



Accurate determination of aldehydes in amine catalysts or amines by 2,4-dinitrophenylhydrazine derivatization



Bhajendra N. Barman*

Huntsman Advanced Technology Center, 8600 Gosling Road, The Woodlands, TX 77381, United States

ARTICLE INFO

Article history:

Received 31 October 2013

Received in revised form

19 December 2013

Accepted 20 December 2013

Available online 30 December 2013

Keywords:

Aldehyde

Derivatization-UV detection

2,4-Dinitrophenylhydrazine

Amine catalyst

Effects of pH

Reversed-phase liquid chromatography

ABSTRACT

Carbonyl compounds, specifically aldehydes, present in amine catalysts or amines are determined by reversed-phase liquid chromatography using ultraviolet detection of their corresponding 2,4-dinitrophenylhydrazones. The primary focus has been to establish optimum conditions for determining aldehydes accurately because these add exposure concerns when the amine catalysts are used to manufacture polyurethane products. Concentrations of aldehydes determined by this method are found to vary with the pH of the aqueous amine solution and the derivatization time, the latter being problematic when the derivatization reaction proceeds slowly and not to completion in neutral and basic media. Accurate determination of aldehydes in amines through derivatization can be carried out at an effective solution pH of about 2 and with derivatization time of 20 min. Hydrochloric acid has been used for neutralization of an amine. For complete derivatization, it is essential to protonate all nitrogen atoms in the amine. An approach for the determination of an adequate amount of acid needed for complete derivatization has been described. Several 0.2M buffer solutions varying in pH from 4 to 8 have also been used to make amine solutions for carrying out derivatization of aldehydes. These solutions have effective pHs of 10 or higher and provide much lower aldehyde concentrations compared to their true values. Mechanisms for the formation of 2,4-dinitrophenylhydrazones in both acidic and basic media are discussed.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Undesirable degradation products, such as formaldehyde and dimethylformamide, were observed and found to grow over time when exposed to air in oxidation-sensitive amines such as tertiary amine catalysts or amines used in the polyurethane industry [1]. The presence of such volatile compounds in an amine catalyst will contribute to emissions of organic compounds from polyurethane or polyisocyanurate products such as insulation for buildings and appliances, flexible foams for beds and car seats, furniture foams, and urea and urethane coatings. Some volatiles, especially aldehydes, are toxic and suspected to be carcinogens. Consequently, they have low exposure limits. For example, Occupational Safety & Health Administration (OSHA) short-term 15 min exposure limit for formaldehyde is 2 ppm and an 8-h time-weighted average permissible exposure limit is 0.75 ppm. Therefore, amine catalysts with no or low concentrations of aldehydes are highly desired. It is equally important to have the required accuracy in aldehyde determination to ascertain such stringent product quality.

In this work, aldehydes are determined as their 2,4-dinitrophenylhydrazone derivatives by reversed-phase liquid

chromatography (RPLC) with ultraviolet (UV) detection at 365 nm. This approach has been applied extensively [2–5]. The derivatization technique is known to be based on the acid-catalyzed reaction of aldehydes and ketones with an excess amount of 2,4-dinitrophenylhydrazine (DNPH). However, to our knowledge, a systematic approach for converting aldehydes present in basic materials such as amines into their 2,4-dinitrophenylhydrazones has not been reported. Insights into the effects of solution pH, derivatization reaction time and the number of active nitrogen atoms in an amine should be helpful for selecting appropriate conditions to determine aldehydes accurately.

Literature data on reaction temperatures and reaction times for derivatization vary widely. For example, conditions such as room temperature and 60 min [2], 40 °C and 60 min [3], and room temperature/40 °C and 30 min [4], were recommended. There are limited data on the dependence of pH on the reaction between carbonyl compounds and DNPH. Usually, buffer solutions at pH 3 were recommended for carrying out derivatization [3]. In a related work for the effect of pH of the substrate on trapping volatile aldehydes, 50 mM citric acid/sodium citrate buffer at pH 4 was recommended for optimum recovery of aldehydes [6]. From a similar study on extraction efficiencies of aldehydes from water samples using solid-phase microextraction, pH 4 was found to be optimal. Acceptable recoveries were achieved at an absorption time of 30 min with reaction temperature at 40 °C [7]. In a study with

* Tel.: +1 281 719 7604; fax: +1 281 719 7666.

