Surface Tension and Derived Surface Thermodynamic Properties of Aqueous Sodium Salt of L-Phenylalanine

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Abstract

Objectives: To investigate experimental data of surface tension of aqueous sodium salt of L-phenylalanine (Na-Phe) at temperatures ranging from 298.15 to 343.15 K and concentration ranging from 0.05 to 0.40 (w). **Methodology**: This work was carried out through an optical contact angle tensiometer (OCA 15 EC). It is a video based instrument which employs a pendant drop method for contact angle measurement. **Findings**: It was observed that surface tension values rise as aqueous Na-Phe concentration increases and decrease with the increase in system's temperature. Experimental surface tension data were used to calculate the dervied surface thermodynamic properties such as surface enthalpy and entropy. Surface enthalpy was found to increase with concentration and tend to decrease with the rise in temperature. While, estimated surface entropy values were found to decrease with the increase in Na-Phe concentration. Temperature and concentration dependent empirical correlation was utilized to predict the surface tension data. A good agreement was found between the experimental and correlated data. **Applications/Improvements:** The findings reported in this study could be helpful significantly for the selection of appropriate solvent, and in the calculations for the efficient design of absorption column.

Keywords: L-Phenylalanine, Surface Tension, Sodium Salt, Surface Enthalphy, Surface Entropy

1. Introduction

Surface tension is the differential change of free energy with the change of surface area[1]. Surface tension of aqueous solutions or water in particular is altered by the addition of salts, electrolytes and surfactants[2]. It expresses the force by which the surface molecules attract each other and thus provide the information regarding the molecular interactions that occurs on the surface of the solution, and in the bulk[1,2]. Surface tension plays a key role in tailoring the wettability and non-wettability of various industrial applications such as paints, lubricants, various engineering materials, oil recovery processes, distillation and absorption columns[3,4]. It is an important physical property which controls the hydrodynamics of the absorber in absorption column[5]. For the designing and development of various chemical processes based on amino acid salts such as acid gas contactors and absorption column, the data on surface tension is very significant[6]. Moreover, the derived surface thermodynamic properties such as surface enthalpy and entropy are also useful for com-

prehensive understanding of interactions between the components occurring at the surface region[7].

Alkali salt of L-phenylalanine is one of the amino acid salt proposed as the probable solvent for CO_2 capture because of negligible volatility due to its ionic structure[8]. Moreover, it has low toxicity and high biodegradability similar to other amino acids such as L-proline, glycine, β-alanine and sarcosine, etc[9–11]. Several researchers have investigated different amino acids salts such as sodium and potassium salts of L-proline, glycine, β-alanine and sarcosine, which proves that these solvents have sufficient potential for CO_2 capture[8,10,12]. Surface tension data have much importance in mass transfer processes between CO_2 gas and solvent used, since it enhances the bubbles size and wettability in the absorption column[13,14]. Various researchers are attempting to comprehend the structural changes occurring at the surface-interface from the experimental data of surface tension and its derived surface thermodynamic properties[7]. Moreover, surface tension is one of the property, which helps in the appropriate selection of solvent for CO_2 capture[13,14]. This makes it essential to carry out the study on the surface tension and derived surface properties of aqueous alkali salt of L-phenylalanine. Despite the importance of surface tension data in the CO_2 absorption, no attempt has been made to investigate the surface tension and derived surface properties of amino acid salts, especially, the aqueous sodium salt of L-Phenylalanine (Na-Phe).

Therefore, in this work, surface tension of aqueous Na-Phe has been investigated at different concentrations and temperatures. In addition, the derived surface thermodynamic properties such as surface enthalpy and entropy have also been estimated from experimental surface tension data in order to understand the interaction between water and Na-Phe molecules in the surface region. This data could be useful in the design of CO_2 absorber. Additionally, temperature and concentration dependent empirical correlation has been used for correlating the surface tension of aqueous Na-Phe solution[15]. Statistical analysis of the applied correlation in the form of different statistical parameters was also performed to evaluate the performance of the correlation used.

