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Properties of surfactants on high salt-affected sandy land in enhanced sand fixation: Salt tolerance, adsorption isotherms and ecological effect

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Highlights

The water solubilization method was used to study the phase behavior of microemulsion.

The adsorption of the surfactants on the sand particles was investigated at different salinities.

The effects of the surfactants on soils microbial growth were evaluated.

Abstract: In present paper the surfactant, for the first time, was used to improve the sand fixing ability of emulsion in high salt-affected sandy land. This study started from the analysis of main components of the sand particles from Golmud sandy land, Qinghai province, China, by X-ray diffraction (XRD). Then, two surfactants, sodium dodecyl sulfate (SDS, an anionic surfactant) and Pluronic L35 (L35, a nonionic surfactant), have been selected and conducted the salt tolerance test before their reaction with the sand from salty desert. The water solubilization method and Fourier Transform Infrared (FTIR) Spectroscopy have been adopted to investigate the salt tolerance of surfactants and their reaction with sand particles, respectively. The adsorption and adsorption characteristics of two surfactants at varied salinities by sand particles have been considered because of its significance for the interaction. In addition, the influence of SDS and L35 on the growth of *Escherichia coli* (*E.coli*) and microbe of sand were evaluated for understanding their ecological effect. The experimental results showed that SDS and L35 can visibly enhance the sand-fixing ability of the emulsion in high salt-affected sand land. The related mechanism is that, first, the SDS and L35 could improve the stability of the emulsion against the salt if the preparation of emulsion was taken SDS and L35 as the emulsifying agents; second, the SDS and L35 could change the morphology of salt in sand (This experimental result we will report

in another paper). The test of the influence of SDS and L35 on the growth of *E.coli* and microbe of sand also showed a dependable ecological effect.

Key words: Soil salinization, Surfactant, Microorganisms, Adsorption isotherm, Salt tolerance, Sand-fixation

1 Introduction

With the increasing use of low quality water and conventional agriculture practice, soil salinization, nutrients poorness and desertization are one of the most serious environmental and worldwide socioeconomic problems, which is considered as the major threat to the sustainability of agriculture and economic development^[1-4]. It is well known that the salinity limit soil fertility because of its accumulation of excess Na^+ in soil, resulting in the destruct of physical and chemical properties of soil, such as the deficiency in essential elements of nitrogen(N), phosphorus(P), and potassium (K)^[5]. And, the excessively exchangeable sodium leads to the welling and dispersion of clays as well as slaking of soil aggregates through the decrease of soil permeability, available water capacity and infiltration rate^[6]. In addition, in the arid zones, the intense evaporation tends to accumulate salts in the upper soil profile, especially when it is associated with an insufficient leaching or where soluble salts move upward in the soil profile from a water table instead of downward^[7]. Desertization in salt-affected soils has been found in more than 100 countries of the world^[8-17]. According to Tòth et al., the total area of salt-affected soil was about one billion hectares, occurring mainly in the arid and semiarid regions of Asia, Australia, Africa and South America^[9]. In China, there were over 99.13 million hectares of salt-affected soils suffering desertization^[10, 15].

For many years humans around the world have been enforced to consider the control of desertified land caused by salinization. Many scientists have conducted a lot of researches to develop a series of measures to reduce or prevent the desertization of salt-affected soil^[18-22]. Although numerous financial resources have been consumed to vegetation restoration and protection of bare saline soil^[23, 24], there were lots of limitations in terms of cost, effectiveness and ratio of seed germination only by vegetation restoration due to the adverse wind erosion and nutrients poorness in high salt-affected sandy land. So, the sand fixation under high salt stress was regarded as the key step for saline soil restoration.

The polymeric materials, as the new sand stabilizers to prevent sand wind erosion, have

received much attention^[25-28]. The polyurethane (PU) designed by TORAY of Japan was used in Qinghai salt-affected sandy land of China^[29, 30]. The experimental results showed that there was excellent sand-fixing capability at the beginning period of using PU; however, with the extension of time, PU began to pulverize and lost the sand-fixation performance. Moreover, PU cost too high to be applied in large-scale. Therefore, the performance and cost became the main consideration for the materials applied in the sand-fixing of high salt-affected sandy land.

Usually, the emulsions, especially the emulsions made of acrylate monomers, had a much lower cost and good adhesive. With its peculiar performance, the emulsions became the all-important choice for desertification and soil salinization control. Generally, properties of emulsions were mainly determined by the monomer composition and emulsifying system^[31]. Especially, the influence of surfactant on the mechanical and chemical (e.g. salt tolerance) stabilities of emulsions was often a matter of major concern.

Due to the negative charge of sand surface, the cationic poly(vinyl acetate-butyl acrylate-co-2-methylacryloylxyethyl trimethyl ammonium chloride) (P(VAc-BA-DMC)) copolymer emulsion designed by Xu Meng et al was used as sand-fixing material^[32]. After the P(VAc-BA-DMC) was sprayed on the sand surface or mixed with sand, the emulsion showed its cementing ability to aggregate sand particles and formed crust by neutralizing the negative charge of sand surface and having the strong intensive. However, they didn't study its salt resistance. Additionally, cationic surfactant and DMC monomer in P(VAc-BA-DMC) emulsion had a negative influence on the growth of soil microbe if spraying too much the emulsion on the sand surface.

In order to improve salt resistance of emulsion used for high salt-affected sandy land, the salt tolerance of surfactant was regarded as the key point for preparing the emulsions with good salt tolerance, in the present work, the surfactants, namely SDS and L35, have been selected and their salt tolerance properties have been intensively studied by spectrophotometric and phase volume methods. Another batch experiments were carried out to determine the adsorptions of surfactant on the sand particles (adsorbent) at different salinity. Additionally, the effects of surfactants (SDS and L35) on the growth of *E.coli* and soil microbe were evaluated.

