Solubility of methylphosphonic acid in selected organic solvents

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ABSTRACT

The solubility of methylphosphonic acid in ethanol, n-propanol, i-propanol, acetone, butanone and ethyl acetate was determined by a static analytical method over a temperature range of 288.15–318.15 K. Quantum chemical calculations utilizing Gaussian 09 indicated that solubility of methylphosphonic acid is dependent on solvent polarities and also on interactions with solvent molecules. The modified Apelblat equation, Wilson, nonrandom two-liquid (NRTL), and UNIQUAC models were applied to correlate the experimental data. Finally, the modified van't Hoff equation was applied to calculate dissolution enthalpy, entropy, and Gibbs energy of methylphosphonic acid in the selected organic solvents.

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1. Introduction

The chemistry of organophosphorus and their derivatives has gained immense attention in the scientific community. Physicochemical properties displayed by this chemical group allow them to be utilized in a wide variety of applications. Methylphosphonic acid $CH_3PO(OH)_2$ (MPA, CAS No. 993-13-5) and its derivatives such as methylphosphonyl chloride are recognized intermediates for the production of esters, free acids and amides, utilized in fungicides, insecticides, surface active agents, petroleum additives, etc., [1]. MPA has recently been indicated as an essential organophosphorous acid for synthesis of metal phosphonates; hybrid organic–inorganic compounds with novel properties for molecular sieves, ion exchangers, ferromagnetic conductors, etc. [2–6]. MPA is generally prepared from dimethyl methylphosphonate by chlorination and hydrolyzation, thus purity of MPA affects properties of the final product.

Fundamental solubility data of MPA is critical for understanding final product characteristics such as crystal size distribution, crystal habits, purity, and yields [7]. Solubility modeling and interpretation of the interactions between MPA and various solvents also rely on this data and are the focus of this study. The solubility of MPA in six solvents was first measured over a temperature range 288.15–318.15 K by a gravimetric method. A quantum chemical calculation was then applied to identify the striking difference of solubility in various solvents. Correlation of experimental data to obtain a comprehensive overview for MPA

solubility data was obtained through application of the modified Apelblat equation, Wilson [8], nonrandom two-liquid (NRTL) [9], and UNIQUAC [10] models. The modified van't Hoff equation was applied to calculate the dissolution enthalpy, entropy, and Gibbs energy of MPA in the selected organic solvents. MPA solubility as related to thermodynamic models capability is discussed to conclude the conducted research.

2. Experimental

2.1. Materials

Table 1 provides a description of solute and solvents utilized in the subject research, including MPA, ethanol, n-propanol, i-propanol, acetone, butanone and ethyl acetate. Additionally, methylphosphonic acid was purchased from Alfa Aesar and all organic solvents were utilized without further purification.

2.2. Thermal properties measurements

Thermogravimetric analysis (TGA) was carried out using a SDT Q600 (TA Instruments) thermogravimetric analyzer. A 5 mg sample was heated from ambient temperature to 873 K at a heating rate of 10 K min^{-1}. A high purity nitrogen stream was continuously passed into the furnace at a flow rate of 100 mL min^{-1}. Determination of the melting temperature T_m and enthalpy of fusion $\Delta_{fus}H$ of MPA was obtained utilizing a differential scanning calorimeter (DSC Q100, TA Instruments) with accuracy and calibration of the instrument similar to background research [11]. A sample was then heated from 313.15 to 393.15 K at 10 K min^{-1} under a 25 mL min^{-1} nitrogen flow.

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Table 1
Description of materials used in this paper.

Chemical name	Source	Mass fraction purity	Analysis method
Methylphosphonic acid	Alfa Aesar	>0.98	HPLC[a]
Ethanol	Shanghai Chemical Reagent Co.	0.995	GC[b]
n-Propanol	Shanghai Chemical Reagent Co.	0.995	GC
i-Propanol	Shanghai Chemical Reagent Co.	0.995	GC
Acetone	Shanghai Chemical Reagent Co.	0.995	GC
Butanone	Shanghai Chemical Reagent Co.	0.995	GC
Ethyl acetate	Shanghai Chemical Reagent Co.	0.995	GC

[a] High-performance liquid chromatography.
[b] Gas–liquid chromatography.

2.3. Solubility measurements

Solubility measurements were conducted as described by Li et al. [12]. Experimental equipment included a jacketed equilibrium cell with a working volume of 120 mL and a magnetic stirrer. A circulating water bath was utilized with a thermostat (type DCY-3006, Shanghai Laboratory Instrument Works Co., Ltd.) capable of maintaining temperature within ±0.05 K. Temperature of the vessel inner chamber was measured by a calibrated mercury-in-glass thermometer (uncertainty of ±0.05 K). Mass of the sample was weighed with precision of ±0.0001 g using an analytical balance (type AB204, Mettler Toledo, Switzerland).

