



# Physicochemical properties of tri(butyl)ethylphosphonium diethylphosphate aqueous mixtures



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## ABSTRACT

This work presents the new experimental data on physical and thermodynamic properties of binary system composed of tri(butyl)ethylphosphonium diethylphosphate and water: solid-liquid equilibrium (SLE) and vapor-liquid equilibrium (VLE) phase diagrams as well as the excess enthalpy of mixing. SLE phase diagram has been determined at wide temperature and composition range using two techniques: dynamic method and differential scanning calorimetry (DSC). Interesting behavior with a solid compound formation was observed for the studied mixture. The isothermal VLE have been measured by an ebulliometric method within temperature range from  $T = (328.15 \text{ to } 368.15) \text{ K}$  and pressure up to 100 kPa. The excess enthalpy for the tested binary system was determined at  $T = 298.15 \text{ K}$  using isothermal titration calorimeter. Liquid density for pure IL and the binary mixtures with water has been determined at temperature range from  $T = (298.15 \text{ to } 348.15) \text{ K}$  and from experimental data, the excess molar volumes were calculated. The influence of temperature and composition on measured properties is discussed in terms of IL-water molecular interactions. Furthermore, the binary mixture under study was discussed as an alternative working pair for the absorption heat pump cycle.

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## 1. Introduction

Ionic liquids (ILs) exhibit exceptional properties, which are undoubtedly very low vapor pressure [1], high chemical and thermal stability [2,3] and a wide temperature range for the liquid phase. A very important feature of this type of compounds is the ability to change the following properties: melting point, viscosity, density and miscibility with different solvents, accordingly to ILs' structure [4]. The ability to modify the anion, or cation structure gives us the opportunity to design novel media for a specific purpose [5,6]. ILs as virtually nonvolatile compounds are regarded as “green solvents” and regarded as ideal replacements for conventional volatile organic solvents. In the face of numerous problems with the adverse effects of the chemical industry on the environment, it becomes necessary to design technologies and processes that are not based on volatile organic compounds. The motivation in both academia and industry is to conduct research on the use of ILs in variety of fields. ILs are tested for possible use as alternative solvents in chemical synthesis [7], as electrolytes for various technologies in the production of batteries, photovoltaics and many other electrochemical devices [8,9], as media for the heat transport and accumulation [10,11], as lubricants [12], or antibacterial and fungicidal

compounds [13]. From the point of view of this study, the ability of using ILs as an absorbent in absorption refrigeration technology is very interesting [14–16].

Generally speaking, absorption refrigeration is attractive because electrical energy is replaced with low value heat energy. Conventional absorption refrigeration systems used on industrial scale are LiBr + water (which is corrosive and exhibits problem with solidification) or water + ammonia (which is toxic and an odor nuisance) [17,18]. The problems associated with the current systems could potentially be avoided by replacing with IL mixtures with the following refrigerants: water [15,16,19–29], carbon dioxide [30–34], or hydrofluorocarbon (HCF) [35–41]. In recent years, ILs have been regarded as the potential candidates for absorbent in absorption refrigeration system [24]. The advantage in applying of ILs as absorbents in absorption refrigeration lies in possible absorption of large amount of refrigerant under low temperature conditions to yield good coefficient of performance (COP) and ensure them not contaminating with refrigerant stream when desorbed. Therefore, in order to evaluate IL and water systems for application in absorption refrigeration technology the thermodynamic measurements and predictive modeling are necessary.

In this work a novel IL, tri(butyl)ethylphosphonium diethylphosphate (abbreviated henceforth as  $[P_{2,4,4,4}][DEP]$ ) is proposed for absorption refrigeration technology. It is worth mentioning that the literature on physicochemical and thermodynamic properties of pure  $[P_{2,4,4,4}][DEP]$  and its

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mixtures with organic solvents and water is very scarce. In particular, only a few papers have reported physicochemical characterization of pure  $[P_{2,4,4,4}][DEP]$  [22,42–45]. Besides, excess enthalpy of aqueous solution of  $[P_{2,4,4,4}][DEP]$  as a function of temperature and concentration was presented in 2010 by Ficke et al. [22]. Moreover, the solubility of carbon dioxide and hydrofluorocarbons in  $[P_{2,4,4,4}][DEP]$  were presented by Mejia et al. [46] and Sousa et al. [47]. Activity coefficients at infinite dilution of different organic solvents by Stark et al. [48] and by our group [45].