2 Experimental

2.1 Materials

Nonionic surfactant, Pluronic L35 was supplied by Haian Petrochemical Corp. (Jiangsu,

China), and was used as received. Anionic surfactant, Sodium dodecyl sulfate (SDS) was purchased from Kelong Chemical Reagent Corporation (Chengdu, China) and was used without further purification. Analytical pure cetyltrimethylammonium bromide (CTAB) procured from Sinopharm Chemical Reagent co., Ltd. (Beijing, China), and was used as received. Sodium Chloride (NaCl) procured from Guangdong Guanghua Sci-Tech Co., Ltd. (Guangdong, China), was used for preparation of brine. Deionized water was used in all preparations.

2.2 Experimental procedures

2.2.1 Preparation of sand particles

Sands used for this investigation from Golmud sandy land, Qinghai province, China. The sands were sieved to get 60 mesh sized particles, and then dried at 353K for 24h for experimental purposes.

2.2.2. XRD analysis of sand particles

The sands were ground to prepare powder sample. XRD measurement was carried out with a Rigaku D/max-RB apparatus (Tokyo, Japan) powder diffractometer and image-plate photography using graphite-monochromatized Cu K α radiation. The data were collected from 10°-90° with a scanning rate of 5(°)/min and analysed with the help of the JCPDS files.

2.2.3. FTIR analysis

The apparatus used for measuring the FTIR spectra of the sand particles before and after surfactant treatment in the range of 450-4000 cm⁻¹, was a PerkinElmer Spectrum version 10.03.07 FTIR spectrometer. The instrument was operated by Spectrum two software supplied by PerkinElmer (USA). For the FTIR analysis, 4mg of dried sample was mixed with potassium bromide (KBr) (~300mg), which was used as a reference standard sample. The mixture was compressed by hydraulic pump to prepare pallet and the pallet was placed in a desiccator to remove moisture of the sample. The dried sample then was used for experimental purpose.

2.2.4 Salt tolerance analysis of surfactant

In order to achieve the improved sand-fixating ability of emulsion in high salt-affected sandy land, the salt tolerance of surfactant becomes the important parameter if the surfactant will be used for preparing the expected emulsion. Meanwhile, the salt tolerance of surfactant also turns into a criterion for evaluating the effectiveness of sand fixation. A spectrophotometer (721, Shanghai XIPU instrument co., LTD) was used to measure the transmittance of surfactants middle layer

aqueous solution with different salinities at 318 K and 600nm. Additionally, the salt tolerance of surfactants can be evaluated by phase volume-fraction diagram to evaluate, also. The pseudo-ternary phase diagram for oil-water-surfactant system was obtained at 318 K^[34].

2.2.5 Adsorption isotherms of surfactant at different salinity

A series of batch experiments were carried out to determine the adsorption isotherms of SDS and L35 on the adsorbent, respectively. 8g of dry sand particles were added to 50ml surfactant solutions with different concentrations in a 150ml conical flask, which were oscillated constantly for 24h at 303K for an entirely adsorption in a temperature controlled horizontal shaker with a speed of 120rpm. Then the surfactant solutions were isolated with the treated sand particles by centrifugation. The equilibrium concentration (C_e) of surfactant solutions were determined by the two-phase titrations^[35] and potassium ferrocyanide titration methods^[36], respectively. The amount of surfactant adsorbed on the adsorbent, Γ (mg/g), was calculated by a mass balance relation:

$$\Gamma = (C_0 - C_e)V/m$$

where, C_0 and C_e are the initial and equilibrium concentrations of surfactant (mg/g) respectively, V is the volume of surfactant solution (L), and m is the weight of the sand particles (g) used.

The effects of the NaCl concentrations on the adsorption capacity of the sand particles to SDS and L35 were also investigated.

2.2.6 Microorganism growth

Microorganisms played an important role in sand fertility and plant nutrition; also they could speed up the transformation of sand to the soil. So the growth of soil microbe was a primary parameter for evaluating the effectiveness of sand fixation. The *E.coli* was used to evaluate the effects of the SDS and L35 on microbial growth at the first stage, then, the microorganisms from the sand of Golmud sandy land, Qinghai province were used for examining the ecological effect of SDS and L35. The sand containing 3% NaCl was first treated using SDS and L35 with the concentration of 1.0, 2.0, 3.0, 4.0, and 5.0%, than kept for one month at room temperature before put them in distilled water for getting the sand microbe for investigation. A spectrophotometer (721, Shanghai XIPU instrument co., LTD) was used to measure the growth condition of *E.coli* at 596nm after surfactant was introduced into medium. According to the method proposed by Mathur et al.^[37] and Lima et al.^[38] with few modifications, the numbers of soil microbe were estimated,

also.

3 Results and Discussion

3.1 Characterization of sand particles and their interaction with surfactants

The sand particles treated with the method described in section 2.2.1 were characterized by XRD study for knowing the components of the sand, and the result was showed in Fig.1. There is a group of single headed peaks at 21° , 42.56° , 50.22° , 60° and 68.25° , etc, indicating that only one phase was present, which is attributed to the characteristic peaks of silicon oxide according to the JCPDS (file no. 832466). And the main peak was obtained at 27.4° .

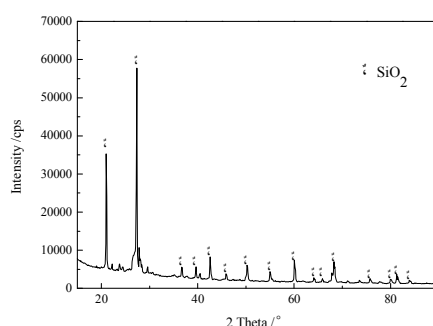


Fig. 1 XRD analysis of the sand particles

The FTIR analysis was used to detect the structure changes of sand particles before and after the treatment with SDS and L35. The Fig. 2(a) told the infrared spectrum of untreated sand, that adsorption peaks at 780.82cm^{-1} and 1084.29cm^{-1} belonged to the symmetric and asymmetric stretching vibration of Si-O group, respectively; and the adsorption bands at 521.98cm^{-1} and 691.57cm^{-1} were related to the asymmetric and symmetric bending vibration of Si-O group, respectively. The results proved again that the sand samples contained silica as main composition, as told in XRD spectrum. And, the peak at 3468.43cm^{-1} indicated a stretching vibration of OH group of water molecule, meaning there was moisture in the sand samples; the peaks at 2922.97cm^{-1} and 2854.54cm^{-1} were the symmetric and asymmetric stretching of $-\text{CH}_2$ group, respectively.

