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Calculation of concentration of alanine in water using the activity coefficient model and *ab initio* model

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In this paper, the NRTL activity coefficient model has been used to predict phase diagram of water-alanine aminoacid. B3LYP ab initio method with 6-311G+(2d,2p) basis set has been used for determination of NRTL model interaction parameters. Zero-point energy correction, BSSE and solvent effects were also regarded. Amounts of AARD error percents for various calculations were obtained that show the current prediction is being in good agreement with experimental results. Amount of AARD% in BSSE computation is less than another computed AARD%. Regarding to these calculations, we found that there are positive and negative deviations from the Rault's law in our concentration range of water+alanine system.

Key Words: Keywords: activity coefficient model, B3LYP, phase diagram, alanine

1. INTRODUCTION

Prediction of mixture properties in a range of temperature and pressure helps to design laboratorial systems to separate them [1]. Lack of enough laboratorial data and high cost of some reactions prevent us from getting experimental data in some required areas. Also working with some materials such as toxins and herbicides is a health risk. Therefore, computational and theoretical methods for predicting phase diagrams have been developed that amongst them equation of state and activity coefficient models could be named. Using the equation of state with mixing rules in conditions of high temperature and pressure has been reported [2.[

Activity coefficient model for asymmetric binary mixtures in moderate and low temperature and pressure is more usual. Various Activity coefficient models such as Wilson, UNIQUAC and NRTL have been developed [3-5].

When the activity coefficient models are being used, estimating of interaction parameters is important which is obtained by fitting the model to experimental data. When there is no enough experimental data, using this method is often difficult. Various methods have been suggested to solve this problem. One of the newest methods is to use the quantum mechanics. Sandler and Sum propose an algorithm by which binary interaction parameters could be estimated [6.[

In this paper the algorithm developed by Sandler has been used to evaluate water+alanine interaction parameters, while solvent effects, zero-point energy and BSSE [7] errors have also been regarded.

2. RESULTS AND DISCUSSION

Alanine is a non-polar amino acid which plays an important role in nitrogen cycle in cells. This amino acid also plays another important role to transfer blood ammonia [8].

The molecular geometries of compounds used in this study fully optimized at B3LYP [9] theory and 6-311G+(2d,2p) levels using the Gaussian 98 Program [10]. The steps listed below were performed regarding to algorithm suggested by Sandler and Sum to predict water-alanine phase diagram:

1. A cluster (12 water + 4 alanine molecules) was designed and optimized by using AM1 semi-empirical method. Two parameters, the size and semi-empirical method were selected in order to obtain an agreement between accuracy of results and cost of calculations. Also, to construct model similar experimental conditions, the number of water molecules selected more than the number of alanine molecules.
2. Symmetric pairs of molecules (water-water and alanine-alanine) and asymmetric ones (water-alanine) were selected and optimized using 6-311G+(2d,2p) basis set and B3LYP method. (see Figs.1 and 2)

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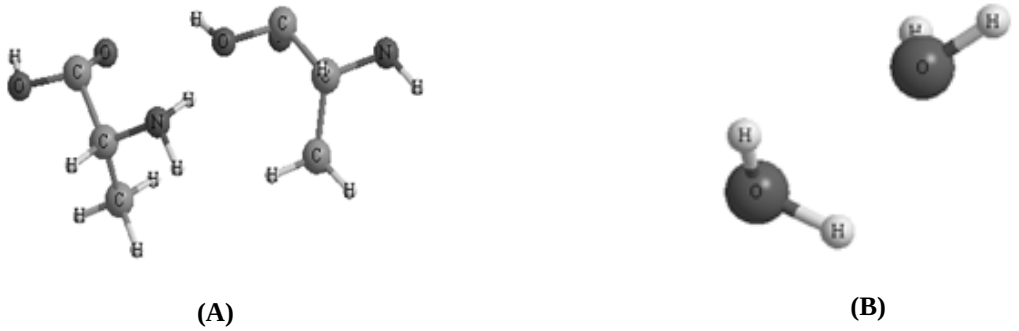

(A) **(B)**

Fig.1 Symmetric pairs of molecules A: alanine-alanine and B: water-water.

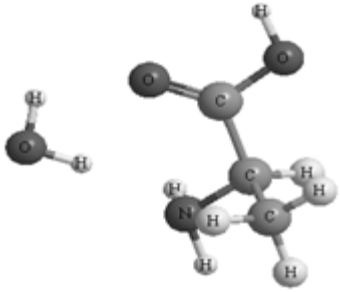

Fig.2 Asymmetric pairs of molecules: alanine-water

3. Frequency computations were performed on optimized pairs in the step before. This was performed in order to consider zero-point energy correction.

