

Nonaqueous charging - Literature review

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1. van der Minne, J.L.; Hermanie, P.H.J. Electrophoresis measurements in benzene-correlation with stability. *J. Colloid Sci.*, 7, 600, **1952**

Summary from Fowkes (1965): Carbon black in benzene:

Designed proper electrophoresis cell that produced a uniform electric field

Dispersants give a charge

Charge depends on chemical nature of dispersant

Stable dispersions require > 25 mV zeta-potential

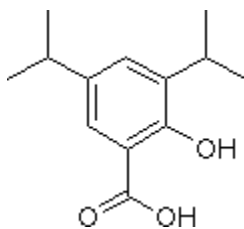
Mixtures of positively charging and negatively charging dispersants counteract one another

From a review of the paper: All about the measurement.

2. van der Minne, J.L.; Hermanie, P.H.J. *J. Colloid Sci.*, 8, 38, **1953**.

Charging agents in benzene were

Calcium salt of diisopropylsalicylic acid (Ca dips)



Tetraisoamylammonium picrate (tiap) (Picric acid is trinitrophenol)

Results:

A minimum concentration of Ca dips is necessary for positive particle charging .

Even the smallest portion of tiap made the particles negative but the absolute values lower than Ca dips.

The agents were antagonistic.

A minimum charge was necessary for stability corresponding to about 21-24 mV.

3. Klinkenberg, A.; van der Minne, J.L., Eds. *Electrostatics in the petroleum industry - The prevention of explosion hazards*; Elsevier Publishing Co.: Amsterdam; **1958**.

"Early in 1954 a large tank in shell's refinery at Pernis exploded 40 minutes after the start of a blending operation in which a tops-naphtha mixture was being pumped into straight-run naphtha. The fire was quickly brought under control and the salvaged contents transferred to another tank. On the following day a second attempt was made to blend these two materials and again an explosion occurred 40 minutes after starting the pumps.

This striking and unusual coincidence could only be explained by the assumption that both explosions had been caused by static electricity. Other possible causes such as pyrophoric scale and even sabotage had been considered and rejected."

Chapter VII. Electric conductivity

The slight conductivity of hydrocarbons is due to foreign matter such as oxidation products, asphaltenes, and metal salts... p. 74

Gemant, A. "Electrical properties of hydrocarbons" - Chapter V, pp 215-240 in Farkas, A., Ed. *Physical Chemistry of the hydrocarbons*, Vol. I, Academic Press: New York; **1950**.

... since the attractive forces are stronger (lower dielectric constant), small structural differences between various electrolytes may give rise to considerable differences for each substance. p. 79.

... mixed solutions often have a much higher conductivity than the sum of their constituents...p. 79. And has been patented: Dutch Patent 83,694 (1956) and British Patent 749,898 (1956).

4. Gemant, Andrew, *Ions in hydrocarbons*. John Wiley & Sons: New York; **1962**.

"Even nowadays the Debye-Hückel theory plays a leading role in electrochemistry, ... This trend helps to explain why solutions of very low conductivity have not been found to be of much interest. The concentration of ions in these solutions is so low that

activity coefficients closely approach unity and the influence of ionic clouds becomes unimportant." (p. 5)

Routes to provide solubility for strong aqueous electrolytes: (1) Instead of metal cations, ammonium, in which hydrogen is replaced by alkyl groups (such as butyl or amyl) can be used. (2) The halogen salts, picrates and thiocyanates of these cations are soluble in solvents of low dielectric constant. (p. 23) (3) An often used solvent which shares with hydrocarbon the essential feature of low dielectric constant is *p*-dioxane. (Also water miscible.) (p. 23)

The concentration of hydrogen ions cannot be measured conductively, but can be measured by titration. (p. 36, 45)

Conductivity of amine-acid solutions - strongly dependent on the presence of a "co-solvent" such as phenol. (p. 55)

Several chapters on specific ion-forming chemistries: Ions from oxidation of ortho-substituted aromatics; Ions from ozonolysis of aromatics.

Metal-complex ions (p. 185f).

5. Fowkes, F.M.; Anderson, F.W.; Moore, R.J. A mechanism for electrical charging of dispersions in nonaqueous liquids; *Div. Of Colloid and Surf. Chem., ACS National Meeting*; Atlantic City, NJ; September **1965**.

By electro deposition of carbon black in hydrocarbon:

Acidic dispersants produce positively-charged particles

Basic dispersants produce negatively-charged particles

Mechanism is proton transfer and resulting ion must be oil-soluble enough that it readily dissociates.

The better dispersants are micellar or oil-soluble polymers

Mechanism explains: stability of electrically-charged dispersions, electro deposition, electrophoresis, streaming potentials, and sedimentation potentials.

Thus showing electrostatic repulsion allows a simultaneous or alternative explanation to that of steric-stabilization

Electro deposition is a rapid screening tool

Used grids for electron microscope, coated with conductive, transparent carbon, as electrodes

Electrode gap at 1.4 cm and usually 500 volts for 30 s.

Polymers:

Neutral polyalkylmethacrylates (200 - 700,000 MW) mostly C12 - C18 methacrylate groups (Acryloid 618, Rohm and Haas)

Similar polyalkylmethacrylates copolymerized with small amounts of weakly basic (pKa 3.3) vinyl pyrrolidone (Acryloid 917, Rohm and Haas) or small amounts of tertiary amine-containing methacrylate (LOA 565, duPont)

Acidic copolymer of maleic anhydride with vinyl acetate and fumarate esters having C16 - C20 alkyl chains (Paratone 460, Enjay Chemical Co.)

Partially imidized polyamine with oil-soluble polyisobutylene chains and some free secondary amine groups (OLOA 1200, Oronite Chemical Co.)

Synthesized polymers: polyaurylmethacrylate, mixed polyalkylmethacrylate (methyl, lauryl, stearyl), and a similar mixed polyalkylmethacrylate copolymerized with a small amount of weakly basic (pKa 4.7) methyl vinyl pyridine

Polymeric dispersants were deoiled by precipitation from benzene, acetone, and methanol

Non-polymeric dispersants

Two basic calcium petroleum sulfonate dispersants

A fatty acid ester of mannitol condensed with ethylene oxide (Tween 81, Atlas Chemical Co.)

Acidic partial ester of lauryl alcohol with phosphoric acid (Ortholeum 162, duPont)

Soot was obtained from a benzene flame on a metal screen and freshly precipitated "asphaltenes" from a standard solution distributed by Rohm and Haas

Screened dispersants at 1% concentration in highly refined naphthenic oil, with 0.5 mg carbon, mixed with vigorous mechanical agitation

Results:

Additive		% Deposition on Positive Electrode	Stability (days)	Dispersancy
Pyridine -containing polyalkylmethacrylate	pKa 4.7	100	> 50	Good
Acryloid 917	pKa 3.3	100	> 50	"
OLOA 1200	pKa >9	100	> 50	"
LOA 565	pKa >0	99.9	> 50	"
Calcium petroleum sulfonate No. 1	pKa >9	99.9	> 50	"
Calcium petroleum sulfonate No. 2	pKa >9	99.9	> 50	"
Cetyl alcohol		95		None
Tween 81		90		"
Dodecylamine		80	3	"
Acetic acid		50	2	"
Acryloid 618		15	1	"
Polyaurylmethacrylate		20	2	"

Oleic acid	15	2	"
Ca dinonylnaphthalene sulfonate	1	1	"
Ditolylphosphoric acid	1	0	"
Ortholeum 162	1	1	"
Paratone 460	0.1	> 50	Good

At low dielectric constant, ionization of acids and bases is suppressed. Dispersants may dissociate at the interface (often slightly moist).

