

Solubility of Thiamine in Pure and Mixed Solvents in Function of Temperature

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The present paper details the solid-liquid equilibrium (SLE) of thiamine in pure dimethylsulfoxide (DMSO) and aqueous solvent mixtures of varying DMSO concentrations. The solubilities were measured in the temperature range of 298.15 K to 323.15 K at 5.0 K intervals, under atmospheric pressure, by employing gravimetric analysis. The experimental results indicate that the vitamin's solubility increases with increasing temperature and the water mass present in the initial solvent mixture. The adjustments using rational models were satisfactory, achieving adequate correlations and predicting the values of the solubility measurements in the laboratory with acceptable accuracy.

Key words

solid-liquid equilibrium, thiamine, vitamin, solvent, rational models, solubility

Introduction

Vitamin B1 ($C_{12}H_{17}N_4OS \cdot HCl$, molecular weight = 337.33 g mol⁻¹), also called thiamine, has great importance in the food industry in general. Thiamine is a vitamin belonging to the B complex, and can be found in the cuticle of rice, brewer's yeast, grains, egg yolk, liver, kidney, pork, fish, peanut, walnut, legumes, as well as in green and leafy vegetables. It acts in different parts of the body and plays a major role in the nervous, muscular and cardiovascular systems, in addition to assisting in glucose metabolism. Thiamine deficiency causes brain damage and in some cases it may be irreversible. Among the diseases caused by vitamin B1 deficiencies are: Beriberi, Wernicke's encephalopathy and Korsakoff's syndrome¹. Thiamine is not stored in large amounts in the body, with provision from the daily diet being necessary. Thiamine is unstable in alkali conditions and is heat stable at acidic pH values.

Thiamine solubility data in water are widely found in the literature. However, solubility data in alternative solvents such as dimethylsulfoxide (DMSO) and DMSO + water mixtures may be important for studies of separation and purification of the feedstock. On the other hand, the crystallization processes of thiamine require a large amount of accurate solubility data. Unfortunately, there is a lack of solubility data that indicates the solubility dependence as a function of temperature and of the initial

solvent mixture composition^{2,4}. Thus, obtaining solubility data for thiamine under known conditions of temperature, pressure and concentration of the initial mixture of solvents is important in order to improve manufacturing processes and purification (crystallization) of this vitamin.

Experimental

Materials

Vitamin B1 with a mass fraction >99.0 % was obtained from Synth[®]. The organic solvent, DMSO was obtained from Vetec[®] with 99.9 % purity. All chemicals were used without further purification.

Apparatus and procedure

In the assays, solubility data of thiamine electrolyte were determined in mixed solvents as a function of temperature by the static method followed by a gravimetric analysis³⁻⁶. The experimental work was performed at atmospheric pressure in the temperature range from 298.15 K to 313.15 K. In this article, the experimental apparatus for measuring the solubility of the vitamin B1 was a jacketed glass cell (volume = 35.0 · 10⁻⁶ m³). The temperature was regulated by a thermostatic bath and the cell temperature was measured by a thermometer with uncertainty ± 0.1 K.

Saturated solutions of the vitamin were prepared with different concentrations in DMSO and double-distilled and deionized water. The solutions

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were prepared to achieve equilibrium with electrolyte excess, while they were subjected to a constant temperature. A magnetic stirrer was used to promote the agitation of the solution and ensure the establishment of equilibrium. The stirring period consisted of 162 minutes, followed by a rest period of 180 minutes. Different stirring periods were tested to determine a suitable equilibrium time. It was found that 162 minutes after stirring had stopped was enough time for thiamine in solvent to reach equilibrium, because repetitive measurements during the following several hours indicated the results are reproducible. Finally, the sampling was made in triplicate. The samples were withdrawn from a previously thermostated syringe according to the temperature of the solution. The sample analysis was made from the gravimetric method. In Figure 1, the layout of the experimental apparatus is presented.