2. Experimental Section

2.1 Materials

The chemicals used in this work were sodium hydroxide (NaOH, ≥ 99% pure) and l-phenylalanine (Phe, ≥ 99% pure). All the chemicals were bought from Merck Malaysia Sdn. Bhd., and were used without any further purification. An equimolar mixture of NaOH and Phe dissolved in double distilled water was used for the preparation of aqueous Na-Phe solutions. A digital electronic balance (Sartorius BSA 224S-CW) having an accuracy of ± 0.0001 g, was used for the weight measurements. The aqueous Na-Phe solution's concentration was in the range of 0.05 to 0.40 (mass fraction) with an increment of 0.05, while the temperature range from 298.15 to 343.15 K with 5 K interval. The uncertainty in the experimental concentration was found to be ± 0.001.

2.2 Surface Tension Measurement

An optical contact angle tensiometer (OCA 15 EC) was utilized to measure the surface tension of aqueous Na-Phe solutions. It is a video based instrument which employs a pendant drop method for contact angle measurement. A digital camera was used to capture the photograph of the droplet, which was adjusted to 20 frames per second (fps) at a resolution of 752 x 480 pixels. In the pendant drop method, a drop of the solution was formed through an injection needle inside a thermostatic unit, and then the integrated camera focused and captured the drop image. The geometry of the drop was recorded by an integrated software (SCA 20). Later, the software calculated the surface tension of the sample automatically by using Young-Laplace equation. A water bath systemwith an accuracy of ± 0.05 K, was used to control the temperature of the thermostatic unit. The instrument was periodically calibrated with double distilled water to maintain the reliability of the measured data. Data reported were the average of five different measurements. Every time before changing the sample, thermostatic unit and sample needle were thoroughlycleaned with acetone to circumvent any contamination. The uncertainty in the measured values of surface tension was found to be ±0.08 mN.m⁻¹.

3. Results and Discussion

3.1 Surface Tension

Surface tension of aqueous Na-Phe solutions was measured in a mass fraction range of 0.05 to 0.40 and temperatures ranging from 298.15 to 343.15 K. The equipment was first calibrated using solvent (i.e., water) with known surface tension. The calibration results are presented in Table 1, and compared with the literature data in terms of percent average absolute deviation (% AAD)[16]. Based on the deviation value shown in Table 1, a good agreement between literature and experimental data is found, which ensures the reliability of method and results presented in this work. However, the existing value of deviation could be attributed due to the difference in the purity of the solvent, measuring equipment with difference in precision.

Table 1. Comparison of experimental and literature data of surface tension of pure water

T (K)	Surface Tension (γ / mN.m^{-1})	
	Experimental	Literature
298.15	71.79	72.01
303.15	71.10	71.21
308.15	70.25	70.42
313.15	69.42	69.52
318.15	68.66	68.84
323.15	67.75	67.92
%AAD	0.2267	

Table 2. Surface tension data of aqueous Na-Phe at 0.1 MPa

T/K	surface tension (γ / mN.m^{-1})							
	Mass fraction(w)							
	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40
298.15	68.39	69.57	70.61	71.49	73.13	74.46	75.48	77.03
303.15	67.65	68.55	69.85	70.63	72.07	73.25	74.87	76.35
308.15	66.42	67.64	68.89	69.91	71.19	72.56	73.78	75.41

