

Phys. Chem. Res., Vol. 4, No. 3, 507-518, September 2016

DOI: 10.22036/pcr.2016.15241

Phase Equilibria of the Ternary System Water + Phosphoric Acid + 1-Nonanol at Different Temperatures

S. Shekarsaraee

Department of Chemistry, University of Guilan, P. O. Box: 41335-19141, Rasht, Iran

(Received 1 February 2016, Accepted 21 May 2016)

The purpose of this research is to measure the phase equilibrium data of the ternary system (water + phosphoric acid + 1-nonanol) at different temperatures. Experimental solubility curves and tie-line points for the system were obtained at $T = 298.2, 308.2$ and 318.2 K and ambient pressure. The binodal curve data were detected by the cloud point method. The mass fractions of each layer were achieved by acid-base and the Karl-Fisher titration, accompanied by refractive index calibration curves. A type-1 LLE phase diagram was observed for this ternary system. The equilibrium tie-line data were correlated *via* the UNIQUAC and NRTL thermodynamic models. The experimental tie-lines of the studied system were satisfactorily regressed to the models. The reliability of the experimental end points was determined using the Othmer-Tobias and Hand plots. Distribution coefficients and separation factors were calculated over the non-miscible parts. For the separation process, separation factor should be greater than one. For the investigated system, the factor was suitable for separation treatment in all concentrations of phosphoric acid and three temperatures.

Keywords: Solubility data, Tie-line points, Phase equilibria, Thermodynamic model

INTRODUCTION

Phosphoric acid (HPO) which has a wide variety of uses could be produced by 3 main commercial processes: wet process, thermal process and dry kiln process. Wet process is nowadays the most common method but the produced acid is diluted with water and various impurities [1-8].

Due to the growing market orders for the pure acid that have vast applications in different industries such as food industry and agriculture, its extraction from dilute aqueous solutions is very important. Several solvents have been tested to extract the acid from dilute solutions. Furthermore, different alcohols, esters and ketones and even hydrocarbons were employed as solvents for the recovery of phosphoric acid from its aqueous solution [9-20]. In this study, 1-nonanol (1-*Nol*) was selected as an organic solvent for the recovery of phosphoric acid from aqueous mixture. Due to the suitable molecular structure, high boiling point and very low solubility in water, 1-*Nol* has a number of

benefits as a high-quality extractant for separating HPO from aqueous solution. This solvent has already been used to extract organic acids from water [21,22].

The present study obtains a practical LLE data for the extraction of HPO from aqueous solutions, for which no such data have never been published before. Total phase diagrams are measured *via* solubility and tie-line data at three different temperatures. Distribution coefficients (D) and separation factors (S) were evaluated using the tie-line points to investigate the possibility of the use of the alcohol for the extraction of HPO from water. The experimental LLE data were correlated by employing two thermodynamic models, the universal quasi-chemical (UNIQUAC) method of Abrams and Prausnitz [23] together with the non-random two-liquid (NRTL) model of Renon and Prausnitz [24].

EXPERIMENTAL

Materials

The materials of this study are 1-Nonanol and phosphoric acid which were purchased from Merck. The mass fraction purity of these materials were 0.98 and 0.85,

*Corresponding author. E-mail: shekarsaraee@guilan.ac.ir

respectively. The purity of the acid was checked through acidimetric titration with 0.5 M NaOH. The compounds were applied without any further purification. Deionized and redistilled water was used throughout all experiments.

Apparatus and Procedure

For the ternary mixtures, the solubility curves were investigated *via* the cloud point method in an equilibrium glass cell [25]. For this purpose, the binary mixtures with specified composition were introduced in to the glass cell

and the cell temperature was controlled by a water bath with the accuracy of ± 0.2 K. The third part of the ternary mixture was added to the binary mixture and the end-point was determined by changing the solution transparency from a homogenous solution to heterogeneous one. The components of the mixtures were obtained by repeating each measurements for three times. The binodal curve data of the investigated system were listed in Table 1.

