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Density, excess molar volume, and COSMO-RS study of reactive aqueous solutions containing formaldehyde

Zhenmin Bai [a, b], Huihong Liu [c], Yansheng Liu [a, b, *], Yu'e Fu [c], Jun Zhao [d], Xinyun Pu [a, b]

[a] College of Chemical Engineering, China University of Petroleum-Beijing, Beijing, 102249, China
[b] State Key Laboratory of Heavy Oil Processing, China University of Petroleum-Beijing, Beijing, 102249, China
[c] Centre of Technology & Research, China BlueChemical Ltd., CNOOC, Beijing, 100029, China
[d] College of Chemical Engineer and Biotechnology, Xingtai University, Xingtai, 054001, China

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ABSTRACT

In this study, the densities of formaldehyde (FA) + water (H_2O) binary systems with formaldehyde fractions (x_{FA}) of 0.05–0.27 at temperatures (T) of 293.15, 298.15, and 313.15 K were measured at 0.1 MPa, as well as those of a formaldehyde + water + methanol (MeOH) ternary system with x_{FA} of 0.05–0.27 and x_{MeOH} of 0.09–0.64. A thermodynamic model was combined with the conductor-like screening model for real solvents (COSMO-RS) coupled with a chemical reaction equilibrium and mass balance to describe the species distribution in the above solutions containing poly (oxymethylene) glycols ($(HO(CH_2O)_nH$, MG_n $n \geq 1$) and poly (oxymethylene) hemiformals ($CH_3O(CH_2O)_nH$, HF_n, $n \geq 1$) produced by the reactions of FA with H_2O and MeOH, respectively. The densities and volumes of these unknown oligomers, MG_n and HF_n, were computed by the COSMO-RS method and were correlated with the polymerization degree, n, and temperature, T. Furthermore, the densities of the FA + H_2O and FA + H_2O + MeOH solutions were calculated based on the species distribution and COSMO-RS simulations, which reproduced the experimental data well. Finally, the excess molar volumes of the FA + H_2O and FA + H_2O + MeOH systems were studied for the first time.

1. Introduction

Polyoxymethylenes (POM) are an important type of engineering plastic, and their production continues to increase. POMs are copolymerized from trioxane and 1,3-dioxolane, both of which are synthesized and distilled from formaldehyde solution [1–3]. In other words, the whole POM production process is carried out in a mixture containing formaldehyde. Thus, information concerning the physical characteristics of this solution system, e.g., the density of the formaldehyde solution, and the dependence on the composition and temperature is not only very important in pipeline systems, formaldehyde solution storage tanks, and mass transfer operations, but must be strictly observed for formaldehyde concentration/absorption and trioxane distillation units. However, aqueous and methanolic formaldehyde solutions are a complex mixture because of the presence of MG_n and HF_n $n \geq 1$, which are generated by a series of polymerization reactions, as shown in equations (1)–(4) [4–6]. These oligomers are quite sensitive to temperature and the overall formaldehyde concentration and cannot be characterized as pure substances. Thus, the experimental study, as well as theoretical modeling, of these complex and reactive formaldehyde solutions is challenging.

$$\mathrm{HCHO\ (FA)} + H_2O \leftrightarrow \mathrm{HOCH_2}OH(MG) \tag{1}$$

$$\mathrm{HO}(CH_2O)_{n-1}H(MG_{n-1}) + \mathrm{HOCH_2}OH(MG) \leftrightarrow \mathrm{HO}(CH_2O)_nH(MG_n) + H_2O(\mathrm{n} = 1, \ldots, \infty) \tag{2}$$

$$\mathrm{HCHO(FA)} + CH_3\mathrm{OH(MeOH)} \leftrightarrow \mathrm{CH_3OCH_2}OH(HF) \tag{3}$$

$$\mathrm{CH_3O}(CH_2O)_{n-1}H(HF_{n-1}) + \mathrm{HOCH_2}OH \leftrightarrow \mathrm{CH_3O}(CH_2O)_nH(HF_n) + H_2O\ (\mathrm{n} = 1, \ldots, \infty) \tag{4}$$

* Corresponding author. College of Chemical Engineering, China University of Petroleum-Beijing, Beijing, 02249, China.
E-mail addresses: 1128bj@163.com, wsuper@cup.edu.cn (Y. Liu).

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The latest density prediction method was reported in 2000 by Winkelman [7]. The authors encountered difficulties and limitations in both technology and measurements, and they calculated the volumes of oligomers as the stoichiometric sum of the volume of the CH_2O units and water for the FA + H_2O solution. This simplified processing method ignores the structures of the existing oligomers and can help to understand better the interactions between molecules, as well as the involved steric effects, which are important for obtaining important density properties. However, Winkelman's method [7] was not applied to FA + H_2O + MeOH ternary systems, which show more complexity, possibly arising from new and unknown species, such as HF_n, and new molecular interactions. Despite the considerable research concerning the measurement of the density of FA + H_2O and FA + H_2O + MeOH mixtures [1], there has been little progress in density measurements, including theoretical prediction methods, for the ternary system with a high methanol concentration. In addition, there has been little physical insight into the density properties at a molecular level for the solution containing formaldehyde. Moreover, no excess volume studies have been reported yet for this reactive mixture.

