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Effects of surfactants and electrolyte solutions on the properties of soil

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Abstract Biosurfactants are frequently used in petroleum hydrocarbon and dense non-aqueous phase liquids (DNAPLs) remediation. The applicability of biosurfactant use in clayey soils requires an understanding and characterization of their interaction. Comprehensive effects of surfactants and electrolyte solutions on kaolinite clay soil were investigated for index properties, compaction, strength characteristics, hydraulic conductivities, and adsorption characteristics. Sodium dodecyl sulfate (SDS) and NaPO_3 decreased the liquid limit and plasticity index of the test soil. Maximum dry unit weights were increased and optimum moisture contents were decreased as SDS and biosurfactant were added for the compaction tests for mixtures of 30% kaolinite and 70% sand. The addition of non-ionic surfactant, biosurfactant, and CaCl_2 increased

the initial elastic modulus and undrained shear strength of the kaolinite–sand mixture soils. Hydraulic conductivities were measured by fixed-wall double-ring permeameters. Results showed that the hydraulic conductivity was not significantly affected, but slightly decreased from 1×10^{-7} cm/s (water) to 0.3×10^{-7} cm/s for Triton X-100 and SDS. The adsorption characteristics of the chemicals onto kaolinite were also investigated by developing isotherm curves. SDS adsorbed onto soil particles with the strongest bonding strength of the fluids tested. Correlations among parameters were developed for surfactants, electrolyte solutions, and clayey soils.

Keywords Surfactant · Atterberg limits · Hydraulic conductivity · Adsorption · DNAPLs

Introduction

Background

Remediation of contaminated soils by soil flushing has been recognized as an effective and innovative technique for dense non-aqueous phase liquids (DNAPLs) sorbed onto soil particles by physicochemical interactions. Surfactants and some feasible electrolyte solutions can be used to enhance the desorption and solubilization of those organic contaminants (Sims et al. 1986; Thornton 1990; Erickson et al. 1991; Mulder et al. 1998; Guha

et al. 1998; Rathfelder et al. 2003; Chu and Kwan 2003). However, the application of chemicals may also change the original geotechnical properties of soils (Uppot and Stephenson 1989; Sai and Anderson 1991; Mitchell 1993; Hueckel et al. 1997). These effects should be carefully studied for the adequate application of soil flushing for the remediation of organic contaminated soils in situ.

Although soil flushing has many advantages over pump-and-treat for the effective recovery of DNAPLs in situ, criticisms of the technique on the point of addition of chemicals into the subsurface cannot be overlooked.

Soil flushing can create secondary contamination by its own flushing agents and furthermore may change the geotechnical properties of the site into undesirable and unpleasant conditions for future land use. Aspects of the secondary contamination from flushing agents are out of the scope of this research. Geotechnical property changes were mainly studied.

Geotechnical index properties of clayey soils can be evaluated by performing Atterberg limits tests and/or hydraulic conductivity tests before and after the flushing of chemicals to find any change in the physical soil properties. Foreman and Daniel (1986) investigated the effect of chemicals on the diffuse double layer of kaolinite, illite, and smectite clays. They concluded that the Atterberg limits of the three clays changed significantly when the pore liquids were varied from water to either methanol or heptane. The organic chemicals reduced or eliminated the plasticity of the soils. Acar et al. (1985) showed that the liquid limit of bentonite dropped from 400 to 50% as the dielectric constant of chemicals decreased from 80 (water) to 2.4 (xylene). The effect of low dielectric constant fluids such as heptane (1.9), benzene (2.3), aniline (6.9), and acetone (20.7) on the diffuse double layer of clayey soil has also been studied for the hydraulic conductivity (Fernandez and Quigley 1985; Dunn 1985; Anderson et al. 1985; Parker et al. 1986; Broderick and Daniel 1990; Li et al. 1996; Lo et al. 1997). Many pure forms of organic compounds of low dielectric constant less than 40 (Bowders and Daniel 1987) tended to reduce the thickness of diffuse double layer, causing the soil skeleton to shrink and decrease in repulsive forces, thus promoting flocculation of clay particles, and to dehydrate interlayer zones of expandable clays, which subsequently became gritty or granular. Consequently, the liquid limit tended to decrease and the hydraulic conductivity increased with the decrease in dielectric constant of organic compound.

Increase in hydraulic conductivity results from permeation with inorganic electrolyte solution as well.

Changes in cation valence or electrolyte concentration of the soil water account for the increases (McNeal and Coleman 1966; Mesri and Olson 1971; Dunn and Mitchell 1984; Broderick and Daniel 1990). On the contrary, Quigley et al. (1987) examined the hydraulic conductivity of natural clays below a 15-year-old domestic landfill and concluded that the decrease in hydraulic conductivity near the interface between waste and clays seemed to correlate directly with increased pollutant concentration of soluble species, total heavy metal concentration, double layer expansion due to sodium adsorption, and a slight decrease in void ratio. Gleason et al. (1997) tested the effect of CaCl_2 and NaCl electrolyte solutions on the Atterberg limits and hydraulic conductivities of calcium and sodium bentonite. They found that increased liquid limit (LL) and plasticity index (PI) occurred with decreased electrolyte concentration, increased dielectric constant, and decreased cation balance. The LL of sodium bentonite dropped from 603% when it was hydrated in distilled water to 86% when it was hydrated in 0.25 M CaCl_2 . The corresponding drop in the LL of calcium bentonite was from 124 to 74%. The hydraulic conductivities increased more than one order when the bentonites were mixed with 1.5 M CaCl_2 solution. Sivapullaiah and Savitha (1999) conducted Atterberg limits tests for illite–bentonite mixtures with NaCl and KCl solutions. Due to reduction in the thickness of the diffuse double layer and consequent particle aggregation in bentonite, the effect of clay–clay interaction was reduced in electrolyte solutions, in which the liquid limit and the plasticity index of bentonite were lower than illite. The PI of bentonite was further reduced in KCl solution.

An overall literature review suggests that the effect of organic chemicals as contaminants has been studied by a number of researchers; however, the effect of flushing agents such as surfactants on the geotechnical properties has not been intensively studied.

Table 1 Test soil properties

Property	Kaolinite	Sand
Liquid limit, LL (%)	47	Not available
Plastic limit, PL (%)	29	Not available
Plasticity index, PI (%)	18	Not available
Specific gravity, G _s	2.63	2.70
Sand (0.074–4.74 mm) (%)	0	100
Silt (0.005–0.074 mm) (%)	7	0
Clay (≤ 0.005 mm) (%)	93	0
Cation exchange capacity (meq/100 g)	3–15 (Mitchell 1993)	Not available
Mineralogy	Mica, silica–gibbsite in 1:1 lattice	Quartz and feldspar
Classification ^a	CL (lean clay)	SP
Source	Dry Branch Kaolin Co., Dry Branch, GA, USA	Tec minerals, Eagle Lake, TX, USA

^aUnified Soil Classification System (ASTM D2487-00)

Objectives of the study

The current research focuses on investigation of the changes in the properties of kaolinite clay due to the addition of surfactants and electrolyte solutions (CaCl_2 and NaPO_3), with or without naphthalene contamination. The interactions between clay soils–surfactants (or electrolyte solutions)–naphthalene were studied by performing comprehensive Atterberg limits tests, pH, viscosity, surface tension, compaction, unconfined strength, hydraulic conductivity tests, and isotherm equilibrium tests in the laboratory.