A transparent water thermostat was utilized to investigate the equilibrium between liquid phases at $T =$

Table 1. Solubility Curve Data in Mass Fractions (w_i) for (Water + HPO + 1-*Nol*) at $T = (298.2, 308.2$ and $318.2)$ K

$T = 298.2$ K		$T = 308.2$ K		$T = 318.2$ K	
w_1	w_2	w_1	w_2	w_1	w_2
0.9995	0.0000	0.9992	0.0000	0.9988	0.0000
0.8868	0.1119	0.9001	0.0988	0.8690	0.1293
0.7977	0.2005	0.8073	0.1913	0.7798	0.2179
0.6404	0.3573	0.6599	0.3372	0.6708	0.3254
0.5747	0.4226	0.5947	0.4021	0.5732	0.4215
0.5233	0.4733	0.5002	0.4951	0.5200	0.4736
0.3950	0.6008	0.4064	0.5883	0.4549	0.5372
0.3164	0.6784	0.3358	0.6573	0.3079	0.6830
0.1909	0.7982	0.2046	0.7839	0.2282	0.7594
0.1474	0.8096	0.1619	0.7956	0.1639	0.7754
0.1204	0.7876	0.1223	0.7854	0.1291	0.7585
0.1002	0.6341	0.1019	0.6500	0.1077	0.6513
0.0871	0.5001	0.0895	0.5224	0.0898	0.5060
0.0662	0.3321	0.0712	0.3578	0.075	0.3412
0.0557	0.2363	0.0619	0.2529	0.0668	0.2569
0.0443	0.1494	0.0569	0.1851	0.0641	0.1943
0.0412	0.0732	0.0471	0.0865	0.0577	0.0846
0.0384	0.0373	0.0366	0.0317	0.0463	0.0443
0.0368	0.0000	0.0371	0.0000	0.0402	0.0000

(298.2, 308.2 and 318.2) K. The equilibrium data were obtained from the prepared ternary mixtures with known compositions. By placing the mixtures into the extraction cell, they were stirred vigorously for 4 h and then left for 4 h, so the phases could be separated. After the phases being separated, two transparent phase were obtained and analyzed to determine their composition. In order to determine the equilibrium tie lines, the aqueous and

the organic phases were weighed and analyzed to gain the composition of the components.

To determine the LLE data, the concentrations of HPO in both phases were measured *via* potentiometric NaOH titration, and methyl orange was utilized as indicator. In the presence of the indicator, HPO is titrated as monoprotic acid and the titration error is reduced sensibly. Karl-Fisher method was used to determine the water content of the

Table 2. Experimental Tie-line Data in Mass Fraction for (Water + HPO + 1-*Nol*) at Different Temperatures^a

Aqueous phase mass fraction			Organic phase mass fraction		
w_1 (water)	w_2 (HPO)	w_3 (1- <i>Nol</i>)	w_1 (water)	w_2 (HPO)	w_3 (1- <i>Nol</i>)
$T = 298.2$ K					
0.779	0.219	0.002	0.040	0.019	0.941
0.709	0.289	0.002	0.042	0.032	0.926
0.651	0.347	0.002	0.039	0.049	0.912
0.594	0.404	0.002	0.041	0.071	0.888
0.558	0.439	0.003	0.045	0.106	0.849
0.507	0.490	0.003	0.048	0.164	0.788
$T = 308.2$ K					
0.767	0.231	0.002	0.038	0.018	0.944
0.696	0.301	0.003	0.038	0.029	0.933
0.638	0.359	0.003	0.040	0.045	0.915
0.586	0.411	0.003	0.044	0.068	0.888
0.539	0.457	0.004	0.050	0.097	0.853
0.493	0.502	0.005	0.055	0.163	0.782
$T = 318.2$ K					
0.749	0.248	0.003	0.044	0.015	0.941
0.686	0.311	0.003	0.045	0.0284	0.927
0.622	0.374	0.004	0.048	0.048	0.904
0.576	0.419	0.005	0.051	0.061	0.888
0.524	0.469	0.007	0.059	0.089	0.852
0.476	0.516	0.008	0.062	0.161	0.777

^aStandard uncertainties u are $u(T) = 0.2$ K, and $u(w) = 0.002$.

organic phase and for this purpose Metrohm-870 KF Titrino plus Karl-Fisher titrator was utilized. The water contents of the aqueous phases were investigated by measuring their refractive indices. To build the standard curves, the refractive indices of both phases were measured at the equilibrium. The standard curves for the studied systems can be only made for the analysis of the aqueous phases, since the refractive indices of the organic-rich phase tie lines are close to each other

Concentration analyses of water and HPO were carried out separately for the organic and the aqueous phases. Therefore, by knowing two variables of each phase (*i.e.* mass of water and acid in aqueous and organic phase), the third one (1-*Nol*) can be evaluated in both phases *via* mass balance rule ($\sum w_i = 1$).

