Experimental and correlated liquid-liquid equilibrium data for water-phosphoric acid-ester

A. Ghanadzadeh Gilani *, M. Nasouri Gazani, B. Mohammadi Khanghah, A. Najafgholizadeh

Department of Chemistry, Faculty of Science, University of Guilan, Rasht, Iran

A B S T R A C T

In this study, experimental liquid-liquid equilibria were studied for the {water + phosphoric acid + ester (n-propyl- and n-amyl acetates)} systems at T = (298.2, 308.2, and 318.2) K and p = 101.3 kPa. The studied systems exhibit type-1 binodal curves. Solubility curves data were measured by cloud-point titration method. Tie line measurements were carried out by acidimetric titration, the Karl–Fischer technique, and refractive index measurements. Correlation of the experimental equilibrium data was carried out using NRTL and UNIQUAC thermodynamic models. The quality of the tie-lines was checked through The Othmer–Tobias correlation equation. Distribution coefficients and separation factors were calculated over the biphasic regions. The experimental results indicate that n-amyl acetate is better solvent than n-propyl acetate for removal of phosphoric acid from water.

© 2018 Elsevier Ltd.

1. Introduction

Knowledge of solvent purification processes, phase equilibria, and thermodynamic behaviour of various aqueous ternary systems including organic or inorganic acids are very important and are always required in a wide range of scientific and industrial fields. Purification of wet process phosphoric acid (PA) by solvent extraction method is extensively reported in the past [1–5].

So far, many important liquid–liquid equilibrium (LLE) data (solubility and tie line data) for various ternary systems containing PA, water, and organic solvents have been reported [6]. Many organic solvents, from different categories, were used to separate PA from water [7–17]. Among different type of organic solvents, esters are good extractants as proton-accepting solvents for separation of PA from water [18,19].

In this work the two esteric solvents (n-propyl- and n-amyl acetates, Fig. 1) were chosen as solvents for extraction and liquid–liquid equilibrium (LLE) measurement of PA from aqueous solutions. In our previous publications [20–23], the LLE data for aqueous solutions of PA in esteric solvents were reported. As an extension of the previous research, we present the results of a LLE study of the (water + PA + n-propyl acetate or n-amyl acetate) systems at T = (298.2, 308.2, and 318.2) K and p = 101.3 kPa.

The quality of the experimental tie-lines was determined through the Othmer–Tobias [24] correlation plots. The experimental tie lines were correlated using the (UNIQUAC) and NRTL models [25–27]. Distribution coefficients and separation factors were determined from the equilibrium data. It is worth to say that there are no data in the available literature on the systems studied.

2. Experimental

2.1. Materials and instruments

All the chemicals used in this experiment were purchased from Merck and used without any further purification. Analytical grade phosphoric acid (mass fraction purity > 0.999) including 85 wt% in water was used as the solute. n-Propyl acetate and n-amyl acetate (stated mass fraction purity higher than 0.98) were used in the current study as organic solvents. The organic solvents were dried over 0.4 nm molecular sieves. The stated purity of the liquids was checked on the basis of their refractive index and density measurements. The acidimetric titration with 0.1 M sodium hydroxide was used to check the purity of the acid. Bi-distilled and deionized water was used throughout all the experiments. Name, source, stated purity, and their measured refractive indices and densities of the liquids used in this study along with their literature values [28–38] are listed in Table 1.

Refractive index and density measurements of the pure liquids were carried out using a Kruss digital Abbe refractometer (AR2008,

* Corresponding author at: Department of Chemistry, University of Guilan, Rasht, Iran.

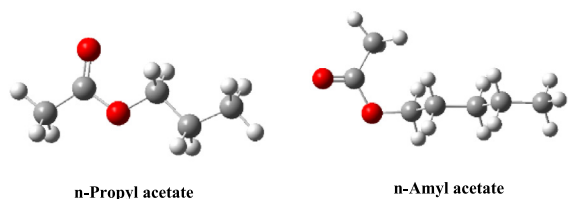*E-mail address:* aggilani@guilan.ac.ir (A. Ghanadzadeh Gilani).

Fig. 1. Chemical structures of the esters used in this study; n-propyl and n-amyl acetate.

Germany) with a manufacturer's stated uncertainty of $0.0002 n_D$ and a Kyoto electronic density meter (DA645, Japan) with a manufacturer's stated uncertainty of 0.05 kg·m^{-3}, respectively. The instruments were calibrated before use with HPLC water. According to the material purity and measurement interval, the uncertainties for the refractive index and density measurements were evaluated to be 0.0005 and 0.5 kg·m^{-3}, respectively. The weighting of the samples with an accuracy of ±0.1 mg were performed with an AND electronic analytical balance (model HR-200, Japan).

