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Experimental Investigations on the Thermophysical Properties of Synthetic Geothermal Fluids

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ABSTRACT

Due to their often very high salt content, the thermophysical properties of geothermal fluids may differ significantly from those of pure water. Therefore, it is of crucial importance for the sustainable design of geothermal power plants to know these properties as exactly as possible. Based on fluids of the North German Basin which are dominated by sodium chloride and calcium chloride, an integrated laboratory study is conducted at GFZ-Potsdam. This study ultimately aims at closing existing data gaps by means of systematic measurements at relevant p-T-conditions. Additionally, suitable site-independent mixing rules are to be found to predict the thermophysical behaviour of a site-specific saline fluid by composition only. Sodium chloride and calcium chloride solutions and mixtures of both serve as a synthetic analogue for this type of geothermal fluid. For this geothermal setting, the thermophysical parameters density, viscosity, electrical and thermal conductivity as well as specific heat and sonic velocity have to be determined systematically in the range between 0 mol·kg^{-1} to saturation, up to 150°C and 450 bars with respect to different mixing ratios of the salts.

In this laboratory study, density, viscosity and electrical conductivity of solutions of sodium chloride, calcium chloride and their mixture were obtained at atmospheric pressure between 20°C and 80°C.

1. INTRODUCTION

In the course of the German energy transition, regenerative energy sources are being researched. These sources of energy should be operated in a sustainable, predictable and economical way. For geothermal energy, this means a low exploration risk and an optimal design of the geothermal cycle. Its operation is much more effective when the whole system is designed according to the site-specific conditions. A key element in the geothermal cycle is the fluid. This serves both as a transport medium and supplies the heat energy. Therefore, it is important to know the properties of the fluid as accurately as possible.

The presented laboratory study relates to the research platform Groß Schönebeck, Germany. At this site operated by GFZ-Potsdam, the value of total dissolved solids (TDS) in the geothermal fluid is 265 g/L. In a depth of 4300 m, the fluid has a temperature of 150°C at about 450 bar (Huenges et al. 2002). When the fluid is pumped out of the borehole, pressure and temperature decrease. At the surface prior to reinjection, the fluid has a temperature of 70°C at 10 bar.

The geothermal fluids within the North East German Basin differ in total molality and salt ratio depending on the specific site. The main solutes are predominantly sodium chloride and calcium chloride. Due to their high proportion in the total molality, these salts determine the physical properties significantly.

Different salt concentrations cause differences in density and viscosity. Combined with changes in temperature and pressure, dramatic impacts on the production efficiency of a geothermal power plant may be caused. In consequence, this may lead to closedown of plant operation and may cause enormous economic damage. Systematic investigations of the properties of the geothermal fluid as a function of pressure, temperature and composition are therefore essential for an understanding of the processes involved and to avoid disruptions in plant operation.

Accurate fluid data are also essential for previews by modelling and simulations. So far, only pure sodium chloride solutions were used as a model fluid due to a lack of existing data for mixed salt solutions of sodium chloride and calcium chloride. To illustrate the need to know the thermophysical properties of the mixed solutions exactly, two hydrothermal simulations were performed.

Figure 1 shows the geological setting at the research platform Groß Schönebeck, Germany. The doublet system extends to 4300 m depth and passes seven different geological layers. Hydraulic stimulation treatments formed several hydraulically induced fractures at the injection side, referred to as "multifrac". Along the deflected production well, there are a water and two gel-proppant fractures. The geological model used is described in detail by Blöcher et al. (2010).

A simulation run with this model illustrates the time-dependent behaviour of the reservoir under production conditions. For example, changes of pressure and temperature are calculated depending on the specified mechanical, hydraulic, thermal and chemical boundary conditions. In this case, two simulations were run with the same boundary conditions. Only density and viscosity data of the geothermal fluid were changed to point out the influence of exact fluid data on the pressure development during production.