E-mail address: bhajendra.barman@huntsman.com

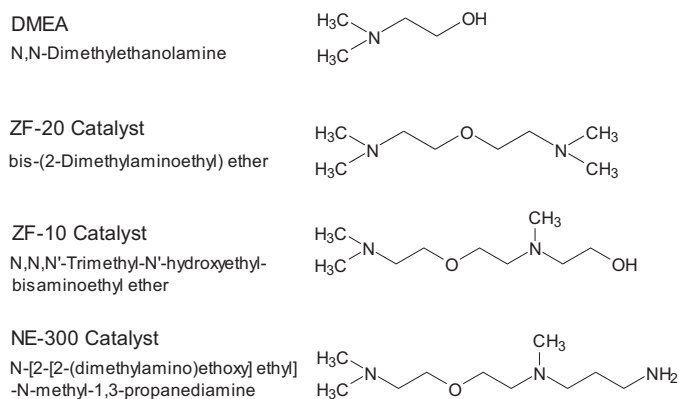


Fig. 1. Amine catalysts.

dabsylhydrazine and monosaccharides, it was observed that the optimum pH for the formation of monosaccharide dabsylhydrazones is around 2–3 [8].

In this work, concentrations of aldehydes present in several amines containing 1–3 nitrogen atoms have been determined under different experimental conditions. The effects of pH have been examined by using sample solutions at pHs ranging from 1 to 12. Several buffer solutions differing in pH have also been evaluated. To establish optimum reaction times, derivatization of aldehydes with DNPH was carried out from 0 to 90 min at 40 °C.

2. Materials and methods

2.1. Equipment and experimental conditions

A Waters (Milford, MA, USA) 2695 Alliance® system with a Waters 2998 diode-array detector was used. The system automation, data collection and data analysis were carried out with Waters Empower® 2 software.

A 7.5 cm × 0.46 cm internal diameter, Kinetex® 2.6 μm, XB C-18, 100 Å column from Phenomenex® (Torrance, CA) was used to separate 2,4-dinitrophenylhydrazones. This short and efficient column was selected to carry out separation with an isocratic conditions to avoid potential overlapping of any emerging peaks. The injection volume was 10 μL. The column temperature was maintained at 30 °C. Solvent flow rate was 0.5 mL/min under an isocratic condition of 40:60 (v/v) water–acetonitrile mixture. The run time of 15 min was found to be enough for complete elution of sample components.

For studies with buffer solutions, 0.2 M buffer solutions were prepared after following the protocols outlined in US Pharmacopeia [9]. The potassium biphthalate and potassium phosphate buffer solutions used in this work cover pHs ranging from 4 to 8. The solution pH was measured by a model S220 pH meter from Mettler-Toledo (Switzerland).

2.2. Samples and reagents

The following commercial amine catalysts from Huntsman (The Woodlands, TX) were used as representative samples: N,N-dimethylethanolamine (DMEA), bis-(2-dimethylaminoethyl) ether (JEFFCAT® ZF-20 or ZF-20 catalyst) and N,N,N'-trimethyl-N'-hydroxyethyl-bisaminoethyl ether (JEFFCAT® ZF-10 or ZF-10 catalyst). Another catalyst, N-[2-[2-(dimethylamino)ethoxy]ethyl]-N-methyl-1,3-propanediamine (DABCO® NE-300 or NE-300 catalyst) from Air products (Allentown, PA) was also studied. The structures of all these amines are shown in Fig. 1.