Micelles or polymers provide local regions of higher dielectric constant thereby shielding the charge.

Basic dispersants pick up a charge from the particle surface, desorb, and leave a negatively charged surface. (The opposite to basic dispersants in water which produce positive particles by preferential adsorption).

Mechanism depends on the chemical nature of the particle surface. Basic dispersants are excellent for the acidic carbon blacks but not very good from basic lead salts.

The calculated area per surface charge is 75K Angstroms squared.

Acid:base ratio for neutrality is different for each pair of acidic and basic dispersants. Particle charge can be changed from negative to neutral to positive.

Some pairs go through electrical neutrality but remain stable because of sufficient steric thicknesses.

Excess dispersant reduces the electro deposition (just as in aqueous dispersions). Can't be double layer compression. Suggests polymer "shrinks" with concentration?

Numerous dispersions are not electrically charged but are still stable. But steric stabilization predicts the thickness is enough for small particles:

Copolymers of octadecene with vinyl alcohol

Copolymer of alkylmethacrylate with a glycol methacrylate (OLOA 6000, Oronite Chemical Co.) Both carbon black and silica.

Streaming and sedimentation potentials:

Electro deposition correlates with these reported phenomena

Streaming potentials with dilute hydrocarbon solutions of acidic or basic dispersants produce the sign of particle charge as expected.

Aluminum picks up hydrogen ions readily and donated them sparingly

Chromium is the opposite; iron in between. (Fowkes, F.M.; *J. Phys. Chem.*, 64, 726, **1960.**)

Can produce solutions of only anions or cations:

Basic (pyridine-containing) polyalkylmethacrylate in highly extracted hydrocarbon

Proposes making electrets of mixtures of acidic and basic dispersants in wax with much higher electric dipoles.

Mixtures of acidic and basic dispersants are 10 times as conductive as either alone.

Micellar dispersants are better conductors than polymers (maybe a 1000 fold).

Conclusions:

Charge on particles in hydrocarbons is created with acidic or basic polar polymers or micelle-forming substances. The process is dissociation at the interface, donation of protons by acidic particles to basic dispersants (or by acidic dispersants to basic particles) and subsequent desorption beyond the shear plane.

Electro deposition experiments are useful.

Mixed dispersant systems are antagonistic. Mixtures of large molecules still produce stable dispersions. Micellar molecules do not.

The acidity or basicity of the particle surface is important.

Excess dispersant decreases the electro deposition.

Streaming potential, sedimentation potential, and electro deposition measure similar properties.

Oil soluble cations and anions can be separated from each other.

Antagonistic dispersant solutions are much more conductive than either alone.

6. Fowkes, F.M. *Disc. Faraday Soc.*, 42, 246, **1966**. (in General Discussion of "Mechanism of de-aggregation and stability of rutile dispersion in organic liquids by Micale, F.J.; Lui, Y.K.; and Zettlemyer, A.C.)

"arging process in non-aqueous media appears to be entirely a proton-exchange... the addition of water tends to make the rutile or alumina surface more basic ... and therefore to make it more positively charged; the aluminum hydroxide is basic and is uninfluenced by added water. ... added water can also make the solution more basic, but the main effect is on the oxide surfaces."

The next comment is from E.J.W. Verwey: "... In support of Fowkes' remarks on the role of "acidity" of particle surface and dispersion medium in determining the charge of oxide particles in various media I would mention some older work (*Rec. trav. chim.*, 60, 625, **1941**) on oxide surfaces" ... SiO₂>TiO₂>ZrO₂ and water>acetone>ethanol>methanol. PZC as determined by titration.

The next comment is from D.W.J. Osmond who calculates the number of charges per particle, small, and therefore the number counterions likely between the particles, also small, therefore the "best" model of repulsion is simple Coulomb repulsion, with minor corrections made if necessary.

7. Fowkes, F.M. The interactions of polar molecules, micelles, and polymers in nonaqueous media from *Solvent Properties of Surfactant Solutions*, Shioda, K., Ed.; Marcel Dekker: New York; **1967**, pp. 65-115.

In hydrocarbons long-chain fatty acids nor sulfonic acids of alkylated aromatics form micelles, but the more ionic Na, Al, or Ca salts do. P. 67

Nearly all micelle-forming solutes are salts, p. 69.

Pearson's classification of hard and soft acids and bases is useful, p. 70-71, especially to determine what combination will form micelles in various solvents.

8. Vijayendran, B.R. Nonaqueous dispersion: Carbon black in heptane solution of manganese and zinc salts of 2-ethylhexanoic acid. *ACS Symp. Ser.*, 9, 211-224; **1975**.

The small number of charges per particle leads to significant dependence on trace impurities. p. 213

Sterling R with Mn and Zn octoates (salts of 2-ethylhexanoic acid). Zn soaps are conductive because of the weak Zn-carboxylate bonds. p. 213. Mn has a stronger bond.

Particles are positive, therefore it is the preferential adsorption of the cation. p. 220.

9. Fowkes, F.M.; Jinnai, H.; Mostafa, M.A.; Anderson, F.W.; Moore, R.J. Mechanism of electrical charging of particles in nonaqueous liquids; *ACS Symp. Ser.*, 200, 307 - 324, **1982**.

Mechanism is adsorption, charge (proton) exchange; and desorption of charged dispersant.

Mechanism was proved by using C-14 tagged copolymers (p. 309). Clean cathode had the higher C-14 count.

Also (p. 312) solvent did not displace adsorbed polymer, but other polymer did (as shown with C-14 labeled polymers.)

Also (p. 312) showed one electronic charge per polymer and one electronic charge per 10^{-11} cm² of particle surface.

For over 30 years, inorganic pigments in hydrocarbons can be charged (van der Minne and Hermaine). But the nature of the oil-soluble ions was not demonstrated.

Materials studied:

Micellar dispersants: dinonylnaphthalene sulfonates, tri-hexyl benzene sulfonates, and petroleum sulfonates.

"Neutral" sulfonates are really acidic, the acid strength increasing in the order: Na^+ , Ba^{++} , Ca^{++} , Mg^{++} , Zn^{++} , Cr^{++} , Al^{+++} .

Basic micelles were obtained with basic sulfonates such as $\text{Ca}(\text{OH})\text{RSO}_3$.

Micelle cores are nearly as concentrated as molten salts.

Fowkes, F.M.; Becher, D.Z.; Marmo, M.; Silebi, C.; Chao, C.C. in *Micellization, solubilization, and microemulsions*, Vol. 2, Mittal, K.L, Ed., Plenum Press: NY; **1977**.

