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Study of the effect of molecular cluster size alanine concentrations in water by using the activity coefficient method and density functional theory

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In this article activity coefficient models UNIQUAC and NRTL are utilized along with the density functional theory to calculate the effect of molecular cluster size alanine concentrations in water. For this purpose, clusters of different sizes were created: 2 alanine + 8 water, 2 alanine + 12 water, 2 alanine + 16 water, 2 alanine + 20 water, 4 alanine + 8 water, 4 alanine +12 water, 4 alanine + 16 water, and 4 alanine + 20 water. Clusters were selected in order to evaluate the effect of the concentration of water and the concentration of alanine. Density functional theory calculations are conducted with B3LYP and basic function 6-311G+(2d,2p). In order to consider the effect of the solvent the PCM model has been used. To consider the effects of the superposition of base functions the BSSE method was used. With consideration for the experimental data of the activity coefficients of alanine in water, the errors in the systems being studied are calculated. The results show the presence of two alanine increase in the amount of water does not significantly impact the reduction of error, while with the presence of four alanine increase in the amount of water the errors show a significant decrease. The results also show that taking into account the error of superposition in all calculations has a higher impact on reducing error.

Keywords activity coefficient, density functional theory, Alanine, UNIQUAC, NRTL

INTRODUCTION

Predicting the behavior of the pressure-temperature mixture using a wide range of temperatures and pressures is very important [1-4]. Therefore, various tests have been recommended and various devices have been provided for the purposes of this experiment. However, due to the cost of the tests and in some cases the danger of the experiment, in high temperatures and high pressure levels, it is customary that the behavior of the mixtures be modeled under optimum conditions. Various activity coefficient models have been used to predict the behavior of the mixtures. These models are based on accounting for the parameters of the interaction between the components of the mixture [5-8].

So far, several activity coefficient models for this calculation of the diagrams in the mixture phase have been presented with the UNIQUAC and NRTL models, in addition to other highly usable models, in this case. These two models are used to predict the behavior during the mixture phase, using components of different sizes [9, 10]. However, in using this method to obtain the parameters of the interaction between the components, various experimental results are required. Therefore, computational methods based on quantum chemistry have been recommended to solve this issue. Among these methods is the density functional theory method. In this method, the electron density of molecules is used in place of the wave function for calculating molecular properties [11-13]. This technique has, in many cases, been used to calculate the structural parameters of molecules.

To use these methods to calculate the parameters of the interaction, the optimum combined structure is required. In this article, clusters with different measurements of water and amino acid alanine have been provided. Using the activity coefficient models, and density functional theory, the activity coefficients of alanine have been calculated. Errors caused in the various clusters have been investigated and calculated.

RESULTS AND DISCUSSION

The following steps were taken to obtain the concentration of alanine, using the UNIQUAC, NRTL model and quantum computing.

A: Clusters with different measurements have been provided: 2 alanine + 8 water (system 1), 2 alanine + 12 water (system 2), 2 alanine + 16 water (system 3), 2 alanine + 20 water (system 4), 4 alanine + 8 water (system 5), 4 alanine + 12 water (system 6), 4 alanine + 16 water (system 7), and 4 alanine + 20 water (system 8). Each of the clusters was optimized using the quasi-experimental PM6 method. In the Fig below, the largest cluster (4 alanine + 20 water) is provided and for the purposes of saving space, the other clusters have been left out (Fig.1).

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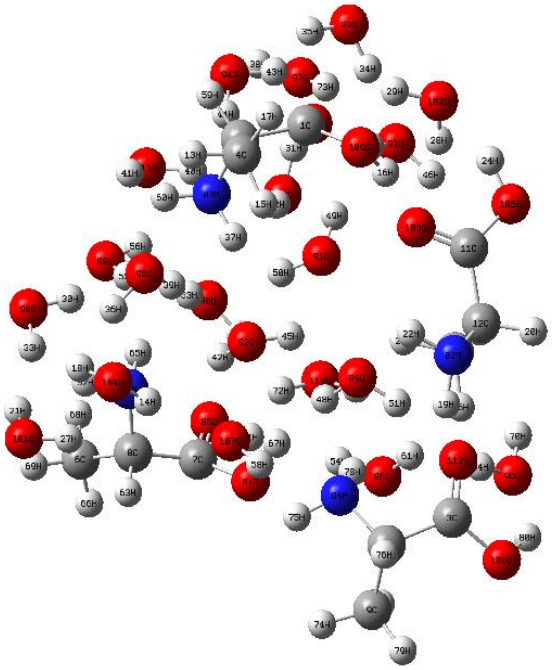

Fig 1. The optimal structure of the cluster containing 4 alanine and 20 water molecules (System 8).