Moreover, the experimental information on the binodal curves along the calculation procedure was used to check the LLE data. By knowing the mass of three components in initial mixtures and utilizing mass balance equations, other parameters like, mass of separated phases, mass of acid content in both phases, the water content in the aqueous phase and the amount of the organic solvent in both phases were obtained. Gomez *et al.* [16] has declared that the application of this method is practical, for the very low water soluble solvents such as 1-*Nol*.

A & D analytical balance with the accuracy of ± 0.0001 g was used for all weightings. The uncertainties in mass fraction were estimated to be about 0.002. A CETI Refractometer (Model quartz-digital semi-automatic refractometer) was utilized to measure the refractive indices and the uncertainty in refractive index value was estimated to be ± 0.0002 .

RESULTS AND DISCUSSION

Equilibrium Data Results

For the (water + HPO + 1-*Nol*) ternary system, the experimental tie-line data was determined at temperatures of 298.2, 308.2 and 318.2 K. Table 2 illustrates the experimental values of the ternary system at each temperature. Figures 1-3 show the LLE phase diagrams of the ternary system at different temperatures. From the LLE phase diagrams it can be concluded that the system exhibited type-1 phase behavior, which has only one liquid

pair of partially miscible (water + 1-*Nol*) and two pairs of completely miscible (water + HPO) and (HPO + 1-*Nol*). The area of the two-phase region depends on the solubility of water in organic phase. 1-*Nol* can be a good candidate for the liquid-liquid extraction process due to its high boiling temperature and very low solubility in water.

In general, the most important factor affecting on the equilibrium characteristics and immiscibility region of the ternary systems is the type of organic solvent. The solubility of water in 1-*Nol* and 1-*Nol* in water, at 298.2 K, are 38.2 $g_{water}/1000 g_{1-Nol}$ and 0.5 $g_{1-Nol}/1000 g_{water}$, respectively.

Investigation of Tie-line Data Quality

The Othmer-Tobias (Eq. (1)) [28] and Hand (Eq. (2)) [29] correlation equations are two common indices of data quality and the linearity of their own plots could be indicative of the quality of the measured data. The consistency and the quality of the experimental tie-line data were determined by the mentioned equations, for the investigated ternary system:

$$\ln\left(\frac{(1-w_{33})}{w_{33}}\right) = A + B \ln\left(\frac{(1-w_{11})}{w_{11}}\right) \quad (1)$$

$$\ln\left(\frac{w_{21}}{w_{11}}\right) = A' + B' \ln\left(\frac{w_{23}}{w_{33}}\right) \quad (2)$$

where w_{11} , w_{23} , w_{21} and w_{33} are mass fraction of water in the aqueous phase, mass fraction of the acid in organic, mass fraction of acid in aqueous phases and mass fraction of the solvent in organic phase, respectively. A and B are the parameters of the Othmer-Tobias and A' and B' is the Hand correlation. The parameters of the Othmer-Tobias and Hand correlations and corresponding plots are also shown in Figs. 4 and 5, orderly. The correlation factor (R^2) of the plots are close to 1 and the linearity of the plots shows the degree of consistency and the quality of the obtained LLE values of the studies.

Extraction Ability of the Solvent

To investigate the ability of the solvent (1-*Nol*) in acid extraction, distribution coefficients for water ($D_1 = w_{13}/w_{11}$), HPO ($D_2 = w_{23}/w_{21}$) and separation factors ($S = D_2/D_1$) were calculated from the experimental data. w_{13} and w_{23} are the

