Streaming Potential Measurements on the Binary Mixture Triethylamine-Water Near the Demixing Phase Transition

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Large density fluctuations developing near the phase transition point of the binary mixture affect physical parameters directly related to the electrokinetic coupling coefficient. Here the first electrokinetic measurements for a porous rock sample are carried out with a critical binary mixture of triethylamine-water, especially around the phase transition point. From the measured streaming potential coefficient, the zeta potential is obtained for the critical composition. The results show that there is no anomaly in the streaming potential coefficient as the temperature approaches the demixing temperature. It is also seen that the streaming potential coefficient and the zeta potential in magnitude decreases with increasing temperature. This observation is opposite to what has been observed in literature. It means that the properties of the electric double layer for the mixtures are different from those for aqueous electrolytes. Additionally, the zeta potential for the critical composition is predicted to fluctuate around the critical point.

1. Introduction

Electrokinetic phenomena are induced by the relative motion between a fluid and a solid surface and are directly related to the existence of an electric double layer between the fluid and the solid grain surface. Electrokinetic phenomena consist of several different effects such as streaming potential, electroosmosis, and electrophoresis. Of electrokinetic phenomena, streaming potential effect plays an important role in geophysical applications. For example, streaming potential could be used to map subsurface flow and detect subsurface flow patterns in oil reservoirs (e.g., [1, 2]), geothermal areas, and volcanoes (e.g., [3–5]). It has also been proposed to use the streaming potential monitoring to detect at distance the propagation of a water front in a reservoir [6]. Monitoring of streaming potential anomalies has been proposed as a means of predicting earthquakes (e.g., [7, 8]). Most experimental measurements of streaming potential in porous media have been performed with electrolyte aqueous solutions (e.g., [9–13]). However, in reality the liquids found underground can be a complicated mixture of water, crude oil, and gas. It should be noted that at a certain condition (high temperature and high pressure), oil and water can mix together. Hence, studying electrokinetics or streaming potential with liquid mixtures may be relevant in oil recovery. The effect of the compositions on the electrokinetic phenomena happening in some liquid mixtures has been reported in the literature. For example, the influences of the compositions on the electrophoresis [14, 15], on the electroosmosis [16, 17], and on the streaming potential [16] have been carried out with liquid mixtures such as methanol-water, ethanol-water, 2-propanol-water, 1-propanol-water, methanol-acetone-water, alcohol-water, and acetone-water. Additionally, the impact of reactive mixing of fluids with different chemical compositions in the subsurface on the resulting effective electrical conductivity that is observed to significantly change over several orders of magnitudes in comparison with the background solution is proposed in [18]. Consequently, it is inferred from those studies that the compositions of the mixtures affect the electrokinetic coupling coefficients. The changes of the electrokinetic coupling coefficients have been explained by both the change of the characteristic parameters of the
mixtures (the electrical conductivity, viscosity, density, and dielectric constant) and the variation of the zeta potential with compositions.

However, to the best of our knowledge the streaming potential measurement in binary mixtures near a demixing phase transition in a porous system has not yet been studied. The transition from the one phase solution to the two phase solution passes through an intermediate state called the spinodal decomposition, which is characterized by a solution that strongly scatters light and becomes opalescent. The reason is that close to the phase separation temperature, the scattering efficiency becomes much larger because not only the density contrast increases but also the length scale of the fluctuating regions grows and starts to match the wavelength of the scattered light [19, 20]. The temperature, corresponding to the state of maximum scattering, is plotted as a function of mass fraction, yielding a phase diagram as shown in Figure 1, for example, for the case of the lower critical solution temperature (LCST). At temperatures below LCST, the system is completely miscible in all proportions, whereas above LCST partial liquid miscibility occurs. The point (LCST) at which the curve has a zero slope is the critical point that corresponds to the critical composition and critical temperature [19]. As shown in Figure 1, the components of a mixture are miscible for all composition below the LCST point.

The motivation for this work is that large density fluctuations developing near the critical point of the binary mixtures affect physical parameters directly related to streaming potential coefficient (the electrokinetic coupling coefficient in general) such as viscosity, electrical conductivity, and dielectric constant [21–23]. From those observations, we investigate how streaming potential coefficient and the zeta potential, one of the most important parameters in electrokinetics, behave near the demixing phase transition.

