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Solubility measurement and thermodynamic functions of 3-nitrobenzaldehyde in different solvents at elevated temperatures

Xinbao Li [a], Chao Cheng [b], Yang Cong [b], Cunbin Du [b], Hongkun Zhao [b,*]

[a] School of Environmental & Municipal Engineering, North China University of Water Resources and Electric Power, ZhengZhou, He'nan 450011, People's Republic of China
[b] College of Chemistry & Chemical Engineering, YangZhou University, YangZhou, Jiangsu 225002, People's Republic of China

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ABSTRACT

The solubility was measured for 3-nitrobenzaldehyde in methanol, ethanol, isopropanol, *n*-butanol, acetonitrile, acetone, ethyl acetate, toluene, *N*,*N*-dimethylformamide, acetic acid, cyclohexane and *n*-propanol by using a high-performance liquid chromatography analysis under pressure of 101.2 kPa. The temperatures of solubility determination were from (273.15 to 303.15) K. The mole fraction solubility of 3-nitrobenzaldehyde increased with the increase in temperature, and obeyed the following order from high to low in different solvents: *N*,*N*-dimethylformamide > (acetone, acetonitrile) > ethyl acetate > toluene > methanol > acetic acid > ethanol > *n*-propanol > *n*-butanol > isopropanol > cyclohexane. Four models, modified Apelblat equation, λh equation, Wilson model and NRTL model were employed to correlate the experimental mole fraction solubility. The largest root-mean-square deviation (*RMSD*) was 6.98×10^{-3}, and the largest relative average deviation (*RAD*) was 1.93% for each set of solubility results. On the whole, the calculated solubility values were in good agreement with the experimental results for the four selected models, and the NRTL provided the best results. Moreover, the mixing Gibbs energy, mixing enthalpy, mixing entropy, activity coefficient at infinitesimal concentration (γ_1^{∞}) and reduced excess enthalpy ($H_1^{E,\infty}$) were computed based on the NRTL model. The experimental solubility, thermodynamic models and thermodynamic properties are very important in the purification process of isomeric mixtures of nitrobenzaldehydes.

1. Introduction

3-Nitrobenzaldehyde (CAS Reg. No: 99-61-6) is pale yellow crystal with molar mass and molecular formula of 151.12 g·mol^{-1} and $C_7H_5NO_3$, respectively. Its chemical structure is shown in Fig. 1. 3-Nitrobenzaldehyde is an important pharmaceutical intermediate and has achieved industrial importance for the synthesis of various pharmaceutical intermediates [1–5]. In recent years, some methods for 3-nitrobenzaldehyde production have been put forward in the literature [6–15]. In general, it can be synthesized by using benzaldehyde [6–14] or 3-nitrotoluene [15] or 3-nitrophenol [16] as the raw materials. The main production method for 3-nitrobenzaldehyde is nitration of benzaldehyde by using mixed nitric acid and sulphuric acid [6–14]. This method of making nitrobenzaldehydes results in mixtures of the isomers. The crude product containing isomers limits its further use in various areas.

There are several ways known for separating the isomeric mixtures of nitrobenzaldehydes. They can be separated by an adsorption–desorption process [17–19], distillation process [20], extraction process [21] and chemical conversion process [22,23]. The decomposition temperature is so near the distillation temperature, for safety reasons, the distillation method is ruled out. Moreover, the high boiling points make separation by distillation energy-intensive. Fractional crystallization is not satisfactory because the melting points are very close (2-: 42–44 °C; 3-: 58 °C). Indirect methods, *e.g.*, conversion of the isomers into acetals, which can be separated by distillation, and then converted back into the nitrobenzaldehyde [23]. So, a method of separating the isomers directly, avoiding costly chemical conversions and reconversion, is still desired.

Solvent crystallization is an important step that determines the quality of the product of 3-nitrobenzaldehyde with low cost and high efficiency. Solubility is an essential physicochemical property that plays an important role in solvent crystallization process. Therefore, it is very significant to know the solubility of 3-nitrobenzaldehyde as a function of temperature in different solvents. For the purification of the desired nitrobenzaldehyde,

* Corresponding author.
E-mail address: hkzhao@yzu.edu.cn (H. Zhao).

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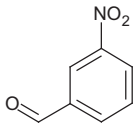

Fig. 1. Chemical structure of 3-nitrobenzaldehyde.

recrystallization from organic solvents can be undertaken [21]. Recently, we report the solubility of 4-nitrobenzaldehyde in some pure organic solvents [24]. Nevertheless, to the best of authors' present knowledge, no study has been made for determining and correlating the solubility of 3-nitrobenzaldehyde in the open publications.