Materials and methods

Soils: kaolinite and sand

The soils used in this research were kaolinite and blasting sand. Hydrite-R kaolinite was purchased from DBK Kaolin Company[®] of Dry Branch, GA, USA. The blasting sand was obtained from Tec Minerals[®] of Eagle Lake, TX, USA. Sand was mixed with the kaolinite to control hydraulic conductivity of the clay.

The physical properties of the soils are summarized in Table 1. Figure 1 shows the particle size distribution curves for the test soils (ASTM D421-85, ASTM D422-63). Figure 2 shows the X-ray diffraction (XRD) analysis of kaolinite. The most prominent peaks were located at 2θ of 12.4° , 24.8° , and 34.5° . These peaks matched well with $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ kaolinite. Thus, these peaks were designated as kaolinite in all subsequent studies. Although soil flushing technique is difficult to apply

directly in clay soils because of their low hydraulic conductivities, tests on kaolinite clay soils and blasting sand mixture samples might provide the general ideas of the characteristics of a clay-containing soil matrix when contaminated by organic hydrocarbons and treated by soil flushing in situ.

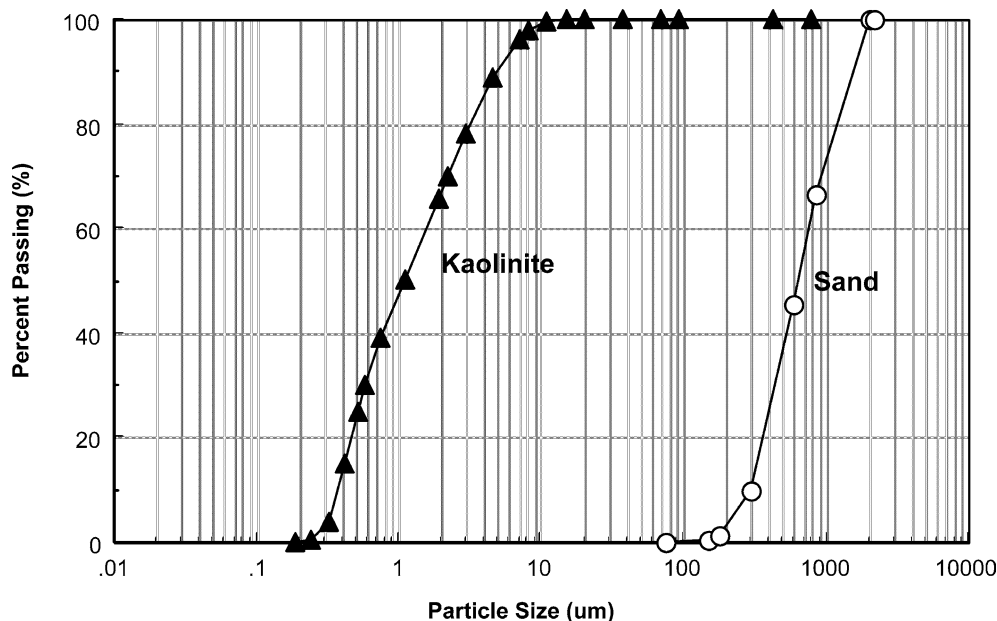
Naphthalene as a contaminant

Naphthalene was chosen for investigating the effect of a contaminant on the given soil properties. Naphthalene is the simplest polycyclic aromatic hydrocarbon (PAH) and has two fused benzene rings (C_{10}H_8) and a molecular weight of 128. The water solubility at 25°C is 31.7 mg/L (Cerniglia 1992). To protect freshwater aquatic life, the permissible concentrations of the compound in water are 2.3 and 0.62 mg/L based on acute and chronic toxicities, respectively (Sitting 1991). Naphthalene was purchased from Fisher Scientific[®] and labeled with a residue after ignition less than 0.002%. Test concentration for naphthalene was maximum solubility at 25°C , which is 31.7 mg/L .

Surfactants and electrolyte solutions

Three different types of surfactant (non-ionic, anionic, and biosurfactants) were selected to examine the effects on the properties of clayey soils. Commercially available Triton X-100 (Acros[®]) and sodium dodecyl sulfate (SDS, Fisher Scientific[®]) represent non-ionic and anionic surfactants, respectively. Biosurfactant was

Fig. 1 Size distribution curves for the test soils



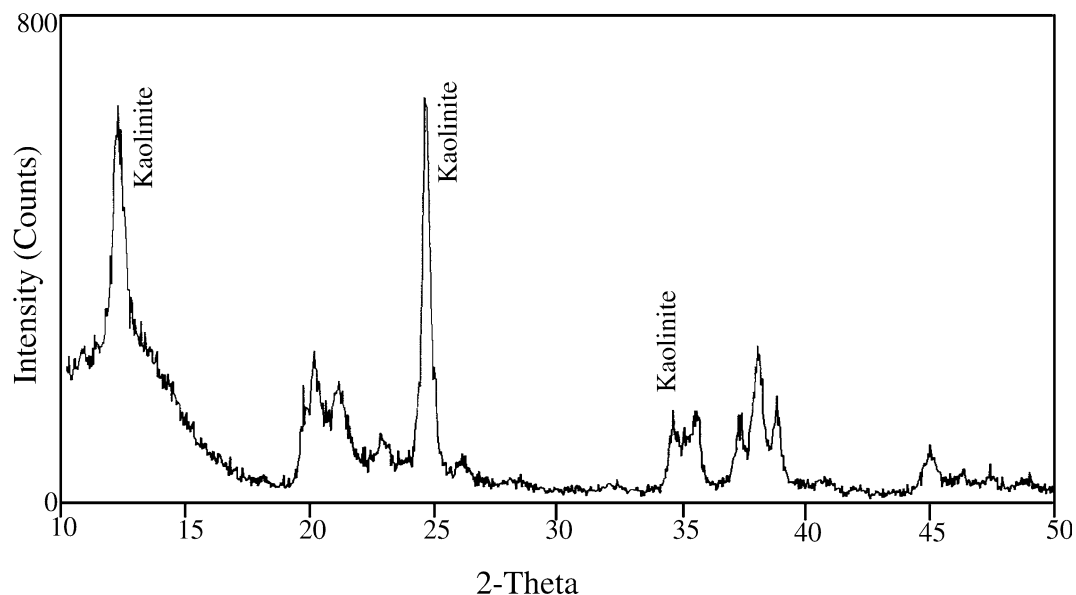


Fig. 2 XRD analysis for the test soil

produced in the laboratory with used vegetable oil (Ren 1998). Biosurfactants have several advantages over chemical surfactants: lower toxicity, higher biodegradability, better environmental compatibility, and the ability to be synthesized from renewable feedstocks. The basic properties of Triton X-100, SDS, and the biosurfactant are summarized in Table 2 (Ren 1998). The concentration for three surfactants in most of the tests was set at 10 times the critical micelle concentration (CMC). The CMC concentrations were picked up from Ren's (1998) values, which are 0.1, 0.2, and 2.37 g/L for Triton X-100, biosurfactant, and SDS, respectively. Surfactants concentrations above CMCs generally facilitate the release of PAHs from soil and thus enhance the overall performance of bioremediation recovery by enhancing aqueous solubility and the mobilization of soil-bound PAHs by lowering the interfacial tension.