Fig. 2(b) gives the IR spectrum of sand treated with SDS. Therefore, the peaks at 2849.18cm^{-1} and 2912.83cm^{-1} were the symmetric and asymmetric stretching vibration of $-\text{CH}_2$ group of SDS, the peak at 1381.55cm^{-1} came from the stretching vibration of the S=O bond of SDS, and the sharp peak at 2912.83cm^{-1} responded to the stretching vibration of alkyl C-H bond of

SDS. All the results indicated that SDS was adsorbed to sands surface after its treatment of sands.

Fig. 2(c) was the FTIR spectra of sands treated with of L35. In this case C-H stretching vibration of L35 showed at 2928.26cm^{-1} instead of 2922.97cm^{-1} , the shift of the absorption band was due to that the ethoxylated group of L35 was adsorbed by sands in solution. As for the peak at 1881.65cm^{-1} , it was also because of the adsorption of ethoxylated group of L35 on sands.

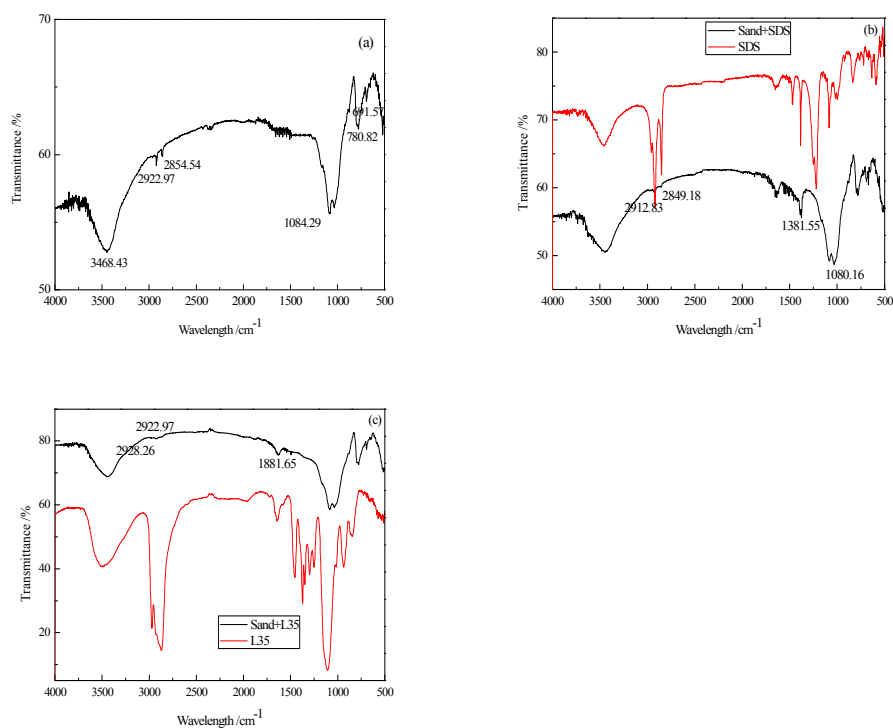


Fig. 2 FTIR spectra of sand particles before and after surfactants treatment in water:
(a) pure sand; (b) treated with SDS; (c) treated with L35.

3.2 Salt tolerance of surfactants

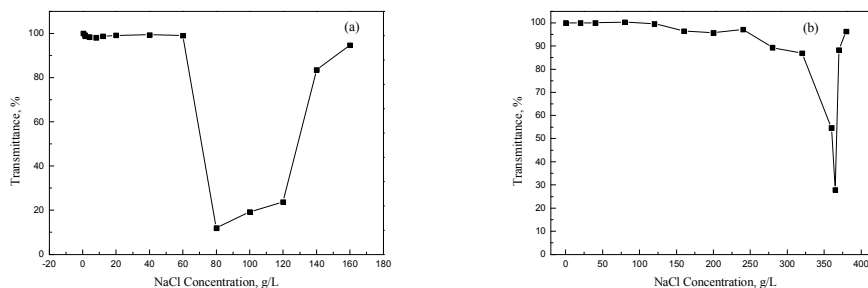


Fig. 3 Transmittance of the surfactants middle layer aqueous solution as a function of electrolyte concentration at 318 K: (a) SDS, (b) L35

The evaluation of polymer emulsion on salt tolerance is very important and necessary, because the polymer emulsion will be used as the sand-fixing material in high salt-affected sandy

land. As we know, the polymer emulsion is an unstable system, and it is sensitive to salt and many chemicals. And the salt tolerance of polymer emulsion was determined by monomer composition and surfactant system, therefore, adopting excellent salt-resistant surfactant was regarded as the key factor for preparing salt-resistant sand-fixing emulsion. Salt tolerance of surfactant could be determined by water solubilization of surfactant with various salinities. Fig.3 showed the transmittance of middle layer aqueous solutions of SDS and L35 with different salinities. From Fig.3, we can see that both the SDS and L35 had a good solubility in water with low salinity; correspondingly, the transmittance of surfactant aqueous solution was similar with water. With the increase in NaCl concentration, water-solubility of SDS decreased due to salting out effect, as for L35, the presence of NaCl could destroy the hydrogen bonding between poly(ethylene oxide-*b*-propylene oxide) chains and water molecules and reduce the hydration degree of L35, so the transmittance of surfactant aqueous solution decreased. And, with the gradual increase of NaCl concentration, at a certain point, a sudden increase of the transmittance of the surfactants aqueous solution occurred because the system came to a phase separation. Therefore, a typical salt concentration, at which the minimum transmittance of SDS and L35 aqueous solutions was obtained, is defined as the biggest salt tolerance of SDS and L35, meaning the surfactants will have an excellent salt tolerance below this salt concentration. The biggest salt tolerances of surfactants were found 80g/L for SDS and 365g/L for L35, respectively. Generally, the salt content in saline sandy lands was less than 3%, so these results indicated that both of the SDS and L35 could meet the requirement for the preparation of a salt-resistant sand-fixing emulsion.

