



The effects of typical salts, acids and ionic liquids on the solubility of formaldehyde in aqueous solutions

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ABSTRACT

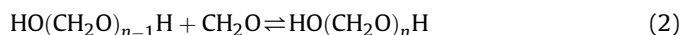
Formaldehyde is an important C1 synthon used in the chemical industry. Formaldehyde is mainly used in aqueous solutions. Solid precipitation from these solutions in the form of poly(oxymethylene) glycols impedes many technical processes. Acids, ionic liquids, and salts have been widely used as catalysts and additives in many technical processes using formaldehyde solutions as reactants. Few data are available in literature on solubility of formaldehyde in aqueous solution containing acids, ionic liquids, and salts. In the present work solubility data is reported for temperatures between 58 °C and 87 °C to investigate the effect of typical acids {H₂SO₄, H₃PO₄, CH₃SO₃H, CF₃SO₃H, C₆H₅SO₃H, C₇H₇SO₃H, C₈H₉SO₃H, C₁₀H₁₆SO₄ or H₄[Si(W₃O₁₀)₄]; the acid concentration is 0.10 mol (kg formaldehyde aqueous solution)⁻¹}, imidazolium ionic liquids {[mim][HSO₄], [mim][CF₃SO₃], [C₃Smim][CH₃SO₃] or [C₃Smim][CF₃SO₃]; [mim]⁺ and [C₃Smim]⁺ stand for 1-methylimidazolium and 1-propylsulfonic-3-methylimidazolium cations; the concentration of the ionic liquid is 0.10 mol (kg formaldehyde aqueous solution)⁻¹}, and salts [NaCl, KCl, LiCl, MgCl₂, ZnCl₂, CH₃SO₃Na, CF₃SO₃Na, C₆H₅SO₃Na, (C₂H₅)₄NBr or ZTS (1-methylimidazolium propanesulfonate); the concentration of the former nine salts is 0.40 mol (kg formaldehyde aqueous solution)⁻¹, and the ZTS concentrations are 0.10 and 0.15 mol (kg formaldehyde aqueous solution)⁻¹, respectively] on the solubility of formaldehyde in aqueous solutions. The results indicate that most acid catalysts and additive salts considered show salting-out effect. More importantly, the acids and salts that can be used as the catalysts and additive salts for trioxane and have salting-in effect are reported. The influence of the structural characteristics of the acids, ionic liquids and salts that were added on their salting-in/out effect is briefly discussed.

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1. Introduction

As one of the most important organic raw materials of chemical industry, formaldehyde (CH₂O) has numerous applications on the synthesis of organic intermediates, resin, medicine, spices, pesticide and fertilizer [1–4]. Formaldehyde plays an important role in production of urea-formaldehyde resin and phenolic resin in the past, and now is applied for synthesis of poly(butyl glycol terephthalate) in electronic industry and polyformaldehyde engineering plastic in automobile industry. Formaldehyde has also been utilized to produce poly(oxymethylene) dimethyl ethers in recent years [5]. However, due to its high reactivity, formaldehyde is mainly used in aqueous solutions, in which a series of chemical

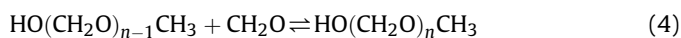
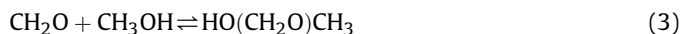
reactions occur and form oligomers, namely, poly(oxymethylene) glycols [HO(CH₂O)_nH] [6]:



The equilibrium distribution of formaldehyde to poly(oxymethylene) glycols depends on the overall concentration of formaldehyde and temperature. If a certain overall concentration of formaldehyde is exceeded at a given temperature, long-chain poly(oxymethylene) glycols precipitate from the solutions. Such precipitation imposes restrictions on many technical processes [7–10]. A comparatively small amount of methanol is added as stabilizer to increase the formaldehyde solubility in aqueous solutions [8,9]. And the addition of methanol induces a variety new reactions [6]:

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In some industrial processes, water-free formaldehyde is needed. As pure monomeric formaldehyde is not available in the industrial scale [8], trioxane $[(\text{CH}_2\text{O})_3]$ is used to circumvent such problem. Trioxane is the cyclic trimer of formaldehyde [1,11] and is usually produced from concentrated aqueous solutions of formaldehyde using an acid such as H_2SO_4 or an ionic liquid as the homogenous catalyst [12]. However, Grützner and Hasse [8] showed that the addition of H_2SO_4 reduces the solubility of formaldehyde in water. The precipitated paraformaldehyde consumes reactant and is very difficult to be removed from reaction mixtures by depolymerization at usual reaction temperatures. It is therefore important to develop new catalysts or salt additives to prevent solid precipitation. This will require investigating solid–liquid equilibrium of acid, ionic liquid, or salt-containing solutions of formaldehyde to uncover the critical factors that control the “salting-out” or “salting-in” specificity of typical acids, ionic liquids and salts.