Usually freshly manufactured catalysts were found to have none or very low concentrations of aldehydes. As mentioned before, tertiary amines degrade over time upon exposure to air into aldehydes and dimethylformamide [1]. Amines used in this study are all aged samples having relatively high concentrations of aldehydes so that their concentrations can be determined with greater level of certainty.

Aldehyde standards as their 2,4-dinitrophenylhydrazones were obtained from Supelco (Bellefonte, PA). Liquid chromatography grade acetonitrile was from Fisher Scientific (Pittsburgh, PA, USA). Water was Milli-Q grade.

2.3. Derivatization of aldehydes

Unless noted otherwise, 2% (w/w) amine solutions (10 mL each) were prepared with water and 2 N hydrochloric acid. The amount of 2 N hydrochloric acid was varied to adjust the solution pH at different levels. For derivatization, typically 200 μL of the above amine solution was transferred to a 1.5 mL chromatography sample vial. 1000 μL of 0.06% (w/v) or 3.03 mM DNPH solution in acetonitrile was then added to the vial. The vial was capped and shaken well before placing in a 40 °C heater block for different time intervals.

Excess DNPH is added to shift the equilibrium for derivatization to favor hydrazone formation. For an example, if 2000 ppm of formaldehyde is present in the amine, under the above approach for derivatization, the ratio of the molar amounts of DNPH to formaldehyde is estimated to be more than 11.

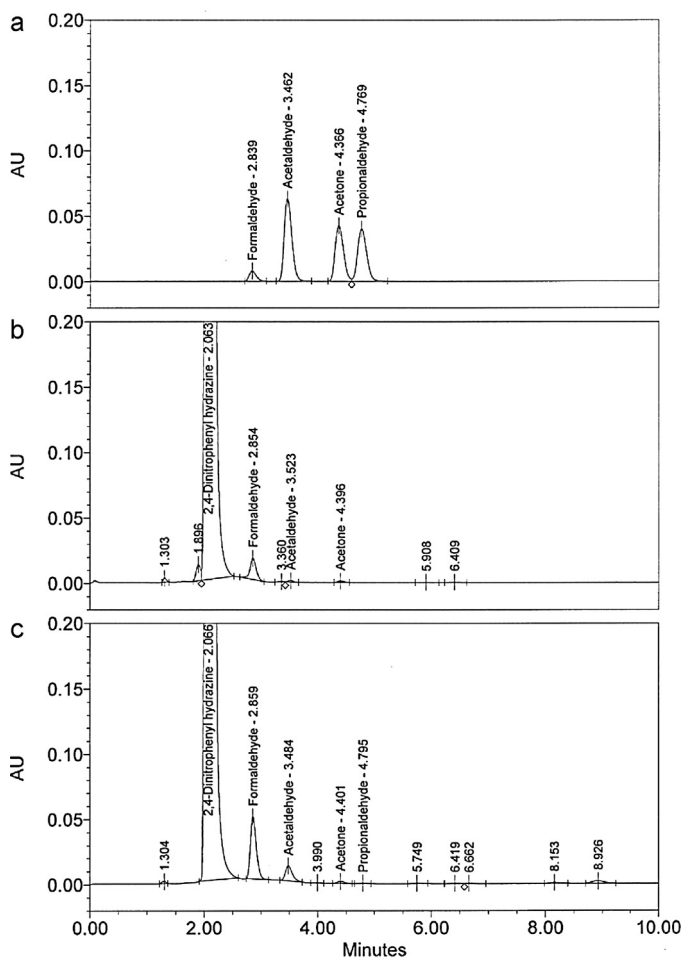


Fig. 2. Chromatograms of (a) hydrazone standards, (b) hydrazones from ZF-20 catalyst at pH 9.16 and (c) hydrazones from ZF-10 catalyst at pH 1.67.

Download English Version:

<https://daneshyari.com/en/article/1199691>

Download Persian Version:

<https://daneshyari.com/article/1199691>

[Daneshyari.com](https://daneshyari.com)