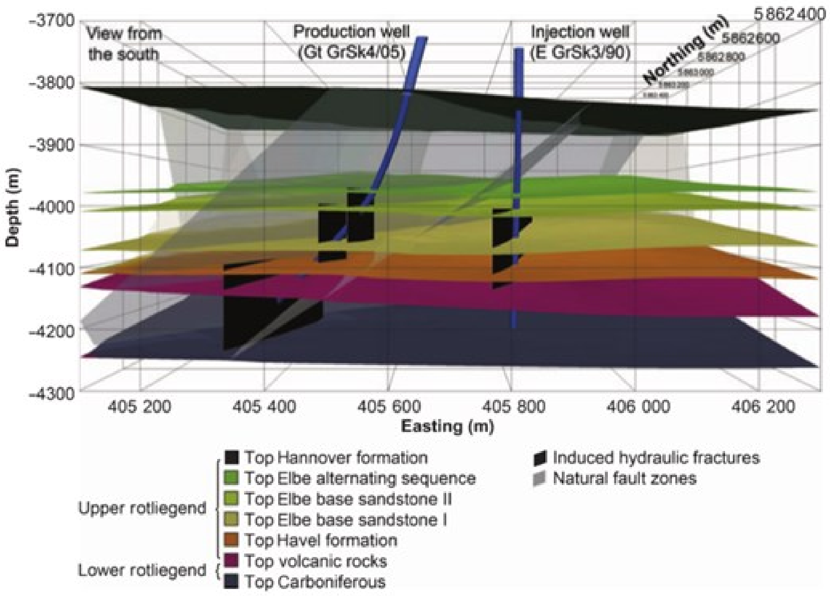
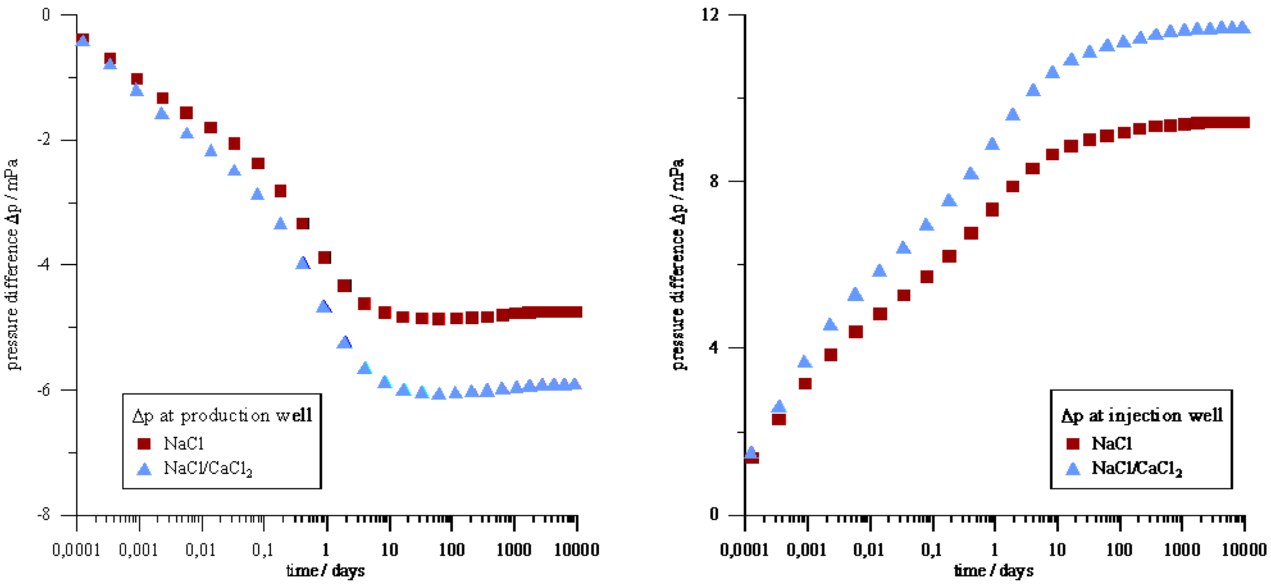


Figure 1: Geological model of the Groß Schönebeck site. The well paths for the deflected production well and the straight injection well are shown in blue. The induced fractures are shown as black rectangles.

The first simulation was run using the viscosity and density data at 80°C for a pure sodium chloride solution (This corresponds to the previous approaches, since there was no real data for mixed solutions.) The second simulation was performed with viscosity and density data at 80°C of a mixture of sodium chloride and calcium chloride (1,2:1) approximately equal to the fluid at the research platform Groß Schönebeck, Germany. **Figures 2 and 3** show the results as a function of pressure over time of the injection and the production side of the reservoir.