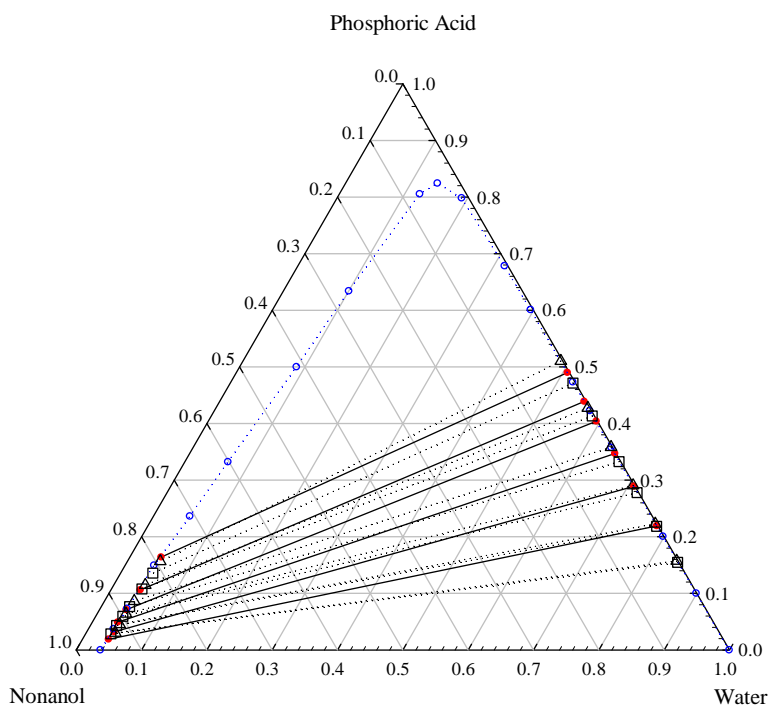


Fig. 1. Ternary phase diagram for LLE of [water (1) + HPO (2) + 1-Nol (3)] at $T = 298.2$ K; (\circ) experimental cloud points (\bullet) experimental tie-lines, (\square) UNIQUAC calculated points, (Δ) NRTL calculated points ($\alpha = 0.3$).

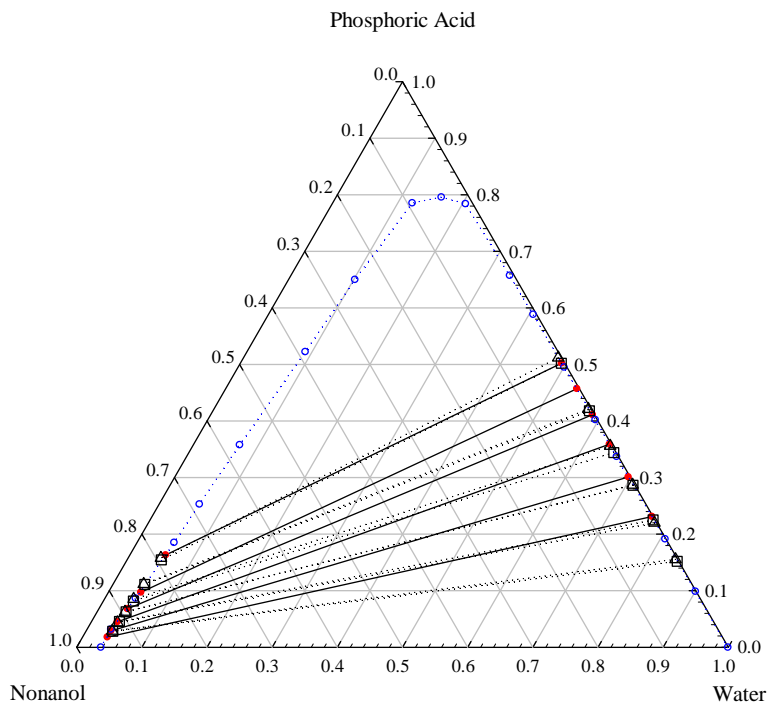


Fig. 2. Ternary phase diagram for LLE of [water (1) + HPO (2) + 1-Nol (3)] at $T = 308.2$ K; (\circ) experimental cloud points (\bullet) experimental tie-lines, (\square) UNIQUAC calculated points, (Δ) NRTL calculated points ($\alpha = 0.3$).

