



Designing new mass-separating agents based on piperazine-containing good's buffers for separation of propanols and water azeotropic mixtures using COSMO-RS method



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ABSTRACT

The isobaric vapor-liquid equilibria of the binary 1-propanol + water, 2-propanol + water, and 2-methyl-2-propanol (*tert*-butanol) + water systems were predicted using the conductor-like screening model for realistic solvation (COSMO-RS) method. The phase behavior of the 1-propanol/2-propanol/*tert*-butanol + water + piperazine-based Good's buffer systems were predicted. The effect of piperazine-containing Good's buffers, 2-[4-(2-hydroxyethyl)piperazin-1-yl]alkanesulfonic acid, as mass-separating agents on the separation of propanols from water were discussed. The influence of alkyl chain length between the zwitterion end groups, *R* = methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, and decyl was evaluated. Further, the effect of 4-(2-hydroxyethyl)piperazine-1-(2-hydroxypropane sulfonic acid) was also evaluated. Piperazine-based Good's buffers are expected to be effective mass-separating agents to have practical application in the separation of propanol from water.

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1. Introduction

Small amphiphilic molecules such as 1-propanol, 2-propanol, and 2-methyl-2-propanol (*tert*-butanol) increase the solubility of sparingly soluble compounds in water. Thus, aqueous solutions of aliphatic alcohols find many uses, ranging from medicine to materials science. The recycling of the alcohols from water in chemical industry is needed. Distillation is one of the most efficient unit operation in the recovery processes due to its ability to produce high purity products. However, these alcohol–water mixtures exhibit azeotropes and, thus, their separation into their pure constituents is not possible *via* distillation alone. There are several potential methods for breaking azeotropes [1] such as extractive distillation, liquid–liquid extraction, membranes, adsorption, and pressure swing distillation. The drawback of these methods that they are uneconomical processes. To facilitate the distillation of the azeotropic mixtures is by adding a third component with high boiling point, called entrainer or mass-separating agent, which altering the relative volatility of alcohol; and therefore, affectively

breaking the azeotrope.

Salts have been used as mass-separating agents in extractive distillation as alternative to solvents [2–6]. Adding salt into alcohol + water mixtures usually forcing out the alcohol molecules from the water network (salting-out) and increases the concentration of alcohol in the vapor phase, which in many cases causes a shifting or breaking the azeotropic mixture. Using salt as entrainer has been used to optimize the separation processes of these mixtures; however, the major drawback of salting out is its high concentrations that corrode the equipment [7]. The phase separation of water–alcohol mixtures induced by the addition of nonelectrolytes (organic separating agents) is very limited in the literature [8,9]. Buffering-out phase separation is a new liquid-liquid two-phase systems which was observed by Taha et al. [10–18], for the separation of various organic solvents from their aqueous solution by adding Good's buffers as mass-separating agents (MSAs). Good's buffers (GBs), organic molecules, are the most commonly used biological buffers. TES [13], HEPES [14], and EPPS [16] buffers have formed aqueous biphasic systems for 1-propanol, 2-propanol, and *tert*-butanol.

The vapor-liquid equilibrium (VLE) data of the above-mentioned systems are necessary for the design of the separation processes. The VLE data of (water + propanol + salt) systems have been

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already explored by many researchers e.g., [19–21]. As far we know, there are no available VLE data for water + propanol + buffer systems. Here, we are trying to find new mass-separating agents based on piperazine-containing Good's buffers for separation of the azeotropic mixtures, 1-propanol, 2-propanol, or *tert*-butanol + water, using the conductor-like screening model for realistic solvation (COSMO-RS) computation method. This model is originally developed by Klamt [22], which considered as an efficient method for the prediction of thermophysical properties of mixtures. COSMO-RS method is based solely on quantum chemical calculations of the chemical compounds. It has been used to predict VLE for binary and ternary systems [23–26]. Several researchers have been used COSMO-RS method to identify the potential entrainers or MSAs for the separation of azeotropic mixtures of ethanol + water [27], 2-propanol + water [27], THF + water [27], 1-hexane + *n*-hexane [28], acetonitrile + water [29], methyl acetate + methanol, and ethyl acetate + ethanol [30].