Polymer dispersants

Random copolymers of long chain alpha olefins or long chain methacrylates

With acidic or basic co-monomers such as:

vinyl acetate, vinyl alcohol, vinyl pyridine, vinyl pyrrolidone, hydroxyethyl methacrylates, etc.

Electro deposition tests; 100V across about 2 cm for 16hours; mixed deposition was often seen.

Particles were soot generated from a toluene flame.

DLVO theory and electrostatically stabilized dispersions in oil

The authors argue the zeta-potentials are high enough.

The Debye lengths are short enough to produce large forces??

And calculates stability ratios for various formulations.

10. Pugh, R.J.; Matsunaga, T.; Fowkes, F.M. The dispersability and stability of carbon black in media of low dielectric constant. 1. Electrostatic and steric contributions to colloidal stability

Stresses the combination of steric (at low concentrations, short range) and electrostatic (at higher surface coverages and long range).

Paper contains the detailed model equations for steric and electrostatic stabilization.

Lots of conductivity, rheology, etc. data.

Synthesis of OLOA-like materials:

de Hek, H.; Vrij, A. *J. Colloid Interface Sci.* 79, 289, **1981**. Have data on silica, 104 nm particles?

Effective non-aqueous dispersants are invariably found to be either acids or bases, and their efficiency increases with acid or base strength. It is also found that the acid or base strength of particle surfaces is quite important ...

Adsorption rates are slow (p. 196) 12 h for equilibrium, but most is by an hour or two.

The necessary dispersant levels are 3% or so. Fig. 9 p.198.

Lyklema, J. *Adv. Colloid Interface Sci.*, 2, 246, **1968**.

11. Pugh, R.J.; Fowkes, F.M. The dispersability and stability of carbon black in media of low dielectric constant. 2. Sedimentation volume of concentrated dispersions, adsorption and surface calorimetry studies. *Colloids Surf.*, 9, 33-46, **1984**.

A maximum in sedimentation volume was found (with OLOA 1200) at <0.25 wt%), higher than that without any dispersant.

Suggests that sedimentation measurements made on the agglomerated dispersions are some sensitive measures of interparticle forces because the gravitational sedimentation is fast and the sediment volumes high.

High dispersant levels, enough to saturate the carbon black are 10%.

12. Pugh, R.J.; Fowkes, F.M. The dispersability and stability of coal particles in hydrocarbon media with a polyisobutene succinamide dispersing agent. *Colloids Surf.*, 11, 423-427, **1984**.

Tested bituminous coal. Found far less dispersant per unit area was needed than with the Sterling NS. The hypothesis is that the coal has a more active surface. Surface chemistry counts.

13. Fowkes, F.M.; Pugh, R.J. Steric and electrostatic contributions to the colloidal properties of nonaqueous dispersions. *ACS Symp. Ser. 240*, 331-354, **1984**.

"Dispersions of finely divided solids in non-aqueous media have been important for paints, inks, reinforced polymers and lubricating oils, but with the development of liquid toner systems and "ultra-structure" **processing of ceramics as fine powders dispersed inorganic media**, the understanding and optimization of such systems is more important than ever." p. 331.

$$A_{\text{carbon / oil / carbon}} = 2.8 \times 10^{-13} \text{ ergs}$$

When the steric barrier is present, the only requirement for the electrostatic repulsion is to eliminate the secondary minimum and this is easily achieved with zeta-potentials far below those required to operate entirely by the electrostatic mechanism. p. 336

OLOA 1200: film balance data give a film thickness of 5 nm. p. 336

Data on Sterling NS (25 m²/gm)

Rates of adsorption are slow, taking about 10 hours. p. 338.

Uses a Deryagin equation of the form:

$$U_{121}^e = 2\pi\epsilon_r\epsilon_0 a\Psi_0^2 \ln(1 + e^{-\kappa H})$$

14. Labib, M.E.; Williams, R. The use of zeta-potential measurements in organic solvents to determine the donor-acceptor properties of solid surfaces. *J. Colloid Interface Sci.*, *97(2)*, 356 - 366 (**1984**).

For most solids the zeta potential changes sign for some value of the solvent donicity. p. 356

Triboelectric series: higher position loses and electron to lower position.

Donicity is taken as the Jensen number: the enthalpy of reaction of a donor molecule with the reference Lewis acid, SbCl₂, using 1,2, dihaloroethane as a solvent. p. 357:

Table 1. Properties of the Solvents Used

Solvent	Viscosity	Donicity	Dielectric	Specific
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	(mPa-s)	(kcal/mole)	constant	conductance ($\Omega\text{-cm}^{-1}$)
1,2-Dichloroethane	0.89	0.00	10.4	6.6×10^{-8}
Nitromethane		2.70	35.9	2.6×10^{-6}
Nitrobenzene	2.03	4.4	34.8	
Acetic anhydride	0.90	10.5	20.7	7.4×10^{-7}
Ethyl acetate	0.46	17.1	6.0	1.2×10^{-9}
Tetrahydrofuran		20.0	7.6	
Dimethylacetamide	0.84	27.8	37.8	1.3×10^{-6}
Dimethyl sulfoxide	2.24	29.8	45.0	7.0×10^{-7}
Ethylene diamine	1.54	55.0	14.2	7.0×10^{-7}

Particles: Calcium carbonate, titania, diamond, zinc sulfide, gold, sodium tungstate, aluminum sulfate, mica, and calcium oxide.

The trend from positive to negative zeta potential is seen for all solids as the That is, when a particle is in a solvent of low donicity, the particle is positive. When a particle is in a solvent of high enough donicity, the particle is negative. Calcium oxide and sodium tungstate were never positive.

A higher donicity value of a **particle** means it is more likely to be positive. That is, since calcium oxide and sodium tungstate were never positive, they always accepted an electron from the solvent. (or lost a proton?)

Water had a large effect! Not too well correlated with contact electrification measurements.

15. Kitahara, A. Nonaqueous systems in *Electrical phenomena at interfaces*, Kitahara, A.; Watanabe, A., Eds.; Marcel Dekker: New York; **1984**, 119 - 143.

Primarily about hydrocarbons or perhalogenated hydrocarbons as solvents.

Reversed micelles are able to solubilize some polar species (an old idea credited to Nelson, S.M.; Pink, R.C. *J. Chem. Soc.*, 1954, 4412, **1954**.) p. 120.

All nonaqueous electrolytes are weak. p. 123

Sticks with the usual: dissociation and micellization independently, then stabilization of ions in micelles. Equations 5.1 and p. 125.

Nonionics produce the same sign charge in nonaqueous as aqueous. p. 128.

The number of charges per particle is so small that the simple application of DLVO theory is suspect. p. 130.

The calculations with DLVO theory show a zero energy crossing at about 10-25 nm. p.132.

Feat and Levine predict that double-layer forces are attractive in concentrated, charged, nonaqueous dispersions. (Feat, G.R.; Levine, S. *J. Colloid Interface Sci.*, 54, 34, **1976**.)

