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Use of HS-SPME for analysis of the influence of salt concentration and temperature on the activity coefficient at infinite dilution of ethanol-water-salt systems

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ABSTRACT

Accurate knowledge of thermodynamic properties is of great importance in optimizing industrial processes of chemical separation. However, traditional techniques have limitations that hinder the use in complex systems, especially involving strong electrolytes. Solid phase micro-extraction (SPME) was used to determine infinite dilution activity coefficients of ethanol in water-salt systems. Different concentrations of inorganic salts were used to verify the influence on the activity coefficient at temperatures of 323.15, 333.15, 343.15, and 353.15 K. Salts evaluated in SPME include potassium chloride (KCl), calcium chloride ($CaCl_2$), and aluminum chloride ($AlCl_3$) at concentrations of 1.125, 1.800, and 2.571 mol/Kg. Comparisons between data obtained using SPME and the theoretical basis and literature data showed good agreement. Thermodynamic parameters such as partial molar excess enthalpy at infinite dilution, partial molar excess entropy at infinite dilution, and partial molar excess Gibbs energy were calculated from the infinite dilution activity coefficient. $AlCl_3$ produced the highest activity coefficient for ethanol at infinite dilution, indicating a strong influence on the separation of ethanol. The results obtained indicate that SPME technique can be considered an alternative method on determination of activity coefficients at infinite dilution.

1. Introduction

Ethanol is used in many industrial applications because it is an excellent alternative fuel and has a virtually limitless potential for expanded use. However, when procedures requires high purity ethanol, expensive and time consuming purification processes such as extractive distillation using a mass separating agent to facilitate separation are necessary [1]. Development of units optimized for the required purity levels requires knowledge of thermodynamic properties [2].

In separation processes involving equilibrium phase, more energy is consumed when the solute is infinitely diluted [3]. The knowledge of activity coefficient at infinite dilution (γ_1^∞) allows the determination of various thermodynamic parameters of industrial and theoretical importance [4]. Many techniques are described in the literature for activity coefficients determinations, nevertheless all methods present limitations in their applications [4]. The gas-liquid chromatography (GLC) is the further used in non-volatile or low volatile solvents [5–8], but presents difficulty or impossibility to determine both activity coefficients of binary mixtures [9,10]. The inert gas stripping allows the determination of γ_1^∞ for many compounds on a single experiment [11–13], however required a system with high relative volatility [9,10]. The HS-SPME is a recent methodology successfully employed in determining partition coefficients and activity coefficients in polymeric and non-polymeric systems [14,15], in organic solvents systems [2,4,16] and in ionic liquid solvent systems [17]. Researchers showed that the SPME can be used in any system (provided that the compound of interest has affinity with the fiber coating) with easiness, lower costs, and accuracy than the conventional methods.

In this study, continuation of a previous research [1], the main objective is extend and validate the SPME methodology in complex systems involving strong electrolytes. It was evaluated the impact of different cations (K^+, Ca^{+2}, Al^{+3}), concentrations and temperature variation on the activity coefficient at infinite dilution of

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ethanol using a proposed theoretical basis. Characteristics of the technique such as advantages, limitations, and result deviations from data reported in the literature were also evaluated.

2. Theoretical basis

Solid Phase Microextraction has been developed as a rapid and solvent-free technique that is compatible with sample preparation methods. It has applications in areas such as environmental analysis, industrial hygiene, process monitoring, and clinical, forensic, food, and drug analyzes [18].

The basic SPME device is a fiber optic rod of fused silica (FS) coated with a polymer thin film with a diameter of 100 μm and a length of 10 mm. Although several types of film coating polymers are commercially available, the most common is the polydimethylsiloxane film (PDMS) [19].

The partition coefficient (K) has been widely used in recent years to quantify the amount of pollutant material or toxic substances in water [20,21]. The partition coefficient has also been used to investigate the sorption phenomena in a substance as well as the affinity of a polymer coating the inside of a chromatographic column or the exterior of a fused silica fiber [22]. The ratio of mass extracted by the fiber relative to the total available mass in the vapor phase may be obtained according to Equation (1). This relationship is also known as fiber-gas partition coefficient (K_{fg}).

$$K_{fg} = \frac{n_1^f}{V_f}\frac{V_g}{n_1^g} \tag{1}$$

Where V_f is the fiber volume, V_g is the vial headspace volume, n_1^f is the number of moles of solute absorbed by the fiber, and n_1^g is the number of moles of solute in the system's gaseous phase.

