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Short Communication

Solubility and thermodynamics of terbinafine hydrochloride in different neat and binary solvents: Measurement, correlation and molecular interactions

Hongwei Shi *, Yong Xie

School of Chemistry and Chemical Engineering, Suzhou University, Suzhou 234000, PR China
Anhui Key Laboratory of Spin Electron and Nanomaterials of Anhui Higher Education Institutes, Suzhou University, Suzhou, Anhui 234000, PR China

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ABSTRACT

The solubility of terbinafine hydrochloride in four pure solvents, including methanol, ethanol, *n*-propanol and ethyl acetate and their binary solvent mixtures, including (methanol + ethyl acetate), (ethanol + ethyl acetate) and (*n*-propanol + ethyl acetate) performed at different mass fractions of methanol, ethanol or *n*-propanol ranging from 0.1 to 0.9, was determined by using isothermal saturation method with temperatures ranging from (278.15 to 313.15) K. The descending order of the mole fraction solubility in pure solvents was as follow: methanol > ethanol > *n*-propanol > ethyl acetate, and for the three mixture with given initial composition, the solubility of terbinafine hydrochloride increased with increasing temperature and mass fraction of alcohol for the three systems including (methanol + ethyl acetate), (ethanol + ethyl acetate) and (*n*-propanol + ethyl acetate). At the same mass fraction of methanol, ethanol or *n*-propanol and temperature, the solubility of terbinafine hydrochloride was greater in (methanol + ethyl acetate) than in the other mixed solvents. The maximum mole fraction solubility of terbinafine hydrochloride was observed in methanol (6.297×10^{-2} at 313.15 K), followed by that in ethanol (3.785×10^{-2} at 313.15 K), *n*-propanol (3.007×10^{-2} at 313.15 K) and ethyl acetate (1.497×10^{-2} at 313.15 K)·The obtained solubility data were correlated with Jouyban-Acree model, van't Hoff-Jouyban-Acree model, modified Apelblat-Jouyban-Acree model and CNIBS/R-K model. The correlation showed good agreement with experimental results, the largest values of relative average deviations (*RAD*) and the root-mean-square deviations (*RMSD*) between the experimental and calculated solubility were 4.32×10^{-2} and 15.28×10^{-4}, respectively. On the basis of the obtained solubility, the standard enthalpy of solution (ΔH^{o}_{sol}), the standard Gibbs energy (ΔG^{o}_{sol}) of solution and the standard entropy of solution (ΔS^{o}_{sol}) of terbinafine hydrochloride dissolved in pure and mixed solvents were obtained by the famous van't Hoff calculations. Thermodynamic treatment of solubility data of terbinafine hydrochloride in these pure and mixed solvents by "Apparent thermodynamic analysis" indicated that the dissolution is an endothermic and entropy-driven process. The experimental solubility and the models in this study could be helpful in purifying the crude terbinafine hydrochloride.

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1. Introduction

Terbinafine, an allylamine derivative, represents the most effective of this new chemical class of antimycotic compounds. It is used topically for superficial skin infections such as jock itch (tinea cruris), athlete's foot (tinea pedis) and other types of ringworm (tinea corporis) [1–3]. Terbinafine hydrochloride (CAS Reg. No. 78628-80-5, its structure shown in Fig. 2) is the main chemical form of terbinafine for pharmaceutical purposes. It is a new drug with broad spectrum of antifungal activity of the allylamine class. The FDA recommends its use in superficial skin and nail fungal infections since it has a broad spectrum of activity against yeasts, dimorphic fungi and dermatophytes [4–5]. The mechanism of action involves irreversible inhibition of the enzyme squalene epoxidase in fungal ergosterol biosynthesis, promoting intracellular squalene accumulation, which compromises the cell wall integrity [6]. Furthermore, terbinafine hydrochloride cream works in about half the time required by other antifungals [7]. Since the discovery of terbinafine in 1984, the effort of many researchers was devoted to the development of applicable methods under commercial conditions for the synthesis of this drug. However, terbinafine hydrochloride is still among the very expensive drugs. To date, terbinafine hydrochloride was mainly prepared from terbinafine and hydrochloric acid via

* Corresponding author at: School of Chemistry and Chemical Engineering, Suzhou University, Suzhou 234000, PR China.
E-mail address: abcchemistry@126.com (H. Shi).

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salification [8–12]. However, under the proposed reaction conditions, researcher obtained terbinafine hydrochloride just containing about 95% [13]. As a final separation and purification technology, solution crystallization is always employed to obtain terbinafine hydrochloride products with high purity and ideal morphology [8–12,13]. The crystallization process strongly relies on accurate equilibrium solubility which is a thermodynamic property of great importance in pharmaceutical area from both practical and theoretical viewpoints. In addition, drug solubility defines the possible state of the pharmaceutical dosage form under consideration. Thus, the solubility of terbinafine hydrochloride in solvents is an important physicochemical property for the purity and quality of the subsequent product. According to the recently patented technology, the purification of terbinafine hydrochloride is recommended via a twofold recrystallization from isopropanol, ethanol aqueous solution or the mixture of methanol and ethyl acetate in the previous publication [8–10,11,12,14]. Recently, the solubility of terbinafine hydrochloride is determined in different pure solvent and aqueous medium (such as: polyethylene glycol 6000 and polyvinyl pyrrolidone K30) at only one temperatures [14]. Nevertheless, according to the aforementioned literature [13], we found that its equilibrium solubility in methanol is large and very low in ethyl acetate. For this reason, ethyl acetate and three alcohol mixtures have been evaluated to increase the solubility of terbinafine hydrochloride in order to provide useful information for developing purification process. It is, therefore, very important to determine systematically their mixed solutions and build better models for describing these behaviors, especially in the cases of non-ideal systems.

