Chapter 6

Streaming potential measurements on the binary mixture Triethylamine - water near the demixing phase transition

6.1 Introduction

In previous chapters, electrolyte aqueous solutions have been used for the streaming potential and electroosmosis measurements. 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 [90]. Therefore, it is worthwhile studying electrokinetic phenomena in liquid mixtures. The effect of the compositions on the electrokinetic phenomena happening in some liquid mixtures have been reported in the literature. For example, the influences of the compositions on the electrophoresis [91, 92], on the electroosmosis [93, 94], and on the streaming potential [93] 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. The results of those studies have shown that the compositions of the mixtures affect the electrokinetic coupling coefficient. The changes of the electrokinetic coupling coefficient 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.

In this chapter, we study the SPCC in binary mixtures near a demixing phase transition in a porous system that 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 [95, 96]. The temperature, corresponding to the state of maximum scattering, is plotted as a function of mass fraction, yielding a phase diagram as shown in Fig. 6.1, for example for the case of the lower critical solution temperature. The point (LCST) at which the curve has a zero slope is the critical point that corresponds to the critical composition and critical temperature [95]. As shown in Fig. 6.1, the components of a mixture are miscible for all compositions below the LCST point.

The motivation for this chapter is that large density fluctuations developing near the critical point of the binary mixtures affect many physical parameters directly related to the electrokinetic coupling coefficient such as the viscosity, electrical conductivity and dielectric constant [97–99]. From those observations, we would like to investigate whether the properties of the electric double layer between grain surface and the mixtures and the Debye length behave differently near the demixing phase transition.
We perform the streaming potential measurements with the Triethylamine-water binary mixture (TEA-W) using an artificial ceramic porous sample. This mixture is a typical partially miscible system that has a lower critical solution temperature near room temperature at atmospheric pressure. The critical composition and critical temperature of the mixture are \( C_c = 32.1 \% \) of TEA mass fraction and \( 18.24^\circ C < T_c < 18.40^\circ C \), respectively [97, 99]. Three different mass fractions of TEA (20\%, 32.1\% and 70\%) are used for the measurements. Based on the measured streaming potential coupling coefficient (SPCC) with the knowledge of the electrical conductivity, viscosity and dielectric constant, the zeta potentials are obtained.

This chapter includes four sections. Section 6.2 presents the experimental setup, materials and procedures for collecting experimental data. Section 6.3 contains the experimental results and discussion. Conclusions are provided in Section 6.4.

### 6.2 Experiments

#### 6.2.1 Setup

The experimental setup for the measurement of the streaming potential is similar as described in chapter 4 for measuring the SPCC as a function of temperature. To control temperature of the mixture, the core holder (see Fig. 6.2) and the
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solution container in which a mixture of TEA and water has been mixed together is immersed in a thermally stabilized water bath (Thermo Fisher Scientific SC150 and A25). The sample in the core holder is surrounded by a conical teflon sleeve inserted into a teflon cell as shown in Fig. 6.2. By tightly twisting the caps, the fluid can be prevented to flow along the interface of the sample. Rubber seals are not used in the setup because TEA dissolves rubber.

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). The electrical potential difference across the sample is measured by two Ag/AgCl wire electrodes. The Ag/AgCl electrodes are made by electrolysis of a wire of clean silver from VWR company in 0.1M NaCl with an electrical current of 20 mA and in 2 minutes [3]. The electrodes are covered by heat shrinkable teflon tubings and their tips are put in the vicinity of each face of the sample but not within the liquid circulation to avoid the electrical noise from liquid movement around the electrodes [36]. The way used to obtain the SPCC as a function of temperature is described in chapter 4.

6.2.2 Materials

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 (32.1% mass fraction of TEA), two other mass fractions (20% and 70%) are also used for the measurements. It should be noted that the mixture of TEA and water used in this chapter may be not really clean because of mineral substances of the sample that may dissolve in the mixture or impurities (e.g., CO₂, H₂O) of the mixtures. Therefore, 32.1% mass fraction of TEA may not exactly be the critical composition as stated in literature, for example in [97–99].

The porous sample is a cylindrical artificial core made of alumina (72%) and fused silica (28%) from HP Technical Ceramics (55 mm in length and 25mm in diameter). The properties of the sample have been reported in Table 3.1 for the one 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.
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6.3 Results and discussion

The experimental measurements are carried out in the single phase in the neighborhood of the demixing phase transition temperature and relatively far from this temperature. The transition temperature for the 32.1% composition is visually identified to be 20.2°C in our laboratory when the opalescence is well developed in the glass container that can be seen through. If the mixture is 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 is shifted to a higher value compared to the known critical temperature $T_c = 18.4^\circ C$ [97] or $18.242^\circ C < T_c < 18.253^\circ C$ [99]. The reason for this discrepancy is likely due to impurities (e.g., CO$_2$, H$_2$O) of the mixtures and the ability of the strongly basic triethylamine to attack glass [95]. Using the same procedure to obtain the demixing temperatures ($T_{demix}$) for two other mass fractions, we get the $T_{demix}$ of 21°C and 19°C for the mass fractions of 20% and 70%, respectively.