NaPO_3 and CaCl_2 were the electrolyte solutions selected to study the effects on the geotechnical properties of kaolinite. NaPO_3 was purchased from ELE International[®]. The test concentration of NaPO_3 was

4% by weight as used in hydrometer tests (ASTM D422-63) for a dispersing agent. CaCl_2 was obtained from Fisher Scientific[®] and has a formula weight of 110.99. The test concentration of the solution was 100 mg/L (9.01 mol/L) to simulate the Ca^{2+} ion concentration mostly found in groundwater conditions.

Test methods

The influence of contaminant and flushing agents on the LL and PI of kaolinite and kaolinite-sand mixtures was evaluated by performing Atterberg limits tests (ASTM D4318-00). The change in the thickness of diffuse double layer of the kaolinite caused by flushing agents with or without naphthalene can result in alteration of the soil matrix and eventually will affect Atterberg limits and hydraulic conductivities of kaolinite. Liquid and plastic limits were measured for water, Triton X-100, SDS, biosurfactant, and NaPO_3 with or without CaCl_2 , and/or naphthalene to model the in situ contaminated

Table 2 Basic properties of chemical surfactants and biosurfactant

	Triton X-100 (octylphenol polyoxyethylene)	SDS (sodium dodecyl sulfate)	Biosurfactant
Molecular formula	$\text{C}_8\text{H}_{17}\text{C}_6\text{H}_4(\text{OCH}_2\text{CH}_2)_{10}\text{H}$	$\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4\text{Na}$	Not determined
Molecular weight	647 (Acros 1995)	288 (Acros 1995)	< 1,000 ^a
Viscosity ^b	1.05	1.45	1.05
CMC (g/L)	0.13 (Jafvert et al. 1994) 0.11 (Edwards et al. 1994) 0.1 (Ren 1998)	2.3 (Valsaraj and Gupta 1988) 2.37 (Ren 1998)	0.2 (Ren 1998)

^aBased on ultrafiltration through YM1 membrane (Amicon, Inc., Beverly, MA, USA)

^bMeasured at 10 CMC by Brookfield Viscometer[®]

soils. Kaolinite was also mixed with test sand (clay:sand 30:70 by weight) to investigate the effect of each solution.

Surface tension of each solution was measured (ASTM D1331-89) using a CENCO-DuNOÛY® interfacial tensiometer. The effects of CaCl₂ on the surface tension of the surfactants were measured because Ca²⁺ ion existing in the subsurface might affect the solubilization and micelle-forming characteristics of surfactants. Surface tension of each solution with or without naphthalene was measured under various CaCl₂ concentrations.

The change in pH and viscosity of the test solutions are good indicators of the physical property alterations. Clay particles have hydroxyls (OH⁻) exposed on their surfaces and edges. The tendency for hydroxyls to dissociate in water is strongly influenced by pH. The higher the pH, the greater the tendency for H⁺ to go into solution and the greater the effect of the negative charges of the particle. As a consequence, pH plays a very important role in the behavior of clay suspensions. A low pH promotes a positive edge to negative surface interaction, often leading to flocculation from suspension. Stable suspensions or dispersions of clay particles often require high pH conditions (Mitchell 1993). The values of pH of each solution with or without naphthalene and/or CaCl₂ were measured (EPA method 9040) by Orion Research Model SA 250®. The viscosity change also can affect the geotechnical property like hydraulic conductivity of soil. The viscosity of each solution was measured by Brookfield Viscometer®.

Standard compaction tests (ASTM D698-90, ASTM D1557-90) and unconfined compression tests (ASTM D2166-85) were performed to study the effect of test solutions on the mechanical properties of kaolinite. Compaction characteristics may be affected by the liquids in the pores and affect the soil structure, which exerts a dominant influence on hydraulic conductivity and strength properties. Unconfined compression tests on the test soils mixed with the test solutions were performed to investigate the effect of the test solutions on the strength properties.

Hydraulic conductivity tests were performed with water and surfactants as permeant solutions in fixed-wall double-ring permeameters. To 70% blasting sand, 30% kaolinite was mixed to control the hydraulic conductivities of the test soils so that permeameter tests could be performed within a reasonable period of time with an induced hydraulic gradient of 40–61. The water content of the specimen was 12%, which is slightly wet of optimum for water (11.6%) because the coefficient of hydraulic conductivity is presumed stabilized at the wet side of the optimum (Das 1997). Soil specimens were prepared using a standard compaction test mold following ASTM D698-90 and ASTM D1557-90. The

mold itself was further used as a rigid-wall permeameter. The 944 cm³ mold contains a specimen of soil, while a ring built into the base plate separates the inflow through the central portion of the soil from the outflow near or along the sidewall. If there is significant sidewall leakage, the rate of flow into the outer collection ring will be much greater than the rate of flow into the inner ring. Double-ring permeameters were first suggested by McNeal and Reeve (1964) as a method of eliminating boundary flow errors. The coefficient of hydraulic conductivity, *k*, of soil specimen was measured by monitoring the effluent solution periodically.

Isotherm equilibrium tests were also performed with naphthalene and three different surfactants onto kaolinite. Series of solutions with various naphthalene (32, 16, 8, 4, 2, 1 mg/L) or surfactants concentrations (10, 5, 2.5, 1.25, 0.625, 0.313 CMCs) were prepared in Pyrex vials. A known amount (0.5 g) of kaolinite was mixed with 10 mL of solution and shaken continuously at 200 rpm. Monitoring of concentration change showed that the adsorption reached maximum after 6 h (Ren 1998). After 24–48 h, samples were taken in centrifuge (Fisher Scientific Centrifuge® centrifuge) and run for 50 min at 9,000 rpm. Supernatant was decanted into a 30 cm³ syringe and passed through 0.22 µm filter unit of Millex®-GP to avoid disturbance while reading in UV-Visible spectrophotometer (CECIL 1020 UV-Visible Spectrophotometer®, Cecil Instruments, Ltd). Naphthalene, Triton X-100, SDS, and biosurfactant showed their peaks at 213.0, 275.6, 220.0, and 202.2 nm, respectively. The amount of adsorption was calculated through mass balance. Calibration curves were drawn using readings for known concentrations of these compounds and developed based on peak absorbance using the regression method. Sorption isotherm parameters were evaluated and used to explain geotechnical property changes of test soils due to the addition of surfactants and naphthalene.

Results and discussion

Atterberg limits and adsorption isotherm parameters obtained through the mixing of test solutions, including naphthalene, with soil particles are the key factors to the behavior of soil-solution mixtures. Soil-solution interactions were investigated based on Atterberg limits and adsorption isotherms. LL and PI can explain the property changes of test soils in terms of soil interactions. Isotherm parameters like *K* and *1/n* can explain the adsorption characteristics of a solute onto soil particles in terms of slurry interactions, thus the mechanism can eventually alter the surface chemistry and affect the soil properties. The behaviors of soil-solution mixtures obtained through performing compaction, compressive

strength, and hydraulic conductivity tests were also analyzed based on the index properties and adsorption characteristics.

