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Determination of Alanine concentration in Alanine-supercritical water mixture, using UNIQUAC methods and density functional theory

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ABSTRACT

In the following paper, density functional method and Universal QUAsi-chemical (UNIQUA) activity index model were applied to calculate the concentration of Alanine I supercritical water. B3LYB method and 6-311G+ (2D, 2P) basic function were used to optimize the molecular structure of Alanine, water and Alanine water complex. Then, reaction parameters of UNIQUAC model were calculated, using formation energy values. PCM method and zero-point energy were utilized to include solvent effect and BSSE effect respectively. The resulted errors indicate that the method in a fairly good agreement with the experimental data. IncludingSSE in the interaction parameter calculations reduces the total error significantly. According to our calculations theAlanine- water complex showed a negative deviation from Raoul's law.

Keywords: supercritical water, UNIQUA, Raoul's Law

INTRODUCTION

In order to design a successful separation method, the behavior of mixture in the upper range of pressure and temperature is very important [1-3]. On the other hand, taking different temperature into account in the experiment is limited for the following reasons:

1) Doing experiment on a large range of temperature and pressure is expensive;
2) Toxic substances are temperature sensitive and not suitable for the experiment at high temperature. Therefore, using the activity coefficient and the equation of state is a common way to model the behavior of mixture [2, 4, 5].

To predict the behavior of asymmetrical mixtures such as water-amino acid, out of the possible methods, activity coefficient method is the most appropriate. On numerous occasions, the activity coefficient model is applied to predict the phase behavior of the mixture [6,7].

To calculate the excess Gibbs energy, Prausnitzand et al, have suggested UNIQUAC model [8]. This model only requires setting parameters for two binary pairs for both types of phase equilibrium. The vapor liquid and liquid-liquid equilibrium are used for binary and multicomponent mixtures.

MATERIALS AND METHODS

UNIQUAC model is taking the difference in size, shape, and energy of various molecules in the mixture, by solving for so-called combination and remaining part equations. The combination part of the equation only includes structural parameters, while the energy difference between molecules is embedded in the remaining part.

The logarithmic equation of activity coefficient for component 'i' is obtained regarding to the relations between Gibbs excess energy and other basic thermodynamic parameters. In this paper, density functional theory (DFT) was used to calculate the binary interaction parameters of UNIQUAC model for water and Alanine system. DFT

accounts for electron correlation in electronic structure calculations and applies electron density instead of electronic wave functions.

RESULTSAND DISCUSSION

The model UNIQUAC and DFT were utilized to obtain the concentration of Alanine as followings:
A) A cluster including 2 molecules of alanine and 16 molecules of water was optimized using semi empirical method, PM6 (Fig1).

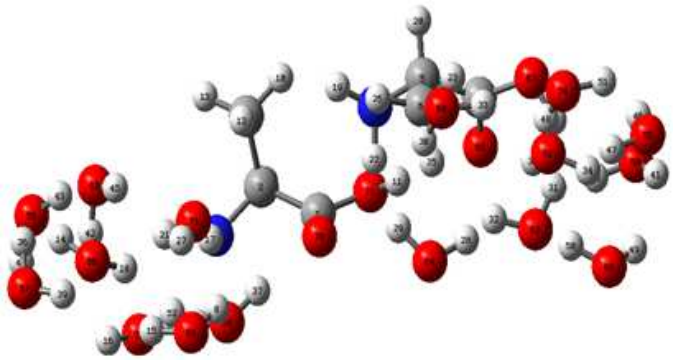

Figure1. Optimized structure of the cluster including 2 molecules of Alanine and 16 molecules of water

B)Pairs of symmetrical molecules of water-water, water- Alanine, Alanine-Alanine and asymmetric pair of these clusters were optimized using DFT with B_3LYP functional [9]. 6-311G + (2d, 2p) was applied as the basis set in DFT calculations. Frequency calculations were performed to confirm that optimized structures have no imaginary frequencies. Optimized structures are shown in figure 2. To refine the results, multiple pairs with different initial structures were selected and the mean results were reported.