Continued

313.15	65.67	66.82	68.02	69.15	70.49	71.89	73.21	74.69
318.15	64.83	66.06	67.14	68.46	69.84	71.23	72.67	74.09
323.15	64.04	65.35	66.36	67.82	69.29	70.59	72.04	73.53
328.15	63.21	64.67	65.57	67.06	68.59	69.96	71.51	72.80
333.15	62.37	64.01	64.71	66.41	67.92	69.35	70.83	72.10
338.15	61.62	63.15	63.93	65.49	67.09	68.66	70.15	71.33
343.15	60.85	62.28	63.32	64.71	66.20	67.91	69.42	70.79
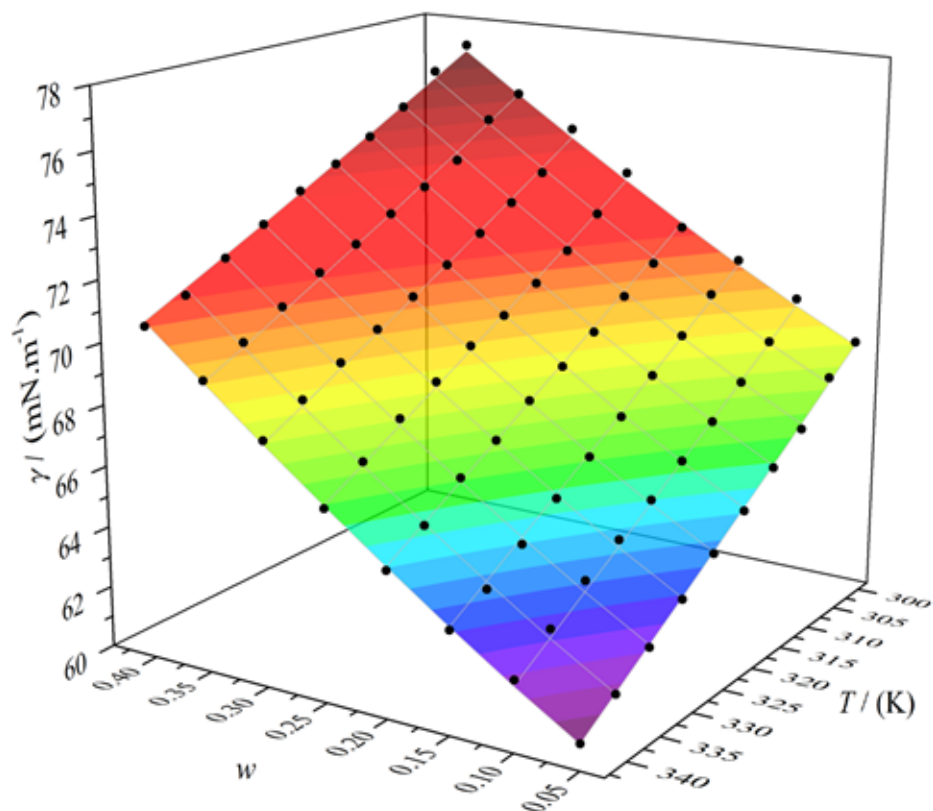
Figure 1. Effect of temperature and concentration on surface tension of aqueous Na-Phe for various mass fractions. Symbols (•) refer to experimental data points and contour surface refers to predicted data points calculated from Equation (3).

The measured surface tension data of aqueous Na-Phe solutions are presented in Table 2. Temperature and concentration effect on surface tension of aqueous Na-Phe solutions is shown in Figure 1. It can be elucidated from Figure 1 that surface tension values decrease linearly as the solution temperature rises at any fixed Na-Phe concentration, while these values increase linearly as the Na-Phe concentration in the solution rises isothermally. With the rise in the solution's temperature, both water and Na-Phe molecules try to move apart, which results in weakening the molecular interactions between them, and thus decreasing the surface tension[7]. While, the rise in surface tension with increasing the Na-Phe concentration is due to the cumulative effect of dispersion forces, electrostatic forces, and ionic hydration[7]. A similar trend in the values of surface tension can be seen in the literature[7,17–19].