B) The pair of symmetrical molecules of water-water, alanine-alanine and the asymmetric pair water-alanine of these clusters were selected and optimized calculations were performed using B3LYP and the basic 6-311G + (2d, 2p), on each cluster. To ensure optimization, frequency calculations is performed, so there is no virtual frequency for the compounds being studied.

C) All the calculations of part B using the PCM model in the solvents phase were repeated until the effect of the solvent on the interaction parameters was considered.

D) All the calculations of part B were repeated while accounting for the superposition error of the basic function BSSE. The BSSE technique is a conventional method for calculating the interaction parameters of singular and multiple systems.

E) The interaction parameters of the UNIQUAC and NRTL model were calculated using the following equation. (1-1)

$$E_{ij} = E_{ij} - \left(E_{ii} + E_{jj}\right)$$

Since alanine is a nonvolatile amino acid the Gibbs-Duhem equation was used and its amount of activity coefficients was calculated based on the amount of the water activity coefficient. Thus, by comparing the experimental results, the error of each calculation was obtained and reported in the following figures.

The figure 2 shows that using the BSSE error instead of solvent effect will result in less error. Also, the two methods UNIQUAC and NRTL have errors that are close to each other.

The figure 3 shows that the BSSE error is less than the error of applying the solvent. Also, the two methods UNIQUAC and NRTL have errors that are close to each other. However, using solvent effect in the UNIQUAC model, PCM has less error than the NRTL.

Figure 4 shows that by increasing the number of water the error related to the different methods is reduced, however, applying the error of the superposition basic functions is more effective than applying solvent effect.

Fig. 5 shows the error values obtained by increasing the number of water has decreased compared to the previous system. However, the procedure for changing errors is the same as past systems. However, the UNIQUAC model compared to the NRTL model is more sensitive to the superposition error.

The figure shows that higher alanine causes a decrease in the model error. Also, the superposition error is more effective than solvent effect.

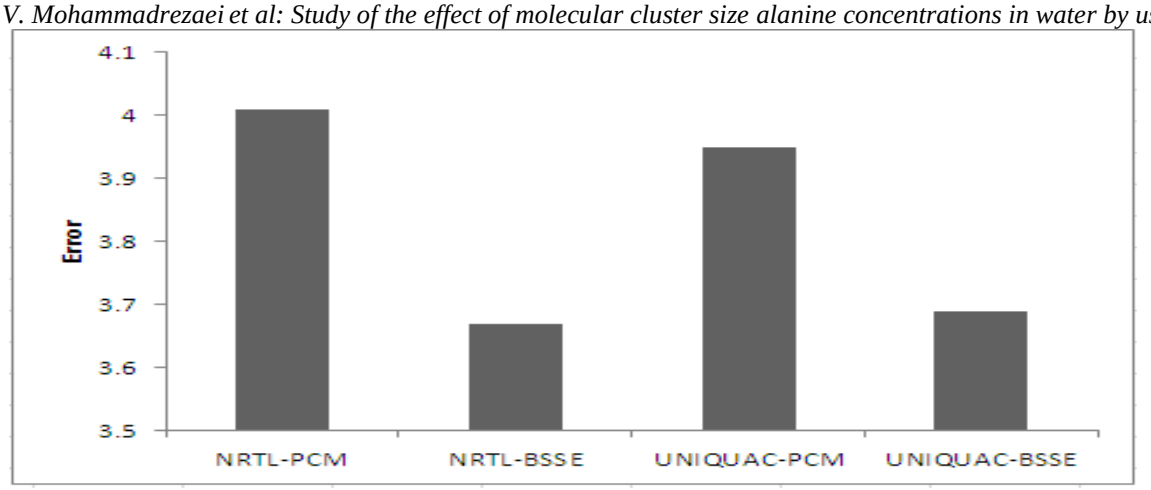

Fig 2. The error values obtained in the different models for system 1.