Figures 2 and 3: Comparison of the simulated pressure development with sodium chloride solution (*red*) and a mixed solution of sodium chloride and calcium chloride (*blue*) at the production side (*left*) and at the injection side (*right*).

The graphs in **Figures 2 and 3** show that the consideration of only sodium chloride in the geothermal fluid leads to a deviation of approximately 20% in the simulation of the pressure behaviour. Subsequently made decisions for power plant design such as the choice of a suitable pump may lead to non-productivity of the reservoir.

This study is to determine the influence of changing conditions on the thermophysical behaviour of geothermal fluids. In a first step, density ρ, viscosity η and electrical conductivity κ of aqueous solutions of sodium chloride and calcium chloride have been measured at atmospheric pressure depending on temperature up to 80°C and salt composition. Due to large data gaps in available literature, a laboratory for thermophysical measurements of salt solutions was built up as introduced in the contribution of Milsch et al. (2015).

Using the measured data, known mixing rules were tested for applicability.

2. MATERIALS AND METHODS

2.1 Sample preparation

As synthetic analogues to the geothermal fluids, aqueous solutions of sodium chloride and calcium chloride were prepared from deionized tap water, sodium chloride[1] and calcium chloride dihydrate[2] by weight. The purity level of both salts was above 99%. The reproducibility of the scale[3] is 0.1 mg which is equivalent to a deviation of less than 1‰ relative to the weighed quantities. To enable the deviation of mixing rules, solutions with only one salt as well as mixed solutions were made. For all samples the total molality was varied approximately up to the saturation level at room temperature (6.14 $mol•kg^{-1}$ for sodium chloride and 6.67 $mol•kg^{-1}$ for calcium chloride). The mixed solutions were prepared in ratios of 1:0, 0:1 and 1:1 of both salts. To avoid bubbles in the measuring devices, the samples had to be heated up before injection. The sample's molalities were verified after the measurements. Therefore, specific amounts of each sample were dried in an oven at 160°C over several days. The actual molalities were determined by weighing the water loss.

2.2 Measuring devices

The viscosity and density measurements were conducted with a combination of an oscillating U-tube densitometer (Anton Paar DMA 4500M) and a falling ball viscometer (Anton Paar AMVn). In order to avoid the formation of bubbles in the measuring devices, the solutions were stirred and heated up before the samples were injected for the measurement. Both parameters were measured simultaneously at different temperatures between 20°C and 80°C and atmospheric pressure. The obtained viscosity data have a deviation of up to 0.5%. For the densitometer, an uncertainty of the measurements lower than $\pm 1.0 \cdot 10^{-4}\ g \cdot cm^{-3}$ is given by the producer. The electrical conductivity data were obtained with a 4-point electrical conductivity probe (WTW TetraCon®325 and Cond3310) with an integrated temperature sensor. All solutions were slowly heated up from 20°C to 80°C while being stirred at constant rate. For the electrical conductivity measurements, an uncertainty lower than 0.5% is given by the manufacturer.

2.3 Literature comparison

The availability of literature data is given for the individual salts in the range between 20°C and 150°C at pressures up to 500 bar for density and viscosity (reviews by Laliberté et al. 2004 and Laliberté 2007). For mixed solutions of sodium chloride and calcium chloride, there are data only at 25°C and 1 bar in ratios of 1:1 and 3:1 or 1:3 respectively (Zhang 1997). Only a few publications deal with concentrations above 3 mol/kg. To compare the electrical conductivity data of pure sodium chloride solutions, the measured data of Janz (1970) were used. The available electrical conductivity data of calcium chloride solutions are insufficient for geothermal applications (Ucok 1980). Data for mixed solutions could not be found.

3. RESULTS AND DISCUSSION

3.1 Measured data

Exemplary for the measurements between 20°C and 80°C, the results at 25°C and ambient pressure for the pure salts' solutions and the 1:1 mixture are shown below.

As expected, density, viscosity and electrical conductivity increase with higher concentrations. For the electrical conductivity of calcium chloride, a maximum is reached at about 3 mol/kg, after which the electrical conductivity decreases with increasing concentration. For all the considered properties, the data of the mixtures are systematically between those of the individual solutions.

