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Vapor–liquid equilibria of binary tri-potassium citrate + water and ternary polypropylene oxide 400 + tri-potassium citrate + water systems from isopiestic measurements over a range of temperatures

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Abstract

Water activity measurements have been carried out on the aqueous solutions of both tri-potassium citrate (K_3Cit) and polypropylene oxide (PPO) 400 + K_3Cit over a range of temperatures at atmospheric pressure. The data obtained is used to calculate the vapor pressure as a function of temperature and concentration. The effect of temperature on the constant water activity lines of aqueous PPO + K_3Cit systems has been studied and it was found that, at higher temperatures the higher concentration of polymer is in equilibrium with a certain concentration of the salt. Also it was found that the vapor pressure depression for an aqueous PPO + K_3Cit system is more than the sum of those for the corresponding binary solutions. The experimental water activities have been correlated successfully with the segment-based local composition Wilson model. The agreement between the correlation and the experimental data is good.

Keywords: Water activity; Vapor–liquid equilibria; Isopiestic; Polypropylene oxide; Potassium citrate

1. Introduction

Ternary aqueous solutions of tri-potassium citrate (K_3Cit) and polypropylene oxide (PPO) separate into a K_3Cit-rich and a PPO-rich phase over part of the composition space. Aqueous two-phase systems of this nature are useful for the separation and purification of biomaterials where the employment of a non-polar solvent/aqueous phase system would lead to degradation of biological activity [1,2]. Citrate is biodegradable and nontoxic and could be discharged into biological wastewater treatment plants and therefore the citrates can be considered as a substitute for inorganic salts, because the citrate forms aqueous two-phase system with PPO which is suitable for protein extraction. In addition to aqueous two-phase systems, aqueous solutions of potassium citrate are of a considerable significance in many other biochemical and chemical processes and this salt is produced in large quantities and used in food, cosmetic, pharmaceutical and chemical industries [3–6].

Thermodynamic properties of aqueous polymer–salt systems are necessary for a fundamental understanding of the phase-forming ability and also for the development of theoretical models for the prediction of the partitioning behavior of the two-phase system. In an ATPS, water constitutes the bulk component of the two phases and therefore water is a special and key component and closely related with the other two-phase-forming components. Thus, the thermodynamic properties of water in these systems should be paid great attention. Also, the activity is an important and key thermodynamic property, because, it is closely related with the other thermodynamic properties and in thermodynamic modeling for separation methods, it is the essential variable. Vapor–liquid equilibria data for several aqueous PPO + salt [7–9] systems have been determined. However, the corresponding data are limited to 298.15 K and there is no information about the effect of temperature on the vapor–liquid equilibria of these systems and it is difficult to correlate the phase behavior of these systems which show a lower critical solution temperature. As far as we know there is no report on the vapor–liquid equilibrium data for binary aqueous K_3Cit and ternary aqueous K_3Cit + PPO systems in the literature.

This work is devoted to obtain the water activities of these systems at 293.15–313.15 K. In this study, the isopiestic method

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[10] is used to obtain the activity of water in the investigated systems. It is based on phenomenon that different solutions, when connected through the vapor space, approach equilibrium by transferring solvent mass by distillation. Equilibrium has been established once the temperature and pressure are uniform throughout the system, provided that no concentration gradients exist in the liquid phase. At equilibrium, the chemical potentials of the solvent in each of the solutions in the closed system are identical. Equality of the solvent chemical potential implies the equality of the solvent activity. Since the solvent activity is known for one or more standard solutions, it will be known for each solution within the isopiestic system. In all of isopiestic measurements, NaCl solutions were used as an isopiestic standard. Finally, the segment-based local composition Wilson [11] model was used for the correlation of the obtained experimental water activity data.

2. Experiments

2.1. Materials

PPO with a quoted molar mass 400 g mol^{-1} was obtained from Fluka. The manufacturer has characterized this polymer as P400 with lot and filling code 1252304 20206282. Potassium citrate ($C_6H_5K_3O_7 \cdot H_2O$) was obtained from Fluka. The polymer and salt were used without further purification, and double distilled, deionized water was used.