Additionally, salt tolerance of surfactants could be evaluated by phase behavior and phase boundary of microemulsion systems, which was usually formed by the surfactants/sec-butyl alcohol/n-heptane/brine system ^[39], and its phase behavior could be determined by water solubilization method with variation of salinity ^[40]. And the phase state diagrams of the microemulsion based on SDS and L35 were shown in Fig.4. It was found from the experimental results that the microemulsion phases were changed from Winsor type-I (showed as Fig.4 (a-1)) to Winsor type-II (showed as Fig.4 (a-6)) through middle phase of Winsor type-III (showed as Fig.4 (a-4)) with salinity increase at a particular temperature. This change in microemulsion phases could be attributable to the reasons: initially at low salinity, surfactants show strong hydrophilic and mainly solve in water phase, so only the oil phase and the lower-phase

microemulsion can be found at the equilibrium situation of the system. And with the increase of salt concentration, the salt ions start to attract more and more H_2O molecules, which decreases the number of H_2O molecules available to interact with the surfactants. In this condition, the systems exhibit a middle-phase microemulsion. And with the gradual increase of NaCl concentration, the surfactant molecules will be precipitated because of the hydrophobic interactions of each other, and then the upper-phase microemulsion and a brine phase occur in the systems at equilibrium. The interfacial film curvature turned from positive value to zero to negative one, corresponding to phase transition from oil–water (O/W) to bi-continuous phase to water–oil (W/O) structure, gradually^[41,42].

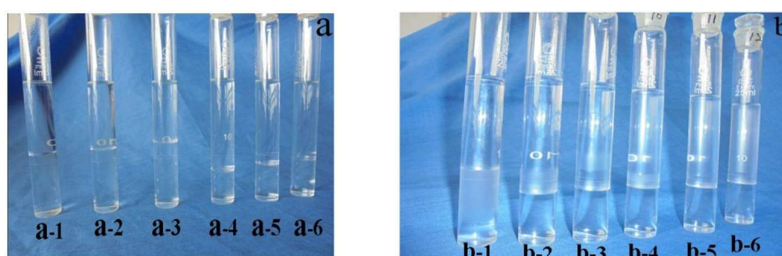


Fig. 4 Phase behavior of the surfactants at 318K: (a) SDS; (b) L35

The salinity, at which water solubilization of surfactant is highest, has been generally termed as “optimal salinity” for the microemulsion system. Usually, the optimal salinity is found in the Winsor type-III region, in this region the solubilization parameters σ_o , σ_w of oil and water in the microemulsion phase were equal, corresponded to the minimum in interfacial tension^[43,44]. Based on the experimental data in Fig.5, the optimal salinities of SDS and L35 obtained by phase behavior were found to be 62g/L and 81g/L for SDS and L35, respectively (see Table 2). Meanwhile, it also could be found that the middle-phase microemulsion had the ability to solubilize equal amounts of oil and brine at the optimum salinity. Therefore, we can say with full confidence that the emulsions prepared by SDS and L35 would be stable at optimum salinity, even it is much higher than the practical salt content in sand land.

Besides, the salt tolerance of surfactant could be evaluated by salinity range, i.e., $\Delta S = S_2 - S_1$ (S_1 was the initial salinity and S_2 is the end salinity for obtaining middle phase emulsion). Because the salt content in the saline sandy land was generally below 3%, which is much less than the salinity ranges (ΔS) of SDS and L35, implying the SDS and L35 are suitable for the preparation of the emulsions used in high salt-affected sandy land (Table 2).

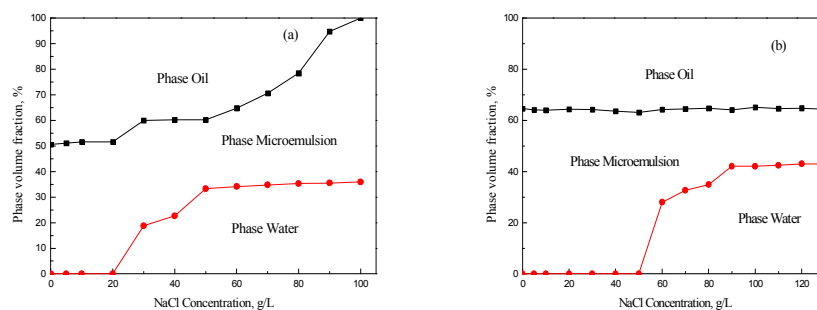


Fig. 5 Phase state diagram of the surfactants/sec-butyl alcohol/n-heptane/brine microemulsion at 318 K: (a) SDS, (b) L35

Table 2 Optimal salinity (S^*), initial salinity (S_1), end salinity (S_2), and salinity range ($\Delta S = S_2 - S_1$) for obtaining middle phase emulsion with SDS or L35 at 318 K

	S^*	S_1	S_2	ΔS
	g/L	g/L	g/L	g/L
SDS	62	30	90	60
L35	81	60	>130	>70

3.3 Adsorption isotherms of SDS and L35 on sand particles

The adsorption of SDS and L35 on sand directly affected the efficient of sand-fixation emulsion in practical application. Owing to the above mentioned FTIR spectra could only provide qualitative result of the adsorption of SDS and L35 on sand, the quantitative results of their adsorption onto sand surface were determined in laboratory, and the Langmuir adsorption isotherm and the Freundlich adsorption isotherm were used to describe the equilibrium adsorption amounts of SDS and L35 on sand particles as well the adsorption mechanism.

The Langmuir equation is related to the amount Γ , of the solid adsorbate adsorbed in the equilibrium liquid concentration at a fixed temperature. The equation was developed by Irving Langmuir^[45] and was expressed in nonlinear form as follows:

$$\Gamma = \frac{\Gamma_{\max} K_L C_e}{1 + K_L C_e}$$

where, Γ is the amount of adsorbate adsorbed (mg/g); $\Gamma_{\max}$ is the maximum amount adsorbed (mg/g); K_L was the Langmuir equilibrium constant (L/mg); C_e is the equilibrium aqueous concentration (mg/L). It is well-known that the Langmuir isotherm is applicable for monolayer adsorption because of the homogeneous surface of a finite number of identical sites. Another

important parameter of the Langmuir isotherm model is the term “ R_L ” which is a nondimensional constant and calls as separation factor or equilibrium parameter, and it is represented by the following equation^[46]:

$$R_L = \frac{1}{1 + K_L C_0}$$

where, C_0 (mg/L) expresses initial adsorbate concentration in aqueous solution. K_L (L/mg) is the Langmuir constant. The R_L parameter is important signs on the compatibility of adsorption for the given adsorbent–adsorbate pair. There are four possibilities for R_L value:

In the case $0 < R_L < 1$, adsorption is favorable;

In the case $R_L > 1$, adsorption is unfavorable;

$R_L = 1$ indicates linearity of adsorption;

In the case $R_L = 0$, the adsorption is irreversible.