Elias et al. [1] used the following assumptions to determine a thermodynamic approach to the calculation of γ_1^∞.Vapor behaves as an ideal gas, therefore, the fugacity coefficient of solute, $\varphi^v = 1$; In infinitely diluted species, only liquid vapor pressure is considered as the fugacity at the standard state ($f_1^0 \approx P_1^{sat} \rightarrow \Delta P_1 \approx 0$) because salt is poorly soluble in this condition [23]; the model is only limited to salts with low solubility in infinitely diluted species.

These assumptions result in Equation (2).

$$\gamma_1^\infty = \frac{1}{P_1^{Sat}}\frac{n_1^f RT}{K_{fg}V_f}\left(\frac{K_{fg}V_f\left(n_{sal} + n_2^L + n_1^0 - n_1^f\right) - n_1^f V_g}{K_{fg}V_f\left(n_1^0 - n_1^f\right) - n_1^f V_g}\right) \tag{2}$$

Where P_1^{Sat} is the calculated ethanol saturation pressure, n_{sal} is the number of salt moles in solution, n_2^L is the number of water moles in solution, n_1^0 is the initial number of moles of added ethanol, R is the gas constant, and T is the system's temperature.

The partial molar excess enthalpy ($H_1^{E,\infty}$) and partial molar excess entropy ($S_1^{E,\infty}$) can also be calculated from γ_1^∞; the partial molar excess Gibbs energies to the reference temperature of 298.15 K can thereby be obtained from Equation (3) and Equation (4) [8].

$$ln\gamma_1^\infty = \frac{G_1^{E,\infty}}{RT} = \frac{H_1^{E,\infty}}{RT} - \frac{S_1^{E,\infty}}{T} \tag{3}$$

$$ln\gamma_1^\infty = \frac{a}{T} + b \tag{4}$$

3. Material and method

3.1. Material

Analytical grade reagents (potassium chloride, anhydrous calcium chloride, and anhydrous aluminum chloride) were obtained from Sigma-Aldrich with purity exceeding the mass fraction of 0.9800. The salt purity was verify with Karl Fischer technique after dried under vacuum at 383.15 K for at least 8 h. Ethanol and ortho-xylene were obtained from Sigma-Aldrich. The purity exceeding the mass fraction of 0.9922, it was verified by gas chromatography and refractometry. Polydimethylsiloxane fiber (PDMS, 100 μm thickness) and holders was obtained from Supelco. Forty mL amber bottles with PTFE/silicone septa were used for confinement and study of the liquid mixtures. Hamilton chromatographic syringes were used in the volumes of 10, 100, 500, and 1000 μL. The sample description can be seen in Table 1.

3.2. Gas chromatography conditions for SPME and liquid injections

The GC-2010 Shimadzu gas chromatograph used in the experiment was equipped with a Flame Ionization Detector (FID) coupled with a 60 m × 0.32 mm x 0.25 μm HP-Innowax capillary column crosslinked polyethylene glycol (PEG) and coupled with a SGE Analytical Science Pty Ltd liner with an internal diameter of 0.75 mm (suitable for SPME). Helium was used as the carrier gas (mass fraction 0.99999) in a column flow of 2.0 mL/min The injector pressure was held constant at 113.0 kPa throughout the analysis period by using the splitless mode for 2 min and a subsequent split ratio of 1:8; the injector and detector temperature were maintained at 523.15 K. The initial column temperature was maintained for 5 min at 323.15 K and then raised by10 K min^{-1} to 353.15 K, a temperature which was maintained for 2 min. The conditions were obtained in order to optimize the resolution of the chromatographic peaks.

3.3. Construction of calibration curves

The calibration curve for ethanol was constructed from gas chromatographic analysis of 1 μL standard solutions of ethanol in o-xylene. The concentrations used in the construction ranged from 8.90 to 2514.41 ng/μL; eight points were used and four to eight replicates were analyzed. The chromatographic conditions were the same as described above.

3.4. Determination of extraction time and fiber-gas partition coefficients

The fiber extraction time was determined in the headspace when the mass extracted by the fiber at the lowest studied temperature no longer varied [18]. The fiber-gas partition coefficient was determined by injecting 1 μL of ethanol in 40 mL amber vials at four studied temperatures, controlled by a thermostat bath (LAUDA Model RM 6B) and calculated from Equation (1) described before.

3.5. Determination of infinity dilution activity coefficients by SPME

The infinite dilution activity coefficient was determined for two types of systems. The first, a binary system (ethanol-water), was prepared according the previous works [1,4]. The purpose was to validate the equation proposed and compared with literature data [1,10]. The second, a ternary system (ethanol-water-salt), was prepared following the salt concentrations of: *i*- 8.39, 13.42, and 19.17 g in 0.1 Kg of water for KCl; *ii*-12.49, 19.98, and 28.54 g in 0.1 Kg of water for $CaCl_2$; and *iii*- 15.00, 24.00, and 34.28 g in 0.1 Kg of water