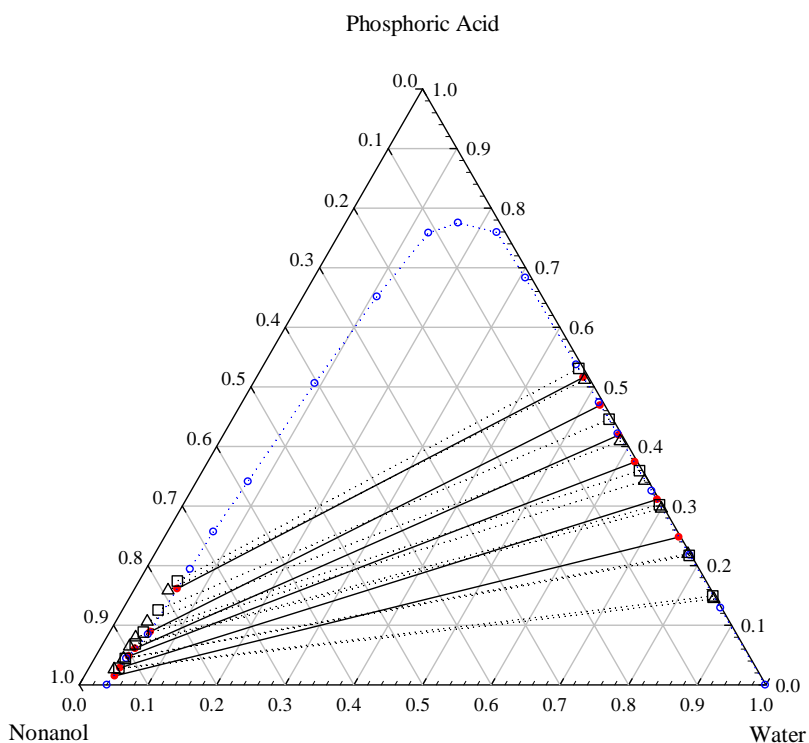


Fig. 3. Ternary phase diagram for LLE of [water (1) + HPO (2) + 1-Nol (3)] at $T = 298.2$ K; (\circ) experimental cloud points (\bullet) experimental tie-lines, (\square) UNIQUAC calculated points, (Δ) NRTL calculated points ($\alpha = 0.3$).

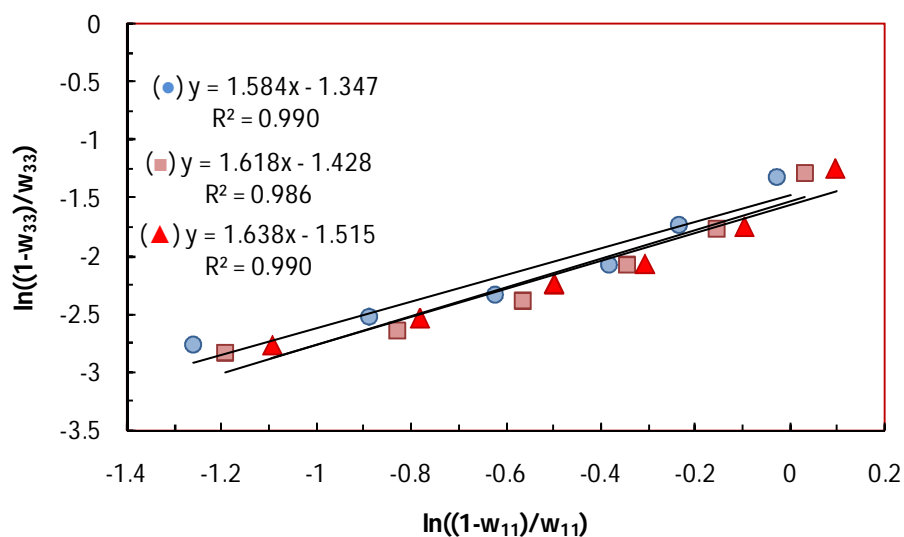


Fig. 4. Othmer-Tobias plot of the (water + HPO + 1-Nol) ternary system at different temperatures; (\bullet) 298.2 K, (\blacksquare) 308.2 K, (\blacktriangle) 318.2 K.

