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## Vapor–liquid equilibrium of ternary aqueous poly (ethylene glycol)+ dipotassium tartrate at solutions at different temperatures



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### ABSTRACT

In this study, water activities for the ternary systems of {dipotassium tartrate ( $K_2Tar$ )+PEG4000+ $H_2O$ } have been measured using an improved isopiestic method at  $T=(298.15, 308.15, 318.15)$  K. From these measurements, values of the vapor pressure of solutions were also determined. The experimental data for the activity of water were accurately correlated with the Wilson model. Also, the performance of an empirical two parameter equation was also tested for representing the experimental water activity data.

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### 1. Introduction

Aqueous two-phase systems (ATPSs) are 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. An ATPS is an aqueous, liquid–liquid, biphasic system which is obtained either by mixture of aqueous solution of two polymers, or a polymer and a salt. It has been found that the latter have more advantages such as low cost, low viscosity and a short time for phase splitting [6]. Polyethylene glycol (PEG), which is a hydrophilic polymer, is often used in aqueous two-phase partitioning studies. This polymer–salt system results in higher selectivity in protein partitioning, leading to an enriched product with high yields in the first extraction step [7]. Tartrates as a substitute for inorganic salts can form ATPS with PEG, which could be suitable for protein extraction [8]. In the ATPS both phases contain mainly water, thus, estimation of the thermodynamic properties of water, such as water activity, is of central importance [9]. In the correlation of the water activity data, local composition models have received more attention due to their simplicity as well as the accuracy of the results. Water activity data for several aqueous PEG+salt [10–17] systems have been determined. There are some reports on the water activity data of the PEG+ $H_2O$  [10–13] and  $K_2Tar$ + $H_2O$  [18] systems at different temperatures. But there is no information about the activity of

water for the aqueous PEG+ $K_2Tar$  system. In this study, water activities of the PEG+ $K_2Tar$ + $H_2O$  system have been determined experimentally using an improved isopiestic method at 298.15, 308.15 and 318.15 K. The experimental data for the activity of water, obtained in this work, were correlated with the Wilson [19] model for aqueous polymer–electrolyte systems.

### 2. Experimental section

#### 2.1. Materials

Poly (ethylene glycol), of molecular weight 4000, was obtained from Merck. Potassium tartrate and sodium chloride with a purity of minimum mass fraction of 0.995 were obtained from Merck. The polymer and salt were used without further purification, and double-distilled, deionized water was used. The number average molar mass and polydispersity of the polymer previously determined [20] to be  $4230 \text{ g mol}^{-1}$  and 1.0638, respectively. The purity of the used materials is shown in Table 1.

#### 2.2. Apparatus and procedure

##### 2.2.1. Water activity measurements

To obtain water activity and osmotic coefficient data of studied systems at  $T=(298.15, 308.15, \text{ and } 318.15)$  K, the isopiestic method was used. The isopiestic apparatus used for determination of water activity of ternary  $\{(K_2Tar)+PEG+H_2O\}$  was similar to the one

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**Table 1**

A brief summary of the purity of the used materials.

Material <sup>a</sup>	Mass fraction purity
NaCl Poly (ethylene glycol) 4000	(GR, min 99.5%) 0.99
Di-potassium tartrate 1.5 hydrate	0.995

<sup>a</sup> All materials were supplied from Merck.

used by Ochs et al. [10]. It consisted of seven-leg manifold attached to round-bottom flasks in measurements of water activity for the ternary solutions. Two of these flasks contained the standard pure NaCl solutions, one flask contained the pure polymer solution, one flask contained the binary aqueous K<sub>2</sub>Tar solution, two flasks contained {(K<sub>2</sub>Tar)+PEG+H<sub>2</sub>O} solutions and the central flask served as a water reservoir. The isopiestic apparatus was slowly evacuated to remove the air and to degas the solutions. It was necessary to evacuate the manifold several times because the dissolved air was slowly released from the solutions. Then isopiestic apparatus was immersed in a constant-temperature bath at least 120 h for equilibrium using a temperature controller (Julabo, MB, Germany) with standard uncertainty of 0.01 K. After equilibrium was reached the air is admitted to the isopiestic apparatus while it was still in the bath. The mass of each flask was calculated using an analytical balance (Shimadzu, 321-34553, Shimadzu Co., Japan) with a precision of  $\pm 1 \times 10^{-7}$  kg. When the difference between the mass fractions of two NaCl solutions were less than 0.1% we assumed that equilibrium was reached. Averages of the duplicate are considered as the isopiestic mass fractions. For the calculation of water activity of standard aqueous NaCl solutions at different concentrations the correlation given by Colin et al. [21] was used. In the measurement of water activity standard uncertainty was estimated to be 0.0005.