3.2 Derived Surface Thermodynamic Properties

Derived surface thermodynamic properties such as surface enthalpy and entropy are important for the detailed understanding of interactions between different components of the surface region[7]. These properties were calculated from the experimental surface tension data of aqueous Na-Phe solution. In order to estimate surface enthalpy and entropy, the surface tension data were linearly fitted with respect to temperature for various concentrations. The surface enthalpy ($H\gamma$) can be calculated using equation (1)[7,20].

$$H^{\gamma} = \gamma - T\left(\frac{\partial \gamma}{\partial T}\right) \qquad (1)$$
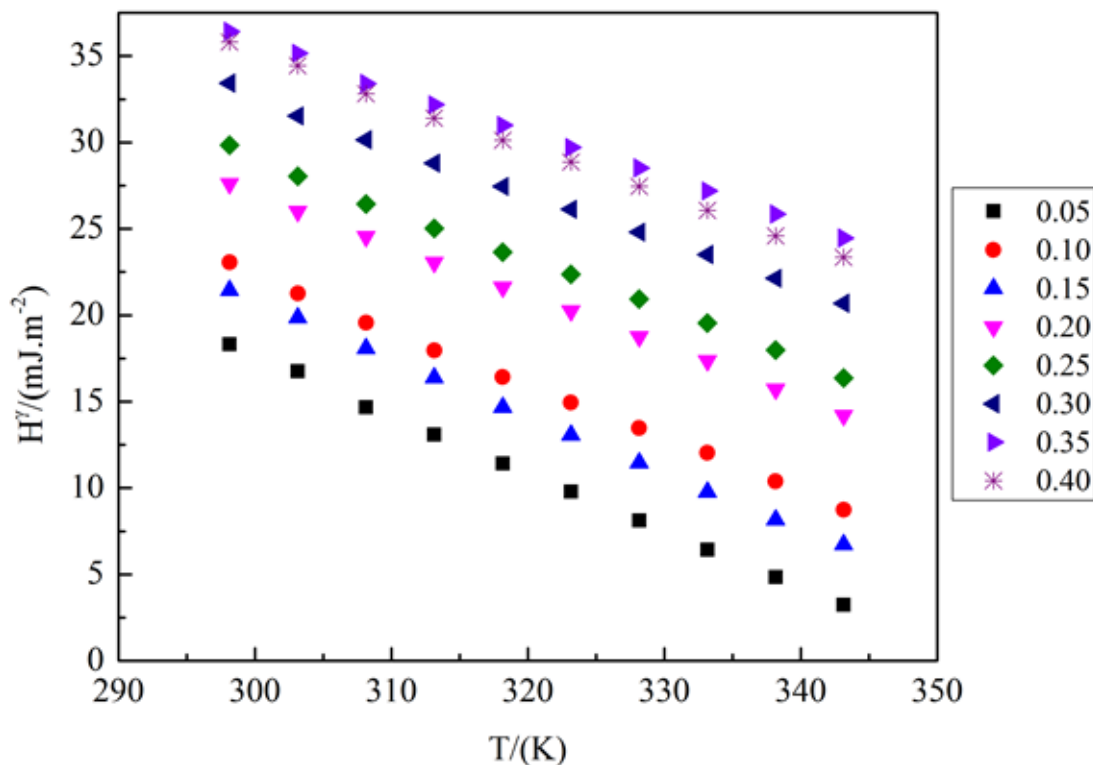