Change in zeta potential with concentration of dispersants (calculated): Equilibrium between dissociation and adsorption, leads to a maximum under some conditions and a steady decrease under others. p. 136.

Effect of water on zeta potential: Especially important for oxide surfaces. Maxima were less for carbon blacks. For carbon blacks and AOT: dispersions stable at low AOT, unstable at intermediate, and stable again at high concentrations (possibly due to a weak flocc structure?). p. 139.

16. Karasawa, S. Reproduction in copying and electrophoretic display in *Electrical phenomena at interfaces*, Kitahara, A.; Watanabe, A., Eds.; Marcel Dekker: New York; **1984**, 413 - 436

Charge control agents - nothing systematic, but examples from Japanese patent (reference number): Polymers (14), block or graft copolymers (15), graft carbon black (16), combination of polymer and monomer (17), polymer and cationic or anionic surfactant (18).

Negative charging of carbon blacks with a copolymer of lauryl methacrylate and dimethylaminomethyl methacrylate and positive charging with metal soaps such as metal naphthenates and nickel di (ethylhexoic acid). (p. 412) in alkanes.

Some discussion of electrophoretic displays and photoelectrophoretic displays.

17. Mikeska, K.R.; Cannon, W.R. Dispersants for tape casting pure barium titanate. in *Forming of Ceramics*, Mangles, J.A., Ed., Vol. 9; 164-183, **1984**.

Dispersions in azeotropic: 34% ethanol- 66% MEK solutions. Need very well dispersed particles to prevent voids in coatings. Hence no flocculation.

In the open literature: menhaden fish oil, corn oil, glycerol trioleate. (p. 167)

Using a standard acrylic binder - Acryloid B7 from Rohm and Haas. (p. 183)

Screened 70 dispersants - Listed in Table 1. (p. 169).

Chose Emphos PS-21 A from Witco Chem, listed as a phosphate ester.

Theory: Emphos is the reaction product of phosphoric acid and two different types of long-chained alcohols (probably 10-15 carbons long) (p. 180). The material is acidic in ethanol/MEK as the pH drops. Free protons are absorbed by the barium titanate, giving it a positive zeta potential. In water the particles are negative. In the organic solvent, positive! (p. 181). Theory is that a hemi-micelle (a second layer) forms in the aqueous dispersion.

18. Labib, M.E. Williams, R. An experimental comparison between aqueous pH scale and the electron donicity scale. *Colloid & Polym. Sci.*, 264, 533 - 541 (1986).

Measured the PZC (pH of no zeta potential) in water and the donicity (Gutmann scale for various solvents) and find a roughly linear correlation between PZC and particle donicity.

19. Labib, M.E.; Williams, R. The effect of moisture on the charge at the interface between solids and organic liquids. *J. Colloid Interface Sci.*, 115(2), 330 -338 (1987).

Using oxides (silica, titania, alumina, and magnesia). Find three regions: When the particles have high charge, the water decreases the potential a little. Added water generally increases the donicity value of the particle (all oxides). Hence water makes particles more likely to be positive; more likely to either donate an electron (or accept a proton).

20. Mikeska, K.R.; Cannon, W.R. Non-aqueous dispersion properties of pure barium titanate for tape casting. *Colloids Surf.*, 29, 305 - 321, 1988.

Ampoteric phosphate ester surfactant was found best to disperse barium titanate in MEK/ethanol. Optimum dispersion was in the azeotropic mixture. Less water was better. Optimum dispersion was at monolayer coverage. Stability is a combination of electrostatic and steric. (p. 305).

Dispersant is Emphos PS21A - equal mixture of mono, di, ethoxylate esters. The ethoxylate is a condensate of a primary C10 alcohol and 7 ethoxy groups. MWs 546 and 994. Density of 0.925 g/cm³ and acid numbers of 130 and 200 at pH 5.5 and 9.5 respectively. (p. 308).

Particles are positively charged. (p. 312). Plots of apparent viscosity, adsorption, and zeta potential are given in Figure 4. (p. 4). (at 25 vol % solids).

21. Chen, W.-J. Stabilization and electrostatic deposition of aqueous and non-aqueous polymeric colloids, PhD Dissertation, Lehigh University; **1988**.

Studies with pigment-embedded polymers (for LID), p. 3f. Shows field-dependent electrophoresis.

In nonpolar dispersions, the charge on the particle is determined by the ternary balance between particle surface chemistry, adjuvant, and medium., p.4

Lists (Table 1-2) dispersants from the literature: Picrate/tetraisoamylammonium; Diisopropylsalicylate/Ca; AOT/Na, Mg, Ca, Ba, Al, Mn; Stearylcylohexyl benzenesulfonate/Ba, Ca, Zn, Ni; Octanoate/Mn, Zn; Tetraoxylethylene nonyl phenyl ether; Methylvinylpyridine alkylmethacrylate copolymer; Polyisobutene succinamide; Petronate/Bacis Ca/Alkyd resin; Melamine resin; Vinylacetate vinyl chloride maleic acid copolymer; Fatty polyamine; Oleate/Cu; Oleic acid; Stearic acid; Caproic acid; Polyether; Epoxy resin; Sorbitan stearate; Cl-PVC; Lecithin; Menhaden fish oil; Tetrabutylammonium chloride; Anthranilate/Cr.

Damerell, V.R.; Mattson, R. **J. Phys. Chem.**, **48**, 134-141 (**1944**).

Damerell, V.R.; Gayer, K.; Laudenschlager, H. *J. Phys. Chem.*, *49*, 436-442 (**1945**).

Rutgers, A.J.; de Smet, M. *Trans. Faraday Soc.*, *48*, 635 (**1952**).

van der Minne, J.L.; Hermanie, P.H. *J. Colloid Int. Sci.*, *7*, 600 (**1952**); *8*, 38 (**1953**).

Preferential adsorption of Ca⁺² onto surface carbonyl groups

Koelmans, H.; Overbeek, J. Th. G. *Discuss. Faraday Soc.*, *18*, 53 (**1954**).

Briant, J.; Bernelin, B. *Re. Inst. Fr. Petroleum Ann. Combust. Liquides*, *16*, 49 (**1961**).
stearylcylohexyl benzenesulfonates; on carbon blacks, Ba⁺² were positive; Ca⁺² and Zn⁺² were negative.

Oyabu, Y.; Kawai, H.; Nakanishi, Y. *Shikizia Kyokaiishi (Color Materials)*, *35*, 98 (**1962**).

Romo, L.A. *J. Phys. Chem.*, *67*, 386 (**1963**).

McGown, D.N.L.; Parfitt, G.D.; Willis, E. *J. Colloid Int. Sci.* *20*, 650 (**1965**).