Soil–solution interaction

Soil interaction: effects of the solutions on the Atterberg limits

Results of the Atterberg limits tests for all soil/liquid combinations are given in Table 3. Comparisons of the limits obtained using water with surfactants and electrolyte solutions, with or without naphthalene, were used to classify the effect of a liquid on a soil. The activity of kaolinite was calculated as 0.51, while Mitchell (1993) listed the values as 0.5 and 1–7 for fkaolinite and smectite, respectively. The higher the activity of a soil, the more susceptible the values to change in factors such as type of exchangeable cations and pore fluid composition. The results for kaolinite showed that naphthalene at solubility concentration (32 mg/L) did not have appreciable effects on the index properties of test soils. The concentration was considered too low to decrease the dielectric constant of the solution and consequently failed to reduce the thickness of the diffuse double layer by which the soil became less plastic. Bowders and Daniel (1987) also concluded that Atterberg limits of kaolinite ($LL_{\text{water}} = 58$, $PL_{\text{water}} = 34$) did not exhibit any appreciable change when heptane and TCE (at their respective solubility limits in water, S_{heptane} at $20^{\circ}\text{C} = 53$ mg/L and S_{TCE} at $20^{\circ}\text{C} = 1,100$ mg/L) were used as the replacement for water ($LL_{\text{heptane}} = 56$, $PL_{\text{heptane}} = 32$ and $LL_{\text{TCE}} = 57$, $PL_{\text{TCE}} = 31$). Thus, one could assume that naphthalene-contaminated soil at concentration less than its solubility does not have appreciable differences in geotechnical properties compared to non-contaminated soil. Surface tension and pH variation of each solution before and after the addition of naphthalene did not change significantly (Table 4); therefore, those properties did not seem to affect geotechnical properties.

However, CaCl_2 (100 mg/L) decreased the plasticity of test soils when mixed with water or Triton X-100.

Ca^{2+} ions adsorb onto kaolinite particles and/or exchange for monovalent ions on the surface of the clay particles, thus altering the soil into more flocculated structures. The effect is an increased LL and decreased PI. This effect was also observed by Gleason et al. (1997). They performed Atterberg limits tests on sodium bentonite with different concentrations of CaCl_2 . The PI dropped from 567 when the soil was hydrated in distilled water to 426 when it was hydrated in 1,000 mg/L CaCl_2 . Sivapullaiah and Savitha (1999) also confirmed that the addition of salts (0.5 N NaCl or KCl) decreased the PI of bentonite. The salts decreased the PI from 250 (hydrated in water) to 50 (hydrated in NaCl or KCl). In contrast, CaCl_2 increased the plasticity of the test soils by approximately 25% when used with biosurfactant (15–21, Table 3). This effect is attributed to the surface tension change due to the addition of CaCl_2 in biosurfactant. CaCl_2 increased the surface tension of biosurfactant from 33 (0 mg/L of CaCl_2) to 50 dynes/cm (140 mg/L CaCl_2), while other solutions remained unaffected or slightly changed (Table 5). The increase in surface tension might increase the cohesion between the soil particles and the pore liquid, which in turn might affect the plasticity of the soil. The effect of CaCl_2 on SDS or NaPO_3 -mixed soils is almost negligible for kaolinite because the small amount of salt (CaCl_2 100 mg/L) is probably not enough to affect soil index properties under the high Na concentration environment caused by SDS or NaPO_3 . Table 5 summarizes the effect of CaCl_2 on the surface tension and pH of each solution.

Both SDS and NaPO_3 decreased the plasticity of test soils as shown in Table 3. For kaolinite, NaPO_3 decreased the PI into an extremely narrow range of 0.3% and turned it into a virtually non-plastic soil. The addition of SDS and NaPO_3 made kaolinite particles flocculate as if the soil was flushed with seawater. The addition of Triton X-100 or biosurfactant did not affect the index properties for kaolinite clayey soil. Results of changes of kaolinite before and after the addition of naphthalene or CaCl_2 are shown in the plasticity chart in Figs. 3 and 4.

The mixture effect of blasting sand with clayey soils was studied. Kaolinite (30%) was mixed with 70% blasting sand. Table 6 shows the LL and PI of kaolinite with various test solutions. As expected, the addition of

Table 3 Atterberg limits of kaolinite with test surfactants and electrolyte solutions

	Water (tap water)			Triton X-100 (10 CMC)			SDS (10 CMC)			Biosurfactant (10 CMC)			NaPO_3 (4% by weight)		
	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)
LL (%)	47	46	49	48	48	49	30	32	33	47	46	49	28	NM	29
PI (%)	18	18	6	17	24	4	7	5	7	15	15	21	0.3	NM	0.5

(1) No other additives; (2) only maximum solubility of naphthalene at 25°C (32 mg/L) added; (3) only CaCl_2 100 mg/L added
 NM not measured

Table 4 Surface tension and pH change by maximum solubility naphthalene

	Water		Triton X-100		SDS		Biosurfactant		NaPO ₃	
	S.T. ^a	pH	S.T. ^a	pH	S.T. ^a	pH	S.T. ^a	pH	S.T. ^a	pH
Before adding naphthalene	77	7.3	34	7.7	36	8.5	33	10.8	52	6.8
After adding naphthalene	76	7.7	32	8.0	35	8.4	31	10.6	51	6.6

^aSurface tension, in dynes/cm

Table 5 Surface tension and pH change by various concentrations of CaCl₂

CaCl ₂ addition (mg/L)	Water		Triton X-100		SDS		Biosurfactant		NaPO ₃	
	S.T. ^a	pH	S.T. ^a	pH	S.T. ^a	pH	S.T. ^a	pH	S.T. ^a	pH
0	77	7.3	34	7.7	36	8.5	33	10.8	52	6.8
60	76	7.6	35	7.7	37	8.4	43	10.8	53	6.8
140	74	7.8	34	7.9	35	8.5	50	10.7	53	6.8
1,000	76	7.8	37	7.8	38	8.3	51	8.9	53	6.4