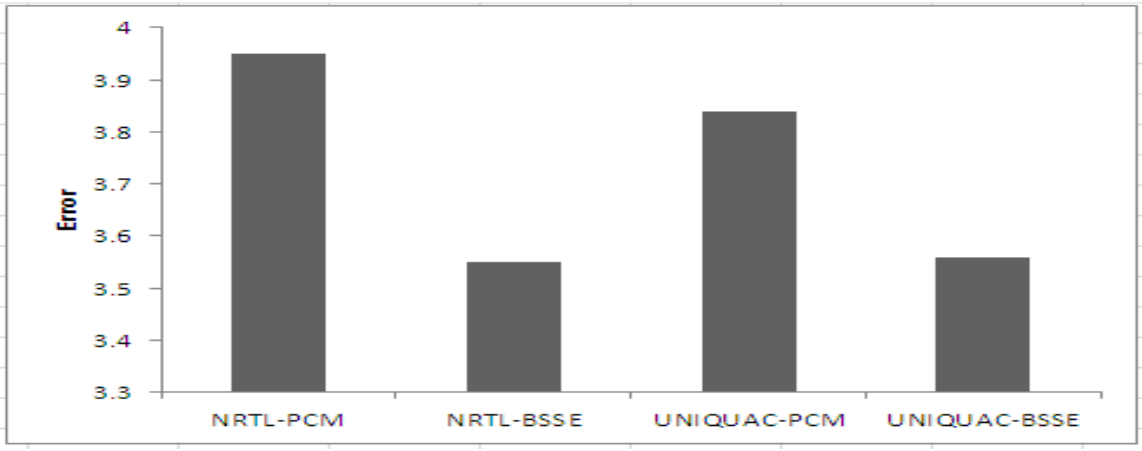

Fig 3. The error values obtained in the different models for system 2.

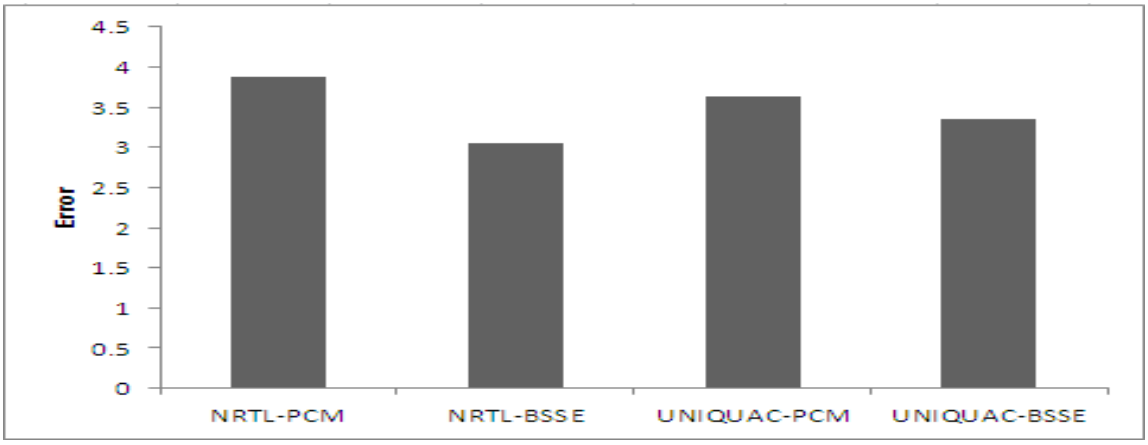

Fig. 4. The error values obtained in the different models for system 3.