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- McGown, D.N.L.; Parfitt, G.D. *Kolloid Z.Z. Polym.*, 220, 56 (1967).
- Kitahara, A.; Karasawa, S.; Yamada, H. *J. Colloid Int. Sci.*, 25, 490 (1967).
- Frankin, M.J.B. *J. Oil Color Chemist's Assoc.*, 51, 499 (1968).
- Kitahara, A.; Komatsuzawa, T.; Kon-no, K. in *Proc. 5th Int. Congr. Surf. Active Substances*, Vol 11, Ediciones Unidas Ed., Barcelona, 1968, p. 135
- Parreira, H.C. *J. Electroanal. Chem.*, 25, 69 (1970).
- carbon blacks, AOT; Na⁺ are negative; divalent (Ba, Ca, Mg) were positive
- Sato, T. *J. Appl. Polym. Sci.*, 15, 1053 (1971).
- Kitahara, K.; Fujii, T.; Katano, S. *Bull Chem. Soc. Jpn.*, 44, 3242 (1971).
- Oyabu, Y.; Yasumori, Y. *Talanta*, 19, 423 (1972).
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- Vijayendran, B.R. *ACS Symp. Ser.* 9, 211 (1974).
- Stotz, S. *J. Colloid Int. Sci.*, 65, 118 (1978).
- Kitahara, K.; Tamura, T.; Kon-no, K. *Sep. Sci. Tech.*, 15, 249 (1981).
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- Fowkes, F.M.; Jinnai, H.; Mostafa, M.A.; Anderson, F.W; Moore, R.J. *ACS Symp. Ser.* 200, 307 (1982).
- Vasconcellos, S.R.; Kosman, J.J.; Rowell, R.L.; Medalia, A.I. *J. Disp. Sci. Tech.*, 4, 409 (1983).
- Fowkes, F.M.; Pugh, R.J. *ACS Symp. Ser.* 240, 331 (1984).
- Kandori, K.; Kazama, A.; Kon-no, K.; Kitahara, A. *Bull. Chem. Soc. Jpn.*, 57, 1777 (1984).
- Kandori, K.; Kitahara, A.; Kon-no, K. *J. Colloid Int. Sci.*, 99, 455 (1984).

Fowkes, F.M.; Huang, Y.C.; Shah, B.A.; Kulp, M.J.; Lloyd, T.B. *Colloid Surf.*, **29**, 243 (1988).

Mechlia, T.; Gosse, B.; Denat, A.; Gosse, J.P. *IEEE Trans. El. Ins.*, *EI-20*, 365 (1985)

Johnson, R.E., Jr.; Morrison, W.H., Jr. *Adv. Ceramics*, **21**, 323 (1987).

22. Morrison, I.D. Criterion for electrostatic stability of dispersions at low ionic strength. *Langmuir*, **7**, 1920 -1922, **1991**.

If the ionic concentration is low enough, the particles repel each other by Coulomb forces. The dispersion force attraction is described in the usual ways. Since the total interaction is a simple equation, the stability ratio can be estimated with an analytic expression.

$$W \approx \left(\frac{Ak^2T^2}{3072D^3\epsilon_0^3a^3\Phi_0^3} \right)^{1/4} \exp\left(\frac{2\pi D\epsilon_0 a\Phi_0^2}{kT} \right)$$

A reasonable approximation for many pigments in oil gives the required zeta potential (mV) for stability as a function of particle radius (μm):

$$\Phi_0^2 > \frac{10^3}{Da}$$

23. Hou, W.H.; Lloyd, T.B.; Fowkes, F.M. The effects of liquid toner composition and toning parameters on electrostatic images. *J. Imaging Sci. Tech.*, **36**(2), 151-161, **1992**.

Polymer-encased (Griltex nylon: nylon 6, nylon 12, and nylon 6/12 copolymer) carbon black particles (Regal L 330), basic barium petronate (negative), cupric naphthenate (positive) toners.

24. van der Hoeven, Ph.C.; Lyklema, J. Electrostatic stabilization in non-aqueous media, *Adv. Colloid Interface Sci.*, **42**, 205-277, **1992**.

Particular attention to roles of dielectric constant and ionic strength. p. 20

Defines; semi-polar: $\epsilon \geq 11$ and low-polar: $11 \geq \epsilon \geq 5$; apolar: $5 \geq \epsilon$ (where electrostatic stabilization may be more problematic).

Data with dodecylbenzene sulphonic acid.

Greater dissociation for larger ionic radii:

p. 223; Popovych, D.; Tomkins, R.T. *Non-aqueous solution chemistry*; Wiley, **1981**.

Could use polyether chains of nonionics: Doscher, T.M. *J. Chem. Phys.*, *53*, 1362, **1949**; and inverse micelles.

25. Lee, B.I.; Rives, J.P. Dispersion of alumina powders in nonaqueous media. *Colloids Surf.*, *56*, 25 -43, **1991**.

Fatty acid (linolenic) and OLOA1200 were good dispersants for 3 different alumina powers in THF and toluene. OLOA1200 was more effective, because the later provided electrostatic repulsion.

Used plate-out cells to measure charge. Some IR data. Some deposition (mass) measurements.

26. Lee, B.I.; Paik, U. Effect of aminosilane adsorption on rheology of silica powders in nonaqueous media. *J. Mater. Sci.*, *27*, 5692 - 5700, **1992**.

Should be that the best dispersions are obtained with combined electrostatic and steric factors, even in nonaqueous dispersions.

Highly purified, 0.45 μ m, particles from hydrolysis and precipitation (Stober). Calcined, amorphous. In chloroform, ethanol, acetone, THF. Treated with N-(3-acryloxy-2-hydroxypropyl)-3-aminopropyl triethoxysilane. Both as crosslinker and binder.

27. Morrison, I.D. Electrical charges in nonaqueous media, *Colloids Surf. A.*, *71*, 1-37, **1993**.

Particles acquire electrical charges either by preferentially adsorbing the ion of one sign or the other, possibly still associated with its stabilizing structure, or by an ion dissociating from its surface to be held in some lyophilic structure in the nonaqueous medium. p. 1.

Labib and Williams have applied the donor-acceptor scales of Gutmann to the problem of characterizing SiO₂, TiO₂, Al₂O₃, and MgO particles in nonaqueous liquids: (1,2-dichloromethane, nitromethane, nitrobenzene, acetic anhydride, acetonitrile, ethyl acetate, tetrahydrofuran, dimethylformamide, dimethylacetamide, dimethylsulfoxide, ethylenediamine, and trimethylamine). p. 11

Instead they (Fowkes et al) propose that the charging of particles comes about by the adsorption of uncharged electrolyte, followed by ion exchange with surface groups and then desorption of charged electrolyte... The most usual mechanism for ion exchange is proton (or hydroxyl) transfer between micelles and particles or container walls... Adsorption of water at the surface of particles is a likely prerequisite for the formation of mobile ions. p. 13

...(Fowkes et al) showed that while adsorbed polymer was so tightly held on the particle surface that it could not be washed off by solvent, polymer in solution replaced some of the adsorbed polymer in just a few minutes. p. 13

Rather the interpretation is that the particles have no charge until the free ions of the electrical double layer are produced. p. 15

28. Morrison, I.D. The influence of electric charges in nonaqueous dispersions. In *Dispersion and aggregation: Fundamentals and applications*, Moudgil, B.M.; Somasundaran, P., Eds.; Engineering Foundation: New York; **1994**.

Surface-active solutes in low dielectric liquids, particularly hydrocarbons, cannot be ionized by the action of the solvent.