This study first predicts the ternary VLE data, by using the COSMO-RS model, for the azeotropic mixtures of 1-propanol + water, 2-propanol + water, and *tert*-butanol + water with the available piperazine (PZ)-based GBs, 2-[4-(2-hydroxyethyl)piperazin-1-yl]methanesulfonic acid (HEPMS, HEP₁S), 2-[4-(2-hydroxyethyl)piperazin-1-yl]ethane sulfonic acid (HEPES, HEP₂S), 2-[4-(2-hydroxyethyl)piperazin-1-yl]propane-sulfonic acid (HEPPS, HEP₃S), 4-(2-hydroxyethyl)piperazine-1-(2-hydroxypropanesulfonic acid) (HEPPSO, HEP₃SO), and 2-[4-(2-hydroxyethyl)piperazin-1-yl]butanesulfonic acid (HEPBS, HEP₄S). The buffers, HEPES, HEPPS, HEPBS, and HEPPSO are commercially available, and HEPMS has been recently synthesized [31]. Second, the study extends to investigated the influence of increasing the alkyl chain length between the zwitterion end groups, 2-[4-(2-hydroxyethyl)piperazin-1-yl]pentanesulfonic acid (HEP₅S), 2-[4-(2-hydroxyethyl)piperazin-1-yl]hexanesulfonic acid (HEP₆S), 2-[4-(2-hydroxyethyl)piperazin-1-yl]heptanesulfonic acid (HEP₇S), 2-[4-(2-hydroxyethyl)piperazin-1-yl]octanesulfonic acid (HEP₈S), 2-[4-(2-hydroxyethyl)piperazin-1-yl]nonane sulfonic acid (HEP₉S), and 2-[4-(2-hydroxyethyl)piperazin-1-yl]decanesulfonic acid (HEP₁₀S); these compounds were here proposed for the first time. The chemical structures of the studied compounds are given in Fig. 1.

2. Computational details

Based on COSMO-RS model, the COSMOtherm (version C30_1401) software [22,32] was used to predict the VLE data of the binary and ternary systems. The COSMOtherm software needs the COSMO and energy files for each compound. Both files were generated by the TURBOMOLE 6.1 [33] software using density functional theory (DFT) level, using the Becke and Perdew functional [34–36] with a triple- ζ valence polarized basis set (TZVP) [37]. The COSMO file is needed to calculate the screening charge density profile (σ -profile) and chemical potential of the individual molecules. This information is necessary to predict the possible interactions in the mixture and the thermodynamic properties. For a given temperature, the COSMOtherm calculates the isobaric VLE data using the following equations:

$$P_{tot} = \sum_i P_i^0 x_i \gamma_i \quad (1)$$

The P_i^0 refer to the pure compound vapor pressures for compound i , and x_i represent the mole fractions of the compound in the liquid. γ_i are the predicted activity coefficients. Ideal behavior of the vapor phase is assumed and the vapor mole fractions y_i are obtained by Eq. (2). The detailed calculation of predicting the activity

coefficient using COSMO-RS can be found elsewhere [38].

$$y_i = P_i^0 x_i \gamma_i / P_{tot} \quad (2)$$

The vapor pressure of pure water, 1-propanol, and 2-propanol were calculated by the Wagner Eq. (3) and their coefficients are given in Table 1.

$$\ln(P_i^0) = \ln(A) + \frac{1}{1-\tau} [C\tau + D\tau^{1.5} + D\tau^3 + D\tau^6]; \tau = 1 - \frac{T}{B} \quad (3)$$

The vapor pressure of buffer was approximated using the exact gas phase energy, while the vapor pressure of *tert*-butanol was calculated by Antoine Eq. (4),

$$\ln(P_i^0) = A - B/(T + C) \quad (4)$$

The coefficients A, B, and C in [kPa]/[K] are, respectively, 14.8398, 2658.29, and -95.5 , taken from COSMOtherm database.