The streaming potential measurements in an artificial ceramic porous sample are performed with a triethylamine-water binary mixture (TEA-W). This mixture is a typical partially miscible system that has a lower critical solution temperature near room temperature at atmospheric pressure. The critical composition of the mixture is 32.1% of TEA mass fraction and critical temperature ranges from 18.24°C to 18.40°C [21, 23]. The experimental measurements are carried out in the single phase solution. Three different mass fractions of TEA (20%, 32.1%, and 70%) are used for the measurements. Based on the measured streaming potential coefficient with the knowledge of electrical conductivity, viscosity, and dielectric constant, the zeta potential is obtained for the critical composition. The results show that there is no anomaly in the streaming potential coefficient as the temperature approaches the demixing temperature for all three mass fractions of TEA. It is also seen that the streaming potential coefficient and the zeta potential in magnitude decrease with increasing temperature. This observation is opposite to what has been observed in literature for aqueous electrolytes. It means that the properties of the electric double layer for the TEA-W mixtures are different from those for aqueous electrolytes. As a consequence of the fluctuations of the viscosity and the dielectric constant of the binary mixture at the critical composition, the zeta potential is predicted to fluctuate around the critical point.

This work has four sections. In the first we briefly describe the theoretical background of streaming potential. In the second we present the experimental measurements. The third section contains the experimental results. Conclusions are provided in the final section.

2. Theoretical Background of Streaming Potential

Surfaces of the minerals of porous media are generally electrically charged, creating an electric double layer (EDL) containing an excess of charge that counterbalances the charge deficiency of the mineral surface (e.g., [28]). Figure 2 shows structure of the EDL: a Stern layer that contains only counterions coating the mineral with a very limited thickness and a diffuse layer that contains both counterions and coions but with a net excess charge. The shear plane that can be approximated as the limit between the Stern layer and diffuse layer separates the mobile and immobile part of the water molecules when subjected to a fluid pressure difference. The electrical potential at the shear plane is called the zeta potential (ζ). The zeta potential is a complicated function of many parameters such as mineral composition of porous media, ionic species present in the fluid, the pH of fluid, fluid electrical conductivity, and temperature (see [29, 30] for more details). In the bulk liquid, the numbers of cations and anions are equal so that it is electrically neutral. Most reservoir rocks have a negative surface charge and a negative zeta potential when they are in contact with ground water.

The streaming current is generated by the relative movement of the diffuse layer with the solid surface due to a fluid pressure difference over the capillary (a porous medium...
Figure 2: Stern model (see [25–27] for more details) for the charge and electric potential distribution in the electric double layer at a solid-liquid interface. In this figure, the solid surface is negatively charged and the mobile counter-ions in the diffuse layer are positively charged.

Figure 3: Development of streaming potential when an electrolyte is pumped through a capillary (a porous medium is made of an array of capillaries).

can be considered as a bundle of capillaries). This streaming current is balanced by a conduction current, leading to the streaming potential (Figure 3). In a fluid saturated porous medium, the electric current density and the fluid flux are coupled, so fluids moving through porous media generate a streaming potential [31] (Figure 4). The streaming potential increases linearly with the fluid pressure difference that drives the fluid flow, provided that the flow remains laminar [11]. The streaming potential coefficient (SPC) is defined when the total current density is zero as (e.g., [27, 32])

\[ C_S = \frac{\Delta V}{\Delta P} = \frac{\varepsilon_r \varepsilon_0 \zeta}{\eta \sigma_{eff}}, \]  

where \( \Delta V \) is the streaming potential, \( \Delta P \) is the fluid pressure difference, \( \varepsilon_r \) is the relative permittivity of the fluid, \( \varepsilon_0 \) is the dielectric permittivity in vacuum, \( \eta \) is the dynamic viscosity of the fluid, \( \sigma_{eff} \) is the effective conductivity, and \( \zeta \) is the zeta potential. The effective conductivity includes the fluid conductivity and the surface conductivity. The SPC can also be written as [33, 34]

\[ C_S = \frac{\varepsilon_r \varepsilon_0 \zeta}{\eta \sigma_f}, \]  

where \( \sigma_f \) is the electrical conductivity of the sample saturated by a fluid with a conductivity \( \sigma_f \) and \( F \) is the formation factor. The electrical conductivity of the sample can possibly include surface conductivity. If the fluid conductivity is much higher than the surface conductivity, one has \( \sigma_{eff} = \sigma_f \). Equation (1) is rewritten as

\[ C_S = \frac{\varepsilon_r \varepsilon_0 \zeta}{\eta \sigma_f}. \]  

3. Experiments

The triethylamine (TEA) is purchased from VWR (Merck). The purity is stated to be 99.95%. The TEA is used without further purification. The water used in this work is deionized water. All mixtures are prepared from weighed amounts of the pure components. Besides the critical composition of 32.1% mass fraction, two other mass fractions of 20% and 70% are also used in our work. The porous sample is a cylindrical artificial rock made of alumina (72%) and fused silica (28%) from HP Technical Ceramics (55 mm in length and 25 mm in diameter). The microstructure properties of the sample have been reported in [35, 36] for the sample labeled DP217: the permeability of 370 mD, the porosity of 45.4%, the solid density of 3652 kg/m³, and the formation factor of 4.5.