To evaluate the results, the measurement data were compared with available literature data (**Figures 4-9**).

The comparison reveals excellent agreement of the measured data and literature values for density, viscosity and electrical conductivity of sodium chloride solutions (**Figures 4-7, 9**).

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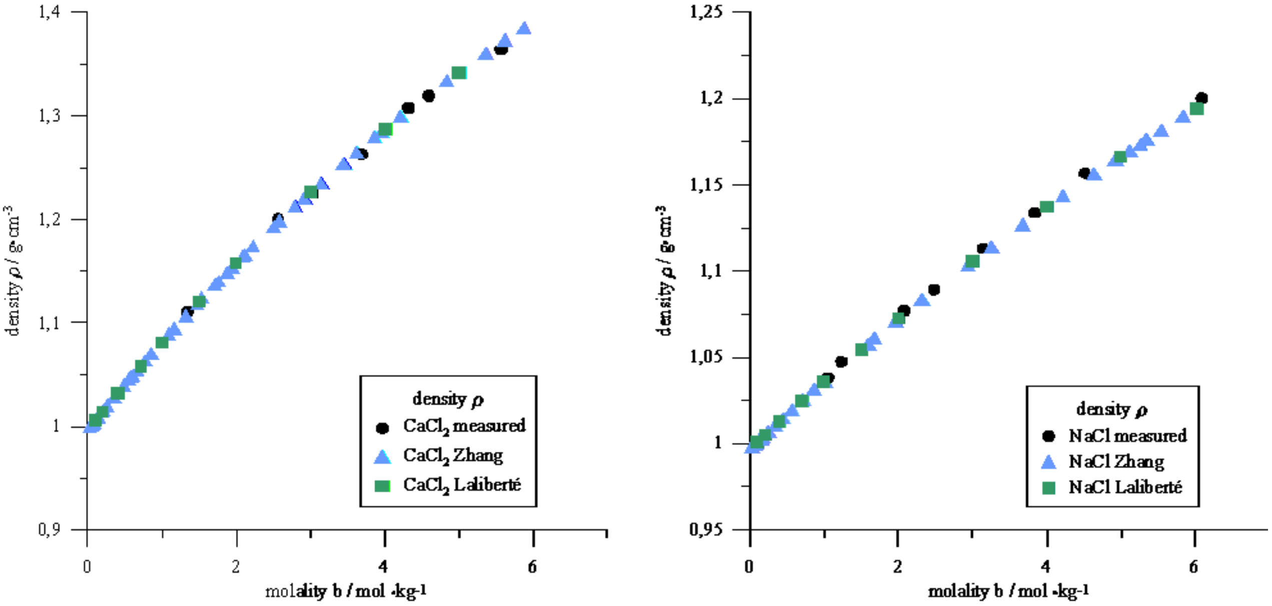
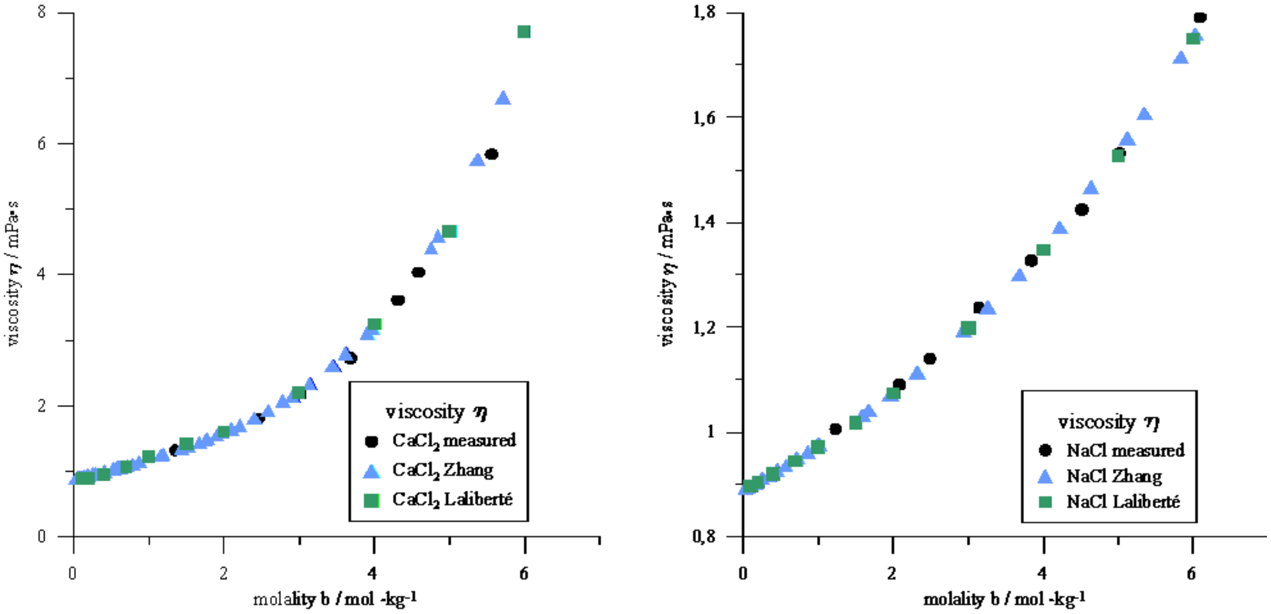
[1] Carl Roth GmbH + CO. KG. Sodium Chloride Cellpure ©, Order No. HN00