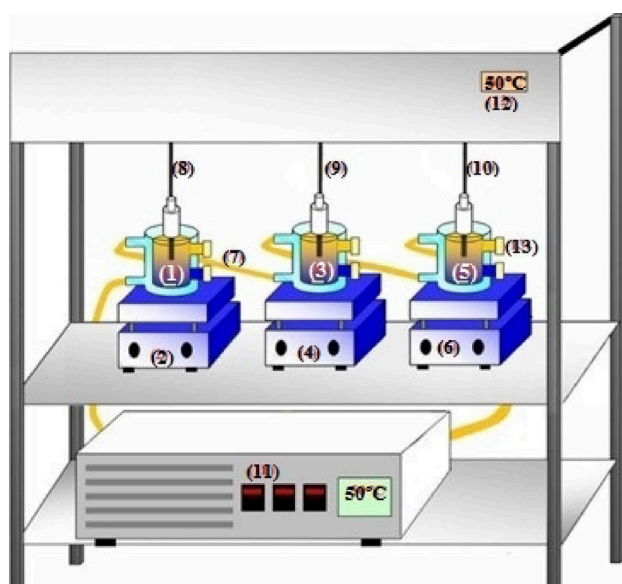


Fig. 1 – Experimental apparatus representation: 1, 3 and 5 Jacketed glass cell; 2, 4 and 6 Magnetic stirrer; 8, 9 and 10 Thermometer; 7 Latex hose; 11 Thermostatic bath; 12 Temperature indicators; 13 Septa

Results and discussion

Solubility data

The data of thiamine mole fraction solubility in mixed solvents as a function of temperature are listed in Table 1 and Figure 2. All experimental data are included in Table 1. In this table, m is the thiamine molality with the experimental standard deviation among three samples. By analyzing the data for each temperature, it can be noted that all of them have a maximum point at the maximum water concentration. This occurs because thiamine is a water-soluble vitamin⁷. From Table 1 and Figure 2, we can conclude that the thiamine solubility in all the mixed solvents increases with the increase in both temperature and mass fraction of water in DMSO solution.

The results suggest that an explanation for the increased solubility of thiamine with increasing mass fraction of water is based on the fact that thiamine is a molecule with a highly polar structure. Thus, the smaller and less voluminous water molecule clusters more easily around the thiamine molecules than the bulkier DMSO.

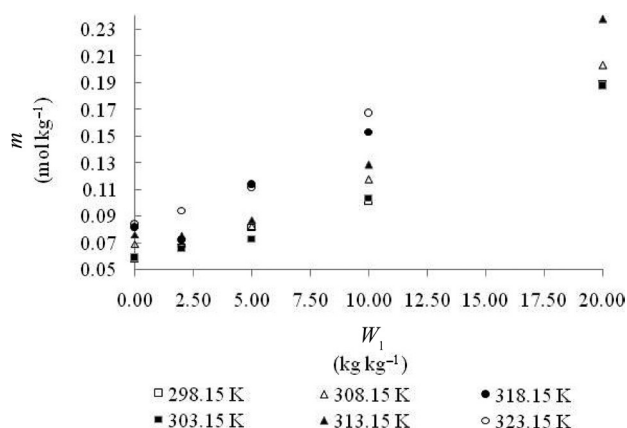


Fig. 2 – Solubility of thiamine (m) in function of mass fraction of DMSO in water + DMSO initial solution without thiamine at four temperatures

Table 1 – Thiamine solubility in aqueous mixtures as a function of the temperature

T(K)	W_{H_2O} (kg kg ⁻¹)				
	0.00	2.00	5.00	10.00	20.00
$m \pm \delta$ (mol kg ⁻¹)					
298.1	0.0574±0.0022	0.0655±0.0004	0.0815±0.0035	0.1007±0.0029	0.1892±0.0016
303.0	0.0585±0.0044	0.0659±0.0009	0.0729±0.0008	0.1037±0.0031	0.1875±0.0032
308.0	0.0691±0.0014	0.0696±0.0024	0.0824±0.0020	0.1175±0.0015	0.2028±0.0099
313.0	0.0762±0.0004	0.0748±0.0008	0.0871±0.0024	0.1285±0.0034	0.2375±0.0024
318.1	0.0812±0.0016	0.0715±0.0027	0.1131±0.0038	0.1532±0.0015	0.2445±0.0009
323.2	0.0834±0.0020	0.0941±0.0022	0.1112±0.0056	0.1671±0.0024	0.2924±0.0042