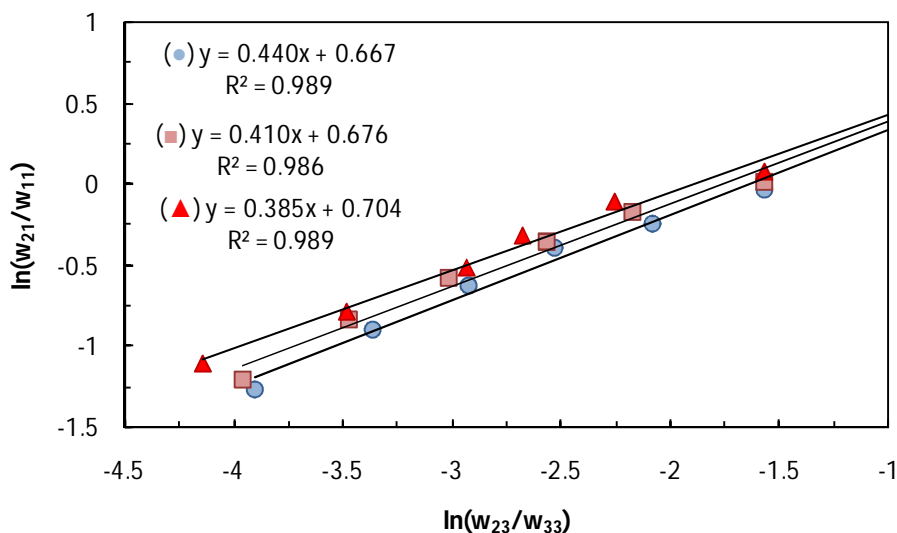


Fig. 5. Hand plot of the (water + HPO + 1-*Nol*) ternary system at different temperatures; (●) 298.2 K, (■) 308.2 K, (▲) 318.2 K.

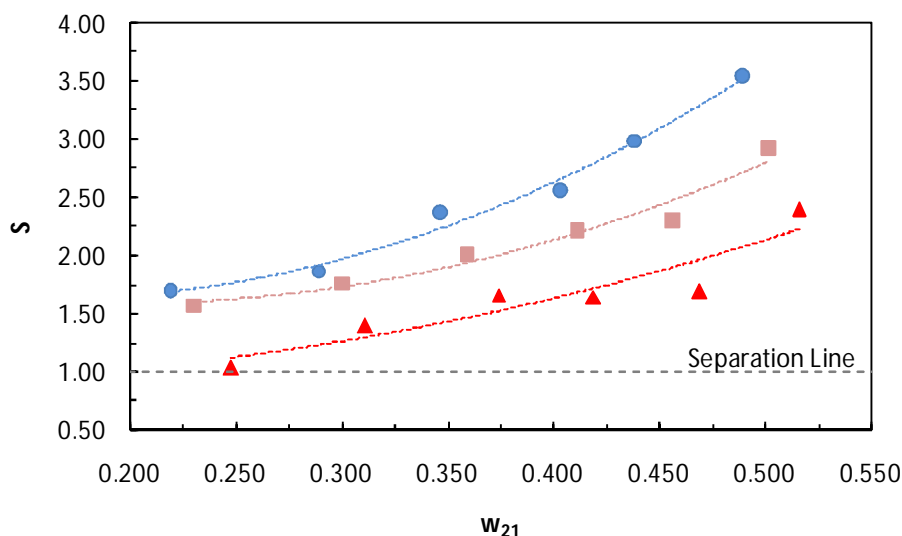


Fig. 6. Plot of the separation factor (S) of HPO as a function of mass fraction of the acid in the aqueous phase; (●) 298.2 K, (■) 308.2 K, (▲) 318.2 K.

mass fractions of water and HPO in the organic phase, respectively, and w_{11} and w_{21} are the mass fractions of water and HPO in the aqueous phase, orderly. The results of distribution coefficients and separation factors for each system are summarized in Table 3. Figure 6 shows the variation of experimental separation factor of HPO as a

function of the acid mass fraction in aqueous phase for (water + HPO + 1-*Nol*) system.

It has been observed that mutual solubilities of the partially miscible liquids have direct relationship to temperature effect [9,12,15,17-20] namely when the intermolecular interactions are more similar and in result

Table 3. Separation Factors (S) and Distribution Coefficients of HPO (D_2) and water (D_1) at $T = (298.2, 308.2$ and $318.2)$ K

T (K)	D_2	D_1	$S (D_2/D_1)$
298.2	0.09	0.05	1.69
	0.11	0.06	1.87
	0.14	0.06	2.36
	0.18	0.07	2.55
	0.24	0.08	2.99
	0.33	0.09	3.54
308.2	0.08	0.05	1.57
	0.10	0.05	1.76
	0.13	0.06	2.00
	0.17	0.08	2.20
	0.21	0.09	2.29
	0.32	0.11	2.91
318.2	0.06	0.06	1.03
	0.09	0.07	1.39
	0.13	0.08	1.66
	0.15	0.09	1.64
	0.19	0.11	1.69
	0.31	0.13	2.40

more soluble to each other, the temperature has stronger effect on mutual solubilities. The temperature effect is often the reason for more solubility but not always. As the temperature of a solution increases, it is easier for the molecules of liquids to move between each other and it makes the solution more disordered. A positive (+) entropy change in a solution process could help the solution to shift to the more dispersed and therefore, more probably solution state.

