Salting out and interfacial tension of methane with electrolyte solutions from computer simulations

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INTRODUCTION

The solubility of methane in water decreases when a small amount of salt (i.e. $NaCl$, $MgCl_2$, Na_2SO_4, …) is present in water. This is usually denoted as the salting out effect (i.e the methane is expelled from the solution when it contains small amounts of salt). In previous work [1] we have studied the salting out effect using the TIP4P/2005 [2] model of water, describing $NaCl$ using the popular Smith Dang model. These previous simulations predict correctly the salting out effect although it was overestimated. In this work we have used Madrid 2019 model [3,4] and we predict both qualitatively and quantitatively the salting out effect. Besides, we have also studied the salting out effect for different salts (i.e. KCl, $MgCl_2$, $CaCl_2$, Na_2SO_4, K_2SO_4).
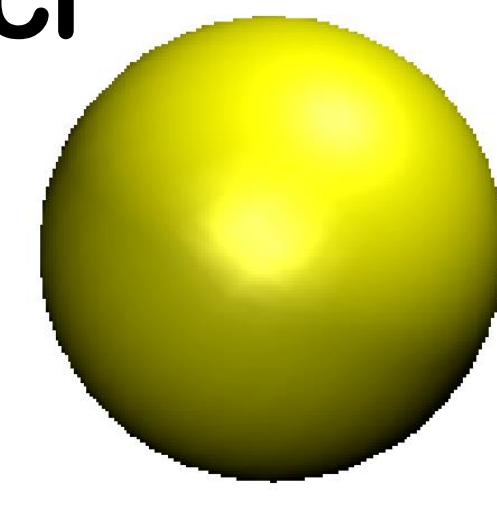
COMPUTER SIMULATIONS AND MODELS

Computer simulations provide an important tool to understand mechanisms that cannot be studied in a laboratory. Simulations give us a microscopic view of the system at short time scales. However, we need good models for a good description of the system.

There are different models to describe $NaCl$ in aqueous electrolyte solutions which have been proposed.

