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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Introduction

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. This work is devoted to obtain the water activities of binary tri-potassium citrate + water and ternary polypropylene oxide 400 + tri potassium citrate + water systems at 293.15–313.15 K.

Key words: Water activity, Vapor liquid equilibria, Isopiestic, polypropylene oxide, potassium citrate

Method

The isopiestic apparatus used in this work was similar to the one used by Ochs et al. The apparatus used for determination of water activity of binary aqueous K₃Cit solutions consisted of five-leg manifold attached to round-bottom flasks. The apparatus
used for determination of water activity of ternary aqueous K₃Cit + PPO solutions consisted of seven-leg manifold attached to round-bottom flasks. The apparatus was held in a constant-temperature bath at least 120 h for equilibrium.

Result

In the present work, in order to describe thermodynamic properties of both binary aqueous K₃Cit and ternary aqueous K₃Cit + PPO solutions, the water activity measurements at 293.15, 298.15, 303.15, 308.15, and 313.15K were carried out for binary K₃Cit+H₂O and ternary K₃Cit + PPO+H₂O solutions to study the vapor–liquid equilibria behavior of these systems. The vapor pressures (p) of various aqueous solutions at each temperature were computed. The effect of temperature on the constant water activity or vapor pressure Of K₃Cit+ PPO+H₂O system has been studied. It was found that at the same concentration, vapor pressure depression for the salt solution is more than those for the polymer solution. This is because the number of moles of ions in the salt solution is more than the number of moles of polymer in the polymer solution with same concentration (the vapor pressure depression is a coligative property) and also the ion–water interactions are stronger than the polymer–water interaction. Vapor pressure depression for several K₃Cit + PPO+H₂O solutions along with those for corresponding binary solutions is studied at different temperatures. This shows that the vapor pressure depression for a ternary aqueous K₃Cit + PPO system is more than the sum of those for the corresponding binary solutions. In the aqueous solutions, each segment of PPO is hydrated strongly with several water molecules. Such binding will result in a reduction in the free water content and consequently in an increase in the effective concentration of the salt. Similarly, ionic species in the aqueous solutions are hydrated and this hydration will result in an increase in the effective concentration of the polymer. Thus, it can be expected that the vapor pressure depression for an aqueous K₃Cit + PPO system to be more than the sum of those for corresponding binary solutions. With increase in the concentration of the polymer or the salt, increase in the effective concentration will increase and ultimately, the system could reach a state where, for entropic reasons, the formation of aqueous two-phase system would become favorable. However, the thermodynamic properties aqueous polymer solutions are very sensitive to the temperature. It was found that, at higher temperatures, hydrogen bond interactions of PPO are weakened. In other words, PPO becomes more hydrophobic with increasing temperature. Thus, by increasing the temperature, water is driven from
PPO-rich solutions to vapor phase and therefore by increasing the temperature of these four systems in equilibrium, increase of concentration for the system with higher PPO concentration is larger than the systems with less PPO concentration.

Reference