Individual ions are stabilized in a liquid when surrounded by a "steric" layer. The required thickness of this layer depends inversely (to first order) on the dielectric constant of the solvent. Therefore the stabilizing layer around ions in low dielectric liquids needs to be substantially thicker than in water... In low dielectric liquids this implies a small concentration of ions and hence low conductivities, slow kinetics of particle charging and slow responses to perturbations.

It is easy to demonstrate the separation of cations from ions by liquid flow... Particle charges can even be determined this way.

The conductivity of micelle-forming surfactants is linear in surfactant concentration. Since these are weak electrolytes, ions are not formed by self-dissociation, but by two-body interactions.

A simple derivation gives the conductivity in terms of viscosity, micelle diameter, equilibrium constant, degree of dissociation, and micelle concentration:

$$\lambda = \frac{2e^2}{3\pi\eta d} K_{eq}^{1/2} (1-\alpha) n_0 \approx \frac{2e^2}{3\pi\eta d} K_{eq}^{1/2} n_0 \quad [1]$$

A simple derivation gives an estimate of the distance between micelle centers in terms on the temperature dependence of the conductivity and the viscosity:

$$\left(\frac{\partial \ln \lambda}{\partial (1/T)} \right) - \left(\frac{\partial \ln \eta}{\partial (1/T)} \right) = - \frac{1.1 \times 10^{-4} M^0 K}{Dd}$$

Zeta potentials are often about the same in oils as in water when these charge-carrying micelles are present.

29. Rosés, M. Ionic equilibria in non-aqueous solvents. Part 3. Effect of homoconjugation. *Analytica Chimica Acta*, 285, 391 - 399, **1994**.

Parts 1 and 2: equations and computer programs for the calculation of pH, dissociation constants and reference potentials from potentiometric data in non-aqueous solvents were developed.

Adds complex ion formation as part of analysis.

30. le Bars, N; Levitz, P.; Messier, A.; Francois, M.; van Damme, H. Deagglomeration and dispersion of barium titanate and alumina powders in an organic medium. *J. Colloid Interface Sci.*, 175, 400 - 410, **1995**.

Dispersion of noncolloidal barium titanate and α -alumina in azeotropic ethanol/butanone mixture. Using phosphate ester. Residual water plays an important

role (and is totally miscible with the solvent). The dielectric constant is high enough to allow ionization. (p. 400)

This phosphate ester does not form micelles in this azeotropic mixture!! The spectroscopic data show that the particle adsorbed head group on the surface. (p. 402).

The adsorption isotherms look normal - very strong adsorption at low concentrations with a plateau. But the adsorption is not reversible. (p. 402).

Water vapor adsorption is nearly reversible but shows hysteresis. (Figure 3). Also water vapor adsorption decreases as phosphate adsorption increases - that is, phosphate displaces water. (p. 403)

The surface charge is always positive, increases with surface coverage, primarily at low coverages, probably between about 40 and 80 mV. (p. 403-4)

Almost no elasticity. (p. 407-8). Viscosities nearly that of the solvent once even a little dispersant is added.

31. Paik, U.; Hackley, V.A.; Choi, S-C.; Jung, Y.-G. The effect of electrostatic repulsive forces on the stability of BaTiO₃ particles suspended in non-aqueous media. *Colloids Surf. A: Physicochem. Eng. Aspects*, 135, 77 - 88 (1998).

Phosphate esters and menhaden fish oil were used as dispersants. The stability by steric stabilization was dependent on fraction covered. The electrostatic repulsions were found to be significantly greater than predicted and mainly dependent on the organic solvent media. (p. 77)

Commercial additives: Emphos PS-21A (Witco) and Defloc Z3 (Reichhold Chemicals) - an oxidized menhaden fish oil containing a complex mixture of triglycerides of saturated and unsaturated fatty acids.

Results were very different for ethanol, ethanol/acetone, and acetone. Conclusions were scant. Other than the charging is much more complex in the organic solvents than in water.

32. Hu, Y.; Veeramasuneni, S.; Miller, J.D. Electrokinetic behaviour of selected alkali and alkaline-earth salts in organic solvents. *Colloids Surf. A: Physico. Eng. Aspects*, *141(2)*, 193 - 203, **1998**.

(No dispersants used?!) Surface charge in methanol is positive as it is in water. The surface charge in other solvents can be positive or negative. The dielectric constants of the solvents tested were high enough the ionic concentration could be estimated adequately (p. 195).

Used FTIR to study the the -OH stretch modes. That with LDV electrophoresis was enough to present a "model" of what ions went where and why.

33. Hughes, D.F.K.; Robb, I.D.; Dowding, P.J. Stability of copper phthalocyanine dispersions in organic media. *Langmuir*, *15(16)*, 5527 - 5231, **1999**.

Only a few mV are sufficient to stabilize dilute dispersions in solvents with dielectric constants less than 20.

Addition of organic acid enhanced stability. Addition of electrolyte: tetrabutylammonium bromide, flocculated all.

Solvents were 1-methoxypropyl 2-acetate, ethylacetate, methanol, and xylene. Acids were ethanoic, propanoic, 2-methoxypropanoic, benzoic, 1-octanoic, and 1-dodecanoic.

Stability correlated with changes in zeta potential. But zeta potentials were small. Lower dielectric constant dispersions were more stable. The hypothesis is that, even though the ionization is less, the repulsion is longer range.

34. Kornbrekke, R.E.; Patrzyk-Semanik, P.; Kirchner-Jean, T.; Raguz., M.G.; Bardasz, E.A. Understanding soot mediated oil thickening. Part 6: Base oil effects

Oil thickening observed in the Mack T-8 test is significantly affected by the aromatic content of the base oil. Increased thickening is accompanied by increased electrical conductivity. After study: the aromatic dispersions had the highest particle charge and conductivity. (p. 135)

Analysis of test results: No apparent agglomeration that could cause oil thickening. The increase in thickening and conductivity are apparent at 100C

Black Pearls 130 was chosen as model for soot. (Previously named Sterling NS) (p. 140)

Table 3: Micelle diameter in various solvents. (Doesn't vary much, even with concentration.) Conductivity data in Figure 6. (All linear.) Explained by the micelle equilibration, not Fuoss et al. Figure 7: Zeta potential and conductivity versus equilibrium concentration.

Suspension stability (p. 143): The estimated required charge is about right (not completely) The difference is suggested to be due to steric effects. (Table 5).

Suggest that the higher ion and charged particle concentration cause a bigger increase in thickening than the less ion and charged particle dispersions. (p. 145)

35. Jenkins, P.; Basu, S.; Keir, R.I.; Ralston, J.; Thomas, J.C.; Wolffenbuttel, B.M.A. The electrochemistry of nonaqueous copper phthalocyanine dispersions in the presence of a metal soap surfactant: A simple equilibrium site binding model. *J. Colloid Interface Sci.*, 211(2), 252 -263, **1999**.

Measure electrophoretic mobilities. Surfactant was zirconium octanoate. In isoparaffin (Isopar G). Maximum in zeta potential occurred at about monolayer coverage.

