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Solubility of Triethylenediamine in Methanol, Ethanol, Isopropanol, 1-Butanol, and Ethyl Acetate between 276.15 K and 363.15 K

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The solubilities of triethylenediamine in methanol, ethanol, isopropanol, 1-butanol, and ethyl acetate between 276.15 K and 363.15 K were measured using a synthetic method at atmospheric pressure. A laser monitoring observation technique was used to determine the disappearance of the solid phase in a solid + liquid mixture. The solubility of triethylenediamine in the above solvents increased in the order methanol > ethanol > isopropanol > 1-butanol > ethyl acetate. An empirical equation was proposed and verified by experimental solubility data.

Introduction

Triethylenediamine (TEDA, CAS No.: 280-57-9, IUPAC name: 1,4-diazabicyclo(2.2.2)octane) is a pure white powdered crystal under standard conditions. TEDA exhibits certain unusual properties which are due to its bicyclic or "cage" structure (Figure 1).[1]

It is an important intermediate and end product in the chemical industry, which is used mainly as a catalyst in the production of polyurethane foams.[2] A number of methods are known in the art for preparing and isolating this compound as a product of commercially acceptable purity.[3] Typically, TEDA is isolated from the reaction mixture as a white crystalline hygroscopic product containing a small amount of byproduct amine compounds. In the final purification step, the TEDA recrystallizes from solution.[4,5] To determine the proper solvent and to design an optimized separation process, it is necessary to know its solubility in different solvents. However, few experimental solubility data of TEDA in solvents have been reported. Farkas reports some solubility data of TEDA in 92 % ethanol as 77 G/100 g at 25 °C, but there are only very few relevant data.[6] According to the properties of the solid studied in this work and the requirement of the industry, the last crystal disappearance method was used to determine the solubility data of TEDA in methanol, ethanol, isopropanol, 1-butanol, and ethyl acetate between 276.15 K and 363.15 K at atmospheric pressure. In this paper, a synthetic method was used to determine the solubility data of TEDA. By this method, solubility data can be obtained much faster and more readily than with an analytical method.[7−9]

Experimental Sections

Materials. White crystalline TEDA powder ($C_6H_{12}N_2$, MW 112.2) was obtained from Shijiazhuang Hejia Health Productions Co., Ltd., China, and had a melting point of (159.25 ± 0.5) K. Its mass fraction purity, determined by GC (SP 6890 with an FID detector, 30 m CP-Sil-5 Chrompack column, i.d. = 0.25 mm, coating 0.25 lm, column temperature 200 °C, injector temperature 200 °C, and FID temperature 250 °C), is higher than 99.75 %. It was dried under a vacuum at 313.15 K for 24 h and stored in a desiccator. The methanol, ethanol, isopropanol, 1-butanol, and ethyl acetate used for experiments were obtained from Tianjin Chemical Reagent Co., Ltd., China. They were all analytical reagent grades and dehydrated with molecular sieves before use. All the solvents used in the experiments have a minimum purity of 99.5 mol %. TEDA is stable in these five solvents.

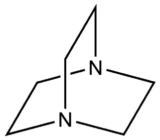

Figure 1. Chemical structure of triethylenediamine.

Procedure. In the experiments, the solubility of TEDA was determined by the last crystal disappearance method. The method is based on sequentially adding known masses of a solid compound to a stirred solution kept at a predetermined temperature. The initial mass of solvent was known precisely. The laser monitoring observation technique was used to determine the disappearance of the last crystal particles in the solid + liquid mixture. The laser set consists of a laser generator, a photoelectric transformer, and a digital display. When a solid increment had completely dissolved, the next portion of solid was introduced. When the solute dissolved completely, the solution was clear, and the laser intensity penetrating through the vessel reached its maximum. If the solute could not dissolve completely, then the laser beam was scattered by the undissolved solute particles in the solution, and the penetrating laser intensity was below the maximum.

The experiment was performed in a cylindrical double-jacketed glass vessel. This vessel with a diameter of 110 mm and a height of 160 mm was maintained at a desired temperature by circulating water from a water bath with a thermoelectric controller. Heated water can be circulated through the jacket. A condenser was connected to the vessel to prevent the solvents from evaporating. A mercury-in-glass thermometer was inserted into the inner chamber of the vessel with an uncertainty of ± 0.05 K. An analytical balance (Mettler Toledo AB204-N) with

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Table 1. Mole Fraction Solubility, *x*, of Triethylenediamine in Pure Solvents

T/K	10^3x^{exptl}	10^3x^{calcd}	T/K	10^3x^{exptl}	10^3x^{calcd}	T/K	10^3x^{exptl}	10^3x^{calcd}
				Methanol				
276.15	9.78	10.1	280.15	10.9	10.6	287.15	11.6	11.6
294.15	11.6	11.6	298.15	14.0	13.6	303.15	14.9	14.8
308.15	15.7	16.0	313.15	17.4	17.5	318.15	19.0	19.1
323.15	20.7	21.0	328.15	22.7	23.0	333.15	25.7	25.3
338.15	28.3	28.0						
				Ethanol				
276.15	6.32	6.70	280.15	7.14	7.02	287.15	8.00	7.69
294.15	8.71	8.53	298.15	9.29	9.10	303.15	10.2	9.91
308.15	10.7	10.8	313.15	11.8	11.9	318.15	13.1	13.2
323.15	14.1	14.6	328.15	15.9	16.2	333.15	17.8	18.1
338.15	20.4	20.3	343.15	22.8	22.8	348.15	26.8	25.7
				Isopropanol				
276.15	4.56	4.80	280.15	5.19	5.09	287.15	5.81	5.68
294.15	6.53	6.40	298.15	7.13	6.88	303.15	7.47	7.55
308.15	8.38	8.32	313.15	9.18	9.20	318.15	10.2	10.2
323.15	11.1	11.4	328.15	12.5	16.7	333.15	13.9	14.2
338.15	15.8	15.9	343.15	17.6	17.8	348.15	19.8	20.0
353.15	23.7	22.6						
				1-Butanol				
294.15	6.51	6.50	298.15	7.08	6.93	303.15	7.55	7.55
308.15	8.27	8.26	313.15	9.07	9.08	318.15	9.85	10.0
323.15	10.7	11.1	328.15	12.1	12.3	333.15	13.3	13.7
338.15	15.6	15.4	343.15	18.0	17.2	348.15	20.6	19.3
353.15	22.5	21.8	358.15	24.3	24.6	363.15	26.3	27.8
				Ethyl Acetate				
298.15	1.24	1.28	303.15	1.67	1.71	308.15	2.28	2.24
313.15	3.03	2.88	318.15	3.57	3.63	323.15	4.46	4.48
328.15	5.20	5.45	333.15	6.17	6.51	338.15	7.42	7.65
343.15	9.50	8.86						