Figure 2. Surface enthalpy of aqueous Na-Phe solution at different temperatures and concentrations.
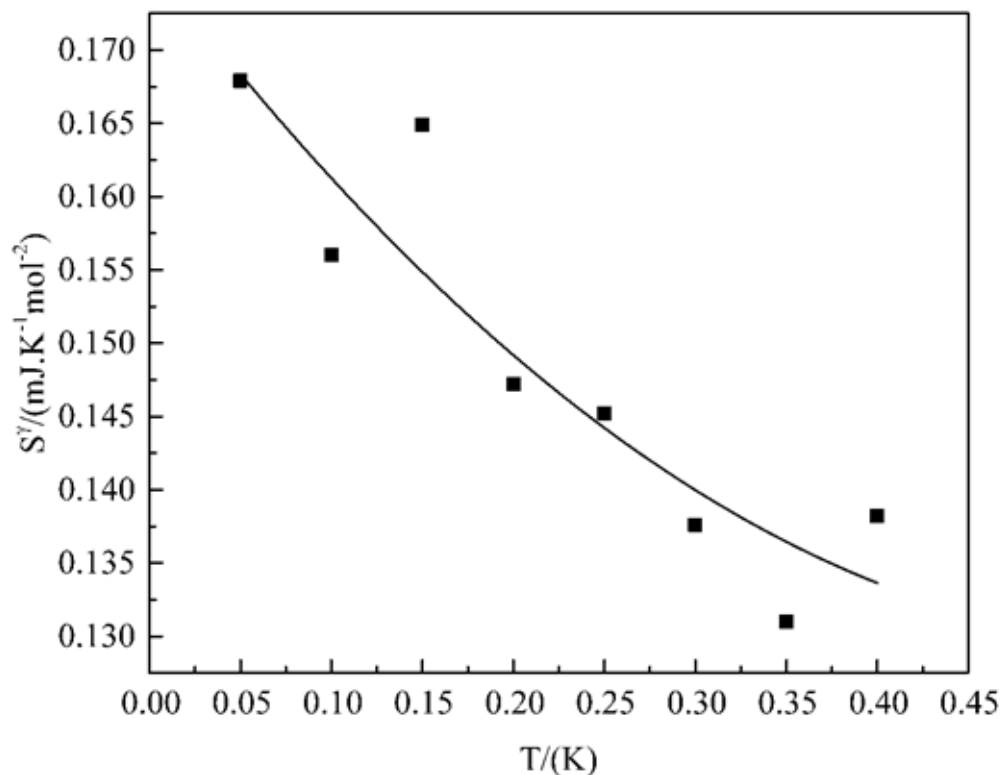
Figure 3. Surface entropy of aqueous Na-Phe solution at different temperatures and concentrations.

While, the surface entropy (S^γ) can be estimated using Equation (2)[7,20].

$$S^\gamma = -\frac{\partial \gamma}{\partial T} \qquad (2)$$

Where γ represents surface tension of aqueous Na-Phe and T represents the absolute temperature.

The estimated surface enthalpy data of aqueous Na-Phe solution are shown in Figure 2. It can be elucidated from Figure 2 that, enthalpy of surface formation mostly follows an increasing trend with the concentration at various temperatures. The observations found in this study are similar to those reported by[2] for various aqueous salt solutions. Moreover, the calculated surface entropy data are shown in Figure 3. The surface entropy values show a slight decreasing trend with the rise in Na-Phe

concentration. The interaction between the charge of the ion and the water-dipole constitute an important factor for the surface entropy of aqueous Na-Phe solutions[2,21]. A steady decrease in the surface entropy values can be seen upon the addition of Na-Phe salt in the water. A possible explanation for this type of behavior is that, the decrease in surface entropy is owing to the antisolvent crystallization of air molecules from the surface region[2,7,19,21]. The same behavior can be seen in the literature also[7,17].

3.3 Correlation Study

In the past, the correlation utilized for the prediction of surface tension data was primarily a function of temperature for different concentrations. As a result, individual equations were required to associate the surface tension data with respect to temperature and every concentra-

tion[22,23]. This makes the correlation study more complex and time consuming due to the various equations and their respective fitting parameters. Therefore, in the present study, the experimental data of surface tension were correlated as a function of both temperature and concentration. A modified Graber equation was used to represent the data of surface tension, as given in Equation (3)[15].

$$\gamma = w * \exp(A_1 + A_2 T^{0.5} + A_3 w^{0.5}) + A_4 + A_5 T^{0.5} + A_6 w^{0.5}$$

(3)

Where γ is the surface tension, w represents the mass fraction, T is the solution's temperature, and A_i (i = 1-6) represents the corresponding fitting parameters of Equation (3). The fitting parameters calculated are tabulated in Table 3. Moreover, in order to check the reliability and accuracy of the applied correlation, statistical analysis has been performed in terms of least-square correlation coefficient (R^2), Standard Deviation (SD), Average Relative Deviation (ARD) and percent Average Absolute Deviation ($\% AAD$). The data of these statistical parameters are presented in Table 4. Following equation were used to estimate the statistical parameters.