The aim of this work is to determine the phase diagrams including solid–liquid equilibrium (SLE) and vapor–liquid equilibrium (VLE), excess enthalpy of mixing ( $H^E$ ) and the liquid density ( $\rho$ ) for aqueous solution of tri(butyl)ethylphosphonium diethylphosphate,  $[P_{2,4,4,4}][DEP]$  as a function of temperature and IL's concentration.

## 2. Experimental Section

### 2.1. Materials

Chemical structure of the IL investigated in this work is presented in Fig. 1. The sample of tri(butyl)ethylphosphonium diethylphosphate,  $[P_{2,4,4,4}][DEP]$  with initial mass fraction purity 0.95 was purchased from IoLiTec. IL was prepared for experiment by drying for 48 h in a Vacuum Drying Ovens (Binder, model VD 23) at a temperature  $T = 373$  K and under reduce pressure ( $P = 4 \cdot 10^{-4}$  mbar) obtained by vacuum pump (Vacuubrand RZ 6). This procedure is used to remove any remaining volatile chemicals and to decrease water content. No decomposition of the IL was observed at the experimental conditions. The water mass fraction of the dried IL was determined using Karl–Fischer titration (model SCHOTT Instruments TitroLine KF) and it was found to be 2100 ppm.

The water used for the experiment was deionized by a reverse osmosis unit with an ion-exchange system with conductivity less than  $0.05 \mu\text{S} \cdot \text{cm}^{-1}$  (Cobrabid-Aqua, Poland) and next degassed in an ELMA Germany ultrasonic bath at about 320 K before each measurement.

Binary mixtures were prepared by weighing the pure components on a Mettler Toledo XA105 balance, with a precision of 0.0001 g. In order to minimize the variation in composition, due to evaporation or absorption of water by IL, each sample was prepared immediately before the experiment.

### 2.2. Solid–liquid phase equilibrium measurements

SLE phase diagram has been determined by dynamic method and confirmed by differential scanning calorimetry (DSC). Binary mixtures were prepared by weighing pure components on Mettler Toledo XA105 balance with an uncertainty of 0.0001 g. In dynamic method, the sample was heated very slow ( $< 2 \text{ K h}^{-1}$ ) with continuous stirring inside of a Pyrex glass cell placed in a thermostat. The temperature of crystal disappearance was detected visually, and measured using an electronic thermometer P 550 (DOSTMANN electronic GmbH) with the probe totally immersed in the thermostatic liquid (water, or ethanol with dry ice, depending on the measurement temperature). The uncertainties of the temperature measurements were estimated to be lower than 0.05 K.

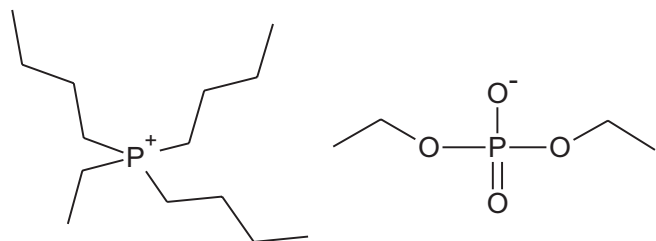


Fig. 1. Chemical structure of ionic liquid studied in this work.