In the recent years, the idea of using scaled charges to describe electrolytes in water is becoming more popular. In these models, the charge assigned to the Na cation or Cl anion is not one (in electron units) but is reduced to a certain fraction. The justification behind this approach is to assume that there is a certain transfer of charge from the hydration water molecules to the ions. Recently a new model with scaled charges has been developed for Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-} in aqueous solution based on the TIP4P/2005 water model. [4]
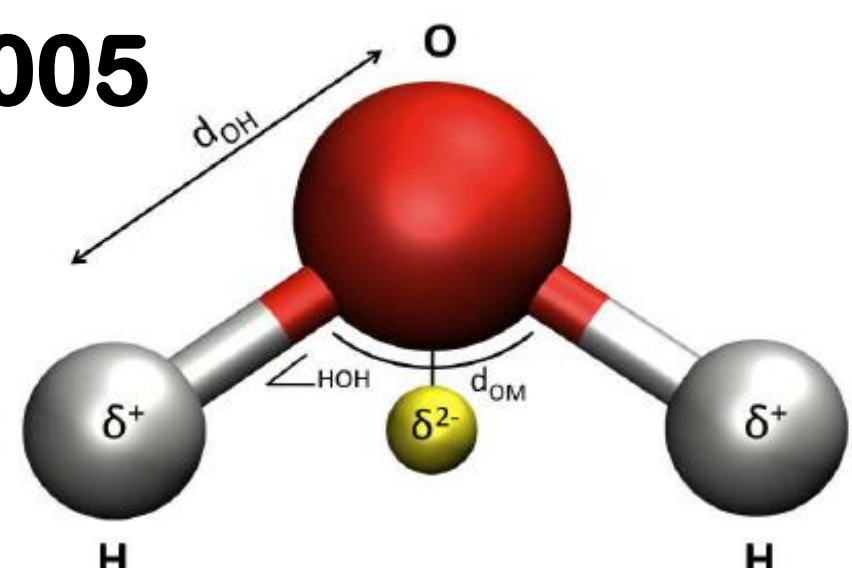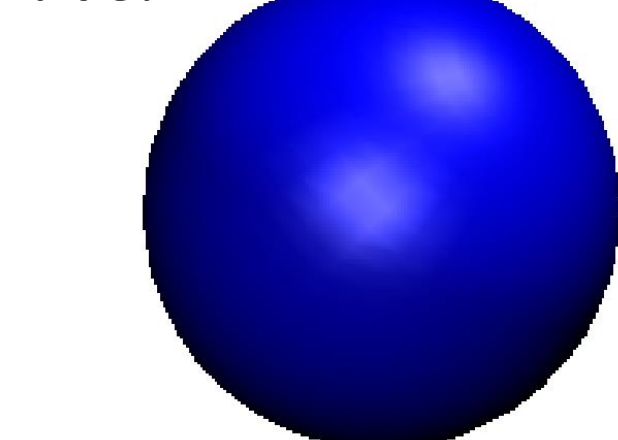
Water TIP4P/2005 | **Na⁺** $q = +0.85\ |e|$ | **Cl⁻** $q = -0.85\ |e|$ | **Mg²⁺** $q = +1.7\ |e|$ | **SO₄²⁻** $q = -1.7\ |e|$ | **CH₄**
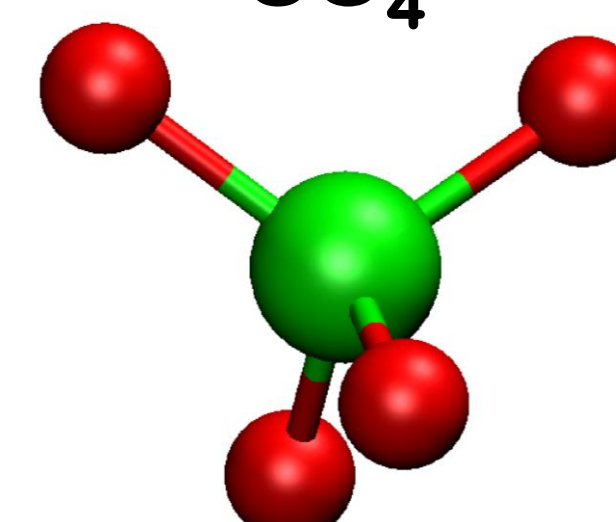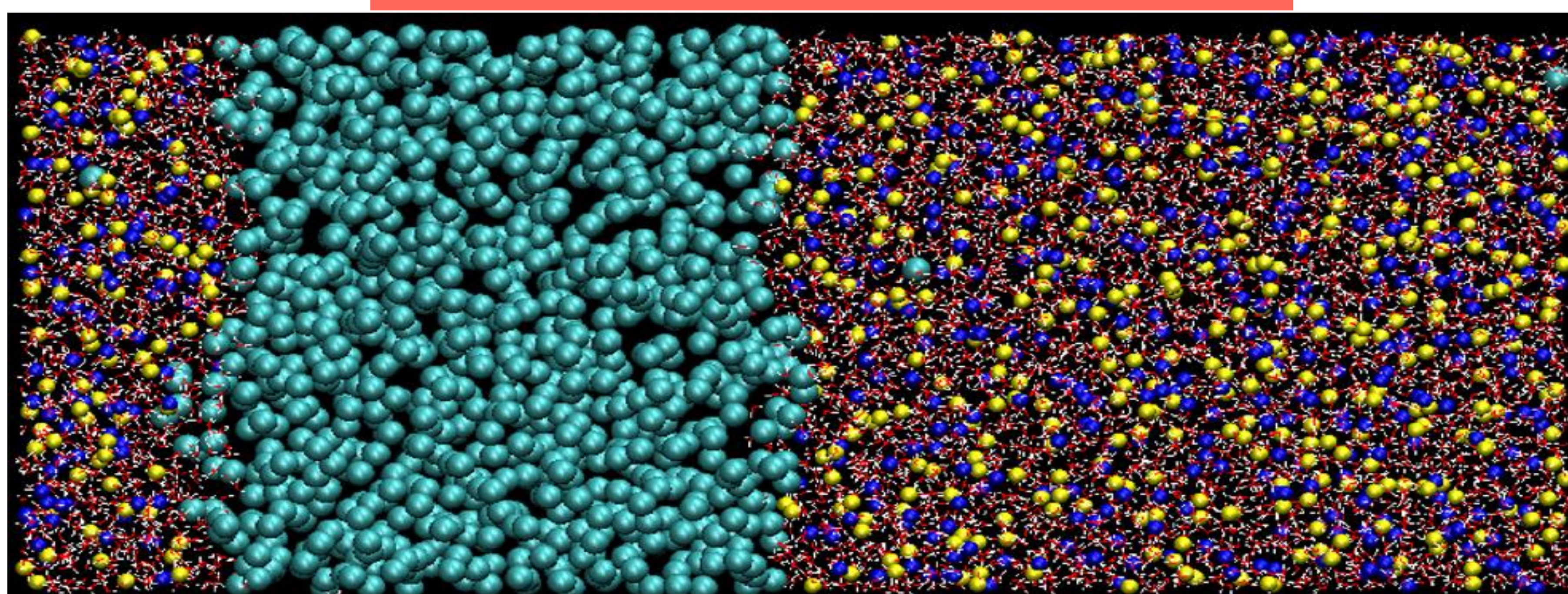
SIMULATION DETAILS

