

Experimental study and modelling of saturation molality of NaCl in quaternary aqueous electrolyte solutions at various temperatures

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ABSTRACT

Saturation molality of sodium chloride in mixed aqueous electrolyte solutions containing NaCl, CaSO₄ and Na₂SO₄ was measured at atmospheric pressure over the wide range of temperatures using an equilibrium cell equipped with an accurate temperature control system. The measurements were carried out at different CaSO₄ and Na₂SO₄ concentrations. In order to check the repeatability of the experimental data for the saturation molality of NaCl, the experiments were replicated three times and the values reported were the average of the replicas. To model the data generated in this work, the PDH+UNIFAC-Dortmund activity coefficient model was used. The model used to predict the mean ionic activity coefficients of NaCl at the saturation molality at various temperatures and at different concentrations for CaSO₄ and Na₂SO₄. The PDH term of the model accounts for the long range interactions between ionic species in solutions, while the modified UNIFAC-Dortmund activity coefficient model was used to account for the short range interactions between the species in solutions. It is worth noting that no new adjustable parameters were introduced into the model and the previously reported values for the interaction parameters of the binary and ternary electrolyte systems were directly used to predict the experimental data of the mean ionic activity coefficients of NaCl at saturation molality. The results showed that the PDH+UNIFAC-Dortmund activity coefficient model can accurately predict the mean ionic activity coefficients for the quaternary electrolyte solutions studied in this work.

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1. Introduction

Electrolyte solutions are of vital importance in many industries such as distillation, extraction, crystallization, water injection operation, natural gas hydrate formation, etc. [1–3]. Deposition of mineral scales due to the incompatibility of the connate and injecting waters during water flooding process has been one of the main pitfalls in the oil and gas industries. The above-mentioned scales are responsible for formation damage and consequently decrease in production rate [4–11]. Study of the scale formation in order to prevent such formation damage in the operational oil reservoirs is indispensable. To do so, a reliable thermodynamic model is needed to estimate the mineral salt solubility in aqueous mixed electrolyte solutions at various electrolyte compositions, temperatures and pressures. Such model is normally used to estimate the mean ionic activity coefficients (MIAC) of electrolytes at various conditions. Although, the importance of models which can quantitatively represent the activities of individual ions have been long

realized [12], the lack of reliable experimental data has been a major hindrance in their development.

A brief introduction of the previously published experimental results along with the models developed to study the single and mixed electrolyte systems was given elsewhere [13].

Very recently, Yousefi et al. measured the saturation molality for aqueous single and mixed binary/ternary NaCl, CaSO₄ and Na₂SO₄ solutions at various temperatures. They also used the PDH+UNIFAC-Dortmund activity coefficient model to correlate their experimental data [13].

In this work, the saturation molality of sodium chloride in mixed aqueous electrolyte solutions containing NaCl, CaSO₄ and Na₂SO₄ was measured at atmospheric pressure over the wide range of temperatures at different CaSO₄ and Na₂SO₄ concentrations. Also, to model the data generated in this work, the PDH+UNIFAC-Dortmund activity coefficient model was used. The model used to predict the mean ionic activity coefficients of NaCl at the saturation molality at various temperatures and at different concentrations for CaSO₄ and Na₂SO₄. The results showed that the PDH+UNIFAC-Dortmund activity coefficient model can accurately predict the mean ionic activity coefficients for the ternary electrolyte solutions studied in this work.

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2. Experimental section

2.1. Chemicals

Analytical grade of NaCl, Na₂SO₄, and CaSO₄ salts with a purity of 99.5% were purchased from Merck GmbH in Germany. Deionised water with the electrical conductivity of 0.2 μs/cm was used throughout the experiments. It should be noted that all chemicals were used as exactly received without further purification or preparation. Also in order to prevent the contamination of the salts with atmospheric moisture, a moist free environment was used to conduct the experiments.

2.2. Apparatus

A schematic diagram for the equilibrium cell used in these experiments was shown in Fig. 1. As seen from this figure, a thermostatic bath was used to keep the temperature of the equilibrium cell constant at atmospheric pressure. In order to constantly measure the temperature of the cell an RTD with an accuracy of ±0.1 K was used. A magnetic stirrer was used to homogenize the mixtures in the equilibrium cell. The solutions were stirred continuously during the experiments. The cell temperature was kept constant at different temperatures using the thermostatic bath.

