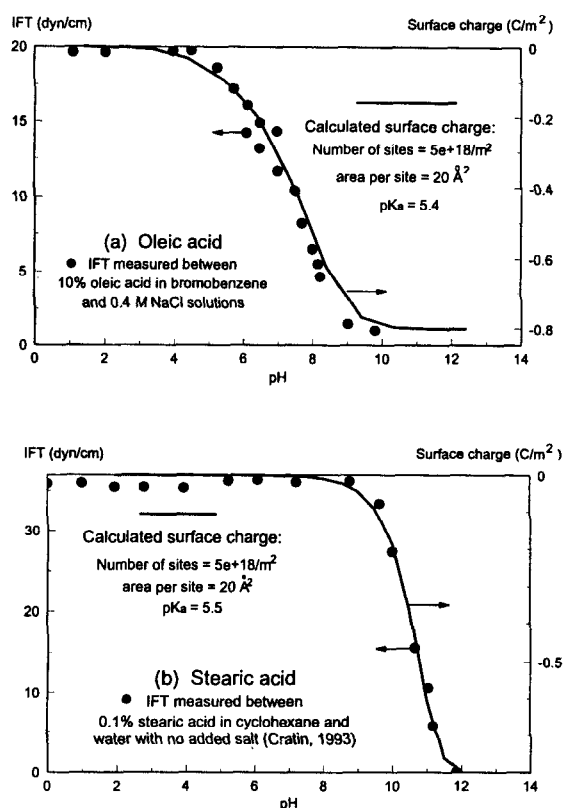

Figure 4: IFT response for two oil-soluble acids correlates with surface charge for a reasonable density of weakly acidic ionizable sites, with pK_a values that are typical of carboxylic acids in aqueous solution, as shown for (a) oleic acid and (b) stearic acid.

Peters, 1931; Danielli, 1937; Cratin, 1993).

On surfaces with ionizable sites, surface charge varies with total ionic strength of the solution as well as its pH, as shown in Fig. 3 for an interface with carboxylic acid sites. Each acid group is assumed to occupy 20 Å^2 (a value of 21 Å^2 has been measured for stearic acid (Tanford, 1973)) and has a pK_a of 5. The
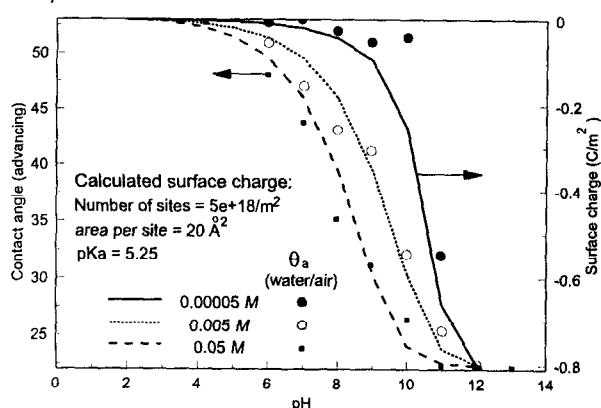

Figure 5: Contact angles on functionalized polyethylene surfaces appear to be related to surface charge. (Contact angle data from Holmes-Farley *et al.*, 1985.)

IFT data for oleic and stearic acids are replotted in Figs 4a and b, together with ISG fits. Assuming pK_a values between 5 and 5.5 and 20 Å^2 per site, gives good fits to both sets of data. The large shift in apparent pK_a for stearic acid occurs because the only
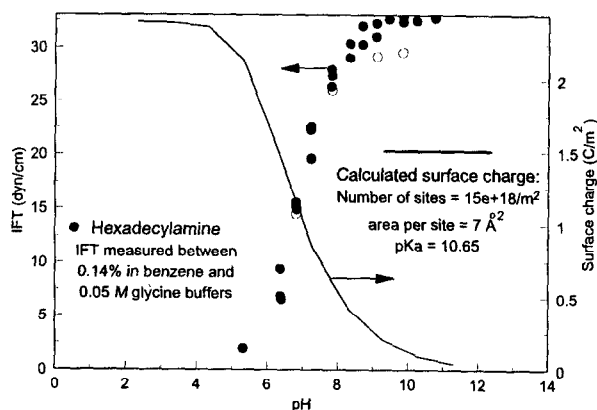

Figure 6: IFT between hexadecylamine solutions in benzene and aqueous buffers correlates with the extent of charge of the positively charged amine surface. (IFT data from Peters, 1931.)

ions in solution were those added to adjust pH; the ionic strength was low and varied with pH. Oleic acid was tested against a buffered 0.4 M NaCl solution, and the apparent pK_a is shifted less at this higher ionic strength. While these fits are not necessarily unique, they do support the validity of the ISG model and of

the underlying assumption that IFT decreases as the extent of negative charge increases.