The values of R_L obtained in this study were between 0.0295 to 0.222, indicating that the SDS and L35 were favorable for adsorption onto the sand surface.

The Freundlich isotherm assumes that, at equilibrium of adsorption process, if the C_e , the concentration of the solute in the solution, is raised to the power $1/n$, the amount of the solute adsorbed is Γ . The $C_e^{1/n}/\Gamma$ is a constant at given temperature, and the nonlinear form of the equation will be expressed as:

$$\Gamma = K_F C_e^{1/n}$$

where, K_F (mg/g) and n are the Freundlich adsorption constants related to adsorption capacity and adsorption intensity, respectively. The Freundlich isotherm has been derived by assuming an exponentially decaying adsorption site energy distribution. The Freundlich isotherm suggests that surfactant adsorption occurs on a heterogeneous surface by multilayer adsorption.

The Freundlich constant ($1/n$) is related to the adsorption intensity of the adsorbent. When, $0.1 < 1/n < 0.5$, the adsorption will be favorable; $0.5 < 1/n \leq 1$, it will be easy to adsorb; however, when $1/n > 1$, meaning it is difficulty to adsorb^[47].

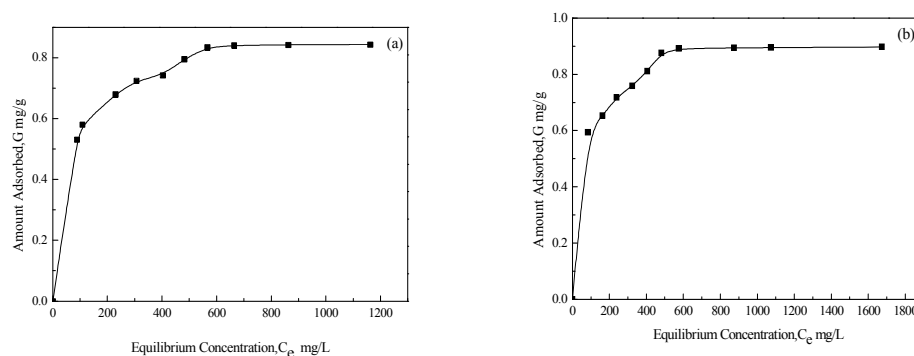


Fig. 6 Adsorption isotherms of the surfactants on sand surface at 303K: (a) SDS, (b) L35

Fig.6 showed the adsorption of SDS and L35 on sand surfaces at 303 K. The Γ_{SDS} and Γ_{L35} , the amount of SDS and L35 adsorbed on the sand particles at equilibrium, depended on the structures and nature of hydrophilic groups of SDS and L35. It was clear that the Γ_{L35} was considerably higher than Γ_{SDS} . Fig.6 indicated that there was a sudden increase in adsorption isotherms with the increasing concentration of SDS and L35. The sudden increase in adsorption isotherm may be related to the surface aggregates of SDS and L35, known as the “hemi micelles” of SDS and L35 molecules on the sand surface derived from the lateral interaction of hydrocarbon chains. This lateral attraction force generated an additional driving force to superimpose the existing electrostatic attraction, causing a sharp increase in adsorption. In all cases the increase of adsorption with concentration up to and then leveling off at a certain point have been observed^[48, 49]. The adsorption of SDS at solid–liquid interface was strongly influenced by the compositions of the sand. Because the XRD and FTIR analyses showed that the main ingredient of the sand was silicate, which made the sand surface negatively charged, therefore, the weak interaction took place with the negatively charged head part of SDS, resulting in a not visibly high adsorption capacity of SDS on sand particles. And, the adsorption of L35 occurred onto sand was based on the weak hydrophobic and hydrogen bond interactions for there were no positive and negative charge existing in L35, so the adsorption capacity of L35 for sands was considerably higher than that of SDS.

To quantify the adsorption capacity of SDS and L35 on sand, the Langmuir and Freundlich adsorption isotherms have been used to depict the different adsorption model. According to the Fig.7 and Fig.8, the calculated results from the curves of Langmuir and Freundlich isotherm adsorption for SDS and L35 have been summarized in Table 3. The values of regression

coefficient (R^2) implied that the adsorption of SDS and L35 on sand surface was well fitted to Langmuir model.

Table 3 Adsorption isotherm parameters of SDS and L35.

Isotherm models	Parameters	Surfactants	
		SDS	L35
Langmuir	$\Gamma_{\max}(\text{mg/g})$	0.897	0.944
	$K_L \times 10^2(\text{L/mg})$	1.578	1.648
	R^2	0.965	0.911
Freundlich	$K_F(\text{mg/g})$	0.257	0.334
	$1/n$	0.178	0.143
	R^2	0.920	0.831