GROMACS
- Direct coexistence method
- Np_zT simulations
- P_z = 200 bar
- N(H_2O) = 6660
- N(CH_4) = 1000
- N($NaCl$) = 240 (2m)
- Runs of 80 ns
- T = 324.65 K

CROSS INTERACTIONS
- Interaction between CH_4 and H_2O
- Lorentz-Berthelot rules

$$\sigma_{CH_4-H_2O} = \frac{\sigma_{CH_4-CH_4} + \sigma_{H_2O-H_2O}}{2}$$

$$\epsilon_{CH_4-H_2O} = \chi\sqrt{\epsilon_{CH_4-CH_4} \cdot \epsilon_{H_2O-H_2O}}$$

- Deviation of Lorentz Berthelot energetic rule χ=1.07

Fig.1: Snapshot of the direct coexistence $NaCl$ solution – methane. The water molecules are represented by red and white sticks. The spheres cyan are methane molecules. The spheres blue and yellow are Na^+ and Cl^- ions.

RESULTS

Traditional models of $NaCl$ (i.e. Smith Dang model) which assigned charges of +1 and -1 to the ions explained the salting out effect qualitatively but overestimated the effect quantitatively. However the Madrid 2019 model which assigns charges of +0.85 and -0.85 to the ions describes both qualitatively and quantitatively the salting out effect.
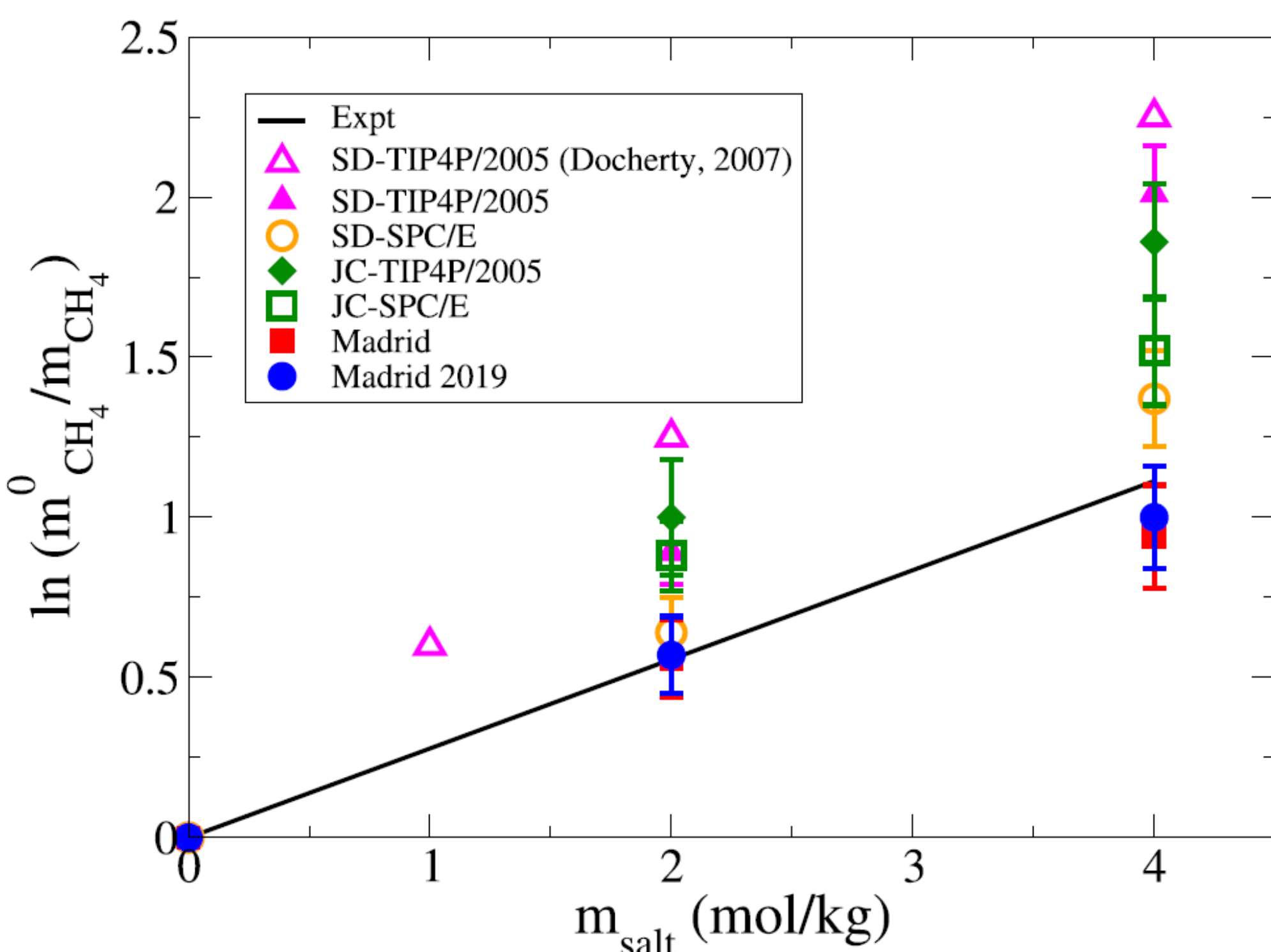
Madrid 2019 model with scaled charges describes the salting out effect of different salts and predicts both qualitatively and quantitatively the salting out effect of the methane

The interfacial free energies between water and a gas under pressure (methane in our study) increases with the addition of salt and the Madrid-2019 model yield results that are within 3 mJ/m² of the experimental ones and reproduce the experimental trend.