A similar pH-dependence has been reported for advancing contact angles (θ_a) between water and air on polyethylene surfaces with carboxylic acid functionality (Holmes-Farley *et al.*, 1985; Whitesides *et al.*, 1991). The shift in apparent pK_a in the θ_a vs pH curve is similar to that for fatty acid/water IFT measurements. Fig. 5 shows the ISG fit to some of the contact angle data, suggesting that carboxylic acid functional groups, fixed at a solid/water interface, behave very similarly to those at the oil/water interface. The water advancing contact angle decreases as the extent of surface charge increases and the surface becomes more hydrophilic.

Interfaces that acquire a positive charge because of the association of a hydrogen ion with a basic nitrogen also show lower IFT as extent of charge increases, and shifts of apparent pK_a consistent with the ISG model, as shown in Fig. 6 for hexadecylamine.

Crude Oil/Brine Interfaces

Polar functional groups in crude oils

Much of the available data for polar constituents in crude oils is focused on the asphaltene fraction. Although the interfacially active components of crude oils are probably not found exclusively in the material that is insoluble in an excess of n-pentane, polar heteroatoms are concentrated in the asphaltene fraction. Studies of asphaltene chemistry thus provide a convenient starting point.

Speight and Plancher (1991) have reviewed the literature on molecular models of the asphaltenes. Oxygen occurs in carboxylic acids, as phenols, and as keto groups. Nitrogen is found in heterocycles of various types, some of them having basic character like pyridine and the remainder in non-basic pyrrol-type rings. Amines occur in minor amounts at most. Sulfur is found in heterocyclic thiophene condensed ring systems, and as sulfides, linking both alkyl and aryl moieties. If present, functional groups that contain both nitrogen and oxygen (e.g. cyclic amides such as 2-quinolone) may give amphoteric, or even zwitterionic character to the interface.

Dissociation constants of a few simple analogs of polar functional groups with acidic or basic character are shown in Table 1. Simple compounds were chosen to illustrate the impact of structural differences on dissociation constant values. For the examples in Table 1, pK_a changes only slightly with alkyl

Table 1: Dissociation constants of selected organic acids and bases.

Compound	pK_a
Acids:	
acetic acid	4.75
n-nonanic acid	4.96
benzoic acid	4.20
naphthenic acid	α) 3.70
	β) 4.17
phenol	9.89
Bases:	
laurel amine	10.63
aniline	4.63
pyridine	5.25
quinoline	4.90
Amphoterics:	
2-hydroxypyridine	0.75
(2-Pyridol)	11.65
4-hydroxypyridine	3.20
	11.12

zwitterionic species than with the most likely acidic and basic compounds.

The compounds shown in Table 1 all have significant water solubility and cannot account for the interfacial properties of crude oils. The polar substituted molecules in the asphaltene fraction have much higher molecular weights. While the absolute molecular weight of molecules in the asphaltene (n-pentane insoluble) fraction is difficult to measure, the ratio of elements is fairly consistent for materials from a wide range of sources (Speight, 1980), and on average can be represented by the empirical formula $C_{100}H_{115}N_1S_3O_2$. The hydrogen-to-carbon ratio indicates a high degree of aromaticity. Nitrogen content varies only a little, while oxygen and sulfur are more variable. None of these polar constituents is present in sufficient quantity to confer significant water solubility on such large organic molecules, but the extent of polar functionality may well contribute to the affinity of these molecules for the oil/brine interface.

substitution. Aryl substitution of amines and incorporation of nitrogen into heterocyclic rings has a greater affect on dissociation, resulting in weakly basic functional groups.

Amphoteric compounds, such as the 2-quinolone illustrated (I), have been reported (Petersen, 1986; Branthaver *et al.*, 1992). These cyclic amides can also exist in the tautomeric form 2-hydroxyquinoline (II). pK_a's of analogous pyridine compounds are reported in Table 1. N-alkylpyrrolidones (III), based on 5-membered rings, have been reported to have surface active properties and to exist, at least partially, as their zwitterionic equivalents (Rosen *et al.*, 1988). A much broader range of pK values is possible with