To see how the SPCC and the zeta potential behave around the phase transition point, temperature is scanned from 10°C to $T_{demix}$ (21°C, 20.2°C and 19°C for the mass fractions of 20%, 32.1% and 70%, respectively). If temperature was raised higher than the $T_{demix}$, the solution pumped through the sample would be either TEA or water rather than the mixture due to the phase separation. The separation between mixed and demixed mixtures is roughly indicated by the faint lines as shown in Fig. 6.3 and Fig. 6.4.
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The SPCC as a function of temperature in one phase solution at 3 different mass fractions of TEA is shown in Fig. 6.3 by the points. It is seen that the SPCC in magnitude decreases with increasing temperature. This observation is opposite to what has been observed in our earlier work (see chapter 4) for the same sample (DP217) but with the NaCl solution in which the SPCC increases with increasing temperature. It suggests that there is a difference in the properties of the EDL between using the TEA-W mixture and using the NaCl solution. Fig. 6.3 also shows that there seems to be no an anomaly of the SPCC when temperature approaches the $T_{\text{demaix}}$.

In order to calculate the zeta potential from the measured SPCC, one needs to know the electrical conductivity, viscosity and dielectric constant of the mixtures. The electrical conductivity of the mixtures as a function of temperature is directly measured by the conductivity meter (Consort C861) and is shown in Fig. 6.4 by the points. It shows that the electrical conductivity of the binary mixture increases with increasing temperature as expected in [100] in which the relationship between the electrical conductivity and temperature is given by Vogel-Fulcher-Tammann (VFT) equation

$$\sigma = A \exp\left(-\frac{B}{T - T_g}\right),$$

(6.1)

where $A$, $B$ and $T_g$ are fitting parameters. By fitting the experimental data to eq. (6.1), the values of the parameters $A$, $B$ and $T_g$ at 3 different mass fractions of TEA (20%, 32.1% and 70%) are found to be 0.42 mS/cm, 78.0$K^{-1}$, 238.0K; 0.37mS/cm, 102.0$K^{-1}$, 241.0K and 0.04mS/cm, 68.0$K^{-1}$, 249.5K, respectively.

According to [100], close to the demixing temperature the electrical conductivity deviates slightly from the regular VFT behavior. This deviation becomes bigger.
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When the temperature of the mixture approaches the demixing temperature, however, the deviation of the electrical conductivity from the regular VFT behavior is not really clear around the demixing point as observed in \cite{100}. Therefore, we use the VFT equation only to relate the electrical conductivity of binary fluid mixtures to temperature in the single phase region \((T \leq T_{\text{demix}})\) as shown in Fig. 6.4 (the solid lines).

Temperature dependence of viscosity of the binary mixtures in the single phase has been experimentally measured at 3 different mass fractions of TEA (20%, 32.1% and 70%) in the works of \cite{97, 100} for the clean mixtures as shown in Fig. 6.5. It is shown that when the temperature approaches the critical temperature \((T_C)\), the critical fluctuations cause a further increase of the viscosity for the critical composition (32.1%). It is also seen that viscosity is maximum at a critical composition (32.1%) of three mass fractions of TEA. That could be explained by the model suggested by \cite{101} in which the viscosity of the liquid mixtures at a given temperature can be calculated by

\[
\ln \eta = w_1 \ln \eta_1 + w_2 \ln \eta_2 + w_1 w_2 G_{12},
\]

where \(w_1, w_2, \eta_1\) and \(\eta_2\) are mass fraction of TEA, mass fraction of water, viscosity of TEA and viscosity of water, respectively. \(G_{12}\) is a parameter depending on temperature. For example, \(G_{12} = 9.01\) at 10°C (see \cite{101}). From eq. (6.2) the variation of the viscosity versus TEA mass fraction for Triethylamine (1) + water (2) mixture at 10°C is shown in Fig. 6.6.

The dielectric constant as a function of temperature in the single phase region...
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Figure 6.6: The variation of the viscosity versus TEA mass fraction for Triethylamine (1) + water (2) mixture at 10°C, \( G_{12} = 9.01 \) (see [101]).

of the binary mixture for the critical composition has been reported by [99]. By extrapolating the experimental data of [99], the temperature dependence of dielectric constant of the mixture at the critical composition is shown in Fig. 6.7. The result shows that the dielectric constant fluctuates near the critical point.

