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Vapor–liquid equilibria of the polyvinylpyrrolidone + $(NH_4)_2SO_4$ + H_2O system at different temperatures

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Abstract

Water activities of the polyvinylpyrrolidone (PVP) + $(NH_4)_2SO_4$ + H_2O system have been determined experimentally using the improved isopiestic method at 298.15, 308.15 and 318.15 K. The effect of temperature on the constant water activity lines has been studied. It was found that the slope of all constant water activity lines increased with increasing temperature. Furthermore, the extended Wilson theory has been used for the correlation of the experimental water activity data. The agreement between the correlation and the experimental data is good.

Keywords: Water activity; Vapor–liquid equilibria; Polyvinylpyrrolidone; Ammonium sulphate; Wilson

1. Introduction

Aqueous two-phase systems (ATPS) can be useful for the separation of various biological materials [1–3], metal ions, dyes, drug molecules and small organic species [4,5] using the liquid–liquid extraction method. There are two types of ATPS: polymer–polymer ATPS and polymer–salt ATPS. It has been found that the latter has more advantages. Liquid–liquid equilibrium data for some aqueous PVP–salt two-phase systems have been reported in the literature [6–9].

In an ATPS, water is a special and key component. Thus, the thermodynamic properties of water in these systems should be given great attention. Also, the water activity is an important and key thermodynamic property, because it is closely related to the other thermodynamic properties. Vapor–liquid equilibria data for aqueous polyethylene glycol (PEG) + salt [10–12] and polypropylene glycol (PPG) + salt [13,14] systems have been determined extensively at 298.15 K. But, vapor–liquid equilibrium data of aqueous PVP–salt systems are relatively scarce. There are some reports on the water activity data of the PVP + H_2O [15] and PVP + NaCl + H_2O [16] systems at different temperatures.

In this study, water activities of the PVP + $(NH_4)_2SO_4$ + H_2O system have been determined experimentally using an improved isopiestic method [10] at 298.15, 308.15 and 318.15 K that have not been previously published. The effect of temperature on the constant water activity lines has been studied. Furthermore, the extended Wilson theory [17] has been used for the correlation of the experimental water activity data.

2. Experimental

2.1. Materials

PVP (K15), of molecular weight 10,000, was obtained from Aldrich. Ammonium sulphate and sodium chloride were obtained from Merck (GR, min 99.5%). The salts were dried overnight at 373.15 K. Double distilled, deionized water was used.

2.2. Methods

In this study, the isopiestic method is used to obtain the activity of water in aqueous PVP–$(NH_4)_2SO_4$ mixtures. This method is based on the phenomenon that different solutions, when connected through a vapor space, approach equilibrium

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by transferring solvent by distillation from one solution to the other. 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. The isopiestic apparatus used in this work was similar to the one used by Ochs et al. [10]. This apparatus consisted of a seven-leg manifold attached to round-bottom flasks. Two flasks contained the standard pure NaCl solutions, one flask contained the pure PVP solution, one flask contained the pure $(NH_4)_2SO_4$ solution, two flasks contained the PVP/$(NH_4)_2SO_4$ solutions and the central flask was used as a water reservoir. The apparatus was kept in a constant-temperature bath for at least 120 h to achieve 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 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 $\pm 1 \times 10^{-7}$ kg. From the weight of each flask 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. [18]. 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 uncertainty in the measurement of solvent activity was estimated to be ±0.0002.

Nomenclature

List of symbols

a	activity
A_x	Pitzer–Debye–Hückel constant
B	second virial coefficient
c	coordination number
D	dielectric constant
e	electronic charge
E	binary parameter in the Wilson model
G^E	excess Gibbs energy
h	enthalpy of interaction
H	binary parameter in the Wilson model
I_x	ionic strength on the mole fraction scale
K	Boltzmann constant
n	number of moles
N_A	Avogadro's number
NP	number of experimental data
OF	objective function
p	vapor pressure
r	segment number
R	gas constant
T	temperature
V	molar volume
w	mass fraction
x	mole fraction
X	effective mole fraction
Z	charge number

Greek letters

ϕ	segment fraction
γ	activity coefficient, permittivity of vacuum
ν	stoichiometric number
ρ	closest approach parameter

Subscripts

a and c	anion and cation
ca	salt
i, j	any species, polymer, ions and water
k, k'	ions
m, m'	neutral species, segment and water
M	neutral species, polymer and water
p	polymer
s	mixed-solvent and segment of polymer
w	water

Superscripts

cal	calculated value
Comb	combinatorial
exp	experimental value
E	excess
LR	long-range
SR	short-range
$'$	salt-free
$\circ$	pure water

3. Thermodynamic framework

In our previous works [19,17], we extended the Wilson model to represent the excess Gibbs energy of multicomponent polymer solutions [19] and polymer + electrolyte solutions [17]. The polymer–electrolyte Wilson model was used for correlation of water activity data of some aqueous polymer + salt systems [17]. In this model, the excess Gibbs energy of aqueous polymer + salt systems, G^E, is expressed as the sum of three contributions:

$$G^E = G^{E,Comb} + G^{E,LR} + G^{E,SR} \qquad (1)$$

where $G^{E,Comb}$ is the combinatorial contribution, $G^{E,LR}$ the long-range interaction contribution and $G^{E,SR}$ is the short-range interaction contribution. The combinatorial term accounts for the configurational entropy of mixing molecules