Surface Charge as a Function of Brine pH

Many crude oils have both acidic and basic ionizable sites at the oil/water interface (Buckley *et al.*, 1989; Dubey and Doe, 1993). As two interfaces approach one another, the DLVO forces between them will vary with net charge, but as separation distance decreases the existence of discrete sites of positive and negative charge becomes important. A simple example, illustrating the disparity between hypothetical surfaces with identical zeta potential curves, is shown in Figs. 7a and b. For equal numbers of acidic and basic sites ($1 \cdot 10^{18}$ of each), pK's of 6 and 8, and low salinity (I = 0.01 M NaCl), two distinct alternatives can be envisioned. If pK_a(acid) is less
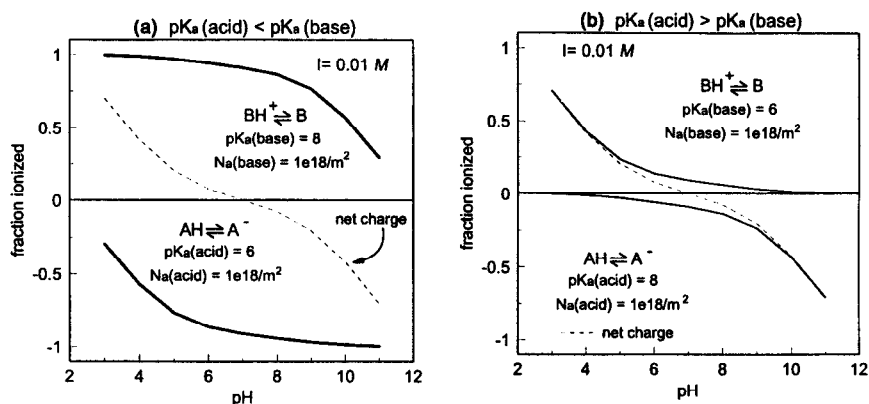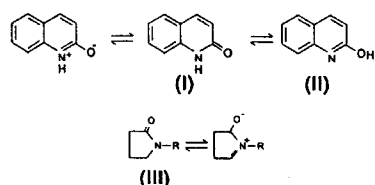

Figure 7: Calculated surface charge for hypothetical zwitterionic surfaces with equal numbers of acidic and basic sites and (a) pK_a (acid) < pK_a (base) or (b) pK_a (acid) > pK_a (base).

Table 2: Ionizable surface group model parameters (Buckley et al., 1989).

Crude Oil	Acidic sites		Basic sites	
	N_a(acid) (number/m^2)	pK_a(acid)	N_a(base) (number/m^2)	pK_a(base)
Moutray	$0.4 \cdot 10^{18}$	4	$0.1 \cdot 10^{18}$	6
ST-86	$2.0 \cdot 10^{18}$	1.75	$2.08 \cdot 10^{18}$	5.8

than pK_a(base), as in Fig. 7a, both acidic and basic species are ionized over a wide pH range. In the opposite case, pK_a(acid) > pK_a(base), the extent of ionization is much less, as shown in Fig. 7b. The net charge (dotted lines) and zeta potentials are the same in both cases, but adsorption of oil components at a charged surface could be quite different for these two cases.

In Fig. 8, the results of calculations of IEP are shown as a function of the logarithm of the ratio of the numbers of acidic to basic sites. The shape of the curve depends on the separation between acidic and basic pK_a values. As the difference between them increases, IEP becomes increasingly sensitive to the surface density ratio.

<u>IFT as a Function of Brine pH</u>

Crude oil/brine IFTs are often reported as a function of pH because low tensions contribute to improved oil recovery in alkaline flooding. Decreases in IFT may occur at both low (less than 4) and high (greater than 8) pH. At the extremes of pH, some oils show transient, ultra-low interfacial tensions that may reflect surfactant production by chemical reactions at the interface, but for less extreme pH values, IFT change is likely related to dissociation, as demonstrated for interfaces of known acidic and basic species.

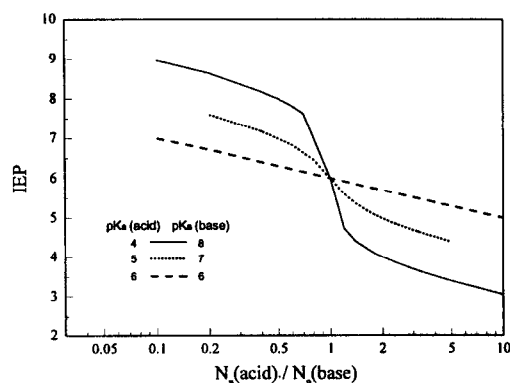Zeta potential measurements for Moutray crude oil

(Fig. 1) have been shown previously to be consistent with a model that includes one type each of acidic and basic sites; the ISG parameters from that study are shown in Table 2 (Buckley et al., 1989). The estimated pK_a values are separated by 2 pH units with pK_a(acid) < pK_a(base) and about four acidic sites for each basic site. Surface charge densities are plotted for this model of the Moutray/water interface as a function of solution pH in Fig. 9. The positive part of this plot is repeated in Fig. 10 for NaCl solutions with I = 0.001, 0.01, and 0.1 M. Also plotted in Fig. 10 are IFT measurements for Moutray and 0.01 M NaCl. There is a good correlation between IFT decrease and the transition from an interface with both negative and positive charges (pH < 8) to one that has negatively charged sites only (pH > 8). A second example comparing positive and negative surface charge and IFT is shown in Fig. 11 for ST-86 crude oil.