3. Results and discussion

The azeotropic temperature (T_{Az}), and liquid-phase composition ($x_{alcohol,Az}$)/vapor-phase composition ($y_{alcohol,Az}$) are 360.8 K and 0.4320 for 1-propanol + water mixture, 353.7 K and 0.6740 for 2-propanol + water mixture, and 353.0 K and 0.5989 *tert*-butanol + water mixture [39], respectively. The predicted $T_{Az}^{COSMO-RS} = 362.3$ K and $x_{alcohol,Az}^{COSMO-RS} = 0.3738$ for 1-propanol + water mixture, $T_{Az}^{COSMO-RS} = 354.6$ K and $x_{alcohol,Az}^{COSMO-RS} = 0.7438$ for 2-propanol + water mixture, and $T_{Az}^{COSMO-RS} = 353.0$ K and $x_{alcohol,Az}^{COSMO-RS} = 0.6178$ for *tert*-butanol + water mixture, respectively. The differences of $T_{Az}^{COSMO-RS}$ and $x_{alcohol,Az}^{COSMO-RS}$ between the COSMO-RS model predictions and literature experimental data were estimated by were $+1.5$ K and -0.06 for 1-propanol + water mixture, $+0.9$ K and $+0.07$ for 2-propanol + water mixture, and 0 K and $+0.02$ *tert*-butanol + water mixture, respectively. It can be observed that the $T_{Az}^{COSMO-RS}$ and $x_{alcohol,Az}^{COSMO-RS}$ were predicted with acceptable accuracy. Nevertheless, the effect of structural variations of piperazine-based Good's buffers can be studied qualitatively for rapid screening of potential MSAs using COSMO-RS. The isobaric-VLE data of 1-propanol/2-propanol/*tert*-butanol (1) + water (2) + MSA (3) systems are given in Figs. S1–S6 in the Supporting Information, at different MSA mole fractions ($x_3 = 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, \text{ and } 0.35$). The experimental VLE data of the binaries, 1-propanol + water, 2-propanol + water, and *tert*-butanol + water, are taken from Refs. [3,40–42]. The isobaric VLE data for the alcohol + water + MSA systems (Figs. S1–S6 in the Supporting Information) reveals that all the studied MSAs break the azeotropic composition. In case of 1-propanol + water + MSA systems, HEP₁S breaks the azeotropic composition at $x_3 \geq 0.25$, and the buffers from HEP₂S to HEP₈S break the $x_{1-propanol,Az}^{COSMO-RS}$ at $x_3 \geq 0.15$. While HEP₉S, HEP₁₀S, and HEP₃SO break the $x_{1-propanol,Az}^{COSMO-RS}$ at $x_3 \geq 0.20$. As for 2-propanol + water + MSA systems, HEP₁S and HEP₃SO break the $x_{2-propanol,Az}^{COSMO-RS}$ at $x_3 \geq 0.10$, while the other MSAs break the $x_{2-propanol,Az}^{COSMO-RS}$ at $x_3 \geq 0.05$. All the studied PZ-based compounds break the azeotropic mixtures of *tert*-butanol + water mixture at $x_3 \geq 0.10$. It can be seen that these compounds appear to be a more effective MSAs for the separation of 2-propanol/*tert*-butanol + water mixture. Figs. 2 and 3 show the predicted isobaric-VLE data of alcohol (1) + water (2) + MSA (3) systems at $x_3 = 0.05$ and $x_3 = 0.15$, respectively.

The optimization of the MSA screening was performed for these azeotropic mixture separations by the relative volatility (α_{12}). The relative volatility of alcohol to water can be calculated as,

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