In this paper we will investigate the solid–liquid equilibrium of formaldehyde aqueous solutions containing the above (Abstract section)-mentioned acids, salts, or ionic liquids that have been (or have the potential to be) used as homogenous catalysts or salt additives to synthesize trioxane from formaldehyde aqueous solutions.

2. Experimental

2.1. Materials and reagents

The analytical grade of paraformaldehyde, H_2SO_4 , H_3PO_4 , $\text{CH}_3\text{SO}_3\text{H}$, $\text{CF}_3\text{SO}_3\text{H}$, $\text{C}_6\text{H}_5\text{SO}_3\text{H}$, $\text{C}_7\text{H}_7\text{SO}_3\text{H}$, $\text{C}_8\text{H}_9\text{SO}_3\text{H}$, $\text{C}_{10}\text{H}_{16}\text{SO}_4$, $\text{H}_4[\text{Si}(\text{W}_3\text{O}_{10})_4]$, KCl , NaCl , LiCl , MgCl_2 , ZnCl_2 , $\text{CH}_3\text{SO}_3\text{Na}$, $\text{CF}_3\text{SO}_3\text{Na}$, $\text{C}_6\text{H}_5\text{SO}_3\text{Na}$, $(\text{C}_2\text{H}_5)_4\text{NBr}$, 1-methylimidazole, 1,3-propanesultone and acetone were supplied by SinoPharm Chemical Reagent Co. Ltd. and Aladdin Industrial Corporation (Shanghai, China), without further purification. The purity levels and sources of these compounds are shown in Table 1. These compounds were stored in a desiccator prior to use. Deionized water was distilled in a quartz still. Its conductivity is $0.8\text{--}1.2 \times 10^{-6} \text{ S cm}^{-1}$ [1,13].

2.2. Preparation of ionic liquids

Fig. 1 shows the structures of the ionic liquids used. $[\text{mim}][\text{HSO}_4]$ and $[\text{mim}][\text{CF}_3\text{SO}_3]$ were prepared using the well-established procedures [14–18]. 1-Methylimidazole was dissolved in acetone, and equal molar quantity of H_2SO_4 or $\text{CF}_3\text{SO}_3\text{H}$ in acetone was added slowly at 273.15 K, respectively. Mixtures were stirred at room temperature for 5 days in a dry N_2 atmosphere. Zwitterion ZTS was prepared from the neutral nucleophiles 1-methylimidazole by reacting with equal molar quantity of 1,3-propanesultone [18]. $[\text{C}_3\text{Smim}][\text{CH}_3\text{SO}_3]$ and $[\text{C}_3\text{Smim}][\text{CF}_3\text{SO}_3]$ were prepared by further syntheses. In the further step, the ZTS acidification was accomplished by combining 1:1 M quantities of ZTS with $\text{CH}_3\text{SO}_3\text{H}$ and $\text{CF}_3\text{SO}_3\text{H}$, respectively. These ionic liquids were recovered and washed by filtration and dried in a vacuum at 343.15 K. Both the literature results [19] and our experiments show that, after having been dried in a vacuum box at 343.15 K for more than 28 h, the prepared ionic liquids have been dried to constant weights. Water contents of these ionic liquids were determined with a ZKF-1 Karl Fischer (KF) Titrator.

2.3. Experimental conditions and apparatus

The apparatus used in this study is similar to that used in Ref. [8]. The experimental setup for determining the solubility consists primarily of a pressure-resistant glass vial that contains the sample and a magnetic stir bar. The vial is immersed in a controlled oil bath (supplied by Beijing Xingde instrument & equipment Co. Ltd) with control accuracy of $\pm 0.1 \text{ K}$. The vial is closed by a pressure-resistant PTFE-aluminum septum through which the solutions can be sampled or the sample and the aqueous solutions of acids, salts, or ionic liquids can be injected by syringes. Temperature inside the vial is measured with a calibrated mercury thermometer, which is inserted through the septum. Solid precipitation upon cooling is determined by visual observation [8].