The reduction in crude oil IFT at high pH is often attributed to dissociation of acidic species. In fact, it appears that a more accurate description of the interfacial charge of crude oil/brine interfaces is that there is a transition from zwitterionic to a negatively charged surface at high pH and that this transition corresponds to reduced IFT values. In terms of the net charge, these two descriptions are indistinguishable. The implications for adsorption and wetting alteration are very different, however. Positive charge, and thus interactions between basic sites and a negatively charged solid surface, may persist to pH conditions far above the IEP. Acid numbers alone may be not be indicative of differences between oils for which equally important parameters are the number of basic species, differences between pK_a's, and the total numbers of each that partition to the interface. Interfacial tension appears to be a sensitive indicator of the transition from zwitterionic conditions to a surface
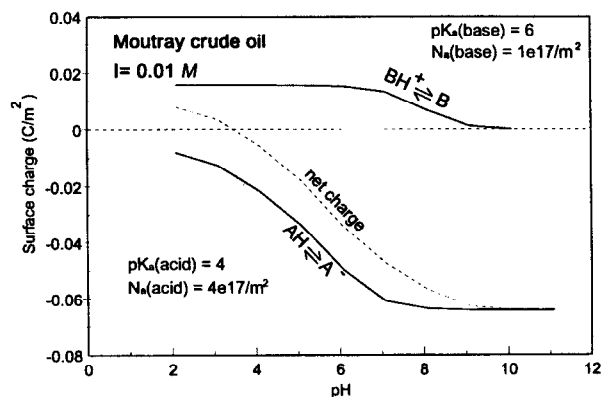

Figure 8: The isoelectric point of a zwitterionic surface depends strongly on the ratio of the numbers of acidic sites and basic sites, and their respective pK_a values.

Figure 9: Surface charge of zwitterionic Moutray crude oil emulsions. (Calculated from data in Buckley et al., 1989.)
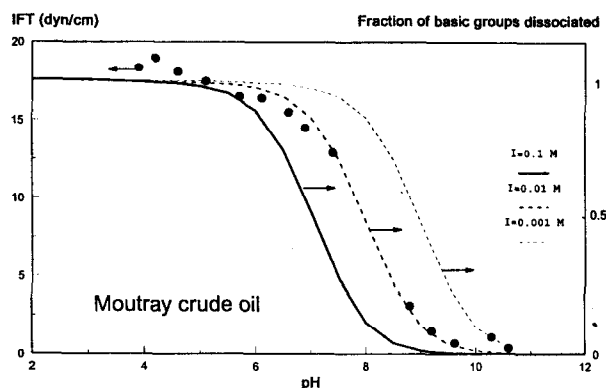
Figure 10: Positively charged ionizable sites for Moutray crude oil with brines of varying pH and ionic strength. The best match to the IFT data for measurements against 0.01 M NaCl brine is with the calculated 0.01 M curve.

that has exclusively positive or negative charged sites.

Conclusions

♦ Oil soluble organic acids and bases lower the IFT between oil and water. IFT depends on aqueous phase pH and ionic composition. The relationship between IFT and aqueous phase properties can be explained by treating the acidic or basic functional groups as ionizable surface sites and applying the ISG model to calculate the extent of charge. IFT decreases in proportion to the increase in either positive or negative charge of the oil/water interface.

♦ Crude oil/brine interfaces have both acidic and basic sites. Brine composition affects the extent of charge. Over a wide range of conditions, sites of both positive and negative charge can coexist. Coexistence of sites of opposite charge has important implications for the short range interactions that affect wetting in an oil reservoir.
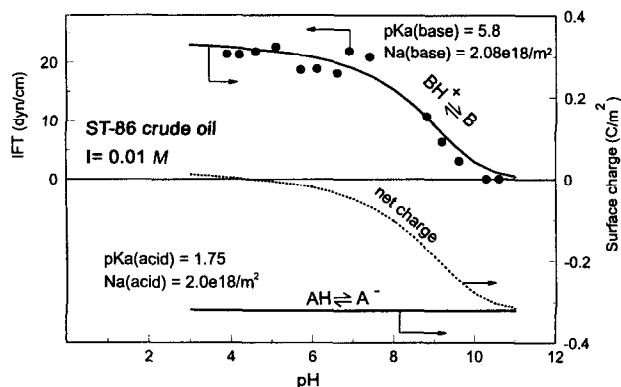
♦ The drop in crude oil/brine IFT as pH increases

Figure 11: Comparison of zwitterionic surface charges and IFT for ST-86 crude oil. (Calculations based on data from Buckley *et al.*, 1989.)

corresponds to a transition from a zwitterionic interface (with both positively and negatively charged sites) to an interface that is exclusively negative in charge.

Acknowledgments

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