The experimental setup for the streaming potential measurement is similar to that described in [35–37] (see Figure 5). To control temperature of the mixture, the core holder
\( \Delta V = V_{P1} - V_{P2} \) is the streaming potential and \( \Delta P = P_{P1} - P_{P2} \) is the fluid pressure difference.

Figure 4: Schematic illustration of streaming potential measurement when an electrolyte is pumped through a porous medium. The pressure transducer is labeled as \( \text{Pressure transducer} \) and the multimeter as \( \text{Multimeter} \).

Figure 5: Experimental setup for streaming potential measurements described in [35, 36]. (1) Core holder; (2) Ag/AgCl electrodes; (3) pump; (4) pressure transducer; (5) solution container.

(Figure 6) and the solution container, in which TEA and water have been mixed together, are immersed in a thermally stabilized water bath (Thermo Fisher Scientific SCi150 and A25). The sample is surrounded by a conical Teflon sleeve inserted into a Teflon cell as shown in Figure 6. By tightly twisting the chambers over the Teflon cell, the fluid can be prevented from flowing along the interface of the sample. The chambers on both sides are made of perspex and are transparent to check whether there is a phase transition around the critical temperature or not (the solution becomes opalescent). Rubber is not used in the experimental setup because it is attacked by TEA. A whole experimental setup is placed in a laboratory fume hood to prevent the terrible smell of triethylamine.

The solution is circulated through the sample until the electrical conductivity of the mixture reaches a stable value. The pressure differences across the sample are created by the high pressure pump (LabHut Series III-Pump) and measured by the pressure transducer (Endress and Hauser Deltabar S PMD75). Electrical potentials across the sample are then measured by a high input impedance multimeter (Keithley Model 2700) using two Ag/AgCl wire electrodes. The input resistance of the multimeter is larger than 10 GΩ. The resistance of the samples is usually smaller than 250 kΩ, which is low compared to input resistance of the multimeter, therefore allowing accurate measurements of electric potentials. The LabVIEW program averages the value of electrical potentials. The Ag/AgCl electrodes are made of electrolysis of a wire of clean silver from VWR company in 0.1 M NaCl with an electrical current of 20 mA and in 2 minutes (for more details, see [27]). The electrodes are covered by heat shrinkable Teflon tubes, and their tips are put in the vicinity of the end faces of the sample but not within the liquid circulation to avoid the electrical noise from liquid movement around the electrodes [33].

4. Results and Discussion

The experimental measurements are carried out in the single phase solution. The solution container is firstly cooled down to 10°C and stirred; a single phase solution is formed in the container. The container is then slowly heated up until the entire volume of the solutions becomes white and the opalescence is easily visible due to strong light scattering. The critical temperature for the 32.1% composition is visually identified to be 20.2°C in our measurements when the opalescence is well developed in the glass container that can be seen through. The critical temperature is shifted to a higher value compared to the known critical temperature \( T_c = 18.4°C \) [21] or \( 18.242°C < T_c < 18.253°C \) [23]. The reasons for this discrepancy are likely the impurities (e.g., CO₂, H₂O) of the mixtures, the dissolution of mineral substances of the sample, and the ability of the strongly basic triethylamine to attack glass as mentioned in [19]. Using the same procedure to obtain the demixing temperatures (\( T_{demix} \)) for two other mass fractions, we obtain the \( T_{demix} \) of 21°C and 19°C for the mass fractions of TEA of 20% and 70%, respectively.

The way used to collect the SPC is similar to that described in [35, 36]. Figure 7 shows an example of the electric potential as a function the pressure difference across the sample for the 32.1% mass fraction at 10°C. From that graph, the SPC as the slope of the straight line is obtained. To see how the SPC and the zeta potential behave around the phase transition point, temperature is scanned from 10°C.
Figure 7: Streaming potential as a function of pressure difference for the 32.1% mass fraction at 10°C. The symbols are the measured data. The solid line is the linear fit.

Figure 8: Streaming potential coefficient as a function of temperature at 3 different mass fractions of TEA (20%, 32.1%, and 70% mass). The symbols are the measured data. The solid lines are the fitting ones.

Figure 9: The variation of the streaming potential coefficient with temperature for NaCl electrolyte only at $5 \times 10^{-3}$ M obtained from [35].