an uncertainty of ± 0.0001 g was used. The mixtures of solute and solvent in the vessel were stirred with a magnetic stirrer. Predetermined amounts of solute and solvent were transferred into the inner chamber of the vessel. The solid + liquid mixture was stirred at a fixed temperature for 1 h. The quantity of solvent was a small excess. Then additional solute of known mass, from about 3 mg to 5 mg, was introduced into the vessel with continuous stirring. This procedure was repeated until the last addition of solute could not dissolve completely. The interval of addition was 30 min. The process needs more than 6 h, and the last increment added is approximately 0.01 g. Then the total amount of the solute used was recorded, and the solubility expressed in mole fraction was calculated. The accuracy of the experimental solubilities was < 0.01 g of TEDA/100 g of solvent.

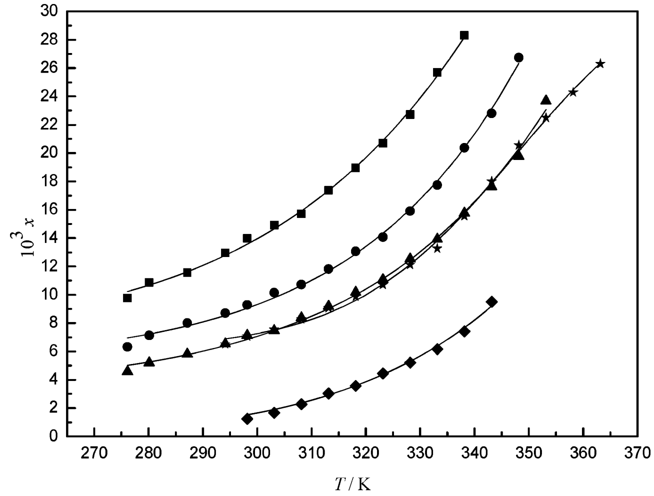

Figure 2. Mole fraction solubility of TEDA, *x*, in different solvents: ■, methanol; ●, ethanol; ▲ isopropano; ★, 1-butanol; ◆, ethyl acetate.

Table 2. Parameters of Equation 1 for Triethylenediamine in Pure Solvents

solvent	A	B	C	10^2rmsd
methanol	−142.1	5266	22.30	1.7
ethanol	−186.8	7165	28.96	2.7
isopropanol	−160.1	5830	25.01	2.3
1-butanol	−178.7	6789	27.71	3.0
ethyl acetate	334.8	−19503	−47.24	4.0

Results and Discussion

The saturated solubilities of TEDA (x^{exptl}) in methanol, ethanol, isopropanol, 1-butanol, and ethyl acetate measured over the temperature range from 276.15 K to 363.15 K are presented in Table 1 and more visually expressed in Figure 1. The temperature dependence of TEDA solubility in pure solvents was described by the modified empirical equation.[10,11]

$$\ln x = A + \frac{B}{(T/\mathrm{K})} + C\ln(T/\mathrm{K}) \tag{1}$$

where x is the mole fraction solubility of TEDA in different solvents; T is the absolute temperature; and A, B, and C are the parameters.

The calculated solubility values of TEDA (x^{calcd}) are also given in Table 1. The values of parameters A, B, and C and the root-mean-square deviations (rmsd's) are listed in Table 2. The rmsd is defined as the following

$$\mathrm{rmsd} = \left\{ \frac{\sum_{i=1}^{N}[(\ln x_{\mathrm{i}}^{\mathrm{calcd}} - \ln x_{\mathrm{i}}^{\mathrm{exptl}})]^2}{N} \right\}^{1/2} \tag{2}$$

where x is the mole fraction solubility of TEDA in different solvents; N is the number of experimental points; and the superscripts calcd and exptl refer to the values calculated from eq 1 and to the data for experimental solubilities, respectively.

From Tables 1 and 2 and Figure 2, we can draw the following conclusions: (1) The solubilities of TEDA in methanol, ethanol, isopropanol, 1-butanol, and ethyl acetate all increase with increasing temperature. (2) The solubility of TEDA in methanol is higher than that in ethanol, isopropanol, and 1-butanol. The solubility of TEDA in ethyl acetate is the lowest. The solubility of triethylenediamine in the above solvents increased in the order methanol > ethanol > isopropanol > 1-butanol > ethyl acetate. (3) The solubility of TEDA decreased according to the decrease of polarity of solvents at the same temperature. (4) These experimental data were able to be regressed by eq 1 for each solvent.

Acknowledgment

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