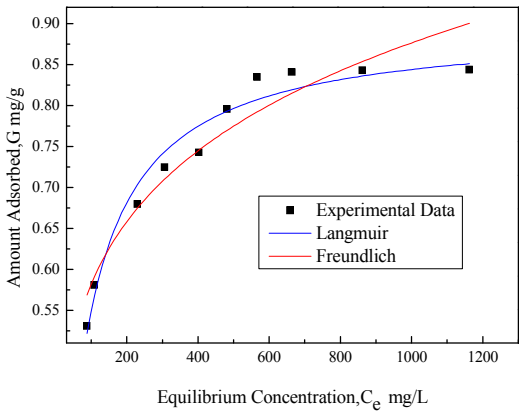


Fig.7 Fitting curves of the adsorption of SDS on sand particles at 303K

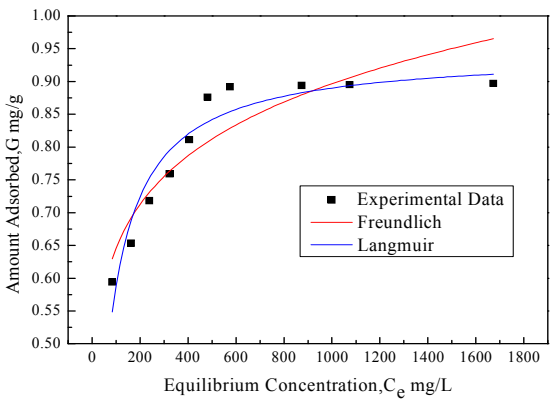


Fig.8 Fitting curves of the adsorption of L35 on sand particles at 303K

3.4 Effect of salt concentration on adsorption isotherm of surfactants

Adsorption isotherms for SDS and L35 solution at varied salinities were shown in Fig.9. At the interface between surfactant and sand particles, there was always an unequal distribution of electrical charges. This unequal charge distribution gave rise to a potential across the interface and formed a so-called electrical double layer^[50]. With the increase of NaCl concentration, the electrical double layer on the surface of adsorbent was compressed, and the electrostatic repulsion between the adsorbed surfactant species decreased, which resulted in the increase of adsorption capacity. The surfactant adsorption capacity increased with the increase in salinity of the system at a constant temperature of 303 K. The phenomenon told that the adsorption of SDS and L35 on sand particle was favored at high salinity and therefore, the adsorption process was found to be a chemical process with increasing salinity.

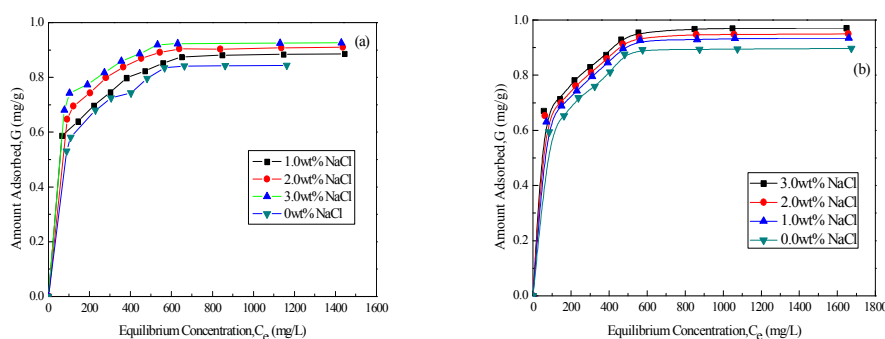


Fig. 9 Adsorption isotherms of the surfactants on sand surface at varied salinities of brine at 303K: (a) SDS, (b) L35

Table 4 Adsorption isotherm parameters of SDS at varied salinities

Salinities (wt% NaCl)	Langmuir parameters			Freundlich parameters		
	$\Gamma_{\max}(\text{mg/g})$	$K_L \times 10^2 (\text{L/mg})$	R^2	$K_F(\text{mg/g})$	$1/n$	R^2
0	0.897	1.578	0.965	0.257	0.178	0.920
1	0.910	2.059	0.981	0.329	0.144	0.959
2	0.929	2.186	0.971	0.397	0.122	0.878
3	0.948	3.11	0.933	0.459	0.103	0.873

Table 4 showed the parameters obtained from two adsorption models. We can see that all the regression coefficients (R^2) from Langmuir model fittings were greater than that of from Freundlich model fittings at corresponding salinities. Therefore, it may be concluded that Langmuir isotherm model presented a better fitting than Freundlich model when SDS and L35

were used to treat the sand.

3.5 Ecological effect of surfactants on sandy land

Microorganisms played a considerable role in sand fertility and plant nutrition, and they could speed up the transformation of sand to the soil. Also, the microorganisms were considered as the most active composition in the land ecological system. So the growth of soil microbe was a key parameter for evaluating the effectiveness of sandy land’s recovery. The culture medium containing 5wt.% SDS and L35 have been taken to test the effect of surfactants on the growth of *E.coli*. As we know, this concentration of SDS and L35 used was much higher than the dosage for preparing emulsions. The experimental results showed in Fig.10 revealed that the growth of *E.coli* was not affected by the SDS and L35 at such a high concentration with the extension of growing time. This result allowed us to strongly believe, that the selected SDS and L35 surely could be used to prepare the salt tolerance emulsions with required ecological effect.

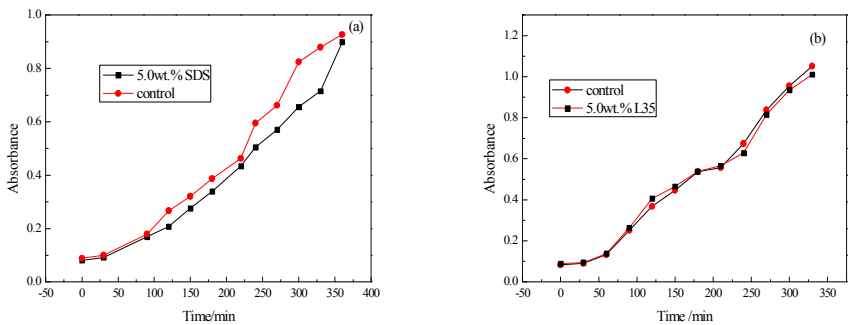


Fig. 10 Effects of SDS and L35 on the growth of *E.coli*: (a) SDS, (b) L35

The *E.coli* and the microorganisms from the sand were used for examining the ecological effect of SDS and L35. The sand was treated followed the procedure described in section 2.2.6. Table 5 showed the quantity of bacteria from the sand treated with 3.0% of salt and SDS or L35 with different concentrations. As observed, when L35 concentration increased, there were no obvious effects on the quantity of sand bacteria. Although SDS could inhibit the bacteria growth of sand at some extent, there was still large quantity of sand bacteria in culture. Moreover, addition of 4.0% concentration of SDS and L35 could obtain sand-fixing emulsions with the desired mechanical strength to resist bigger outside stress without cracks. These results indicated that SDS and L35 at the tested concentrations were harmless to growth of sand microbe, and the emulsions prepared with SDS and L35 will not only provide with the anti-erosion, but the

ecological effect when they are used for sand-fixing in high salt-affected sandy land.

