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Solubility determination and thermodynamic dissolution functions of 1,3-diphenylguanidine in nine organic solvents at evaluated temperatures

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ABSTRACT

The solubility of 1,3-diphenylguanidine was determined in ethanol, isopropanol, *n*-propanol, *n*-butanol, *i*-butanol, ethyl acetate, toluene, acetone and acetonitrile by a high performance liquid chromatography (HPLC) within temperature range from (273.15 to 313.15) K under pressure of 101.3 kPa. The solubility of 1,3-diphenylguanidine in the selected solvents increased with the increase in temperature. On the whole, the solubility of 1,3-diphenylguanidine in these solvents followed the order: acetone > ethyl acetate > *n*-butanol > *n*-propanol > ethanol > *i*-butanol > acetonitrile > isopropanol > toluene. The acquired solubility of 1,3-diphenylguanidine were correlated with the Apelblat equation, λh equation, Wilson model and NRTL model, and the corresponding model parameters were obtained. The Apelblat equation provided better results than the other three models. Furthermore, the apparent dissolution enthalpy and excess enthalpy of solution were obtained from the experimental solubility. The solubility would be helpful in optimising the purification process of 1,3-diphenylguanidine on the industrial scale.

1. Introduction

1,3-Diphenylguanidine (CAS No. 102-06-7, chemical structure shown in Fig. 1) is an important industrial chemical. The uses of 1,3-diphenylguanidine and its derivatives are widely spread in rubber industry, biology, medicine, and many other fields [1–7]. The preparation process of 1,3-diphenylguanidine in commercial scale is using diphenylthiourea as raw material. It can be prepared by treating diphenylthiourea and zinc oxide with liquid ammonia [8–9], or by treating diphenylthiourea and cyanogen chloride with ammonia [10,11] or by treating diphenylthiourea and oxygen with ammonia [12,13] and or by diphenylthiourea and hydrogen peroxide with ammonia [14]. Although the yield of 1,3-diphenylguanidine is relatively high by these methods, the crude product usually contains some unreacted diphenylthiourea. The difficulty is encountered in separating 1,3-diphenylguanidine with high purity from the reaction mixture because of its extremely poor solubility in water. With the development of industry, the requirements for the product purity are becoming higher. The crude 1,3-diphenylguanidine restricts its uses in many aspects.

In general, 1,3-diphenylguanidine is purified by dissolving the crude product in water, extracting this solution with the mixture of at least one water insoluble, a polar hydrocarbon and at least one polar organic compound, and precipitating 1,3-diphenylguanidine from the solution by the addition of alkali metal hydroxide [9–15]. However, the cost of the process is relatively high. It is commonly known that solvent crystallization is an important unit operation during purifying a solid compound. It is of great importance for knowledge of solubility in designing the chemical industrial process of 1,3-diphenylguanidine. Unfortunately, to the best of the authors' present knowledge, the solubility of 1,3-diphenylguanidine in solvents cannot be found in previous publications. Solubility and dissolution thermodynamic properties can be used to optimise the basic design of the solvent crystallization process and improve the purity of 1,3-diphenylguanidine. Therefore, it is very necessary to study the solubility of 1,3-diphenylguanidine in different solvents at evaluated temperatures and the thermodynamic properties of solution in order to obtain the high purity product.

The purposes of the present work are to (1) obtain the 1,3-diphenylguanidine solubility in different solvents, including ethanol, isopropanol, *n*-propanol, *n*-butanol, *i*-butanol, ethyl acetate, toluene, acetone and acetonitrile at different temperatures by high performance liquid chromatography (HPLC); (2) correlate the acquired solubility data via Apelblat equation, λh equation, Wilson model and NRTL model; and (3) compute the dissolution

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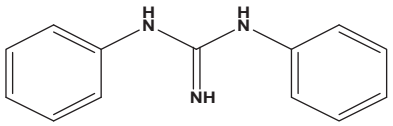

Fig. 1. Chemical structure of 1,3-diphenylguanidine.

thermodynamic properties of 1,3-diphenylguanidine in different solvents.