Excess mass of MPA was added to a pure solvent in each measurement and the solution stirred continuously at a constant temperature. Stirring ceased following a minimum 4 h and the solution left undisturbed to settle and obtain clarity. A preheated on–off injector with a 0.2 μm PTFE filter was then utilized to extract and transfer the clear supernatant into a pre-weighted 5 mL vial and covered immediately. Total weight was measured and sample evaporated in a vacuum drying oven at $T = 353.15$ K. Repeated sampling was recorded until a constant weight was achieved. Each experiment was repeated three times, at minimum, to verify replication of the solubility determination. Three samples were taken for each solvent at each temperature and the mean value was used to calculate the mole fraction solubility. The mole fraction solubility of MPA in solvents was calculated as follows:

$$x = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2} \tag{1}$$

where m_1, m_2 represent the mass of the solute, solvent, and M_1, M_2 are the molecular weight of the solute, solvent, respectively.
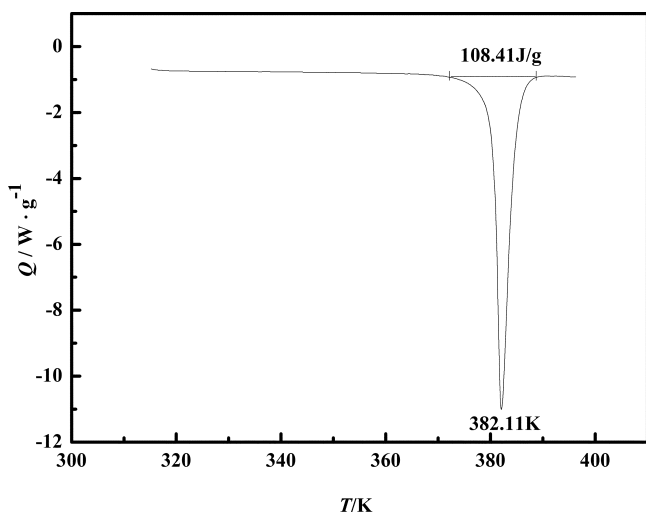
2.4. Computational methods

Density functional theory (DFT) calculations were conducted utilizing the Gaussian 09 method [13] to identify different solubility profiles of MPA in various solvents. Previously, the method was carried out to study the structure and properties of MPA [14,15]. Geometry optimizations for all structures carried out at the B3LYP/6-31 + G** levels and frequency analysis also carried out at the B3LYP/6-31 + G**. Frequency analysis also included calculation of the zero-point correction to the energies and thermochemical information at 298.15 K and 1 atm. Convergence criteria were adopted Gaussian default values. The interaction energy was defined as:

$$E_{inter} = -(E_{0-1} - E_0 - E_1) \tag{2}$$

where E_1, E_0 and E_{0-1} denote the total energies of MPA, solvent and MPA with solvent, respectively.

3. Results and discussion

3.1. Characterization of MPA

MPA demonstrates an initial degradation temperature 427.9 K (1% mass loss), as presented in Fig. 1 TGA data results, and experiences a minimum two-step thermal degradation with 21% charred residue following 868.7 K. Initial degradation transpires at 427.9–600.9 K prompting MPA to degrade gradually with 20% mass loss as related to dehydration from the OH ending groups of the molecule. Mass loss of approximately 40% is observed in the second degradation at 600.9–660.3 K, attributed to volatilization of the parent compound and elimination of phosphorus containing hydrocarbons. DSC measurement results of MPA are presented in Fig. 2. Melting point of MPA was characterized at 382.11 K;
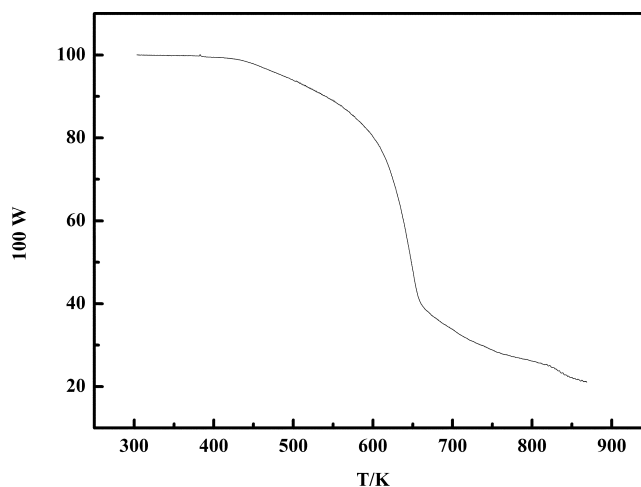

Fig. 1. TGA thermograms of MPA under N₂.

Fig. 2. Experimental heat Q flow from DSC measurement of MPA.