In this regard, the conductor-like screening model for real solvents (COSMO-RS) is an acceptable method for the prediction of the thermophysical properties of fluids without experimental data [8,9]. COSMO-RS can provide important insights into liquid phase thermophysical properties by calculating the required surface charge density distributions (σ-profiles) and statistical thermodynamic analysis of the effective solvent chemical potentials (σ-potentials). The complete theory of COSMO-RS can be found in the work of Klamt and Eckert [10]. Most importantly, COSMO-RS includes hydrogen bonding terms parameterized into the σ-potential applied to the chemical reactions [11]. In the cited work, the COSMO-RS model has been successfully applied to predict the density and volume values of many molecular structures and has gained popularity in chemical engineering [12–15].

As an extension of work concerning formaldehyde solutions [16–19], this study aims to overcome the shortcomings of the previous correlation method and give more detailed information concerning the density and excess molar volume based on the COSMO-RS method, thus avoiding the experimental difficulties associated with FA + H_2O binary and FA + H_2O + MeOH ternary systems. This article is divided as follows: Section 2 provides an introduction to the method and models, including experimental methods for the density measurement, theoretical computational details, and a predictive model for the species distribution. Section 3 first presents our experimental density data and then presents the conformers of MG_n and HF_n that have been calculated and analyzed by our COSMO*conf* program. Thirdly, we performed, for the first time, COSMO-RS simulations to predict the volumetric properties, such as the density and molar liquid molecular volume, of oligomers in the formaldehyde solutions, and, here, we show the correlation with the polymerization degree, n, and temperature, T. Furthermore, the density values calculated by our model for the binary and ternary systems were compared with those obtained experimental data. Finally, we used an innovative technique to simulate the excess molar volume (V^E) for the required systems and interpreted the influence on V^E of the introduction of methanol. Our conclusions are drawn in Section 4.

2. Method

2.1. Experimental method

The designed experiment mainly aims to observe the influence of the amount of methanol on the density of the formaldehyde aqueous solution. Formaldehyde aqueous solutions were rotary evaporated to remove methanol and then titrated with sodium sulfite [1]. No undesired substances were present according to gas chromatography (GC) results for the prepared solutions. The prepared and stoichiometric formaldehyde aqueous solutions were diluted by the addition of water or methanol. Water was determined by the Karl Fisher titrator (Metrohm 870 KF Titrino plus). Methanol with a purity of 99.99% was obtained from TCI (Shanghai) development Co., Ltd.

The concentration of formaldehyde was determined using equation (5) [1].

$$x_{FA} = c\,V \cdot 0.003003 \cdot 100/m \tag{5}$$

Here, x_{FA} is the formaldehyde molar fraction, c is the concentration of the sulfuric acid standard solution and is constant, V is the volume of the sulfuric acid standard solution, and m is the mass of the sample. The combined standard uncertainty of concentration measurement of formaldehyde (u_x) is less than 0.3% [19]. The details of chemicals used in this work are stated in Table 1.

An Anton Paar SVM3000 was used to measure the densities of solutions containing formaldehyde. The uncertainties of the instrument are $\mu_T = \pm 0.05\,^{\circ}C$ and $\mu_\rho = \pm 2 \times 10^{-4}\,g \cdot cm^{-3}$ for the temperature and density, respectively. The accuracy of density data were verified by comparing the our measured data of water at different temperatures with the reference data [20], as shown in Table S1, indicating that the measurement accuracy is about $0.0002\,g \cdot cm^{-3}$. The densities were measured at formaldehyde concentrations, x_{FA}, of 0.01–0.23 and temperatures, T, of 291.15, 298.15, and 313.15 K. All measurements were performed twice to obtain average values.

2.2. Theory and computational details

The COSMO-RS method based on dielectric continuum model with statistical thermodynamic calculations for the pure compound and mixtures has gained popularity because of its predictive power. Two steps are needed to carry out the COSMO-RS calculations. The first step is to carry out density functional theory (DFT) calculations with the continuum solvation model method (COSMO), which yields the optimized geometry, the mapping of the polarized charge densities onto the σ-surface, and the total energy in the conductor. The second step is to use statistical thermodynamics to determine the different forces that affect the H-bonding and non-H-bonding interactions. The calculations determine the energy of a molecule in the chosen

Table 1
Purity of chemicals used in this study and their details.

Chemical name	Source	Purification method	Purity (mass)	Analysis method	Abbv.
Formaldehyde aqueous solution	Sinopharm Chemical Reagent Co. Ltd.	rotary evaporator	36.61%	GC and sodium sulfite	FA
Methanol	TCI (Shanghai) development Co., Ltd.	none	99.99%	GC	MeOH
Water	China University of Petroluem (Beijing)	Ion-exchanger and distillated	Milli-Q	Karl Fisher titrator	H_2O