2.2. Experimental procedure

The solubility curves data of the (water + phosphoric acid + n-propyl or n-amyl acetate) systems were obtained using the cloud point titration method [39]. The binary mixtures of known concentration were prepared by mass in a double layer glass cell (50 ml). The *temperature of the equilibrium cell was controlled* to within ± 0.1 K. The third component is either solvent and or water was added step by step into the cell using a Brand Transferpette micropipette with ±0.001 ml accuracy. The mixtures were sturdily stirred by a magnetic stirrer at the working temperature. The endpoint detection was visually achieved using the mixture turbidity. The mixtures were sturdily stirred by a magnetic stirrer at the working temperature. The endpoint detection was visually achieved using the mixture turbidity. Based on the several visual

measurements and using the method of standard uncertainties [40], the uncertainty in the mass fraction of the solubility data was evaluated to be 0.0050.

Tie line measurements for the ternary systems including water, phosphoric acid, and the esters carried out using a 50 ml equilibrium glass cell at T = (298.2, 308.2, and 318.2) K. The temperature of the cell was controlled by a water jacket and maintained with an accuracy of within ±0.1 K. The mixtures were agitated strongly for 4 h, and then left to settle for 4 h, where these times were long enough to achieve equilibrium. The procedure of phase separation, measurement, and analysis was the same as those described in our previous publication [20].

It should be noted that the preliminary tests including refractive index, density and UV–visible absorption measurements showed that no chemical reaction occurred between the components over the time required to achieve equilibrium. In this work, no variation of composition with resting time was established. So far, many literature sources on LLE for water + phosphoric acid + esters at various temperature and pressure conditions have been reported [18,19,23].

The mass fractions of phosphoric acid in both phases were analysed by NaOH titration in the presence of phenolphthalein as indicator. The quantity of water in the organic phase was measured

Table 2
Equations for refractive index (n_D) as a function of water mass fraction in the aqueous phase at different temperatures and p = 101.3 kPa for the studied systems.[a]

T/K	Equation	R^2
[water (1) + phosphoric acid (2) + n-propyl acetate (3)]		
298.2	$n_D = -0.1057\ w_{11} + 1.4417$	0.9989
308.2	$n_D = -0.1038\ w_{11} + 1.4364$	0.9985
318.2	$n_D = -0.1035\ w_{11} + 1.4314$	0.9933
[water (1) + phosphoric acid (2) + n-amyl acetate (3)]		
298.2	$n_D = -0.1068\ w_{11} + 1.4376$	0.9989
308.2	$n_D = -0.1055\ w_{11} + 1.4336$	0.9985
318.2	$n_D = -0.1074\ w_{11} + 1.4313$	0.9994

[a] Standard uncertainties u are u(T) = 0.1 K, u(n_D) = 0.0005, u(p) = 0.5 kPa, and u(w) = 0.0025

Table 1
Source, purity, refractive index (n_D), density (ρ) and the UNIQUAC structural parameters (r and q) of the pure liquids at T = 298.2 K and p = 101.3 kPa.[a,b,c,d,e,f,g,h]

Component	Source	Purity (mass fraction) [b]	Analysis method	r [e]	q [e]	n_D		ρ/kg·m^{-3}	
						Exp.	Lit.	Exp.	Lit.
n-Propyl acetate	Merck	> 0.98	GC	4.153	3.656	1.3830	1.3828 [28]	882.26	882.5 [28]
							1.3840 [29]		882.3 [29]
							1.3821 [35]		882.54 [35]
							1.3817 [36]		882.20 [36]
							1.3818 [37]		882.55 [37]
n-Amyl acetate	Merck	> 0.98	GC	5.502	4.736	1.3991	1.40004 [38]	872.02	871.9 [30]
							1.4027 [31] [c]		872.22 [38]
									871.46 [35]
Water		Deionized & bi-distilled	Conductometry [d]	0.920	1.400	1.3325	1.3322 [32]	997.01	997.08 [32]
Phosphoric acid	Merck	> 0.999 [f]	Acid-base titration	3.000	4.000	1.4320	1.4321 [33] [g]	1682.7	1683 [34] [h]

[a] Standard uncertainties u are u(T) = 0.1 K, u(n_D) = 0.0005, and u(ρ) = 0.5 kg.m^{-3}, u(p) = 0.5 kPa.
[b] Stated by the supplier
[c] T = 293.13 K
[d] Electrical conductivity was less than 8 μS · cm^{-1} at T = 298.2 K.
[e] Taken from Refs. [23,49,51].
[f] Concentration of aqueous solution of the acid is 85.0 wt% (The standard uncertainty in concentration of aqueous phosphoric acid was estimated to be lower than 0.2 wt%).
[g] Concentration of the acid is 85.0 wt%.
[h] Concentration of the acid is 84.7 wt%.