Table 1

Experimental solid–liquid (SLE) phase equilibrium data as a function of IL mole fraction ( $x_1$ ) and temperature ( $T$ ).<sup>a</sup>

$x_1$	$T^{\text{SLE}}/(\text{K})$	$x_1$	$T^{\text{SLE}}/(\text{K})$	$x_1$	$T^{\text{SLE}}/(\text{K})$
Dynamic method					
0.0000	273.15	0.0231	274.48	0.0554	271.71
0.0050	272.70	0.0254	275.06	0.0631	270.16
0.0082	271.93	0.0280	275.44	0.0712	268.38
0.0124	271.24	0.0300	275.46	0.0777	266.78
0.0146	271.21	0.0335	275.18	0.0860	264.12
0.0154	271.65	0.0359	274.98	0.0994	259.69
0.0171	272.46	0.0395	274.55	0.1172	253.27
0.0189	273.18	0.0451	273.58	0.1297	246.48
0.0206	273.77	0.0495	272.71		
DSC technique <sup>b</sup>					
0.0070	271.8	0.0208	273.99	0.0562	270.21
0.0099	270.7	0.0222	274.31	0.0680	267.71
0.0110	269.9	0.0235	274.87	0.0794	263.77
0.0141	269.7	0.0280	275.10	0.0905	256.09
0.0149	271.0	0.0298	274.75	0.1023	254.36
0.0166	272.4	0.0350	273.84	0.1174	246.85
0.0172	272.7	0.0392	273.65		
0.0190	273.8	0.0480	272.08		

<sup>a</sup> Standard uncertainties  $u$  are as follows:  $u(x_1) = \pm 1 \cdot 10^{-4}$  and  $u(T) = \pm 0.05$  K.

<sup>b</sup> The solidus temperature is 268.2 K.

The procedure of DSC technique was similar to that for pure IL described in our previous paper [45]. Small samples (about 10 mg) of the binary mixture were weighted and placed in hermetic aluminum pans. The sample was cooled to 223.15 K and equilibrated at that temperature for 5 min. After that, the sample was heated (at a heating rate of  $1 \text{ K min}^{-1}$ ) up to 298.15 K. The experimental data were analyzed using STAR software. The standard uncertainty in the temperature determination is better than 0.31 K and the uncertainty of enthalpy is better than  $3.3 \text{ J} \cdot \text{g}^{-1}$ .

### 2.3. Vapor–liquid phase equilibrium measurements

The VLE measurements for the tested binary mixture were performed using an ebulliometer designed by Rogalski and Malanowski [49]. Apparatus was connected to the pressure stabilizing system which consist of the container (volume of  $50 \text{ dm}^3$ ) enabling the pressure to be kept constant within  $\pm 0.1$  kPa and to dampen the pressure fluctuations caused by the bumping of the liquid boiling in the

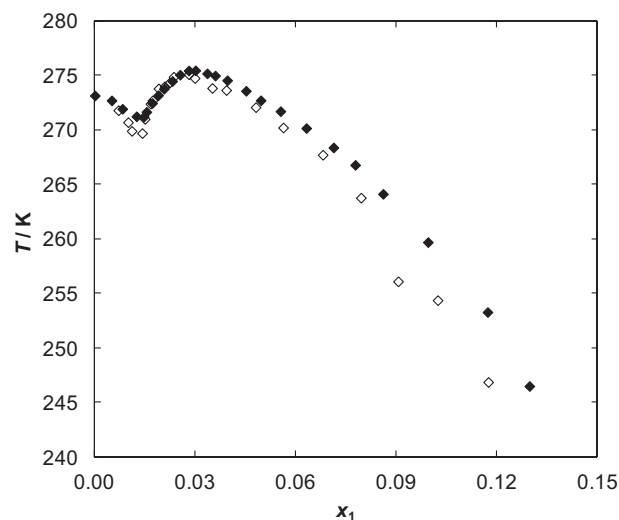


Fig. 2. Experimental and calculated solid–liquid (SLE) phase equilibria for  $[P_{2,4,4,4}][DEP]$  (1) + water (2) binary system:  $\blacklozenge$ , experimental data obtained using dynamic method;  $\diamond$  experimental data from DSC technique.

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