### 3. Results and discussion

In the present work, the isopiestic measurements were carried out for {(K<sub>2</sub>Tar)+PEG+H<sub>2</sub>O} solutions. At isopiestic equilibrium, the activity of the solvent in the reference and sample solutions must be the same. We also used the following relation between the osmotic coefficient  $\varphi$  and the solvent activity  $a_w$  [22]:

$$\varphi = \frac{\nu_R \varphi_R m_R}{\nu m} \quad (1)$$

where  $\nu_R$  and  $\nu$  are the sum of stoichiometric numbers of the anion and cation in the reference solution and the solution of ionic liquid respectively;  $m$  is the molality of the ionic liquid solutions;  $m_R$  is the molality of the reference standard in isopiestic equilibrium with this solution; and  $\varphi_R$  is the osmotic coefficient of the isopiestic reference standard, calculated at  $m_R$ . The necessary  $\varphi_R$  values at any  $m_R$  were calculated from the correlation given by Colin et al. [10]. From the calculated osmotic coefficient data, the activity of water and the vapor pressure of these solutions were determined at isopiestic equilibrium molalities, with the help of the following relations [22]:

$$\varphi = - \frac{\ln a_w}{\nu m M_w} \quad (2)$$

$$\ln a_w = \ln \left( \frac{p}{p_w^0} \right) + \frac{(B - V_w^0)(p - p_w^0)}{RT} \quad (3)$$

where  $a_w$  is the activity of water,  $M_w$  is the molar mass of the water, and  $B$  is the second virial coefficient of water vapor.  $V_w^0$  is

**Table 2**Water activity ( $a_w$ ) and vapor pressure ( $p$ ) for {PEG (p)+K<sub>2</sub>Tar (s)+H<sub>2</sub>O (w)} at  $T=298.15$  K. The four entries given for each  $a_w$  are those in isopiestic equilibrium with each other and the NaCl reference solution.<sup>a</sup>

$w_p$	$w_s$	$a_w$	$p_{exp}$ (kPa)
0.2961	0.0000		
0.0560	0.0633		
0.0268	0.0723	0.9855	3.127
0.0000	0.0801		
0.3139	0.0000		
0.0871	0.0636		
0.0365	0.0815	0.9832	3.120
0.0000	0.0937		
0.3608	0.0000		
0.0826	0.0956		
0.0376	0.1140	0.9753	3.095
0.0000	0.1312		
0.3800	0.0000		
0.1513	0.0838		
0.0725	0.1189	0.9706	3.080
0.0000	0.1521		
0.3840	0.0000		
0.1290	0.0955		
0.0604	0.1270	0.9697	3.077
0.0000	0.1564		
0.3850	0.0000		
0.1279	0.0987		
0.0573	0.1307	0.9690	3.074
0.0000	0.1607		
0.4110	0.0000		
0.1687	0.1009		
0.0822	0.1421	0.9626	3.054
0.0000	0.1884		
0.4240	0.0000		
0.1802	0.1062		
0.0841	0.1544	0.9584	3.042
0.0000	0.2055		

<sup>a</sup> Standard uncertainties  $u$  for mass fraction, temperature, osmotic coefficient, water activity and vapor pressure of water are  $u(w)=0.0001 \text{ mol kg}^{-1}$ ;  $u(T)=0.01 \text{ K}$ ;  $u(\varphi)=0.002$ ;  $u(a_w)=0.0005$ ;  $u(p)=0.001 \text{ kPa}$ , respectively.

the molar volume.  $p$  and  $p_w^0$  are the vapor pressure of solutions and the pure water, respectively. The second virial coefficient of water was calculated using the equation provided by Rard and Platford [23]. Molar volumes of liquid water were calculated using density of water at different temperatures [24]. The vapor pressures of pure water were calculated using the equation of state of Saul and Wagner [25]. After the establishment of isopiestic equilibrium, water activities were calculated using Eq. (2). The values of  $p$  for studied systems were calculated using Eq. (3). The results are collected in Tables 2–4. Tables 2–4 report the water activities and vapor pressures of the ternary {(K<sub>2</sub>Tar)+PEG+H<sub>2</sub>O} system at  $T=(298.15, 308.15, \text{ and } 318.15) \text{ K}$ .

The lines of constant water-activity of {(K<sub>2</sub>Tar)+PEG+H<sub>2</sub>O} system at  $T=(298.15, 308.15, \text{ and } 318.15) \text{ K}$  are plotted in Figs. 1–3. As can be seen in Tables 2–4, in fact four points on each line in Figs. 1–3 has a constant water activity or chemical potential, and thus these points are in equilibrium. To check the quality of the water activity values obtained for (PEG+H<sub>2</sub>O) solutions in Fig. 4a, the measured water activity results at  $T=298.15 \text{ K}$  in this work have been compared with the values reported in the literature [17]. As can be seen from Fig. 4a, our results are in good agreement with the literature [17]. Similarly, for aqueous K<sub>2</sub>Tar system in Fig. 4b, the comparison of water activity data obtained in this work and the literature [18] is shown at  $T=298.15 \text{ K}$ . The data sources used in preparing Fig. 4a and b are reported as supplementary materials. This Figure shows that there is a good agreement between two series of data. Here we also tested (Zdanovskii–Stokes–Robinson) equation [26] to see if there is a possible deviation of our experimental water activity data from this rule. As can be seen

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