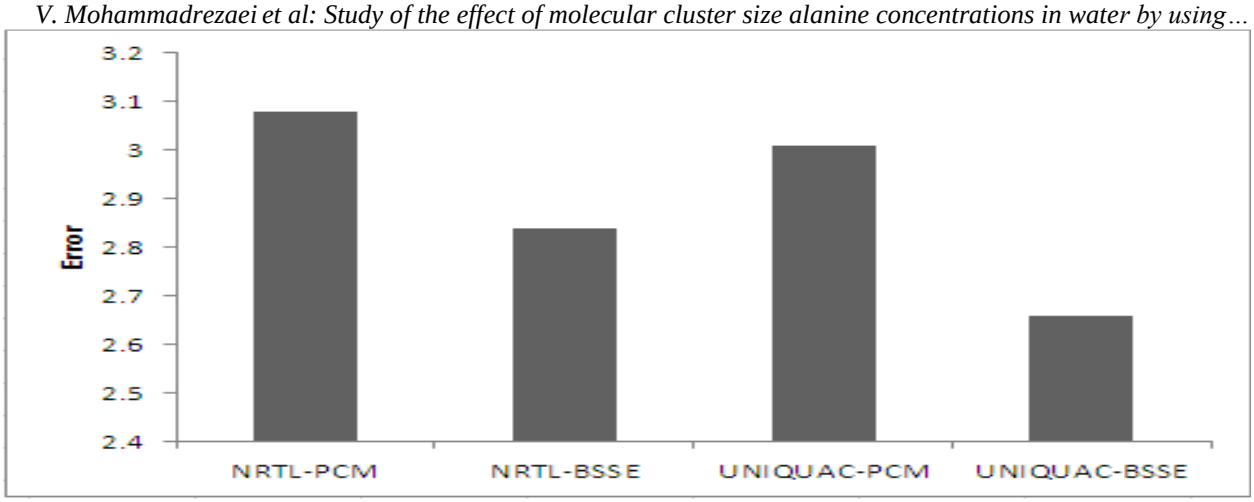

Fig 5. The error values obtained in the different models for system 4.

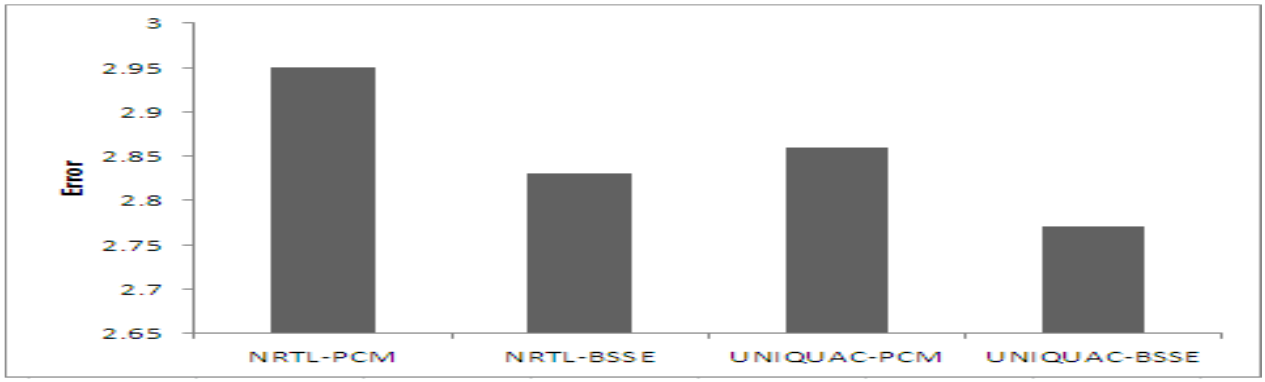

Fig. 6. The error values obtained in the different models for system 5.

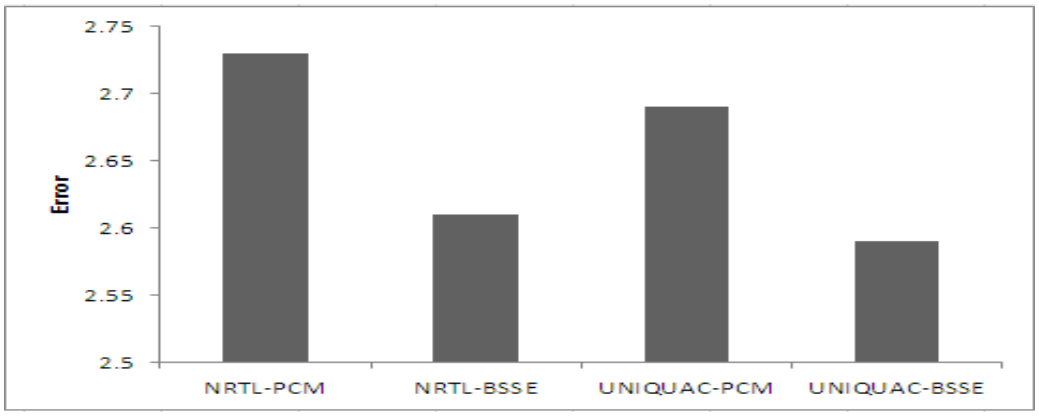

Fig. 7. The error values obtained in the different models for system 6.