Used poly (vinyl acetate) lattices to coat the particles? (p. 253).

Photoelectrophoresis is mentioned but not addressed here. (It could be a real problem.) (p.254). Zeta potential increased to a maximum of about 40 mV at about the monolayer capacity. Water increased the charge. (p. 263) A simple site model was sufficient to fit the data.

36. Kosmulski, M. Zeta potentials in nonaqueous media: how to measure and control them. *Colloids Surf., A.*; 159, 277 - 281, **1999**.

Trace water is overrated in published literature. Trace impurities is overlooked in published literature..

Small ions are stabilized by homoconjugation and amphiphilic nonionic compounds.

Siffert et al (ref. 4) found linear relation between electrokinetic charge (differentiated from electrokinetic potential?) and:

$$(DN_{solid} - DN_{liquid})(AN_{solid} - AN_{liquid})$$

Uses the nonlinearity of ion selective electrodes at low salt concentrations to detect trace impurities. These are more reactive than water, hence more important.

Perchloric acid is stronger than HCL in organic solvents. p. 279.

Homoconjugation of low MW acids and bases can also produce large ions. (ref 17).

Polyether chains can form complexes with alkalai metal cations whose structure is similar to crown ether complexes by cyclic polyethers. (ref. 18).

37. Jenkins, P.; Ralston, J.; Thomas, J.C.; Nicholls, S.L.; Staples, P.E. Copper phthalocyanine-mica interactions in nonaqueous media. *J. Colloid Interface Sci.*, 211, 11 - 17, **1999**.

In isoparaffin with AFM. In the presence of water and zirconium octanoate. Force against distance curves show steric stabilization only. No interaction beyond about 5 nm. (Figure 3) at 3.82 mmol dm⁻³.

38. Keir, R.I.; Quinn, A.; Jenkins, P.; Thomas, J.C.; Ralston, J.; Ivanova, O. Electrokinetic properties of copper phthalocyanine pigment dispersions. *J. Imaging Sci. Tech.*, 44(6), 528 - 533, **2000**.

Used combinations of particle charging agent (zirconium octoate) and particle dispersing agents (one an acrylic copolymer containing an amide functional group and another a methacrylate polymer). Measured adsorption isotherms (of the zirconium octoate), conductivities and zeta potentials, as a function of electric field. Fitted data to a series of equilibria. Successfully.

39. Suparno, *Charging behavior in nonpolar colloidal system*, PhD Thesis, The University of South Australia, **2000**.

For particles small compared to the double layer thickness uses a Derjaguin approximation (from 3rd edition of Heimenz with Rajagopalan):

$$W = 4\pi R^2 \epsilon \Psi_0^2 e^{-\kappa(r-2R)/r}$$

Silica (7 μm)/decane with AOT

PALS and AFM

AOT micelles are 20-30 monomers and size is reasonably consistent with concentration; CMC is 0.73 mM in decane, p. 7

Proposes a negative charging model based on premicellar species, p. 99.

Damerell, V.R.; Urbanic, A. *J. Phys. Chem.*, *48*, 125-133 (**1944**).

Zulauf, M.; Eicke, H.F. *J. Phys. Chem.*, *83*, 480-486, **1979**.

Ekwall, P. Stenius, P. *Phys. Chem.*, *7*, 215-248, **1975**.

40. Kosmulski, M. Electrical interfacial layer in nonaqueous solvents. in *Interfacial dynamics*, Kallay, N., Ed., *Surf. Sci. Ser.*, *88*, 273 - 312, **2000**.

Water is thought to have a different structure at interfaces than in the bulk. (p. 274)

In mixed water/solvent or polar, aprotic solvents, the same should apply. (p. 277)

Gives references on various solvent scales. (Table 6 - Empirical solvent scales and relative permittivities.)

Analysis of data for many oxides in mixed solvents.

41. Lemaire, E.; Merhi, D.; Pérez, A.T.; Valverde, J.M., *J. Electrostat.*, *53*, 107, **2001**.

Ordered 10/26/05.

42. Raj, P. M.; Cannon, W.R. Electrosteric stabilization mechanisms in nonaqueous high solids loading dispersions. *Surf. Sci. Ser., 104 (Polymers in Particulate Systems)*, 27 - 61 , **2002**.

Recent examples of nonaqueous dispersions from the literature:

Powder	Solvent	Dispersant	Anchoring moiety	Stabilizing moiety	Ref
Al ₂ O ₃	MEK/Ethanol	Fish oil	C=C, C=O	Alkyl chains	
Al ₂ O ₃	Toluene	Glycerol trioleate	Carboxylic acid	Alkyl chains	
Al ₂ O ₃		Polyethylene imine	Imine	Alkyl chains	
BaTiO ₃	MEK/Ethanol	Fish oil	C=C, C=O	Alkyl chains	
Lead zirconate titanate	MEK/Ethanol	Amine derivative of an oligomeric polyester			
Si ₃ N ₄	MEK/ 2-Butanol/ 2-Propanol	(2-Aminopropyl)-o'-(2-methoxyethyl)polypropylene glycol	Amine	Propylene glycol and polyethylene glycol	
Si ₃ N ₄	Decalin (nonpolar)	Hypermer KD3	Zwitter-ionic head groups	Polyester-type stabilizing moieties	
SiC	Aldehydes, ketones	No dispersants			

SiO ₂	Ethanol/Acetone THF	N-(3-acryloxy-2-hydroxypropyl)-3-amino-propyltriethoxysilane	Alkoxy silane	Acryloxy, hydroxyl, and amine groups
Zirconia	MEK/Ethanol	KDI, Phosphate ester	C=C, C=O	Alkyl chains
BaTiO ₃	Hexane	Di-isopropoxytitanium distearoyloxy stearate	Alkoxy titanate	Alkyl chains
Poly(vinyl acetate)	Aliphatic hydrocarbons	Poly(vinyl acetate) Poly(ethyl hexyl methacrylate)	Vinyl acetate	Poly(ethyl hexyl methacrylate)

Discussion of properties of stabilizer: high HLB numbers for decreased solubility; high enough MW, possibly better dispersion energy match with solvent, p. 31f

Table 2 Physical properties of typical solvents includes: Acid/Base nature, Donor and Acceptor numbers, Electrostatic force, HBI (Hydrogen bonding index), surface tension, fractional polarity (water has a value of 100), and dielectric constant.

Graphical description of steric, electrostatic and electrosteric stabilizations. (p. 37)

The effectiveness of electrosteric stabilization has been illustrated by the work of Mikeska and Cannon. In their study, 61 commercial dispersants were screened for use in dispersing barium titanate in a reasonable high dielectric constant medium, the azeotrop of ethanol and MEK. The average dielectric constant for the solvent mix is 20. One of the tow dispersants that showed exceptional ability to lower the viscosity was a phosphate ester. The authors showed evidence that electrostatic repulsion contributed strongly to this very low viscosity and, therefore, good dispersion. (p.38)

Discussion of phosphate esters in MEK/ethanol. Extra conductivity when particles added indicates the charging of the particles. Adsorption increased monotonically.