^aSurface tension, in dynes/cm

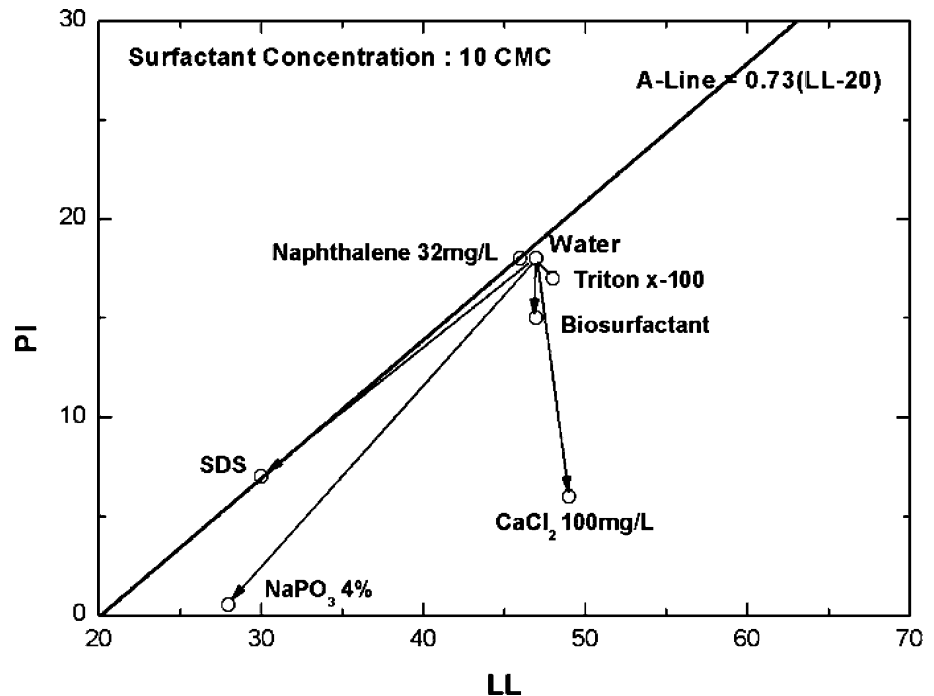
sand decreased the LL and PI for kaolinite. Figure 6 shows the influence of sand mixture on the index properties of kaolinite. Activity for kaolinite decreased from 0.51 to 0–0.20, which is the same as for muscovite or calcite.

Slurry interaction: effects of adsorption characteristics of solutions

Batch organic sorption was investigated to assess the adsorption characteristics of kaolinite for naphthalene,

Triton X-100, SDS, and biosurfactant, respectively. The partition mechanism of organics onto soil particles, called *slurry interaction*, is a good indicator for the alteration of surface chemistry of soil particles. An attempt was made to explain the geotechnical change of clayey soils when mixed with organic solutions by adsorption isotherm parameters.

Equilibrium sorption of naphthalene and surfactants onto kaolinite was studied. The data for the test solutions were fitted using linear isotherm equations. The linear isotherm is expressed as

Fig. 3 Index property change after the addition of test solutions

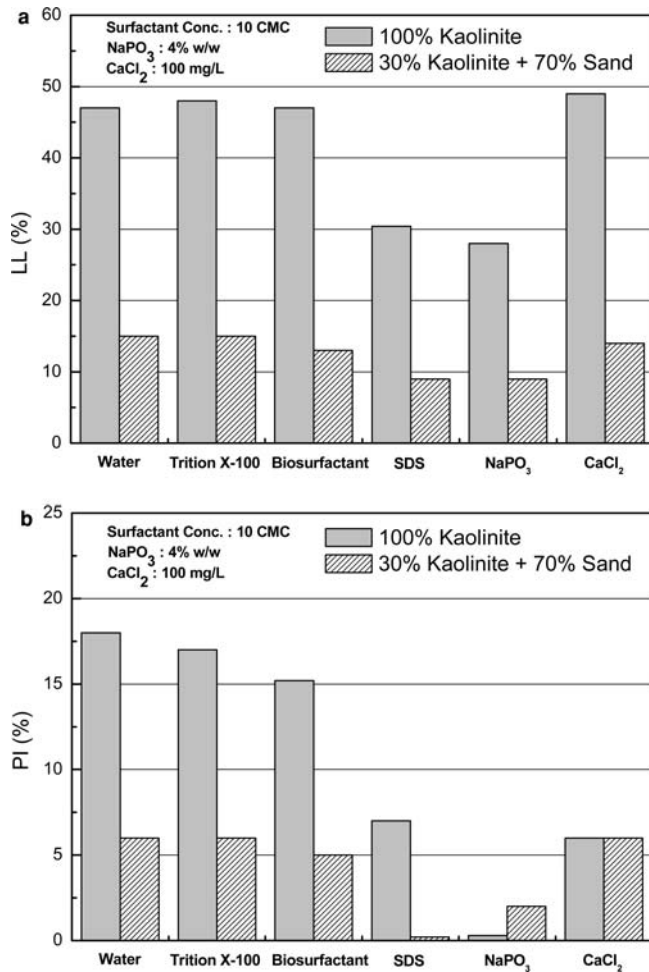


Fig. 4 Index property change after the addition of sand: **a** LL change after the addition of sand, **b** plasticity change after the addition of sand

$$C_s = K_d C_e, \quad (1)$$

where C_s is the loading amount, mass of a solute adsorbed per unit mass of adsorbent (mg/kg); K_d the distribution coefficient; and C_e the solution equilibrium concentration (mg/L). Generally, the more hydrophobic solute has higher value of K_d under the same soil conditions, including organic matter content. For a non-linear adsorption isotherm relationship, the Freundlich isotherm equation is well fitted and expressed as

$$C_s = K C_e^{1/n}, \quad (2)$$

where K and $1/n$ are known as Freundlich isotherm parameters. If the parameter $1/n$ is one, the Freundlich isotherm becomes linear, and K becomes identical to the distribution coefficient, K_d .

The linear adsorption isotherm test results are shown in Fig. 5. The distribution coefficients for naphthalene, Triton X-100, SDS, and biosurfactant are 43.6, 17.5, 65.0, and 181.8, respectively. The sorption coefficients of kaolinite decreased in the order: biosurfactant > SDS > naphthalene > Triton X-100. The results mean that Triton X-100 is the most hydrophilic and is not highly adsorbed onto kaolinite, but solubilized most easily in water. Biosurfactant shows most hydrophobic character of all the surfactants and adsorbs most onto soil particles rather than remaining in water. However, the distribution coefficients of kaolinite for naphthalene and three different surfactants did not show significant correlation with PI values, for which SDS decreased most remarkably at the concentrations tested. K_d values were related to the compaction test results to some extent.

Soil–solution mixture behaviors

Solution effects on compaction behavior

The effect of test solutions on the compaction characteristics of kaolinite–sand mixtures was studied. Figure 6 and Table 7 show the standard proctor compaction test results for clay:sand 30:70 mixtures. The addition of surfactants and electrolyte solutions generally increased the maximum dry unit weight and decreased the optimum moisture content. The maximum dry unit weight and optimum moisture content of kaolinite compacted with water were 18.9 kN/m³ and 11.6%, respectively. But when compacted with biosurfactant, the values became 19.5 kN/m³ and 10.0%. The effect was more remarkable for NaPO₃ solution, with values of 19.7 kN/m³ and 9.0%. Surfactants decrease surface tension (Table 4) so that the solution could move more freely through the pores in the soil. This effect could help saturate soil more easily with less water, resulting in lower optimum moisture content. Consequently, the surfactants could lower the optimum moisture content of the kaolinite mixtures. As

Table 6 Mixture effect of blasting sand on the index properties of kaolinite

	Water	Triton X-100 (10 CMC)	Biosurfactant (10 CMC)	SDS (10 CMC)	NaPO ₃ (4% by weight)	CaCl ₂ (100 mg/L)
LL ^a	15	15	13	9	9	14
PI ^a	6	6	5	0	2	6