Fig. 2: Evaluation of the salting out effect of methane in $NaCl$ solutions with different models [5] and experimental data. [6]
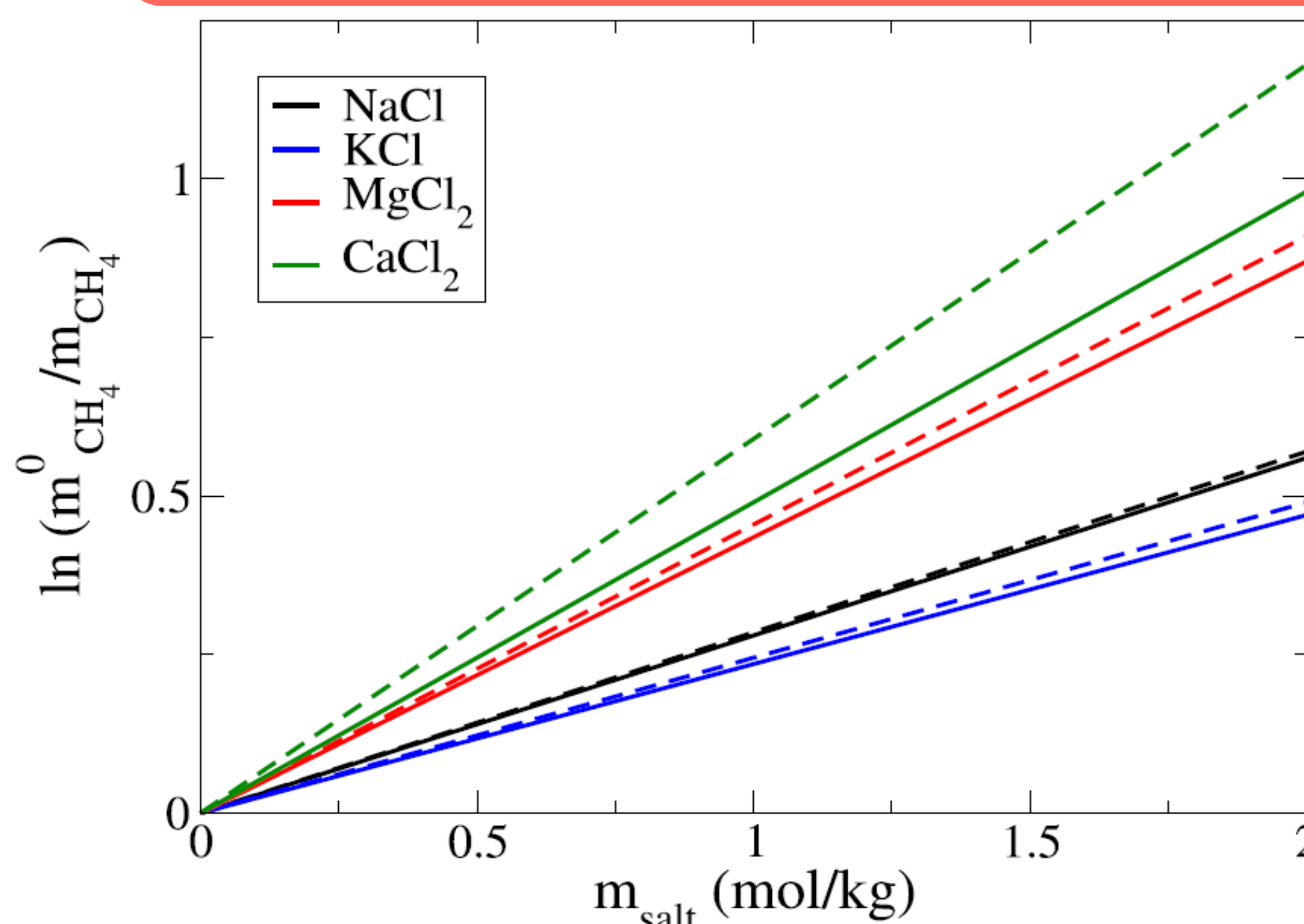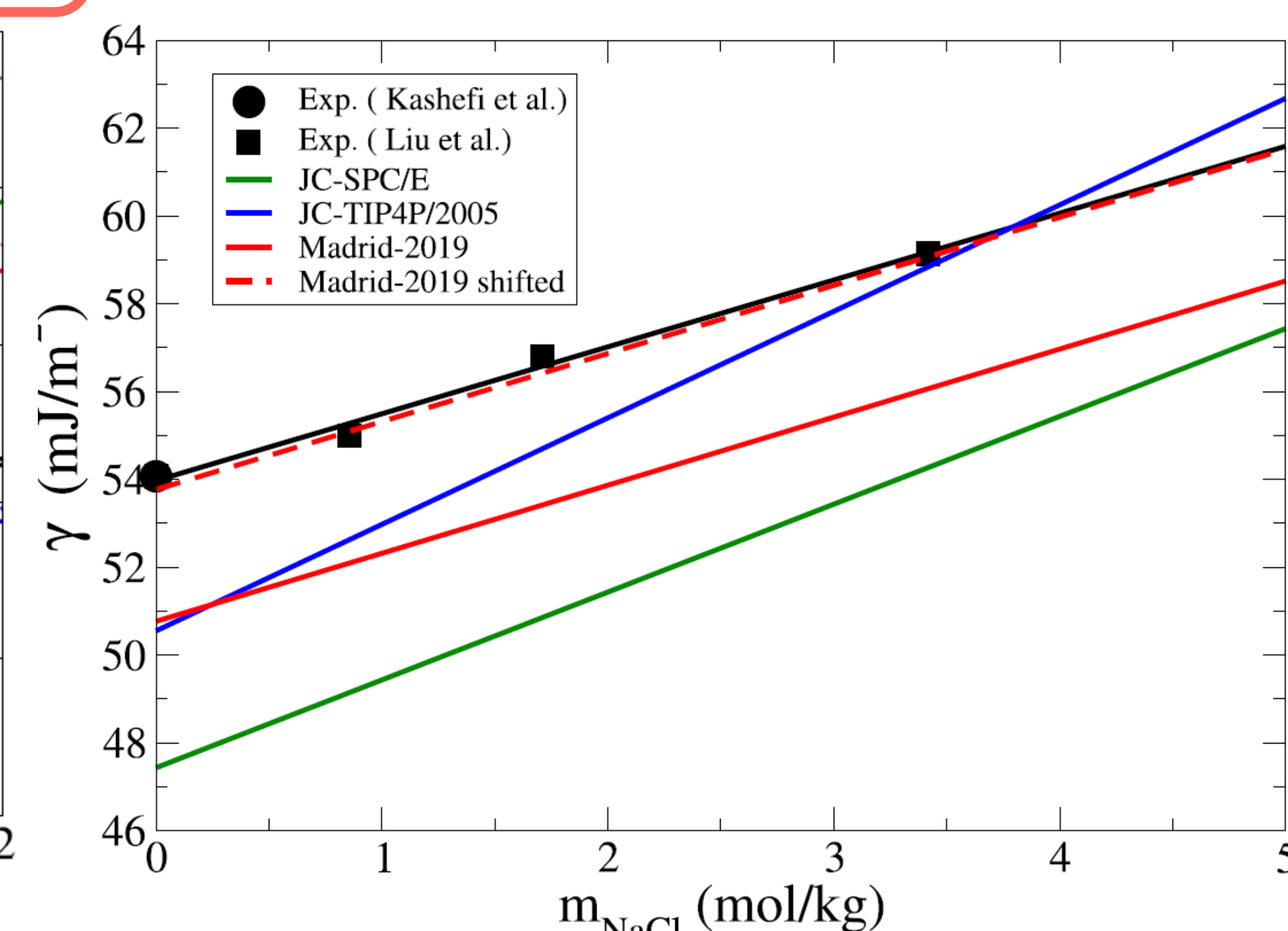
Fig. 3: Evaluation of the salting out effect of methane in different chloride solutions with Madrid-2019 model [5]. Dashed lines are simulations results and solid lines the experimental data [6].

Fig. 4: Evaluation of the interfacial tension between methane and $NaCl$ solutions with different models [5] and experimental data. [7]

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