[2] Carl Roth GmbH + CO. KG. Calcium Chloride Dihydrate, p.a. ACS, Order No. 5239

[3] KERN & SOHN GmbH. ABJ 220-4M

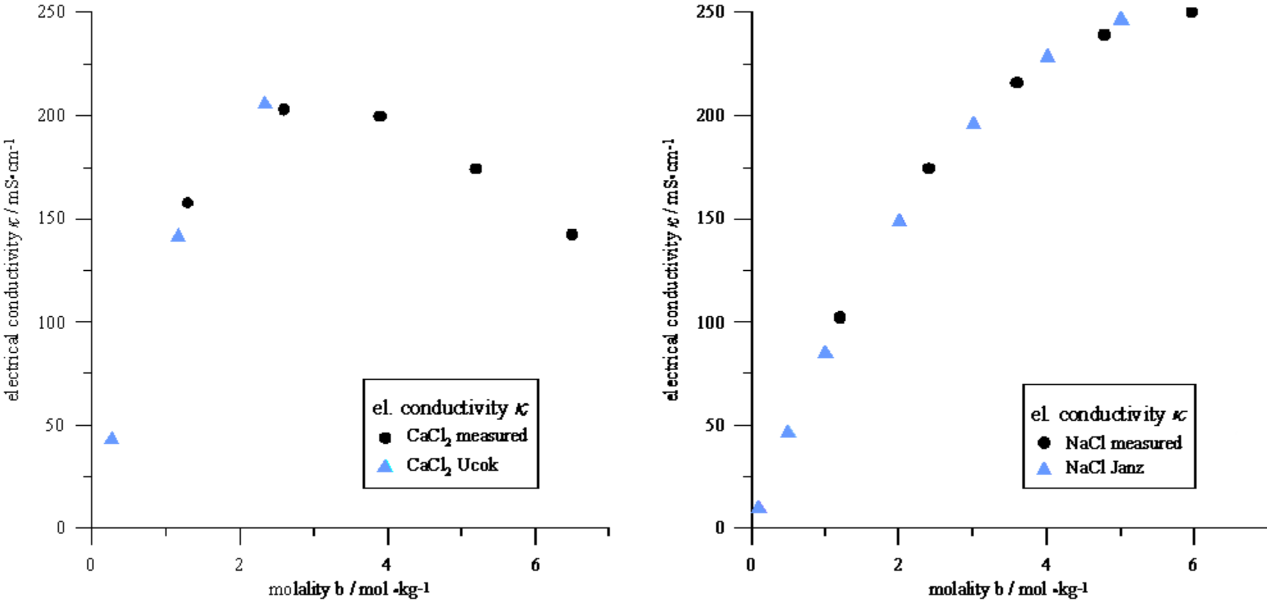


Figures 4 and 5: Literature comparison of the measured density data at 25°C and atmospheric pressure for calcium chloride (*left*) and sodium chloride (*right*) with Zhang et al. (1996, 1997) and Laliberté et al.(2004).