^aKaolinite:sand 30:70

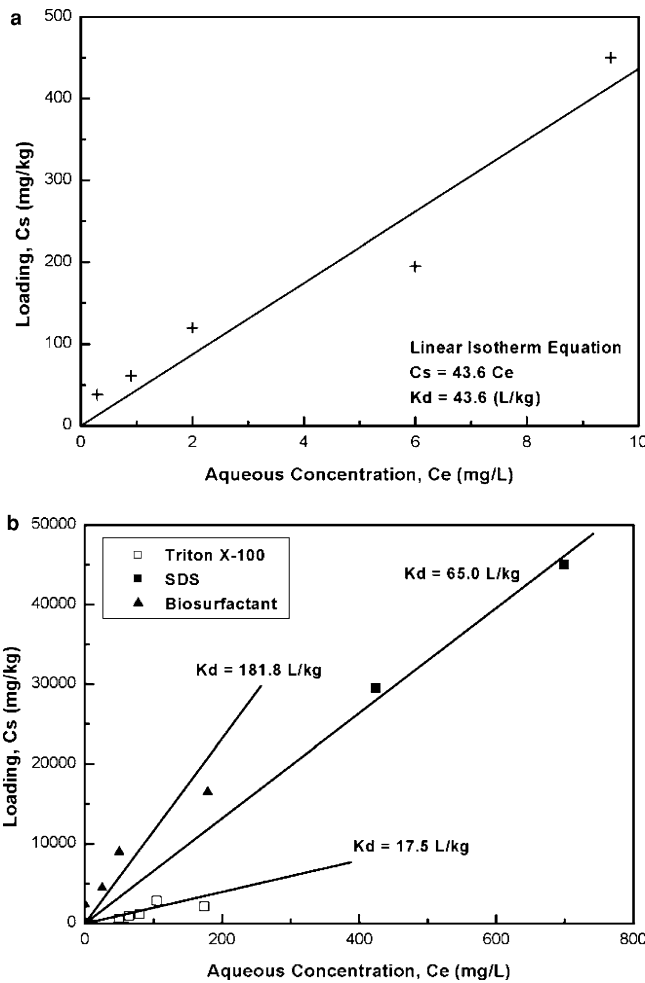


Fig. 5 Linear isotherm curves on kaolinite: a naphthalene, b surfactants

surfactants contents increased, the soil particles developed larger surrounding surfactant films, which lubricated the particles and made them easier to move around and reorient into a denser configuration. The effect can be explained by distribution coefficients. Biosurfactant has the highest value of K_d , thus it can be most adsorbed onto the kaolinite particles and has better lubrication between soil particles compared with other surfactants with lower K_d . Biosurfactant can make the soil into the densest configuration (Fig. 7). Although SDS is a surfactant and was expected to behave as same as other surfactants, the effect of increasing the maximum dry unit weight was not remarkable. Too much foam developed when it was mixed with soils. The foam prevented effective compaction, which resulted in lower unit weights compared with the values obtained from Triton X-100 and biosurfactant. Electrolyte solutions like $CaCl_2$ and $NaPO_3$ also decreased the optimum moisture content of the kaolinite mixtures. These solutions caused

the soil to be more flocculated. Flocculation of clayey soils generally increases the maximum dry unit weight and lowers the optimum moisture content.

For clayey soils, the maximum dry unit weight tends to decrease and the optimum moisture content tends to increase as plasticity increases (Johnson and Sallberg 1960). Figure 8 shows that surfactants and electrolyte solutions also follow the trend. However, no significant trends were found between K_d and optimum moisture content. The PI values were obtained from 100% kaolinite, not from 30% clay and 70% sand mixtures. However, the curves were sufficient to give general relationships between the parameters.

Solution effects on unconfined compressive strength

Unconfined compression tests were performed to study the effects of additive solutions on the strength properties of test soils (30% kaolinite and 70% sand). All the

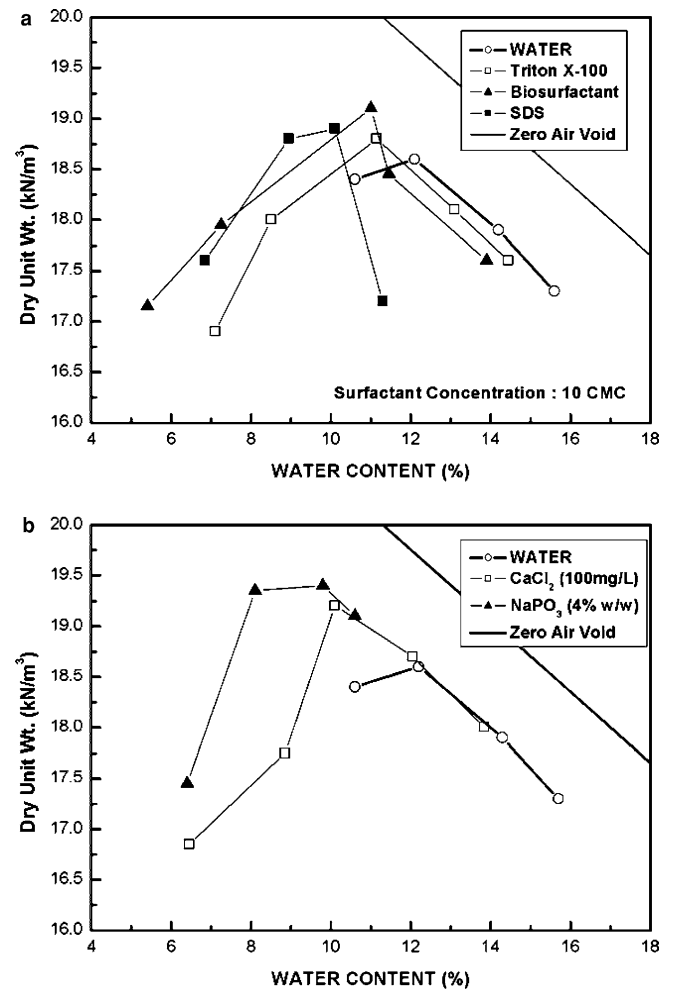


Fig. 6 Compaction test results for 30% kaolinite and 70% sand mixture: a surfactants, b electrolyte solutions

Table 7 Standard compaction test results for 30% kaolinite and 70% blasting sand mixture

	Optimum water content, ω_{opt} (%)	Maximum dry unit weight, $\gamma_{d,max}$ (kN/m ³)
Water	11.6	18.9
Triton X-100 ^a	10.2	19.2
Biosurfactant ^a	10.0	19.5
SDS ^a	9.7	19.0
CaCl ₂ ^b	10.3	19.2
NaPO ₃ ^c	9.0	19.7

^a10 CMC

^b100 mg/L

^c4% solution

samples were remolded by compacting at their optimum moisture contents and maximum dry unit weights of standard proctor tests. The samples were tested after 7 days of curing in a humidity-controlled room. Test results are shown in Fig. 9 and Table 8. Effects of the

