

Solubilities and thermodynamics of TPP in propionic acid + water and TPPMnCl in *N,N*-dimethylformamide + water solvent mixtures at (303.2–343.2) K



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ABSTRACT

By static analytical equilibrium method, the solubilities of 5,10,15,20-tetraphenylporphyrin (TPP) in propionic acid + water solvent mixtures and 5,10,15,20-tetraphenylporphyrin manganese(III) chloride (TPPMnCl) in *N,N*-dimethylformamide + water solvent mixtures were measured from 303.2 K to 343.2 K under atmosphere pressure. The results show that both the solubilities of TPP and TPPMnCl increased with temperature from 303.2 K to 343.2 K. The solubilities of TPP were maximal in pure propionic acid and TPPMnCl were maximal in pure *N,N*-dimethylformamide, afterwards, the solubility markedly decreased as the mole fraction of water increased in binary solvents mixture at experiment temperatures. The modified Apelblat equation was applied to correlate the experimental data. The solubilities calculated by the modified Apelblat equation were in good agreement with experimental data. The thermodynamic parameters including dissolution enthalpy, dissolution entropy, isobaric heat capacity, and Gibbs free energy of TPP in propionic acid + water solvent mixtures and TPPMnCl in *N,N*-dimethylformamide + water mixtures were obtained by combining both the modified Apelblat equation and Clark–Glew equation.

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1. Introduction

5,10,15,20-Tetraphenylporphyrin (TPP) and 5,10,15,20-tetraphenylporphyrin manganese(III) chloride (TPPMnCl), are known as their widely applications in photodynamic therapy agents [1,2], molecular electronics and sensors [3,4], functional organic materials [5], non-linear optics [6] and field-effect transistors [7]. In the recent decades, TPPMnCl is widely used as oxidation catalyst [8–12]. This kind of metal porphyrin gradually taking the place of traditional catalysts in catalyzing the inert hydrocarbon bond, because of its excellent bio-catalytic effect, the catalytic effect of metal porphyrin is the same as that of cytochrome P-450 monooxygenase [13,14].

The synthetic methods of TPP and TPPMnCl have been well-investigated by many researchers. Usually, TPP is synthesized by the reaction of benzaldehyde with pyrrole at atmospheric pressure [15]. Usually the solvent is propionic acid (abbreviated in PA), TPP and water are the main products. When the reaction is completed, the solution is cooled to room temperature, the main product TPP

would crystallized out from the solution. TPPMnCl is synthesized by the reaction of manganese(II) chloride tetrahydrate with TPP under atmospheric pressure [16]. In the manufacturing process of TPPMnCl, usually the solvent is *N,N*-dimethylformamide (abbreviated in DMF), when the reaction is completed, TPPMnCl must be separated from aqueous DMF. The solution crystallization, which is an important technology to produce crystalline solids from solutions, has a significant effect on the quality of product. The design and operation of the solution crystallization process strongly relies on accurate solubility data, however the solubility is a thermodynamic variable that depends on temperature and the solution composition. To better understand the crystallization process and design an optimum crystallization step for TPP and TPPMnCl, it is crucial to establish the systematic study of solid–liquid equilibrium of TPP in propionic acid + water binary solvent mixtures and TPPMnCl in DMF + water binary solvent mixtures.

According to the above analysis, the solubility characteristics of TPP and TPPMnCl in given solvents have a considerable influence on the design and operation of the solution crystallization process, it is crucial to know the solubility data and thermodynamic parameters of TPP and TPPMnCl. However, until now, there is no experimental data for solubilities of TPP and TPPMnCl in literatures. In our previous work [17,18], the solubilities of similar

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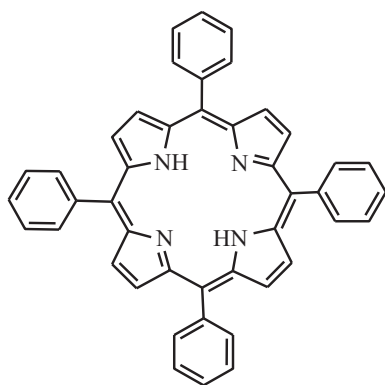


Fig. 1. Chemical structure of 5,10,15,20-tetraphenylporphyrin.

compounds such as 5,10,15,20-tetrakis(*p*-chlorophenyl)porphyrin in propionic acid + water binary solvent mixtures and 5,10,15,20-tetrakis(*p*-chlorophenyl)porphyrin manganese(III) chloride in *N,N*-dimethylformamide + water binary solvent mixtures have been measured.

The aim of this work was to investigate the solubilities of TPP in propionic acid + water binary solvent mixtures and TPPMnCl in DMF + water binary solvent mixtures at temperatures ranging from (303.2 to 343.2) K under atmospheric pressure. The modified Apelblat equation was selected to correlate the solubilities of TPP and TPPMnCl with the temperature and solvent composition. At the same time, the thermodynamic parameters including dissolution enthalpy, dissolution entropy, isobaric heat capacity, and Gibbs free energy of TPP and TPPMnCl were obtained by combining both the modified Apelblat equation and Clark–Glew equation.