Figures 6 and 7: Literature comparison of the measured viscosity data at 25°C and atmospheric pressure for calcium chloride (*left*) and sodium chloride (*right*) with Zhang et al. (1996, 1997) and Laliberté (2007).

As shown in **Figure 8**, only few literature data could be found for electrical conductivity of calcium chloride solutions. Since the available literature data do not exceed molalities higher than 3 mol/kg, a direct comparison is not possible. The new measured data show, that a maximum electrical conductivity of calcium chloride solutions is reached at around a molality of 3 mol/kg, after which the electrical conductivity is decreasing with increasing molality.



Figures 8 and 9: Literature comparison of the measured electrical conductivity data at 25°C and atmospheric pressure for calcium chloride (*left*) and sodium chloride (*right*) with Janz (1970) Ucok (1980).

3.2 Mixing rules

For the prediction of the thermophysical properties, the applicability of known mixing rules was tested. Therefore, the data of the pure solutions were combined by the respective equation and compared with the measured data of the mixtures.

Figures 10, 12 and 14 show the measured data of the solutions of sodium chloride, calcium chloride and the 1:1 mixture. Since the values of the mixtures fall systematically between those of the single salt' solutions for all three properties, most mixing rules base on a weighted average (e.g. Viswanath et al., 2010).

For each property, both the arithmetic mean and the Arrhenius approach (geometric mean) (**Equations 1-2**) were used. For density, an additional mixing rule by Iulian et al. (after Patwardhan and Kumar, 2008) (**Equation 3**) was used, for viscosity, the one of Kendall and Monroe (**Equation 4**) was tested.

$$(\eta/\rho/\kappa) = \frac{\sum_i \chi_i \cdot (\eta/\rho/\kappa)_i}{\sum \chi} \tag{1}$$

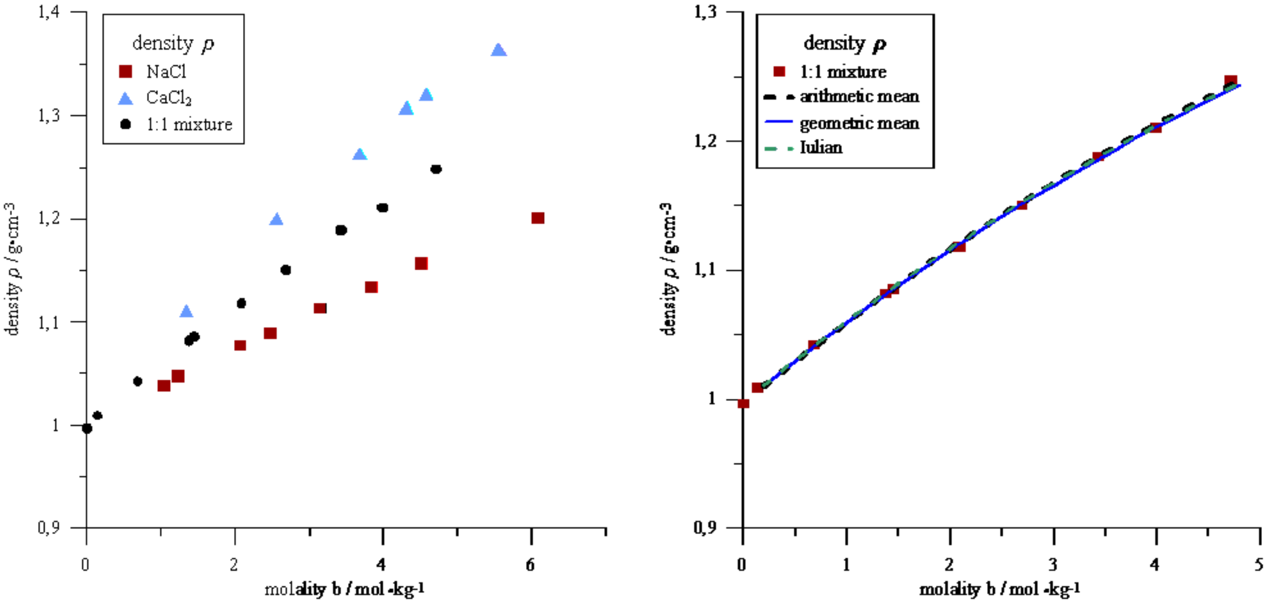
$$\log(\eta/\rho/\kappa) = \sum_i (\chi_i \cdot \log(\eta/\rho/\kappa)_i) \tag{2}$$