$$R^2 = \frac{\sum_{i=1}^{i=n}\left(x_{exp} - x'_{pred}\right)^2 - \sum_{i=1}^{i=n}\left(x_{exp} - x_{pred}\right)^2}{\sum_{i=1}^{i=n}\left(x_{exp} - x'_{pred}\right)^2}$$

(4)

$$SD = \sqrt{\frac{\sum_{i=1}^{i=n}\left(x_{exp} - x_{pred}\right)^2}{n-1}}$$

(5)

$$ARD = \frac{\sum_{i=1}^{i=n}\left|x_{exp} - x_{pred}\right|}{n}$$

(6)

$$\% AAD = \frac{100}{n} * \sum_{i=1}^{i=n}\left|\frac{\left|x_{exp} - x_{pred}\right|}{x_{exp}}\right|$$

(7)

Table 3. Fitting parameters for surface tension measurement using Equation (1)

Measurement	Parameters		No. of data points, n
	i	A_i	
	1	0.9511	
	2	0.1231	
	3	0.3109	
Surface Tension	4	172.6	80
	5	-6.081	
	6	-2.132	

Table 4. Evaluation of statistical parameters for surface tension

Parameter	Value
R^2	0.9984
SD	0.1506
ARD	0.1244
%AAD	0.1805

where x_{exp}, x_{pred}, x'_{pred}, and n are experimental data, predicted data, mean predicted data and number of data points respectively. Data presented in Table 4 shows that the applied correlation have good prediction ability and could be used for any future calculations.