Data correlation

The relationship between the solubility measured by the molality and the temperature was proposed by mathematical models available in the literature^{8–10} represented by Equations 1, 2 and 3, respectively.

$$\ln m = A + \frac{B}{T} + C \cdot \ln T \quad (1)$$

$$\log m = A' + \frac{B'}{T} + \frac{C'}{T^2} \quad (2)$$

$$\ln m = A''T^2 + B''T + C'' \quad (3)$$

Equations 1, 2 and 3 were proposed by Heidman *et al.* (1985), Yaws *et al.* (1993) and Rasmuson *et al.* (2006). Thus, the superscripts h , y and r were used to differentiate the parameters obtained in the fits. In this article, the Heidman, Yaws and Rasmuson models have been changed in order to obtain better results. These modified models are represented by Equations 4, 5, and 6, respectively, similar to the literature⁶.

$$\ln m = A^h + \frac{B^h}{T} + C^h \cdot C_{DMSO} \cdot \ln T \quad (4)$$

$$\ln m = A^y + \frac{B^y}{T} + \frac{C^y \cdot C_{DMSO}}{T^2} \quad (5)$$

$$\ln m = A^r T^2 + B^r T + C^r C_{DMSO} \quad (6)$$

The experimental points were fitted by non-linear regression using the Levenberg-Marquardt method¹¹ to obtain the dimensionless parameters A^h , B^h , C^h , A^y , B^y , C^y , A^r , B^r , and C^r to solve the optimization problem. The objective function was used to minimize the sum of squared residuals. In three fittings, the parameters presented low standard deviations. The parameters calculated for these models have shown low standard deviation. The accuracy of the adjustments was also verified by the observed quadratic correlation coefficients (R^2). All correlation coefficients were >97 %, indicating that the calculated parameters with more than 97 % of the variability in the data could be explained by the rational models employed. In all settings, the averages of relative deviations between the values obtained by the model and the values obtained in the laboratory were calculated. The average to relative deviations, σ^h , σ^y and σ^r were calculated by the following equations:

$$\sigma^h = \frac{\sum_{i=1}^{NP} \left[\frac{(m - m^h)}{m} \right]}{NP} \quad (7)$$

$$\sigma^y = \frac{\sum_{i=1}^{NP} \left[\frac{(m - m^y)}{m} \right]}{NP} \quad (8)$$

$$\sigma^r = \frac{\sum_{i=1}^{NP} \left[\frac{(m - m^r)}{m} \right]}{NP} \quad (9)$$

Where m is the experimental data and NP is the number of experimental points.

The values obtained for the modified models of Heidman, Yaws and Rasmuson identified by H, Y and R, respectively, are shown in Table 2.

Table 2 – Data fitting

		Estimated parameters	Standard error
H	A^h	2.50	0.47
	B^h	-1612.24	146.61
	C^h	1.04	0.032
	R^2	0.978	
Y	A^y	3.50	0.53
	B^y	-1909.70	164.23
	C^y	573160.20	19554.3
	R^2	0.978	
R	A^r	0.00	0.00
	B^r	-0.03	0.01
	C^r	5.98	0.17
	R^2	0.990	

The average for the relative deviations of the fitted data for the system thiamine + water + DMSO were 0.054 %, 4.261 % and 0.279 % for Heidman, Yaws and Rasmuson fittings, respectively. The experimental standard deviations for the thiamine solubility data in mixtures of solvents (DMSO + water) are shown in Figures 3, 4 and 5, respectively.

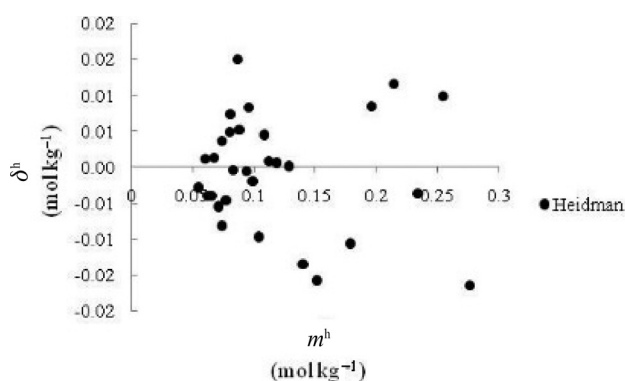


Fig. 3 – Experimental standard deviations for the data of solubility of thiamine in mixtures of solvents (DMSO + water) for adjustments Heidman