Zeta potential reached a maximum about where viscosity hit a minimum. 25 vol % solids at about 1.5 cps viscosity. Particles are BaTiO₃. They were positive. In water dispersions, they are negative. Explains with ideas due to micelle formation.

Describes Le Bars et al (1995): Hexaoxyethylene undecyl monoester phosphate to disperse BaTiO₃ in azeotrope of Ethanol/Butanone. Conjecture is a electrical double layer "on" the particle? Saw a large effect on zeta potential. Hence phosphate esters are powerful dispersants in nonaqueous systems.

Discussion of interactions of polymer, dispersant, and solvent. (pp. 45 - 49).

Table of dispersants for BaTiO₃, PZT, Al₂O₃, TiO₂, and carbon black (p. 48) and the charge on the particles. Dispersants were: hexaoxyethylene undecyl monoester phosphate, phosphate ester, acidic phosphate ester, linolenic acid, OLOA 1200, petroleum sulfonate, and n-butylamine.

Discussion of the role of water. (pp. 49 - 52.) Good, but the usual references.

Various electrostatic stabilization theories (including Morrison, 1991). (pp. 52 - 57.)

Optimum MW requirements: (p. 57). Surfactants are adsorbed head group down. Get steric effects unless the polymer chains entangle. Therefore need a balance to keep the viscosity down.

43. Briscoe, W.H.; Horn, R.G. Direct measurement of surface forces due to charging of solids in a nonpolar liquid. *Langmuir*, 18(10), 3945 - 3956, **2002**.

Between mica surfaces in the presence of AOT (millimolar) in n-decane. Results fit a counterion only model. Get surface charge density of about 1mC/m² (160 nm²/charge?).

Surfactants or crown ethers can form large structures such as inverse micelles and chelates which are effective in stabilizing counterions. (p. 3947)

Uses the usual (and wrong) assumption that all the counterions are contained between the interacting surfaces. (p. 3948).

The interaction energy should decrease as D^{-1} rather than exponential (from an earlier publication). Comes from a model of counterions only, contained between the interacting surfaces.

Find weak, long-range forces. And a strong steric barrier of about 2nm which is large compared to AOT molecules (about 1.1 to 1.2 nm). (p. 3952)

Tries to deny credit to Fowkes (too bad). (p. 3954)

44. Aranowski, R.; Nalaskowski, J.; Hupka, J.; Miller, J.D. Influence of surfactants on interaction forces between polyethylene surfaces in a hydrocarbon solvent. in *Functional Fillers and Nanoscale Minerals*; Kellar, J.J.; Herpfer, M.A.; Moudgil, B.M., Eds.; Society for Mining, Metallurgy, and Exploration: Littelton, CO; **2003**, pp 139 - 150.

The colloidal probe technique (Ducker, Quate, and Gerber 1986) is now used in NA media. A small polymer bead is attached to the cantilever and a flat polymer surface is created by melting. They used n-tetradecane to mimic polymer matrix.

The lauric acid gave -4.78 mV zeta potential. The dodecylamine, +12.4 mV; +/-2 mV (p. 143-144) (Used Smoluchowski equation).

Used the force/particle radius equation:

$$\frac{F(D)}{R} = -\frac{A}{6D^2} + \frac{4\pi\sigma^2}{\epsilon\epsilon_0\kappa} e^{-\kappa D} \quad [2]$$

where σ is the surface charge. (This is peculiar because in the limit of long Debye lengths the electrostatic term is unbounded?)

The Hamaker constant was calculated from that of crystalline hydrocarbon PE (7.1×10^{-20} J) and n-tetradecane (5.1×10^{-20} J). The data were fitted to Equation [2]. For both surfactants, they get Debye length of about 10 nm and surface charge densities of .109 $\mu\text{C}/\text{m}^2$ for lauric acid and 0.204 for dodecylamine.

See modulations in the force at short distances, 0.8 nm which is too small for micelle.

45. Reuter, S.; Franke, S. Models for the charging of particles in liquid toners: A summary. *J. Imaging Sci. Tech.*, 48(4), 319 - 323, **2004**.

Essentially a series of simultaneous equilibria. Adsorption of anions, cations, neutral micelles, dissociation of micelles. (Might be a good place to start to formulate the issues.)

46. Tolpekin, V.A.; van den Ende, D.; Duits, M.H.G.; Mellema, J. Flow electrification in nonaqueous colloidal suspensions, Studied with video microscopy. *Langmuir*, 20(20), 8460 - 8467, **2004**.

Essentially, hydrophobic silica, suspended in chloroform, subjected to high shear, in the presence of glass, became positively charged. Possibly, acidic silanol groups on the glass transfer to the particles and solvent.

47. Briscoe, W.H.; Horn, R.G. Electrical double layer interactions in a non-polar liquid measured with a modified surface force apparatus. *Prog. Colloid Polym. Sci.*, 123, 147 - 151, **2004**.

Ordered 10/26/05

48. Pérez, A.T.; Lemaire, E. Measuring the electrophoretic mobility of concentrated suspensions in nonaqueous media. *J. Colloid Interface Sci.*, 279, 259 - 265, **2004**.

Index matched PMMA particles in cyclohexyl bromide. Refers to work on the packing of particles at the electrode - electrical and adhesional effects. (Ref. 3)

49. Ryoo, W.; Dickson, J.L.; Dhanuka, V.V.; Webber, S.E.; Bonnecaze, R.T.; Johnston, K.P. Electrostatic stabilization of colloids in carbon dioxide: Electrophoresis and dielectrophoresis. *Langmuir*, 21, 5914 - 5923, **2005**.

Steric stabilization is known. This paper shows that water droplets (about 1 micron) are charged with a few elementary charges per square micron. Up to 5 vol%. Protons are transferred to micelles, formed with a low molecular weight branched hydrocarbon

surfactant. Leaving excess carbonate in water, up to 70 mV potential. The dielectric constant is even lower than hydrocarbons, at about 1.5.

(n.b. The Bjerrum length is the distance where Coulomb potential and kinetic energy are equal:

$$l_B = \frac{q^2}{4\pi\epsilon_r\epsilon_0kT} \quad [3]$$

is approximately 0.7 nm for water and 28 nm for alkanes.)

The micelle-forming surfactant is: octa-(ethylene glycol) 2,6,8-trimethyl-4-nonylether (Prevention of ion pairing of counterions with water/CO₂ microemulsions would be of interest for stabilizing other types of micrometer-size colloids in CO₂ based on related studies in apolar solvents.)

The charged droplets form crystals in CO₂ in which the droplet spacing is 3x the droplet diameter indicating a Debye length on the order of 10 microns.

Water/CO₂ interface is about 20mN/m. The surfactant lowers that to about 2 nN/m.

This surfactant does not have a sharp cmc and the micelle size probably increased with concentration.

Dielectrophoresis lead to chain formation.

50. Smith, P.G., Jr.; Ryoo, W.; Johnston, K.P. Electrostatically stabilized metal oxide particle dispersions in carbon dioxide. *J. Phys. Chem.*, 109(43), 20155 - 20165, **2005**.