In order to view the graphical representation of the experimental and correlated values, % relative error curve and cross-plot were drawn, and shown in Figures 4-5. In Figure 4, the data sets which are near to the line y = 0 show more accuracy than the data slightly dispersed. Similarly, in Figure 5, the data sets near to the line y = x show less error than the scattered ones. Figures 4-5 show that a large number of data points do not scatter much, which suggest that the applied correlation is suitable for the prediction of surface tension data.
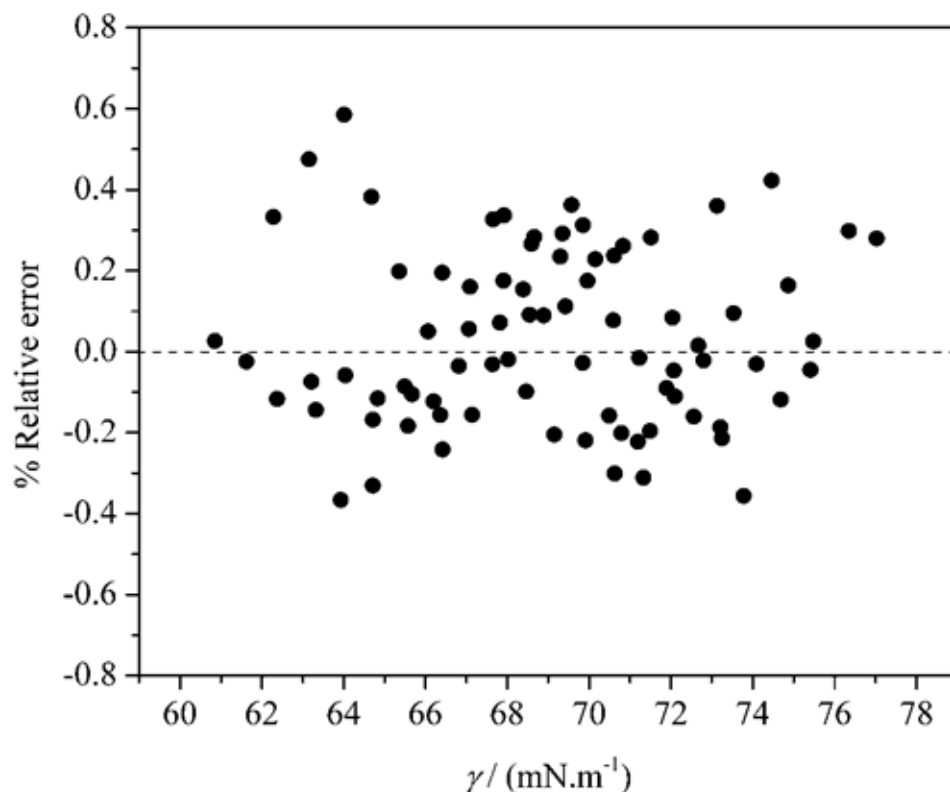
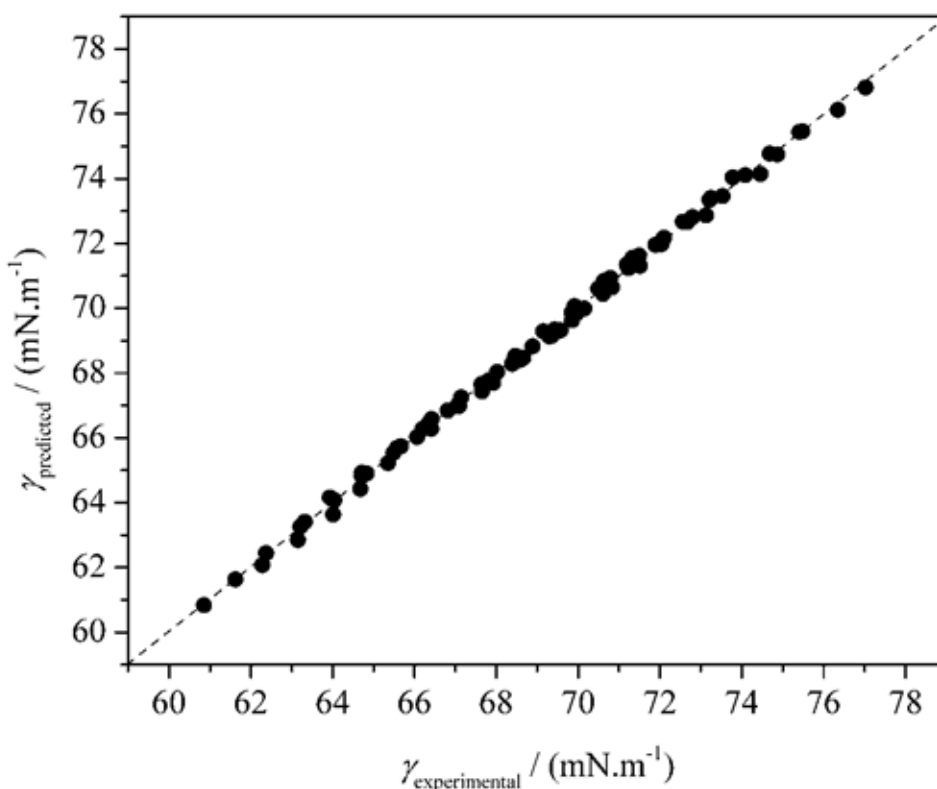**Figure 4.** Relative error distribution of surface tension data.

Figure 5. Comparison between experimental and predicted data of surface tension.

4. Conclusion

Surface tension of aqueous Na-Phe solution was measured over a concentration range of 0.05 to 0.40 mass fraction and temperature ranging from 298.15 to 343.15 K. The reported data showed that surface tension increased with increase in Na-Phe concentration, and decreased with the rise in system's temperature. Derived surface thermodynamic properties such as surface enthalpy and surface entropy were calculated from experimental surface tension data of aqueous Na-Phe solution. The values of surface enthalpy showed increasing trend with the rise in concentration; however, these values decreased with the rise in temperature. While, the values of surface entropy decreased slightly with the rise in concentration of Na-Phe. Moreover, applied empirical correlation was satisfactorily used for correlating the surface tension data. Detailed statistical analysis showed that the applied correlation could be used for the prediction of surface tension data at various temperatures and concentrations. The results obtained in this study could be helpful significantly for the selection of appropriate solvent, and in the calculations for the efficient design of absorption column.

5. Acknowledgement

6. References

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