2.2. Method

The isopiestic apparatus used in this work was similar to the one used by Ochs et al. [10]. The apparatus used for determination of water activity of binary aqueous K_3Cit solutions consisted of five-leg manifold attached to round-bottom flasks. Two flasks contained the standard pure NaCl solutions, two flasks contained the pure K_3Cit solutions and the central flask was used as a water reservoir. The apparatus used for determination of water activity of ternary aqueous K_3Cit + PPO solutions consisted of seven-leg manifold attached to round-bottom flasks. Two flasks contained the standard pure NaCl solutions, one flask contained the pure PPO solution, one flask contained the pure K_3Cit solution, two flasks contained the PPO + K_3Cit solutions and the central flask was used as a water reservoir. The apparatus was held in a constant-temperature bath at least 120 h for equilibrium. During the equilibration process the manifold was removed at least once a day and the samples were agitated. After the third day the samples were not agitated, but left in the bath to approach their final equilibrium conditions. The temperature was controlled to within ±0.01 K. After equilibrium had been reached, the manifold assembly was removed from the bath, and each flask was weighed with an analytical balance with a precision of $\pm 1 \times 10^{-4}$ g. From the weight of each flask after equilibrium and the initial weight of salt and polymer, the mass fraction of each solution was calculated. The water activity for the standard aqueous NaCl solutions at different concentrations and temperatures has been calculated from the correlation of Colin et al. [12]. It was assumed that the equilibrium condition was reached when the differences between the mass fractions of two standard solutions were less than 1%. In all cases, averages of the mass fractions of two standard solutions are reported. The accuracy of the method depends upon the standard solutions, sample mixing during the equilibrium period, temperature stability, and the time allowed for the equilibrium process. The uncertainty in the measurement of solvent activity was estimated to be $\pm 2 \times 10^{-4}$.

3. Results and discussion

3.1. Experimental results

In the present work, in order to describe thermodynamic properties of both binary aqueous K_3Cit and ternary aqueous K_3Cit + PPO solutions, the water activity measurements at 293.15, 298.15, 303.15, 308.15, and 313.15 K were carried out for binary K_3Cit + H_2O and ternary K_3Cit + PPO + H_2O solutions to study the vapor–liquid equilibria behavior of these systems. Table 1 reports the water activity data of binary K_3Cit + H_2O system at 293.15, 298.15, 303.15, 308.15, and 313.15 K. Tables 2–6 report the water activities of K_3Cit + PPO + H_2O system at 293.15, 298.15, 303.15, 308.15, and 313.15 K, respectively. In Fig. 1, comparison of the experimental water activity data measured in this work with those taken from Refs. [13,14] has been made for PPO + H_2O system at 303.15 K. That is to say, two samples of the same polymer, e.g., equal in weight average molecular weight may exhibit different physicochemical properties if they differ in their molecular-weight distribution. However, the polymer used in this work has a small molar mass and therefore the polydispersity of this polymer is small. In fact, Fig. 1 shows that there is a good agreement between our data and the literature. Also, Fig. 1 shows larger negative slope of the water activity against polymer mass fraction, w_p, above mass faction 0.8, implies that the interaction between the water and PPO molecules at high mass fractions of PPO

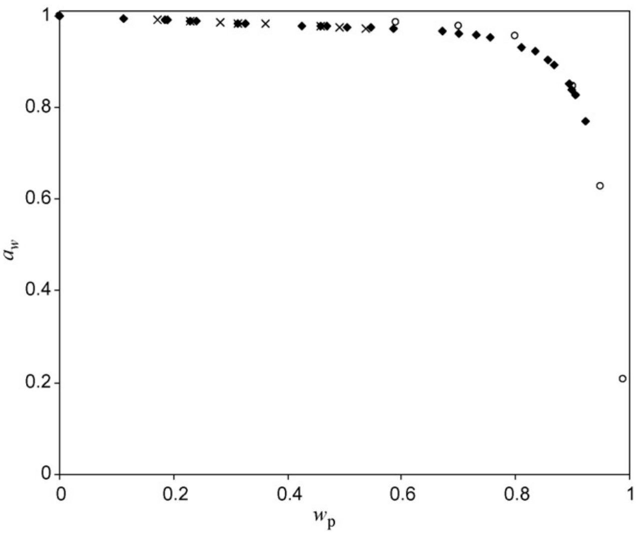

Fig. 1. Comparison of measured water activity data for PPO + H_2O solutions at 303.15 K: (×) this work; (♦) Ref. [13]; (○) Ref. [14].