2.3. Procedure

To measure the saturation molality, the equilibrium cell was charged with 1 kg of aqueous electrolyte containing CaSO₄ and Na₂SO₄ with predetermined concentration ratios. Then sodium chloride salt was gradually added to the aforementioned mixed aqueous electrolyte solution while the temperature of the system was kept constant using a thermostatic bath. Addition of sodium chloride salt to the electrolyte solution continued until the super-saturation condition in solution was attained. At this stage, the stirrer was switched off and the system was left to reach the equilibrium condition. Then, in order to analyze the saturation molality of NaCl, three samples were taken out from the original supersaturated solution. It should be stressed that the amount of each sample taken out for each measurement has been 50 cm³ of the mixture containing

the electrolytes. The samples were weighed and put in the Ben Marry bath at 90 °C. The partially dried samples were kept in a vacuum oven at 120 °C for at least two hours to completely dry the samples. Samples were then brought to room temperature and weighed up using a balance with an accuracy of ±0.001 g. Finally, the saturation concentrations for the sodium chloride salt solutions were estimated using the values for the weights of electrolyte solutions and dried electrolyte samples in terms of molality.

3. Modelling

The activity coefficient for a component (i) in a mixture can be considered as sum of two major terms, i.e., the short – range as well as the long – range terms. Therefore, for each component, the activity coefficient takes the following form [14]:

$$\ln \gamma_i^m = \ln (\gamma_i^m)_{LR} + \ln (\gamma_i^m)_{SR} \tag{1}$$

The PDH model can be written as below for mixed electrolyte solutions:

$$\begin{aligned} \ln \gamma_{\pm, MX} = & |z_+ z_-| F + \frac{v_{\pm}}{v} \sum_a m_a \left(2B_{Ma} + ZC_{Ma} + 2 \frac{v_{\pm}}{v_+} \phi_{Xa} \right) \\ & + \frac{v_{\pm}}{v} \sum_c m_c \left(2B_{cX} + ZC_{cX} + 2 \frac{v_{\pm}}{v_-} \phi_{Mc} \right) \\ & + \sum_c \sum_a m_c m_a v^{-1} (2v_+ z_+ C_{ca} + v_+ \psi_{Mca} + v_- \psi_{caX}) \\ & + \sum_{c < c} m_c m_c \frac{v_{\pm}}{v} \psi_{ccX} + \sum_{a < a} m_a m_a \frac{v_{\pm}}{v} \psi_{Maa} \end{aligned} \tag{2}$$

where, quantity F includes the Debye–Hückel term and other terms as follows:

$$\begin{aligned} F = & -A_{\phi} \left[\left(\frac{I^{\frac{1}{2}}}{1 + bI^{\frac{1}{2}}} \right) + \frac{2}{b} \ln(1 + bI^{\frac{1}{2}}) \right] + \sum_c \sum_a m_c m_a B_{ca} \\ & + \sum_{c < c} m_c m_c \phi_{cc} + \sum_{a < a} m_a m_a \phi_{aa}. \end{aligned} \tag{3}$$

Other parameters introduced in Eqs. (2) and (3) can be found elsewhere [13–17]. It should be noted that, the binary and ternary

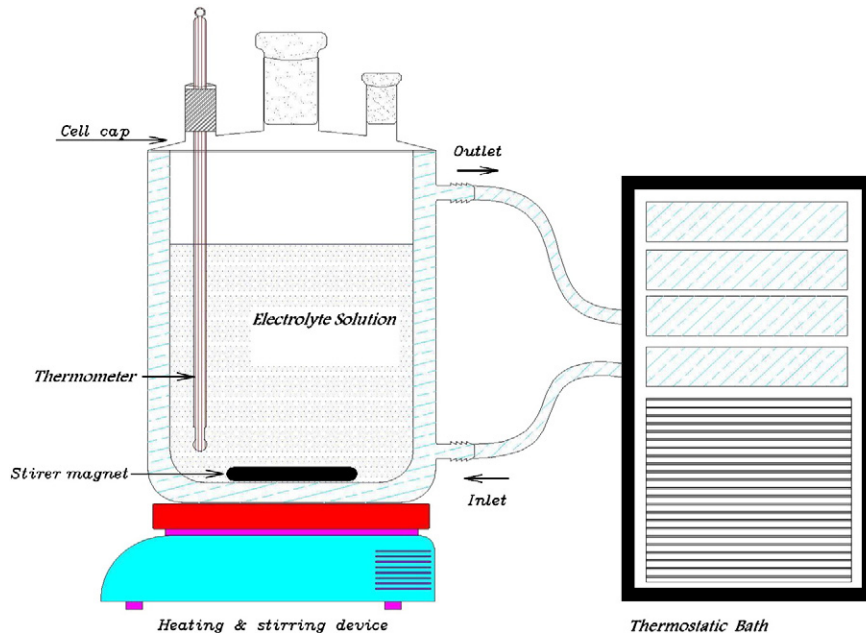


Fig. 1. Schematic diagram of equilibrium cell used in this work.

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