Since the dielectric constants of the binary mixtures at the other two mass fractions (20% and 70%) are not yet available in literatures, we use a parallel plate copper capacitor to measure them. When the plate capacitor is gradually immersed, the capacitance changes in proportion to the depth by which the plates are immersed into the dielectric liquid. Fig. 6.8 shows the capacitance against the depth for TEA only and 70% mass fraction of TEA at 10°C. From the slopes of the straight lines, the dielectric constants of TEA only and 70% mass fraction of TEA are determined to be 16.2 and 2.6, respectively. The dielectric constant of 2.6 for TEA only is in good agreement with that mentioned in [54] (2.42). That shows the validity of the dielectric constant measurement. For 20% mass fraction of TEA, the electrical conductivity of the mixture is too high to measure the dielectric constant for our setup. We approximately use the dielectric constant of water (80) for the mixture of 20% mass fraction of TEA. According to [54], the dielectric constants of TEA only and water change only 0.8% in the temperature range 10°C to 21°C. We therefore assume that the dielectric constants are constant over temperature for the purpose of calculating the zeta potential.

Because the binary mixtures that we use for the measurements may be different from those used in the works of [97, 100] and [99] due to the impurities. This is indicated by the shift of \( T_C \) to higher temperatures at the nominal critical composition of 32.1%. The variations of viscosity and dielectric constant of the
Figure 6.7: Temperature dependence of the dielectric constant of the binary mixture at a critical composition obtained from the experimental data of [99]. The dash line is the one connecting the experimental points.

Figure 6.8: Capacitance against depth of the capacitor that are dipped in the binary mixture of TEA only and 70% mass fraction of TEA

binary mixtures used in the measurements against temperature, in particular near the demixing phase transition are currently still unknown and needs additional measurements. Therefore, the zeta potential can not be calculated using our experimental data.

However, if the clean binary mixtures were used, temperature dependence of viscosity and dielectric constant would follow experimental data of [97, 100] and [99], respectively. To see how the zeta potential varies near the demixing phase transition for the clean mixtures, we assume that there is also the same behaviors for the SPCC and the electrical conductivity for the clean mixtures near the demixing phase transition as observed for the binary mixtures we use for the measurements (see Fig. 6.3 and Fig. 6.4). To simplify the calculation of the zeta potential in the studied range of temperature, the surface conductance is ignored and thus
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Figure 6.9: The prediction of the zeta potential as a function of temperature at three different mass fractions of TEA for clean binary mixtures. The dash lines are the ones connecting the experimental points.

the zeta potential is calculated using eq. (1.2). By fitting the experimental data shown in Fig. 6.3 and Fig. 6.4 (see solid lines), the relationship between the SPCC and the electrical conductivity against temperature at three different mass fractions of clean mixtures are obtained. With the knowledge of viscosity and dielectric constant obtained from [97, 100] and [99], the zeta potential as a function of temperature at three different mass fractions is obtained and shown in Fig. 6.9.

The prediction shows that zeta potential at the critical composition (32.1%) for clean mixture may behave differently around the critical point if the viscosity and dielectric constant follow what has been measured in [97, 100] and [99]. However, it seems that there is no an anomaly happening around the demixing point for the other two mass fractions. Absolute values of the zeta potential decreases with increasing temperature. That is opposite to what has been observed in our earlier work (see chapter 4) in which the zeta potential increases with increasing temperature for the NaCl solution. It means that the TEA-W binary mixtures change the properties of the electric double layer and the zeta potential compared to normal aqueous electrolytes. Fig. 6.9 also shows that the zeta potential varies with compositions of the mixtures as observed [91–94] for liquid mixtures such as methanol-water, ethanol-water, 2-propanol-water, 1-propanol-water, methanol-acetone-water, alcohol-water and acetone-water.

6.4 Conclusions

The streaming potential measurements for the porous material saturated with a binary mixture of triethylamine-water with three different mass fractions have
been carried out. The results show that there is no anomaly in the SPCC as the temperature approaches the demixing temperature for the 32.1%. As a consequence of the fluctuations of the viscosity and the dielectric constant of the clean binary mixture at a critical composition, the zeta potential is predicted to fluctuate around the critical point. However, it does not happen to the other two mass fractions (20% and 70% mass). To verify the behavior of the SPCC and the zeta potential near the critical phase transition, the viscosity and dielectric constant of the own binary mixtures used in the SPCC measurements need to be measured as a function of temperature. Besides the measurements of the viscosity and dielectric constant, the TEA-W mixtures needs to be degassed by the Freeze-Pump-Thaw technique [102] and protected from the atmosphere.

The results also show that the TEA-W binary mixtures change the behaviors of the electric double layer compared to electrolytic solutions such as NaCl or KCl and the zeta potential varies with compositions of the mixtures. This work, along with the conductivity and viscosity results from [97, 98], the dielectric constant results from [99], the refractive index results from [103] and the mass density results from [104] create a better understanding of the critical behavior of TEA-W binary mixtures near the demixing phase transition.