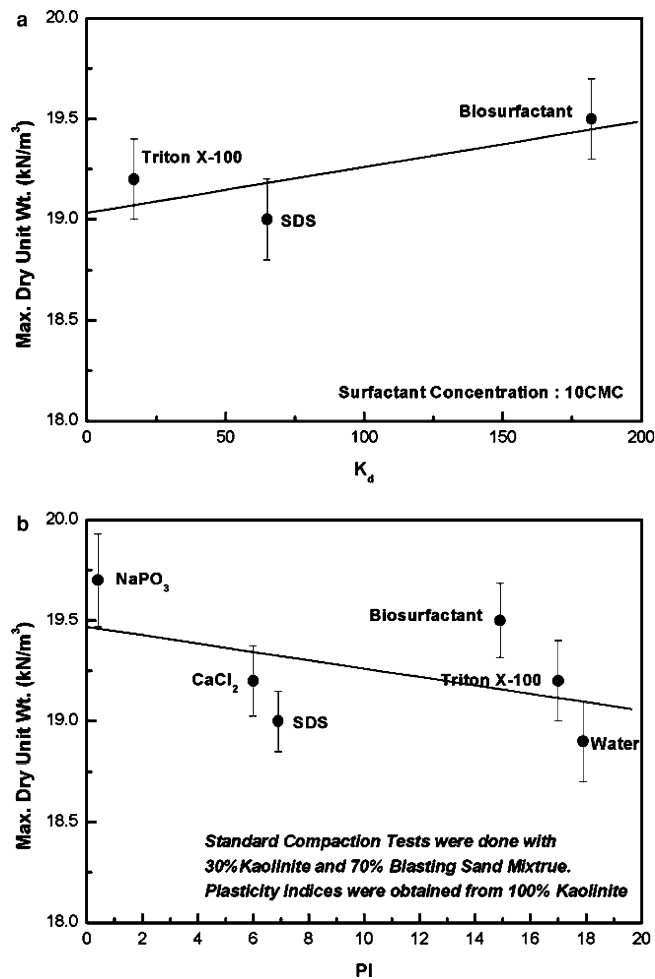


Fig. 7 Effects of K_d and PI on the maximum dry unit weight: **a** K_d -max. dry unit wt, **b** PI-max. dry unit wt

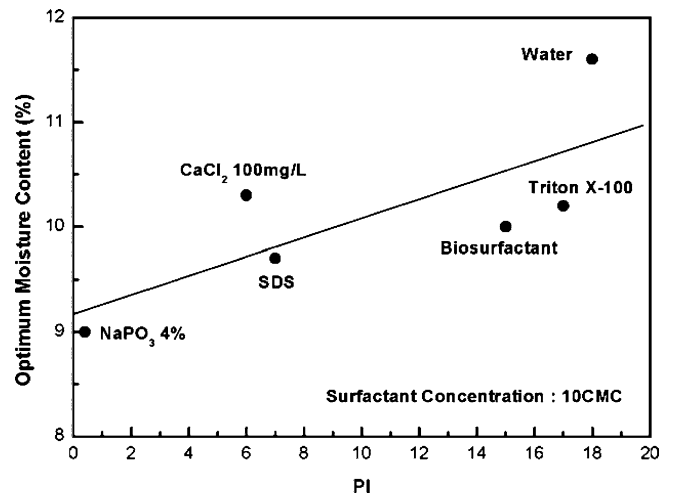


Fig. 8 Effects of plasticity index on the optimum moisture content

additive solutions on the stress-strain behavior of kaolinite seemed appreciable. For kaolinite, the Triton X-100 and biosurfactant acted as lubricant materials, lowering particle friction and making the soil into denser configuration. This effect could possibly increase the undrained shear strength, c_u (defined as a half of unconfined compressive strength, q_u), and elastic modulus, E , of kaolinite mixtures. SDS did not show any increase of c_u and E because of the foam mobilization. The addition of the electrolyte solutions caused the increase in electrolyte concentration, which decreased the double layer thickness. Surfactants concentrations above CMCs generally facilitate the release of PAHs from soil by enhancing their aqueous solubility and increasing their mobilization through PAH-water interfacial tension reduction. Figure 10 shows the relationship between the PI and the undrained shear

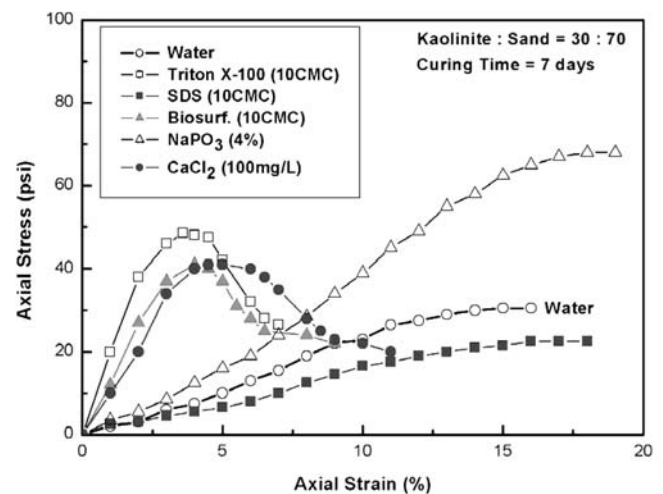


Fig. 9 Stress-strain relationship of kaolinite with various solutions

Table 8 Unconfined compression test results of test soils

	Water	Triton X-100	Biosurfactant	SDS	NaPO ₃	CaCl ₂
c_u (psi)	15.0	24.0	20.5	11.0	34.5	20.5
E (psi)	260	2,500	2,180	160	490	1,360

Kaolinite:sand 30:70, curing time of soil sample 7 days

strength. The undrained shear strength (q_u) decreases as PI increases for test soils. No trend was found between the PI and K_d . As the maximum unit weights of kaolinite mixtures with surfactants and electrolyte solution increased, the strength of the test soils also increased. In addition, as the optimum moisture contents decreased, the strength of the test soils increased (Tables 7, 8). Some of the test surfactants and electrolyte solutions enhance compaction behavior and increase the strength of test soils. Attempts were made to correlate parameters like surface tension, pH, viscosity, CMC, K_d of the test solutions with PI, γ_d , ω_{opt} , c_u , and E . However, significant correlation was not found.

Solution effects on coefficient of hydraulic conductivity

Fixed-wall compaction-mold permeameter tests with double-ring bottom plate were performed to investigate the effects of surfactants on kaolinite mixture (clay:sand 30:70) samples. Table 9 summarizes the test results. There were no large differences between inner and outer k values for all the test solutions, which meant no significant sidewall leakages were detected during the tests. The tests were generally continued until two pore volumes of permeant liquid (1 pore volume \approx 250 mL) passed through the specimens. The hydraulic conductivities were very well stabilized throughout the tests. The duration of the tests ranged from 3 to 7 weeks. The surfactants generally decreased the hydraulic conductivity down to 70% of the hydraulic conductivity of water at 10 CMC. The concentrations of the surfactants seemed so low that even if they had produced physico-chemical changes, it is unlikely that major changes in hydraulic conductivity would have been observed. There

Table 9 Hydraulic conductivity tests for kaolinite–sand mixtures with the test surfactants at 10 CMC

Permeant solutions	k_{in} ($\times 10^{-7}$ cm/s)	k_{out} ($\times 10^{-7}$ cm/s)	k_{avg} ($\times 10^{-7}$ cm/s)
Water ^a	1.3	0.6	1.0
Triton X-100 ^b	0.3	0.3	0.3
Biosurfactant ^c	0.4	0.5	0.5
SDS ^c	0.3	0.2	0.3