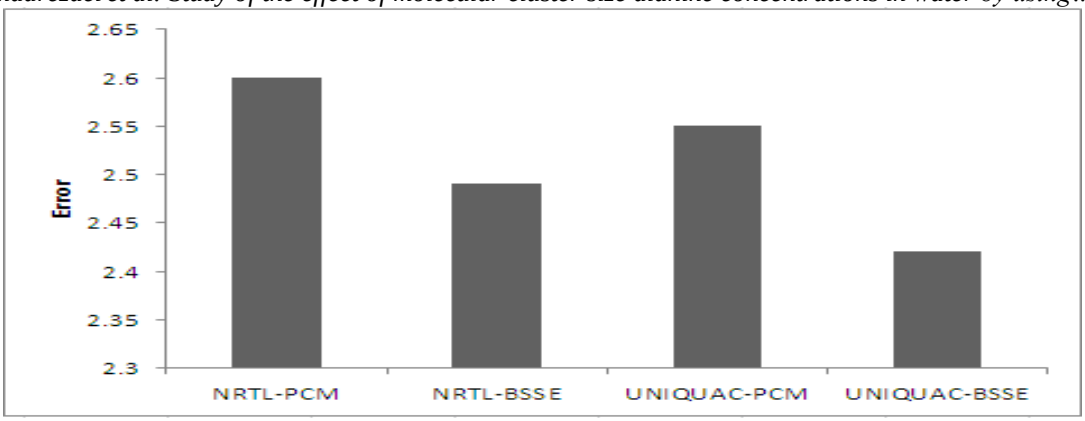

Fig 8. The error values obtained in the different models for system 7.

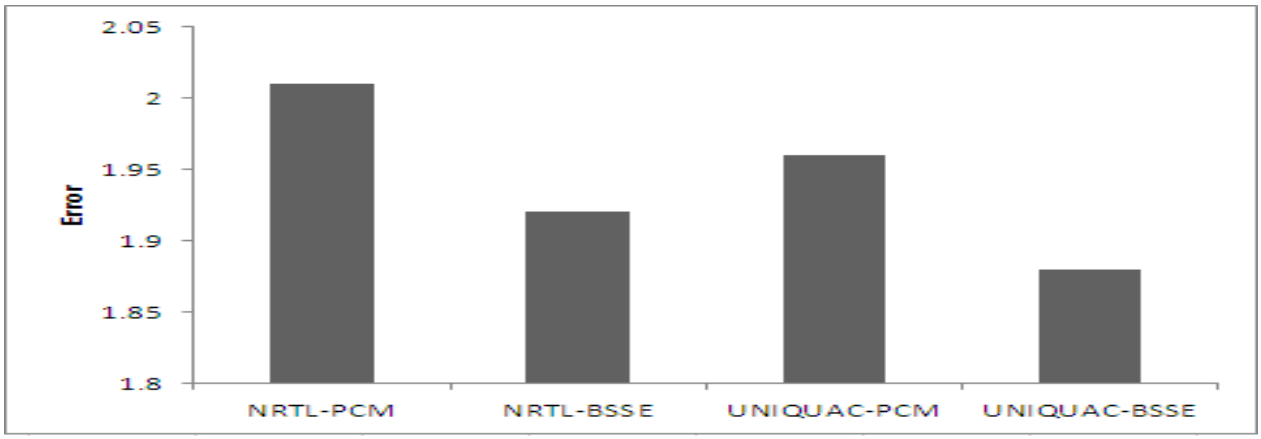

Fig. 9. The error values obtained in the different models for system 8.

When considering the figures, an increase in the size of the clusters causes a decrease in the error of the models. Additionally, in all cases, the effect of considering the superposition error is higher than that of considering the solvent PCM model. The results also show that the greater the number of amino acid alanine, the greater the impact on the accuracy of the models, compared to the increase in the amount of water. On the other hand, the UNIQUAC model has fewer errors compared to the NRTL model, although, the difference between the two methods in different clusters is not significant. Also, the UNIQUAC model compared to the NRTL model is more sensitive while considering the superposition error. In general, given the fact that the error in the models is not considerable, this method for calculating the activity coefficients and the amino acid alanine concentration in water appears to be appropriate.

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