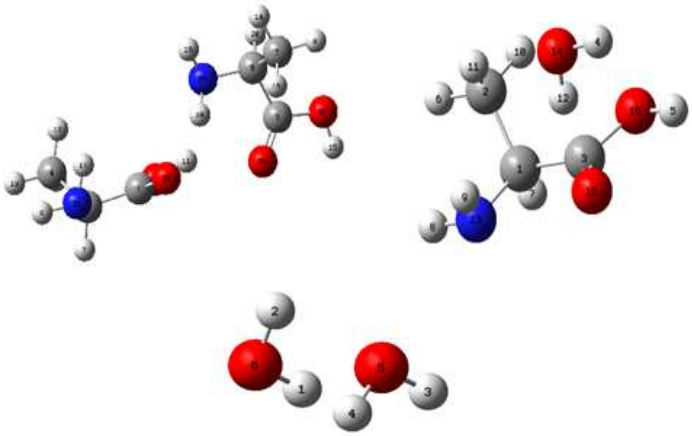

Figure 2.Symmetrical structure of water-water, alanine-alanine and asymmetrical structure of water-alanine optimized using density functional theory

C) All the calculations of step B were repeated using PCM model to include solvent effects.
D) All the calculations of step B were repeated considering basic function of superposition error (BSSE). BSSE is a common method in calculation of Binary and multiple interactions systems.
Interaction parameters of UNIQUAC model were calculated by the following equation:

$$\Delta E_{ij} = E_{ij} - \left(E_{ii} + E_{jj}\right) \qquad (1-1)$$

Corresponding parameter values are reported in Table 1.

Table 1.Corresponding parameter values

	Opt	Freq	SCRF	BSSE
E_{11}	0.013253	0.03424	0.03642	0.09136
E_{22}	0.036347	-0.02841	-0.02471	0.23088
E_{12}	0.023215	-0.02051	-0.01418	0.15822
ΔE_{12}	5539.9373	13070.6116	28090.1828	-192541.4
ΔE_{21}	31019.8671	141172.6290	128195.0789	175637.3

The optimized energies are also reported in table 1. Since alanine is a nonvolatile amino acid, Gibbs-Duhem equation was used. The activity coefficients values were obtained based on water activity coefficient values.

Table2. Activity coefficient values calculated for Alani

X	γ^{exp}	γ^{cal}opt	γ^{cal}freq	γ^{cal}scrf	γ^{cal}bsse
0.9981781	0.99960	1.00006	1.00009	1.00006	0.99953
0.9972956	0.99960	1.00001	1.00004	1.00002	0.99896
0.9963968	0.99950	1.00005	1.00003	1.00003	0.99812
0.9954996	0.99970	1.00009	1.00005	1.00004	0.99712
0.9937297	1.00030	1.00002	1.00006	1.00008	0.99441
0.9928106	1.00000	1.00007	1.00011	1.00011	0.99265
0.9919482	1.00020	1.00004	1.00013	1.00012	0.99070
0.9910449	0.99940	1.00019	1.00016	1.00017	0.98862
0.9840495	1.00030	1.00037	1.00045	1.00045	0.96430
0.9798037	1.00080	1.00053	1.00078	1.00078	0.943561
0.9776979	1.00100	1.00061	1.00096	1.00090	0.93165
0.9756183	1.00130	1.00084	1.00112	1.00114	0.91889

Error bars obtained for each method is reported in figure 3.

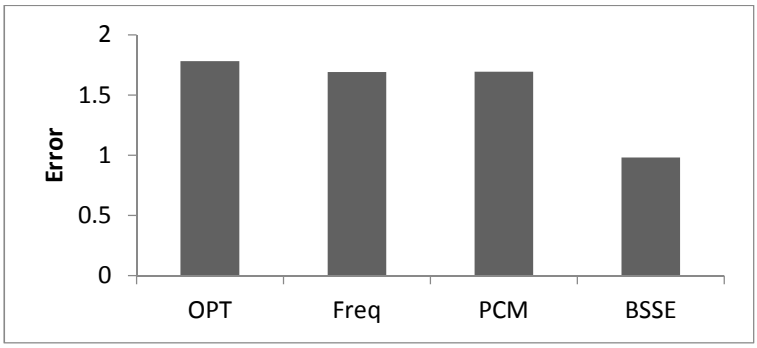

Figure 3. Error bars for different calculations

According to Figure3, superposition error of basic functions dramatically affects the interaction energies and decreases the total error. Also, solvents effects and zero-point energy have reduced calculation errors equally. Activity coefficient values are all more than 1 so all solutions have negative deviation from Raoul's law.

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