Figure 10: Electrical conductivity of the mixture as a function of temperature at the critical composition (32.1%). The square symbols are the measured data and the solid line is the fitting one from (4) with the parameters $A = 0.37$ mS/cm, $B = 102.0 K^{-1}$, and $T_g = 241.0 K$.

measured result in this work is opposite to what has been reported for the same sample with NaCl electrolyte only. It suggests that there is a variation in the properties of the EDL between using the TEA-W mixture and using aqueous electrolytes. The result also shows that there is no anomaly of the SPC when temperature approaches the $T_{demix}$ for three mass fractions of TEA.

In order to calculate the zeta potential from the measured SPC at the critical composition, for example, one needs to know the electrical conductivity, viscosity, and dielectric constant of the mixture. Due to the availability of the viscosity and dielectric constant of the mixture in literature, the zeta potential is only obtained for the critical composition (32.1%).

The SPC as a function of temperature in one phase solution for three different mass fractions of TEA is shown in Figure 8. It should be noted that the separation between mixed and demixed mixtures is roughly indicated by a faint line for clarity in Figure 8. It is seen that the SPC in magnitude decreases with increasing temperature. To remove the electric potential disturbance of the solid particle or noise from the setup itself, the variation of the SPC with temperature for NaCl electrolyte only at $5 \times 10^{-3}$ M has been reported in [35] for the same sample is indicated in Figure 9. It is seen that the SPC in magnitude increases with increasing temperature for NaCl electrolyte only, which is in good agreement with those normally observed for aqueous electrolyte-rock systems (e.g., [26, 38]). Consequently, the
The binary mixtures used in our work with temperature, in particular near the demixing phase transition, are not yet measured due to the limitations of experimental condition and equipment. Therefore, we use temperature dependence of viscosity and dielectric constant reported in literature [21, 23, 39] on the well defined mixtures to obtain the zeta potential.

To predict how the zeta potential varies near the demixing phase transition point for the well defined mixture at critical composition, we assume that the SPC and the electrical conductivity for the well defined mixture behave similarly to those observed in this work (see Figures 8 and 10). By fitting the experimental data shown in Figures 8 and 10 (see solid lines), the relationship between the SPC and the electrical conductivity against temperature for the critical composition of the well defined mixture is obtained. With the knowledge of viscosity and dielectric constant obtained from [21, 23, 39], the zeta potential as a function of temperature is obtained using (3) and shown in Figure 13 (because the electrical conductivity of TEA-W mixture is always larger than 0.30 S/m as shown in Figure 10, the surface conductance is ignored as reported in [36] for the ceramic artificial rock).

The result predicts that zeta potential at the critical composition (32.1%) behaves differently around the critical point if the viscosity and dielectric constant follow what has been reported in [21, 23, 39]. To better understand the behavior of the zeta potential, additional studies on the variation of the viscosity and dielectric constant of the own binary mixtures used in this work with temperature need to be performed. It is also seen that the magnitude of the zeta potential decreases with increasing temperature. That is opposite to what has been observed in our earlier work [26, 35, 38] in which the zeta potential in magnitude increases temperature for aqueous electrolytes. It means that the TEA-W binary mixtures may change the properties of the electric double layer compared to normal aqueous electrolytes.

5. Conclusions

The streaming potential measurements for a porous sample saturated with a binary mixture of triethylamine-water with three different mass fractions have been carried out. From the measured SPC, the variation of the zeta potential with
temperature in single phase solution is predicted for the critical composition. The results show that there is no anomaly in the SPC as the temperature approaches the demixing temperatures for all three mass fractions of TEA. It is also seen that the streaming potential coefficient and the zeta potential in magnitude decrease with increasing temperature. This observation is opposite to what has been observed in literature for aqueous solutions. It means that the properties of the electric double layer for the TEA-W mixtures are different from those for aqueous electrolytes. The zeta potential for the critical composition is predicted to fluctuate around the critical point. To verify the behavior of the SPC and the zeta potential near the critical phase transition, the viscosity and dielectric constant of the own binary mixtures used in this work need to be measured as a function of temperature. In addition to the measurements of the viscosity and dielectric constant, the TEA-W mixtures need to be degassed by the Freeze-Pump-Thaw technique [40] and protected from the atmosphere. To remove the effect of temperature, few more different ionic strengths of electrolyte mixed with TEA may be performed in our proposed future work. This work, along with the conductivity and viscosity measurements from [21, 22], the dielectric constant measurement from [23], the refractive index measurement from [41], and the mass density measurement from [42], creates a better understanding of the critical behavior of TEA-W binary mixtures near the demixing phase transition.

Data Availability
The data used to support the findings of this study are included within the article.

Conflicts of Interest
The authors declare that there are no conflicts of interest regarding the publication of this paper.

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