In the present study, by using the isothermal saturation method [15,16], the solubility of terbinafine hydrochloride in methanol, ethanol, *n*-propanol, ethyl acetate, (methanol + ethyl acetate), (ethanol + ethyl acetate) and (*n*-propanol + ethyl acetate) solvents were experimentally determined with temperatures ranging from 278.15 K to 313.15 K under atmospheric pressure. To extend the applicability of the solubility, values of the experimental solubility were correlated with Jouyban-Acree model, van't Hoff-Jouyban-Acree model, modified Apelblat-Jouyban-Acree model and CNIBS/R-K model. Besides, the standard enthalpy of solution (ΔH^{o}_{sol}), the standard Gibbs energy (ΔG^{o}_{sol}) of solution and the standard entropy of solution (ΔS^{o}_{sol}) for the solution process of terbinafine hydrochloride in different binary solvent mixtures were calculated and discussed.

2. Thermodynamic and correlating models

In this work, four models are employed to correlated the solubility of terbinafine hydrochloride in binary solvent mixtures (methanol + ethyl acetate), (ethanol + ethyl acetate) and (*n*-propanol + ethyl acetate) at different temperatures, which correspond to Jouyban-Acree model [17,18], a combination of Jouyban-Acree model with van't Hoff equation [18,19], a combination of Jouyban-Acree model with modified Apelblat equation [18,19], and CNIBS/R-K model [20–22]. The parameters of four models are acquired by regressed the experimental solubility data by MathCAD software.

2.1. Jouyban-Acree model

The Jouyban-Acree model provides accurate mathematical descriptions for the solubility dependence on both temperature and solvent composition for binary and ternary mixed solvents [17,18], and is described as Eq. (1).

$$\ln x_{w,T} = w_1 \ln x_{1,T} + w_2 \ln x_{2,T} + \frac{w_1 w_2}{T}\sum_{i=0}^{2} J_i (w_1 - w_2)^i \quad (1)$$

where $x_{w,T}$ is the solubility of solute in mole fraction in the binary solvent mixtures at temperature T in Kelvin; w_1 and w_2 denote the mass fraction of solvents 1 (methanol, ethanol or *n*-propanol) and 2 (ethyl acetate) in the absence of the solute (terbinafine hydrochloride), respectively; $x_{1,T}$ and $x_{2,T}$ are the mole fraction solubility of solute in pure solvent, and J_i stands for the Jouyban-Acree model parameters. In order to calculate the model parameters, the model requires the solute solubility in pure solvent at the lowest and highest temperatures.

2.2. Van't Hoff-Jouyban-Acree model

A linear van't Hoff equation is established for providing precise predictions of solute dissolved in solvent at a limited temperature range. It describes the dependence of the natural logarithm of the mole fraction solubility on the reciprocal of absolute temperature and is expressed as Eq. (2) [23]. The solubility of a solute in pure solvent at different temperatures can be calculated with the van't Hoff equation.

$$\ln x = A + B/T(\mathrm{K}) \quad (2)$$

where A and B are equation constants. Substituting Eqs. (2) into (1), one can obtain the Van't Hoff-Jouyban-Acree model expressed as Eq. (3) [18,19].

$$\ln x_{w,T} = w_1\left(A_1 + \frac{B_1}{T/\mathrm{K}}\right) + w_2\left(A_2 + \frac{B_2}{T/\mathrm{K}}\right) + \frac{w_1 w_2}{T/\mathrm{K}}\sum_{i=0}^{2} J_i (w_1 - w_2)^i \quad (3)$$

Here A_1, B_1, A_2, B_2 and J_i are the model constants. This model can provide an estimation of the solute solubility in binary solvent mixtures at different temperatures and composition of solvents.

2.3. Modified Apelblat-Jouyban-Acree model

The modified Apelblat equation is a semi-empirical model. It is employed to correlate the solute solubility against temperature at the same solvent composition and is described as Eq. (4) [24].

$$\ln x = A + \frac{B}{T/\mathrm{K}} + C \ln(T/\mathrm{K}) \quad (4)$$

Table 1
Detailed information on the materials used in the work.

Chemicals	Molar mass / g·mol^{-1}	Source	Initial mass fraction purity	Final mass fraction purity	Purification method	Analytical method
Terbinafine hydrochloride	327.89	Wuhan Dahua Pharmaceutical Co., Ltd. (China)	0.997	0.997	Recrystallization	HPLC[a]
Methanol	32.04	Sinopharm Chemical Reagent Co., Ltd.,China	0.995	0.995	–	GC[b]
Ethanol	46.07		0.997	0.997	–	GC
n-Propanol	60.10		0.995	0.995	–	GC
Ethyl acetate	88.11		0.995	0.995	–	GC

[a] High-performance liquid phase chromatograph.
[b] Gas chromatograph.

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