2. Experimental

2.1. Materials

TPP (molecular mass 614.74, CAS registry No. 917-23-7, chemical structure shown in Fig. 1 [19,20]) and TPPMnCl (molecular mass 703.11, CAS registry No. 32195-55-4, chemical structure drawn in Fig. 2 [21–23]), were synthesized by the method described in detail elsewhere [15,16], with both the purity of TPP and TPPMnCl greater than 98% in terms of mass fraction. Propionic acid and *N,N*-dimethylformamide were obtained from Aladdin Chemistry Co., had the declared purity of 99.5% and 99.9% in terms of mass fraction, respectively. The water content in propionic acid and DMF was verified to be less than 0.1% by Karl Fischer method. The water was purified to the resistivity of 18.2 M Ω cm by a laboratory ultrapure water machine (Master-Q, purchased from

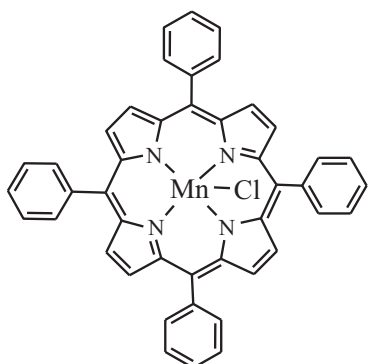


Fig. 2. Chemical structure of 5,10,15,20-tetraphenylporphyrin manganese(III) chloride.

Table 1
Suppliers and mass fraction purity of the chemicals in the experiment.

Chemical name	Suppliers	Purity	Analysis method
TPP ^a		98.0%	HPLC ^c
TPPMnCl ^b		98.0%	HPLC ^c
Propionic acid	Aladdin Chemistry Co.	99.5%	GC ^d
<i>N,N</i> -dimethylformamide	Aladdin Chemistry Co.	99.9%	GC ^d
Ethanol	Aladdin Chemistry Co.	99.7%	GC ^d
CH ₂ Cl ₂ ^e	Aladdin Chemistry Co.	99.5%	GC ^d

^a 5,10,15,20-tetraphenylporphyrin.

^b 5,10,15,20-tetraphenylporphyrin manganese(III) chloride.

^c High-performance liquid chromatography.

^d Gas chromatography.

^e Dichloromethane.

Shanghai Hitech Instruments Co., Ltd.). In this work, the purity of TPP and TPPMnCl was checked by HPLC, and the purity of propionic acid and DMF was verified by GC. All the chemicals were used without further purifications. The purities and sources about the chemicals used in this work are given in Table 1.

2.2. Apparatus and procedures

The experimental apparatus and procedures carried out in this work have been described in detail by Li et al. [17,18] and Wang et al. [24]. Briefly, an excess amount of TPP or TPPMnCl was taken into 100 mL glass bottles, the bottles were filled with known mass fraction of PA + water solvent mixtures or DMF + water solvent mixtures, and were sealed by rubber stopper to stop the solvent from evaporating. The bottles were placed in a constant temperature bath, and the constant temperature bath was heated to the desired temperature, the temperature was kept within ± 0.1 K by thermoelectric controlling system. The mixtures were stirred with Teflon-coated magnetic stirrers to accelerate the dissolution of solute TPP or TPPMnCl. Preliminary experiments indicated that at least 3 h of continuously stirrer was required to reach solid–liquid equilibrium. After the magnetic stirrer was stopped, the mixtures were allowed to settle in the following several hours. To verify the attainment of solid–liquid equilibrium, the clear supernatant solutions were sampled once an hour, and the concentration of TPP or TPPMnCl was determined. Results show that 6 h was required after stirring to allow the solid phase to precipitate down, because repetitive measurements during the following several hours indicated the results were reproducible with $\pm 3\%$. For assurance, after stirring was stop at each temperature, the solutions were kept isothermal and undisturbed for at least 24 h to ensure that the solutions have reached solid–liquid equilibrium.

For TPP, in each measurement, a pre-weighed plastic syringe was prepared, defined as m_0 . Subsequently, about (0.12–0.4) mL of the clear supernatant solution in bottle was withdrawn with the plastic syringe. The plastic syringe with clear saturated solution was quickly weighted again, recorded as m_1 , and then the solution in the syringe transferred quickly into a 50 mL volumetric flask (uncertainty of ± 0.05 mL). The difference between m_1 and m_0 is the mass of sampled saturated solution. In order to collect the possibly crystallized solute in the syringe, the syringe was washed with ethanol at least five times. The solution in the volumetric flask was diluted with ethanol to 50 mL, afterwards the solubility of TPP in binary PA + water solvent mixtures could be determined by the method introduced in Section 2.3.

For TPPMnCl, the sampling process was the same as for TPP, except that about (0.15–1.0) mL of the clear upper solution in bottle was withdrawn, the solution is diluted to 50 mL with CH₂Cl₂, afterwards about 0.6 mL of solution was withdrawn with a suction pipet, and diluted to 50 mL with CH₂Cl₂ once more.

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