2. Experimental

2.1. Materials

1,3-Diphenylguanidine with a mass fraction of 0.97 was provided by Sigma–Aldrich Co. LLC. It was crystallized three times in ethanol. The composition of the recrystallized sample was 0.997 in mass fraction, which was confirmed by a high-performance liquid phase chromatograph (HPLC). The solvents of ethanol, *n*-butanol, *i*-butanol, *n*-propanol, isopropanol, toluene, ethyl acetate, acetonitrile and acetone were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd., China. They were employed in solubility determination without further purification. The details of 1,3-diphenylguanidine and these solvents were tabulated in Table 1.

2.2. Melting properties measurement

The melting temperature T_m of 1,3-diphenylguanidine was reported in the publications [16–21], nevertheless the difference between them is a little large. For example, this temperature was (449–451) K determined by Scherz and co-workers [16]; (421–423) K, by Naunton [18]; and (414.2–416.2) K, by Michelle [21]. In addition, the fusion enthalpy $\Delta_{fus}H$ of 1,3-diphenylguanidine has not been reported until now. In this work, in order to correlate the solubility values of 1,3-diphenylguanidine in solvents with thermodynamic models, the melting point and melting molar enthalpy were determined by using a DSC instrument (Pyris-Diamond, PerkinElmer) under a nitrogen atmosphere. The DSC instrument was pre-calibrated with indium as the reference substance before testing. About 4 mg of 1,3-diphenylguanidine were put in a DSC pan, and then the sample was heated with a heating rate of 2 K·min^{-1} at the temperatures range from (323 to 480) K.

2.3. Solubility determination

The binary solid–liquid phase equilibrium for the systems of (1,3-diphenylguanidine + solvent) was achieved with the isothermal saturation [22] in the temperatures ranging from (273.15 to 313.15) K under 101.3 kPa, and the solubility of 1,3-diphenylguanidine was measured using the high-performance liquid chromatography (HPLC) [23,24]. The experimental apparatus for the solubility measurements is shown graphically in Fig. 2, which included a 50 mL jacketed glass vessel with a magnetic stirrer and a circulating water bath used to keep the temperature. The smart thermostatic water bath (Type of DZKW-4 with a standard uncertainty of 0.01 K) was employed to control the water temperature. The mass of the solute, solvent and solution was determined using an analytical balance (Mettler AE240) with the standard uncertainty of 0.0001 g.

The experimental saturated solutions were made by placing excessive 1,3-diphenylguanidine in the 50 mL glass vessel filled with about 20 mL solvent. To avoid the solvent from escaping, a condenser was connected to the glass vessel. The temperature of the vessel was controlled by circulating water from the

Table 1
Detailed information of 1,3-diphenylguanidine and the selected solvents.

Chemicals	Molar mass g mol^{-1}	Melting point K	Melting molar enthalpy kJ mol^{-1}	Density kg m^{-3}	Source	Mass fraction purity	Purification method	Analysis method
1,3-Diphenylguanidine	211.26	421.15[a] 449–451[b] 423[c] 421–423[d] 420–421[e] 419–420[f] 414.2–416.2[g]	22.52[a]	1190.0[h]	Sigma–Aldrich Co. LLC.	0.997	Recrystallization	HPLC[j]
n-Butanol	74.12			801.8[i]	Sinopharm Chemical Reagent Co., Ltd., China	0.995	None	GC[k]
Ethanol	46.07			789.3[i]		0.997	None	GC[k]
n-Propanol	60.06			805.3[i]		0.995	None	GC[k]
Isopropanol	60.06			803.5[i]		0.997	None	GC[k]
Ethyl acetate	88.11			900.3[i]		0.995	None	GC[k]
Acetone	58.05			784.5[i]		0.995	None	GC[k]
Acetonitrile	41.05			776.8[i]		0.990	None	GC[k]
Toluene	92.14			871.0[i]		0.995	None	GC[k]
i-Butanol	74.12			801.9[i]		0.995	None	GC[k]

[b,c,d,e,f,g] Taken from Refs. [16], [17], [18], [19] and [20], respectively.
[a] This work, determined under 101.3 kPa. The standard uncertainties u are $u(T) = 0.5$ K, $u(p) = 450$ Pa and $u(\Delta_{fus}H) = 400$ J mol^{-1}.
[h] Taken from "International Chemical Safety Cards" data obtained from the National Institute for Occupational Safety and Health (US).
[i] Taken from Ref. [31].
[j] High-performance liquid chromatography.
[k] Gas chromatography.