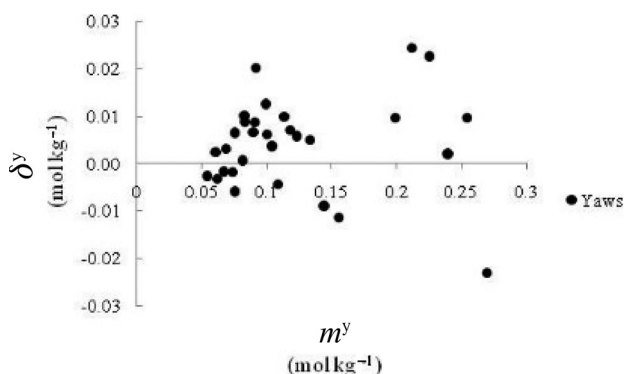


Fig. 4 – Experimental standard deviations for the data of solubility of thiamine in mixtures of solvents (DMSO + water) for adjustments Yaws

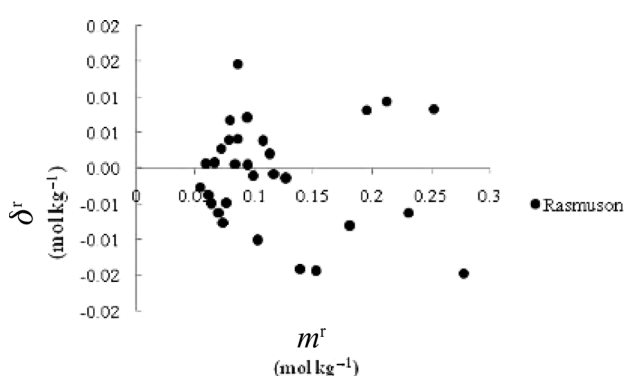


Fig. 5 – Experimental standard deviations for the data of solubility of thiamine in mixtures of solvents (DMSO + water) for adjustments Rasmuson

According to Figures 3, 4 and 5, it is possible to observe that the fitting of the three models displayed no biased characteristics. In all cases, the average of relative deviations calculated was lower than 4.3 %. This fact indicates that the models have adjusted well to the experimental data. One can also say that the three equations presented are able to predict with good accuracy the solubility values for the systems studied in the cited conditions.

It is noted in this case that the average of relative deviations was smaller than 4.3 %, which shows little variation between the results correlated by the models and those obtained experimentally. On the other hand, the correlation coefficients for the three models showed values higher than 97.8 %. Given the above, it can be seen that these models are also suitable for the correlation/prediction of the experimental data obtained in the laboratory under specified conditions.

Conclusion

The thiamine solubility data in the solvent mixture (water + DMSO) demonstrates, in an isothermal system, that the solubility of the vitamin is very

high in water (highly hygroscopic solution); it increased before increasing the concentration of water as a cosolvent in combination with DMSO. This is common behavior among vitamins as observed in the literature⁷. Additionally, it is observed that thiamine solubility also increases with increasing temperature, as observed in the literature^{7,12–14}. An adequate relationship between the experimental results and the results described by the fitting models was observed. Finally, it was observed that the models satisfactorily accounted for the variability of experimental data obtained.

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List of symbols

- A^h, B^h, C^h – parameter for polynomial Eq. (4)
- A^y, B^y, C^y – parameter for polynomial Eq. (5)
- A^r, B^r, C^r – parameter for polynomial Eq. (6)
- m – molality (mol kg^{-1})
- T – temperature (K)
- W – concentration (kg kg^{-1})
- NP – number of experimental points
- DMSO – dimethylsulfoxide
- SLE – solid–liquid equilibrium
- σ – average for relative deviations
- δ – experimental standard deviation
- H – Refers to Heidman model
- Y – Refers to Yaws model
- R – Refers to Rasmuson model

List of superscripts and subscripts

- h – Heidman
- y – Yaws
- r – Rasmuson

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