Table 5 The quantity of soil bacteria change of sand specimen with spraying different conc. of surfactant after 30 days

The surfactant concentration (%)	Bacteria (/g) of spraying SDS	Bacteria (/g) of spraying L35
0	7.084×10^4	7.084×10^4
1	6.635×10^4	6.933×10^4
2	6.219×10^4	6.958×10^4
3	5.874×10^4	6.691×10^4
4	5.663×10^4	6.927×10^4
5	5.149×10^4	6.544×10^4

4. Conclusion

The adsorption of SDS and L35 onto sand particles has been systematically studied. The FTIR and XRD studies showed the presence of silica in the sand which provided with the active sites for adsorption of SDS and L35. The salt tolerance of SDS and L35 was improved by the phase behavior of microemulsions comprising of the surfactants/sec-butyl alcohol/n-heptane/brine with the salinity. And the growth of *E.coli* and soil microbe at high conc of SDS and L35 proved the ecological effect of these two surfactants. The adsorption of SDS and L35 on sand particles conformed a favored interaction between sand and SDS and L35. All these results indicated that SDS and L35 could enhance the sand-fixing ability of prepared emulsions, which will be used for ecological restoration of high salt-affected sandy land.

References

- [1] T.J. Flowers, A.R. Yeo, Breeding for salinity resistance in crop plants, Aust. J. Plant Physiol, 1995, 22:p.875-884.
- [2] T. Darwish, T. Atallah, M. Moujabber, N. El Khatib, Salinity evolution and crop response to secondary soil salinity in two agro-climatic zones in Lebanon, Agric. Water Manage, 2005, 78:p.152-164.
- [3] A. Lakhdar, C. Hafsi, M. Rabhi, A. Debez, F. Montemurro, C. Abdelly, N. Jedidi, Z. Ouerghi, Application of municipal solid waste compost reduces the negative effects of

- saline water in *Hordeum maritimum* L., *Bioresour. Technol*, 2008, 99:p.7160-7167.
- [4] A. Lakhdar, M. Rabhi, T. Ghnaya, F. Montemurro, N. Jedidi, C. Abdely, Effectiveness of compost use in salt-affected soil, *Journal of Hazardous Materials*, 2009, 171:p.29-37.
- [5] C. Kaya, H. Kirnak, D Higgs, Enhancement of growth and normal growth parameters by foliar application of potassium and phosphorus in tomato cultivars grown at high (NaCl) salinity. *Journal of Plant Nutrition*. 2001, 24, 357-367.
- [6] A. Lauchli, E. Epstein, Plant response to salinity and sodic conditions, in: K.K. Tanji (Ed.), *Agricultural Salinity Assessment and Management*, American Society of Civil Engineers, New York, Mann. Rep. Eng. Pract. 1990, 71, 113-137.
- [7] S.A. Isabelo, E.R. Jack, Phosphogypsum in agriculture, *Adv. Agron.* 1993, 49, 55-118.
- [8] P. Rengasamy, World salinisation with emphasis on Australia, *Comp. Biochem. Phys. A*, 2005, 141:p.337-348.
- [9] G. Tóth, L. Montanarella, E. Rusco, Updated Map of Salt Affected Soils in the European Union Threats to Soil Quality in Europe, *European Communities*, 2008, pp.61-74.
- [10] Y.F. Zhang, et al., Arbuscular mycorrhizal fungi improve reestablishment of *Leymus chinensis* in bare saline-alkaline soil: Implication on vegetation restoration of extremely degraded land. *Journal of Arid Environments*, 2011, 75(9):p.773-778.
- [11] A. Mashali, D.L. Suarez, H. Nabhan, R. Rabindra, *Integrated Management for Sustainable Use of Salt-affected Soils*, *FAO Soils Bulletin*, Rome, 2005.
- [12] G. Varallyay, Soil data base for sustainable land use—Hungarian case study, in: *Proc. Int. Symp. On soil Resilience and Sustainable Land Use*, Bp, 28 September- 2 October, 1992.
- [13] M. Khel, Saline soils of Iran with examples from the alluvial plain of Korbal, Zagros Mountains, in: *Soil and Desertification-Integrated Research for the Sustainable Management of Soils in Drylands Proceedings of the International Conference*, Hamburg, Germany, May, 2006.
- [14] *FAO (Food and Agriculture Organization of the United Nations), Global Network on Integrated Soil Management for Sustainable Use of Salt-affected*, 2000.
- [15] G.V. Dobrovol'skii, N.V. Stasyuk, *Fundamental Work on Saline Soils of Russia*, vol. 41, *Eurasian Soil Science*, Pleiades Publishing, Ltd., 2008, pp.100-101.
- [16] A. Yuvaniyama, Managing problem soils in northeast Thailand, in: S.P. Kam, C.T. Hoanh,