4. The second step computations were repeated by the help of PCM model [11] in order to consider solvent effect.

5. Basis Set Superposition Error (BSSE) was calculated in the second step of computations.

Structural energies along with NRTL model interaction parameters are reported in Tables 1. Using the values in Table 1 and considering the Gibbs-Dohem equation, water-Alanine activity coefficients calculated and reported tables 2, 3. Since Alanine is none volatile solute,

we used Gibbs-Dohem equation for computing its activity coefficient based on water's activity coefficient.

Error values in each calculation have been reported in Table 4. Regarding to these tables the following points are to be mentioned:

a. The relationship between computation errors is as follows:

BSSE<SCRF=FREQ<OPT

This shows that the BSSE correction proportion has been more effective than solvent proportion.

a. Since activity coefficient $\gamma=\frac{P^{\exp}}{P^{id}}$ then $\gamma<1$ $\Rightarrow \frac{P^{\exp}}{P^{id}}<1 \Rightarrow P^{\exp}<P^{id}$ thus, negative deviation from Rault's law was observed.

Table 1- Structural energies along with NRTL model interaction parameters (kJ/mol)

	Opt	Freq	SCRF	BSSE
E_{11}	0.012252	0.0312628	0.0354241	0.0913378
E_{22}	0.026348	-0.027485	-0.024749	0.2308475
E_{12}	0.02421899	-0.022507	-0.0137837	0.1582726
ΔE_{12}	5589.9363	13070.0016	28790.1828	-190545.4
ΔE_{21}	31419.86765	141172.6099	129195.0789	175737.3174

Table 2- water activity coefficients at concentration ranges

X	γ^{exp}	γ^{cal}opt	γ^{cal}freq	γ^{cal} scrf	γ^{cal}bsse
0.9981781	0.9996	1.0000046	1.0000066	1.0000068	0.99952584
0.9972956	0.9996	1.00001	1.0000145	1.0000149	0.99895573
0.9963968	0.9995	1.0000178	1.0000257	1.0000264	0.9981473
0.9954996	0.9997	1.0000278	1.0000401	1.0000411	0.99711177
0.9937297	1.0003	1.0000541	1.0000777	1.0000793	0.99440262
0.9928106	1	1.0000711	1.000102	1.000104	0.99264929
0.9919482	1.0002	1.0000892	1.0001277	1.0001301	0.99079014
0.9910449	0.9994	1.0001105	1.0001578	1.0001606	0.98862197
0.9840495	1.0003	1.0003518	1.0004955	1.0004995	0.96439163
0.9798037	1.0008	1.0005655	1.0007893	1.0007911	0.94356948
0.9776979	1.001	1.0006905	1.0009594	1.0009587	0.93164594
0.9756183	1.0013	1.0008263	1.001143	1.0011387	0.91888837

Table 3- Alanine activity coefficients at concentration ranges

X	γ^{exp}	γ^{cal}opt	γ^{cal}freq	γ^{cal} scrf	γ^{cal}bsse
0.0018219	0.9901	0.9981998	0.999001	0.9989314	0.99915851
0.00270438	0.9853	0.9963496	0.9978178	0.9976727	0.99814837
0.00360319	0.9805	0.994028	0.9961609	0.995918	0.99671817
0.00450038	0.9758	0.9913891	0.9940657	0.9937092	0.99488934
0.00627035	0.9666	0.9855814	0.9886927	0.9880835	0.99011899
0.00718938	0.9619	0.9823825	0.9852825	0.9845363	0.98704152
0.00805176	0.9576	0.9793263	0.9817145	0.9808415	0.98378608
0.00895512	0.953	0.9761024	0.9776089	0.9766087	0.97999913
0.01595047	0.9184	0.9524445	0.9346526	0.9332137	0.9383027
0.02019631	0.9002	0.9402287	0.9007885	0.899859	0.90329943
0.02230208	0.8909	0.9348417	0.8823525	0.8819494	0.8835776
0.02438167	0.882	0.9299424	0.8632843	0.8635881	0.86272805

Table 4- Error values

Opt	1.6816115
Freq	1.59161776
Scrf	1.5910117
bsse	0.8701227

3. CONCLUSION

In the present study, we have provided a comparison among Solvent effect, BSSE correction and zero point energy correction in prediction of phase diagram of water-alanine binary system. A conclusion central to our study is that the ab initio method is a good technique to predict phase diagram of asymmetric systems like water-alanine binary system. The results have shown a good consistency between calculated and experimental activity coefficients.

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