From many species of organic solvents, we select twelve commonly used organic solvents (methanol, ethanol, isopropanol, *n*-butanol, acetonitrile, acetone, ethyl acetate, toluene, *N*,*N*-dimethylformamide, acetic acid, cyclohexane and *n*-propanol) he in industrial purification process. In order to enrich our knowledge of the solubility and provide fundamental basis for separating the three isomers, the main objectives of this work are to (1) determine the solubility of 3-nitrobenzaldehyde in the selected solvents over the temperature range from (273.15 to 303.15) K under atmosphere pressure; (2) correlate the obtained solubility with different solubility models; and (3) evaluate the thermodynamic properties for the solution process of 3-nitrobenzaldehyde in the selected solvents.

2. Experimental

2.1. Materials

A pale yellow crystal of 3-nitrobenzaldehyde was supplied by Maya Reagent Co., Ltd, China. It was recrystallized twice in pure acetone. The final mass fraction of 3-nitrobenzaldehyde was 0.995, which was confirmed by a Shimadzu-6A high-performance liquid phase chromatograph (HPLC). The solvents including methanol, ethanol, isopropanol, *n*-butanol, acetonitrile, acetone, ethyl acetate, toluene, *N*,*N*-dimethylformamide, acetic acid, cyclohexane and *n*-propanol were all supplied by Sinopharm Chemical Reagent Co., Ltd., China, and used in solubility determination without additional purification. The details of these materials are given in Table 1.

2.2. Apparatus

The experimental apparatus employed in the solubility determination is shown in Fig. 2. It involved a 100 mL jacketed glass vessel with a magnetic stirrer and a circulating liquid system. The temperature was controlled at a desired value by circulating (water + isopropanol) mixture from a smart thermostatic circulator bath through the outer jacket. The volume ratio of water and isopropanol was about 4:1. The smart thermostatic circulator bath (Model: DZKW-4) having a standard uncertainty of 0.02 K) was provided by Ningbo Scientz Biotechnology Co., Ltd., China. The real temperature of solution was displayed with a mercury glass micro thermometer (standard uncertainty: 0.02 K) inserted in the inner chamber of the jacket glass vessel. In order to avoid the solvent from escaping, a condenser was attached with the jacketed glass vessel. Before experiment, the reliability of experimental apparatus was verified by determining the benzoic acid solubility in toluene [25,26]. The mass of the solute, solvent, and saturated solution was determined by using an analytical balance (model CPA225D), which was provided by Sartorius Scientific Instrument (Beijing) and had a standard uncertainty of 0.0001 g.

2.3. Solubility determination

During the experiment, the solid-liquid phase equilibrium was established by using the isothermal solution saturation method [25,26] within the temperature range from (273.15 to 303.15) K, and the solubility values of 3-nitrobenzaldehyde in the twelve solvents were determined by using a high-performance liquid chromatography analysis.

Table 1
Details of 3-nitrobenzaldehyde and solvents.

Material	Molar mass/ g·mol^{-1}	Melting point (T_m)/ K	Melting Enthalpy/ kJ·mol^{-1}	Source	Density (293 K)/ kg·m^{-3}	Purification method	Mass fraction purity	Analysis method
3-Nitrobenzaldehyde	151.12	328.22[a]330–332[b]329-320[c]327–329[d]315–316[e]	19.90[a]	Maya Reagent Co., Ltd, China	1338[f]	Recrystallization	⩾0.995	HPLC[h]
Methanol	32.04			Sinopharm Chemical Reagent Co., Ltd., China	810.0[g]	None	⩾0.993	GC[i]
Ethanol	46.07				789.3[g]	None	⩾0.992	GC
n-propanol	60.01				805.3[g]	None	⩾0.994	GC
Isopropanol	60.01				785.1[g]	None	⩾0.994	GC
1-Butanol	74.12				810[g]	None	⩾0.993	GC
Acetonitrile	41.05				787.5[g]	None	⩾0.995	GC
Acetone	58.05				789.9[g]	None	⩾0.995	GC
Ethyl acetate	88.11				902.3[g]	None	⩾0.994	GC
Toluene	92.14				863.6[g]	None	⩾0.994	GC
N,*N*-dimethylformamide	73.09				945[g]	None	⩾0.994	GC
Acetic acid	60.05				1051[g]	None	⩾0.994	GC
Cyclohexane	84.18				778[g]	None	⩾0.992	GC

[a]This work, determined under 101.2 kPa. The standard uncertainties u are u (T) = 0.5 K, u (p) = 0.45 kPa, u ($\Delta_{fus}H$) = 400 J·mol^{-1}.
[b,c,d,e,g]Taken from Refs. [27–31], respectively.
[f]Calculatedusing Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994–2016 ACD/Labs).
[h]High-performance liquid chromatography.
[i]Gas chromatography.