$$\rho = \frac{\sum_i \Psi_i}{\sum_i (\frac{\Psi_i}{\rho_i^0})} \text{with } \psi_i = 1000\chi_i + b_i M_i \tag{3}$$

$$\eta^{\frac{1}{3}} = \sum_i \chi_i \cdot \eta_i^{\frac{1}{3}} \tag{4}$$

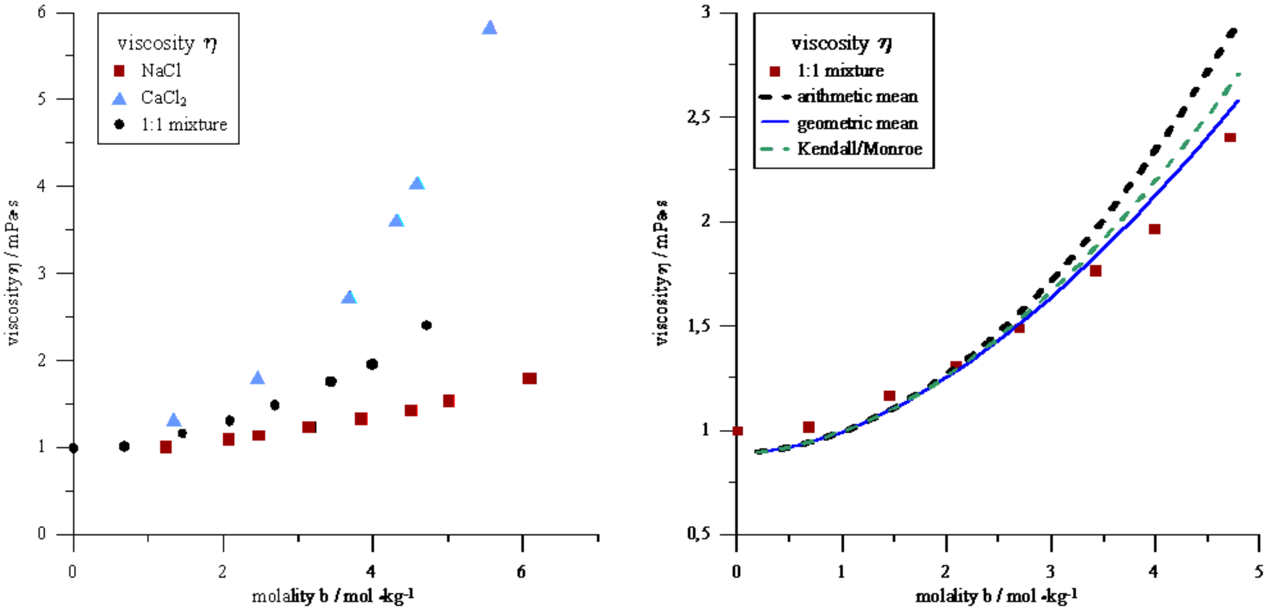
where η, ρ, κ, χ, b, M are viscosity, density, electrical conductivity, mole fraction, molality and molar mass, respectively.

As shown in **Figure 11**, all applied mixing rules provide a (for geothermal purposes) sufficiently accurate calculation of the mixture's density at the given conditions, 25°C and atmospheric pressure.