2.4. Details of experiments

Aqueous solutions of formaldehyde, (formaldehyde– H_2O), were prepared by dissolving paraformaldehyde in bidistilled water at higher temperatures [1,11]. The formaldehyde stock solution, whose formaldehyde concentration (w_1) is greater than the formaldehyde concentration (w_2) used in the following experiments, was obtained by evaporating the dilute formaldehyde aqueous solutions using rotary evaporators [1,11]. The mass of water ($m_{\text{H}_2\text{O}}$) that was required to dilute a defined mass of the stock solution (m_{stock}) to the desired concentration of formaldehyde was calculated with formula $m_{\text{H}_2\text{O}} = m_{\text{stock}} \cdot w_1/w_2 - m_{\text{stock}}$. Also, the corresponding masses of M and N (m_{M} and m_{N} ; N stands for ZTS and $[\text{mim}][\text{CF}_3\text{SO}_3]$ and M stands for acids and the rest of salts and ionic liquids considered) that were required for preparation of the stock solutions $[\text{M}–\text{H}_2\text{O} (m_{\text{H}_2\text{O}})]$ and $[\text{M}–\text{N}–\text{H}_2\text{O} (m_{\text{H}_2\text{O}})]$ with desired concentrations of M and N (c_{M} and c_{N}) were calculated with formula $m_{\text{M}} = c_{\text{M}} \cdot (m_{\text{stock}} + m_{\text{H}_2\text{O}}) \cdot M_{\text{M}}$ and $m_{\text{N}} = c_{\text{N}} \cdot (m_{\text{stock}} + m_{\text{H}_2\text{O}}) \cdot M_{\text{N}}$ (M_{M} and M_{N} is the molar mass of M and N). The calculated results ($m_{\text{H}_2\text{O}}$, m_{M} and m_{N}) were used to prepare stock solutions $(\text{M}–\text{H}_2\text{O})$ and $(\text{M}–\text{N}–\text{H}_2\text{O})$. These stock solutions were prepared by mass from double-distilled deionized water and M and N using a Sartorius CT225D balance with a precision of $1.0 \times 10^{-5} \text{ g}$ [1,11], with the masses of M, N, and H_2O being m_{M} , m_{N} , and $m_{\text{H}_2\text{O}} \text{ g}$, respectively. All solutions were prepared afresh before use.

The formaldehyde solution (formaldehyde– H_2O) was equilibrated at $T \geq 120 \text{ }^\circ\text{C}$ for 5 h in a pressure-resistant vessel. Then, the solution was cooled to lower the pressure so that we can use a pipet to take a defined amount of sample. The aqueous solution $(\text{M}–\text{H}_2\text{O})$ or $(\text{M}–\text{N}–\text{H}_2\text{O})$ was also equilibrated at about $100 \text{ }^\circ\text{C}$. The solutions (formaldehyde– H_2O) and $(\text{M}–\text{H}_2\text{O})$ or $(\text{M}–\text{N}–\text{H}_2\text{O})$ were filled into the glass vial and the vial was closed with the septum cap. The masses of the solutions (formaldehyde– H_2O) and $(\text{M}–\text{H}_2\text{O})$ or $(\text{M}–\text{N}–\text{H}_2\text{O})$ filled into the vial were determined by weighing. Note that the glass vials and pipets have been heated to temperatures above $110 \text{ }^\circ\text{C}$ before they came into contact with the concentrated formaldehyde solution. Upon mixing, the solution was stirred by the small magnetic stir bar in the vial. All these procedures were carried out in such a way that no solid precipitation occurred. After the vial was filled with the mixed solution of the desired composition, it was re-equilibrated at $T \geq 120 \text{ }^\circ\text{C}$ for at least 30 min. Then traces of sample was sampled by using the heated microliter syringe through the septum and was analyzed (the microliter syringe was heated up prior to use). Samples were analyzed by the following methods [1,6,8,20,21]: For the formaldehyde concentration by applying the sodium sulfite method [1,8,21], for the concentrations of chloride salts and $(\text{C}_2\text{H}_5)_4\text{NBr}$ by titration of Cl^- or Br^- with AgNO_3 method [20], and for the concentrations of acids by acid–base titration using potentiometric titrimeter (Leici ZDJ–5) [1,11]. The relative error of the experimental results for the

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