- G. Trebuil, B. Hardy (Eds.), Natural Resource Management Issues in the Korat Basin of Northeast Thailand: An Overview, IRRI Limited Proceedings No. 7, 2001, pp. 147-156.
- [17] D. Wichelns, An economic model of waterlogging and salinization in arid regions, *Ecol. Econ*, 1999, 30:p.475-491.
- [18] B. Li, Z.C. Wang, Z.G. Sun, et al, Resources and sustainable resource exploitation of salinized land in China, *Agricultural Research in the Arid Areas*, 2005, 23:p.154-158.
- [19] A. Lakhdar, et al., Effectiveness of compost use in salt-affected soil. *J Hazard Mater*, 2009, 171(1-3):p.29-37.
- [20] M. Tejada, et al., Use of organic amendment as a strategy for saline soil remediation: Influence on the physical, chemical and biological properties of soil. *Soil Biology and Biochemistry*, 2006, 38(6):p.1413-1421.
- [21] K.C. Ravindran, et al., Restoration of saline land by halophytes for Indian soils. *Soil Biology and Biochemistry*, 2007, 39(10):p.2661-2664.
- [22] E.G. Barrett-Lennard, Restoration of saline land through revegetation. *Agricultural Water Management*, 2002, 53: p.213-226.
- [23] P. Johnson-Green, N.C. Kenkel, T. Booth, Soil salinity and arbuscular mycorrhizal colonization of *Puccinellia nuttalliana*. *Mycological Research*, 2001, 105:p.1094-1100.
- [24] P.H. Thrall, L.M. Broadhurst, M.S. Hoque, et al., Diversity and salt tolerance of native *Acacia* rhizobia isolated from saline and non-saline soils. *Austral Ecology*, 2009, 34:p.950-963.
- [25] J Yang, F Wang, L Fang, T Tan, The effects of aging tests on a novel chemical sand-fixing agent-Polyaspartic acid. *Compos. Sci. Technol*, 2007, 67 (10):p. 2160-2164.
- [26] J Yang, H Cao, F Wang, T Tan, Application and appreciation of chemical sand fixing agent-poly (aspartic acid) and its composites. *Environ. Pollut*, 2007, 150 (3):p.381-384.
- [27] J Liu, B Shi, Y Lu, H Jiang, et al., Effectiveness of a new organic polymer sand-fixing agent on sand fixation. *Environ. Earth Sci*, 2011, 65 (3):p. 589-595.
- [28] S.M. Lahalih, N. Ahmed, Effect of new soil stabilizers on the compressive strength of dune sand. *Constr. Build. Mater*, 1998, 12 (6-7):p.321-328.
- [29] Y Wang, J Liu, Use of polyurethane foams complex material to preserve moisture and fertility. *Polym. Plast. Technol. Eng*, 2007, 46 (10):p.943-947.

- [30] W. Gao, Z. Wu, Study of Mechanism of the W-OH Sand Fixation. *Journal of Environmental Protection*, 2012, 3(9):p.1025-1033.
- [31] C. Heldmann, et al., Influence of nonionic emulsifiers on the properties of vinyl acetate/VeoVa10® and vinyl acetate/ethylene emulsions and paints. *Progress in Organic Coatings*, 1999, 35:p.69-77.
- [32] X. Meng, et al., Synthesis and Sand-Fixing Property of Cationic Poly (Vinyl Acetate-Butyl Acrylate-DMC) Copolymer Emulsions. *Polymer-Plastics Technology and Engineering*, 2013, 52:p.931-939.
- [33] J.L. Chai, J.R. Zhao, Y.H. Gao, X.D. Yang, et al., Studies on the phase behavior of the microemulsions formed by sodium dodecyl sulfonate sodium dodecyl sulfate and sodium dodecyl benzene sulfonate with a novel fishlike phase diagram. *Colloids Surf A*, 2007, 302:p.31-35.
- [34] J.L. SALAGER, et al., Optimum Formulation of Surfactant/Water/Oil Systems for Minimum Interfacial Tension or Phase Behavior. *SPEJ*, 1979, 19:p.107-115.
- [35] D. Wei, et al., Adsorption Performance of Series Alkyl Aryl Sulfonates on Oil Sand of Daqing Oilfield. *ACTA PETROLEI SINICA (PETROLEUM PROCESSING SECTION)*, 2012, 28(5):p.834-839.
- [36] M.J. Rosen, et al., Systematic analysis of surface-active agents. 2d ed, 1972: p.353.
- [37] A.K. Mathur, C.B. Majumder, S. Chatterjee, Combined removal of BTEX in air stream by using mixture of sugar cane bagasse, compost and GAC as biofilter media. *J. Hazard. Mater.*, 2007, 148:p.64-67.
- [38] T.M.S. Lima, L.C. Procópio, et al., Evaluation of bacterial surfactant toxicity towards petroleum degrading microorganisms. *Bioresour. Technol*, 2011, 102:p.2957-2964.
- [39] R.L. Cash, et al., Model Crude Oils for Low Interfacial Tension. *SEP*, 1978, 5813.
- [40] M. Roshanfekr, R.T. Johns, Prediction of optimum salinity and solubilization ratio for microemulsion phase behavior with live crude at reservoir pressure. *Fluid Phase Equilib*, 2011, 304:p.52-60.
- [41] L. Chen, et al., Middle-phase microemulsion induced by brine in region of low cationic Gemini surfactant content. *Colloids Surf A*, 2007, 305:p.29-35.
- [42] A. Bera, K. Ojha, T. Kumar, A. Mandal, Phase behavior and physicochemical properties of

- (sodium dodecyl sulfate/brine/propan-1-ol/heptane) microemulsions. *J Chem Eng Data*, 2012, 57:p.1000-1006.
- [43] Q. Li, T. Li, J. Wu, Water solubilization capacity and conductance behaviors of AOT and NaDEHP systems in the presence of additives. *Colloids Surf A*, 2002, 197:p.101-109.
- [44] J.J. Sheng, Optimum phase type and optimum salinity profile in surfactant flooding. *J Pet Sci Eng*, 2010, 75:p.143-153.
- [45] I. Langmuir, The constitution and fundamental properties of solids and liquids: Part I. Solids, *J. Am. Chem. Soc*, 1916, 38:p. 2221-2295.
- [46] M.M. Ayad, A.A. El-Nasr, Adsorption of cationic dye (Methylene Blue) from water using polyanilines nanotubes base. *J. Phys. Chem. C*, 2010, 114:p.14377-4383.
- [47] B. Samiey, M. Dargahi, Kinetics and thermodynamics of adsorption of Congo red on cellulose. *Central Eur. J. Chem*, 2010, 8:p.906-912.
- [48] A. Bera, T. Kumar, K. Ojha, A. Mandal, Screening of microemulsion properties for application in enhanced oil recovery. *Fuel*, 2014, 121:p.198-207.
- [49] A. Bera, T. Kumar, K. Ojha, A. Mandal, Adsorption of surfactants on sand surface in enhanced oil recovery: Isotherms, kinetics and thermodynamic studies. *Appl Surf Sci*, 2013, 284:p.87-99.
- [50] A.V. Pethkar, K.M. Paknikar, Recovery of gold from solution using *Cladosporioides* biomass beads. *J. Biotech*, 1998, 63:p.211-220.