Kaolinite:blasting sand 30:70

^aThe k values were the average of four different column tests

^bThe k values were obtained from single tests

^cThe k values were obtained from duplicate tests

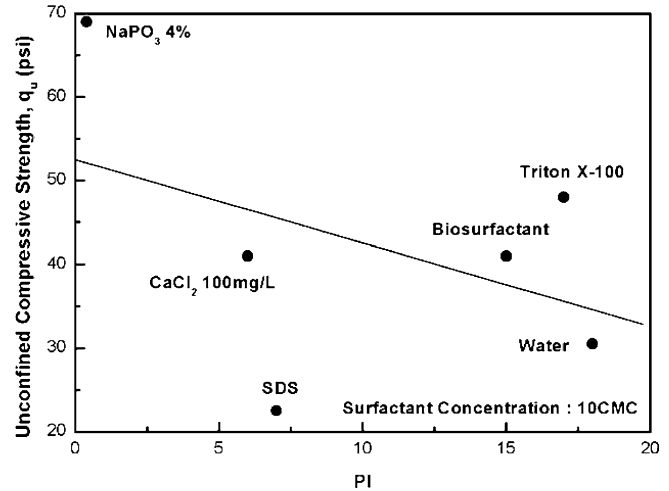


Fig. 10 Effects of plasticity index on unconfined compressive strength

were not many differences in hydraulic conductivities among the three surfactants used. The slight decrease of the hydraulic conductivity by surfactants might be attributed to several possible factors. One possibility is pore clogging caused by the free migration of fine particles activated by surfactants. Higher viscosity of the surfactants (Table 2 and Fig. 11) than water could be another factor. Hydraulic conductivity decreases as viscosity increases. This trend was observed for permeation tests with pure form of organic compounds from a number of researchers (Anderson et al. 1985; Bowders and Daniel 1987; Broderick and Daniel 1990). In the current tests, all three surfactants showed a similar trend of decreasing hydraulic conductivity even though concentrations were not in pure form. The flocculation effect and the increase of hydraulic conductivity by SDS were not observed. The hydraulic gradient was increased from

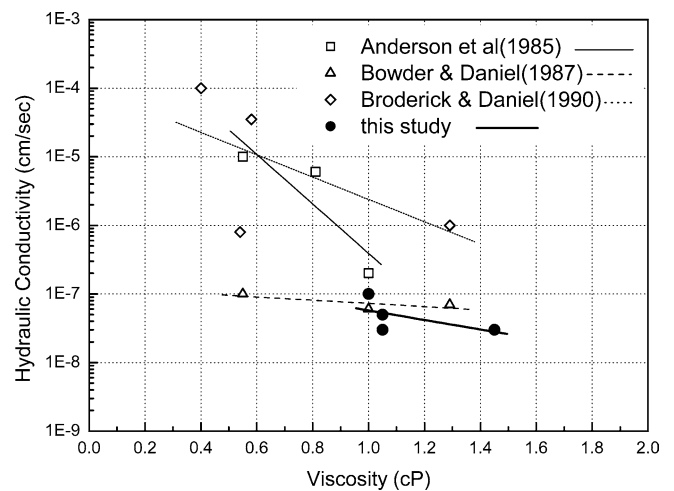


Fig. 11 Hydraulic conductivity and viscosity

42.3 to 60.8 during the tests to speed up the test duration; however, the change of hydraulic conductivity was not measurable for each test. This result is similar to Dunn's (1985) results in which hydraulic conductivities changed less than 0.1 order when hydraulic gradients were sequentially increased from 20 to 200 for two different clayey soils of CH and CL. The values of pH can also play a role in the behavior of clay suspensions. Theoretically, a high pH hinders negative surface interaction, often leading to dispersion from suspensions. This effect can stabilize and decrease the hydraulic conductivity of the clayey soils. In this test, SDS (pH 8.5) and Triton X-100 (pH 7.7) showed the lowest hydraulic conductivities of 0.3×10^{-7} cm/s, while biosurfactant (pH 10.8) had a value of 0.5×10^{-7} cm/s, which was supposed to be the lowest in terms of pH- k relationship. The effect of pH might play a greater role in suspension form than in compacted specimens. Other parameters such as compaction parameters, K_d , surface tension, and plasticity did not much affect the hydraulic conductivity of the kaolinite mixture when permeated with surfactants at 10 CMCs. No specific correlation was found.

Conclusions

Based on this study, the following conclusions are drawn:

1. Naphthalene at its solubility concentration (32 mg/L at 25°C) did not have appreciable effects on the index properties of kaolinite. However, CaCl_2 (100 mg/L) decreased the plasticity of kaolinite when mixed with water or Triton X-100. Both SDS and NaPO_3 also decreased the plasticity of the test soil. For kaolinite, NaPO_3 decreased the PI into an extremely narrow range of 0.3 and turned it into virtually non-plastic soil.
2. The sorption coefficients of kaolinite decreased in the order: biosurfactant > SDS > naphthalene > Triton X-100. Triton X-100 was the most hydrophilic and was not highly adsorbed onto kaolinite, but solubilized most easily in water. Biosurfactant showed most hydrophobic character of all the surfactants and is considered to adsorb most onto soil particles rather than remaining in water. As biosurf-
- actant has the highest value of K_d , it can be adsorbed easier onto the kaolinite particles and gives better lubrication between soil particles compared with other surfactants. This can make the soil into the densest configuration. However, the distribution coefficients for naphthalene and three different surfactants on kaolinite did not show significant correlation with PI values. The concentrations used in this test were not high enough to correlate K_d and other soil index parameters.
3. For the clayey mixture (clay:sand 30:70), the addition of surfactants generally increased the maximum dry unit weight and decreased the optimum moisture content. Electrolyte solutions like CaCl_2 and NaPO_3 also decreased the optimum moisture contents and increased the maximum dry unit weight of the kaolinite mixtures. These solutions caused more soil flocculation. The effects of electrolyte solutions on kaolinite mixture were that flocculation of clayey soils generally increased the maximum dry unit weight and lowered the optimum moisture content.
4. For kaolinite, Triton X-100 and biosurfactant acted as lubricant material lowering particle friction and making the soil into denser configuration. This effect could possibly increase the c_u and E of kaolinite mixtures. SDS did not show any increase in c_u and E because of the foam mobilization. The addition of the electrolyte solutions caused an increase in electrolyte concentration, which decreased the double layer thickness. The large increase in interparticle attraction made possible by the reduction of the diffuse double layer was responsible for the flocculation of the clay mixture on mechanical remolding. This effect resulted in increased strength of kaolinite mixtures.
5. In the fixed-wall permeameter tests, the surfactants generally decreased the hydraulic conductivity down to 70% of the hydraulic conductivity of water at 10 CMC ($k_{\text{water}} = 1.0 \times 10^{-7}$ cm/s). The concentrations of the surfactants seemed so low that it is unlikely that major changes in hydraulic conductivity would have been observed. There were not many differences in hydraulic conductivities among the three surfactants.

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