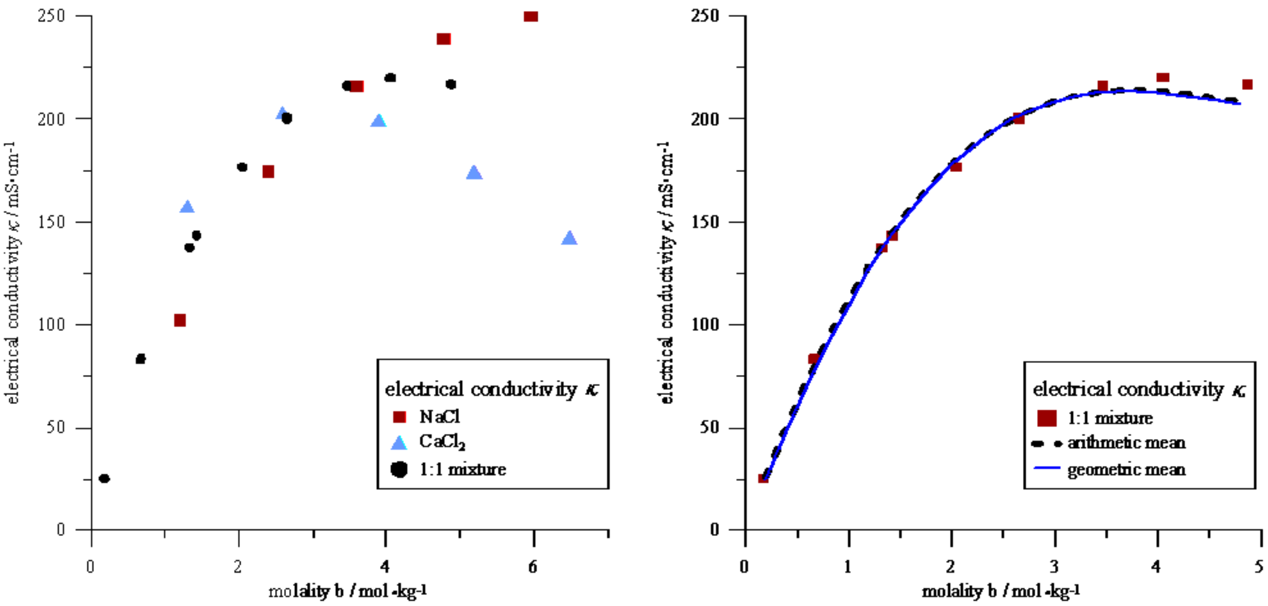
Figures 10 and 11: Measured density data for sodium chloride and calcium chloride solutions and their 1:1 mixture at 25°C and atmospheric pressure (*left*) and applied mixing rules (*right*).

The calculated viscosity values at 25°C and atmospheric pressure do not satisfactorily match the measured data for the 1:1 mixture, as shown in **Figure 13.** Not only the values for molalities below 2 mol/kg but also those for molalities higher than 3 mol/kg differ significantly from the measured data.



Figures 12 and 13: Measured viscosity data for sodium chloride and calcium chloride solutions and their 1:1 mixture at 25°C and atmospheric pressure (*left*) and applied mixing rules (*right*).

Figure 15 shows that the mixing rules reproduce the measured electrical conductivity data for molalities lower than 3 mol/kg sufficiently accurate. For higher molalities, further modification of these mixing rules is required.



Figures 14 and 15: Measured electrical conductivity data for sodium chloride and calcium chloride solutions and their 1:1 mixture at 25°C and atmospheric pressure (*left*) and applied mixing rules (*right*).

While the mixing rules for density predict the data of the mixture sufficiently, the calculated data for viscosity and electrical conductivity are not sufficiently accurate. All mixing rules presented need actual measured data of the single salts' solutions at the desired temperature and pressure conditions. Since measurements at elevated temperature and pressure conditions are significantly more complex, predictions with those mixing rules for geothermal fluid behaviour will not provide time saving compared to direct measurements of the real fluid. Therefore, a concept for mixing rules is necessary which does not need the single salts' data.

4. CONCLUSION

The present study provides new laboratory data for density, viscosity and electrical conductivity of mixed solutions of sodium chloride and calcium chloride. A literature comparison where possible shows that the data are correct and accurate. Especially for electrical conductivity of calcium chloride, new data exceeding the molality range in available literature sources were obtained.

The prediction of the fluid properties using known mixing rules is sufficiently accurate for density. For the prediction of viscosity and electrical conductivity data, further investigations are necessary. Since all mixing rules presented require actual fluid data of the single salts' solutions, an approach without this demand is needed for time saving predictions of geothermal fluid behaviour.

The consideration of pure sodium chloride solutions instead of mixed solutions leads to deviations in the result of numerical simulations of the reservoir behaviour. For a more precise determination of these deviations, real data for density and viscosity at higher pressures and temperatures than obtained in this study are needed and require ongoing measurement efforts.

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