As seen, the temperature effect on the separation factors of the ternary system is small at the temperatures studied probably because of low mutual solubility of water and the solvent. However, a comparison of the extracting

capabilities of the solvent was made with respect to separation factor values. This factor is found to be greater than 1 ($S > 1$) for the system investigated, which means that extraction of HPO by the solvent is possible.

Thermodynamic Correlations

Universal quasi-chemical (UNIQUAC) method of Abrams and Prausnitz [23] and the nonrandom two-liquid (NRTL) model of Renon and Prausnitz were [24] used to correlate the experimental LLE data. Table 4 illustrates the calculated data for ternary system at each temperature. The UNIQUAC structural parameters r (the number of segments per molecules) and q (the relative surface area per

Table 4. Calculated UNIQUAC and NRTL Tie-line Data in Mass Fraction for (Water + HPO + 1-*Nol*) at Different Temperatures

Aqueous phase				Organic phase			
w_1 (water)		w_2 (HPO)		w_1 (water)		w_2 (HPO)	
UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL
$T = 298.2$ K							
0.843	0.840	0.155	0.157	0.039	0.045	0.029	0.030
0.779	0.775	0.218	0.223	0.040	0.044	0.043	0.045
0.720	0.707	0.278	0.291	0.042	0.044	0.059	0.064
0.665	0.640	0.333	0.358	0.043	0.046	0.077	0.086
0.583	0.569	0.413	0.427	0.047	0.048	0.108	0.115
0.525	0.487	0.471	0.510	0.049	0.050	0.136	0.157
$T = 308.2$ K							
0.846	0.841	0.152	0.156	0.041	0.040	0.028	0.029
0.772	0.777	0.225	0.220	0.043	0.041	0.046	0.044
0.710	0.710	0.286	0.287	0.044	0.043	0.063	0.063
0.652	0.641	0.344	0.356	0.046	0.045	0.082	0.085
0.578	0.575	0.418	0.421	0.049	0.047	0.111	0.112
0.493	0.483	0.502	0.512	0.053	0.050	0.154	0.158
$T = 318.2$ K							
0.848	0.852	0.149	0.144	0.044	0.038	0.028	0.026
0.780	0.777	0.217	0.220	0.045	0.042	0.044	0.044
0.694	0.700	0.302	0.296	0.047	0.041	0.069	0.064
0.636	0.652	0.359	0.343	0.049	0.042	0.088	0.080
0.549	0.584	0.446	0.409	0.052	0.046	0.126	0.106
0.462	0.480	0.531	0.512	0.056	0.050	0.174	0.159

molecules) were computed from the number of molecular groups and the individual values of the van der Waals volume and area of the molecule by the Bondi method [30,31]. Table 5 illustrates the r and q values for this ternary system and the value of non-randomness α was set constant at 0.3.

Sorensen [32] developed an objective function to optimize the equilibrium model. The objective function is

the sum of squares of the difference between the experimental and calculated mass fractions. Figures 1-3 show the correlated results and experimental values of the ternary system (water + HPO + 1-*Nol*). The experimental LLE results were also used to determine the optimum UNIQUAC and NRTL binary interaction parameters between each pair of components (see Table 6). To determine the optimum UNIQUAC and NRTL binary

Table 5. The UNIQUAC Structural Parameters (r and q) for Pure Components

Component	r	q
Water	0.920	1.400
Phosphoric acid	3.000	4.000
1-Nonanol	7.296	6.368

Table 6. Correlated Results from the UNIQUAC and NRTL ($\alpha = 0.3$) Models and the Corresponding Binary Interaction Parameters (a_{ij} and a_{ji} for UNIQUAC and b_{ij} and b_{ji} for NRTL) for the Ternary System

UNIQUAC				NRTL			
water + HPO + 1-Nonanol							
i-j	a_{ij} (K) ^a	a_{ji} (K)	$rmsd$ (%)	i-j	b_{ij} (K) ^b	b_{ji} (K)	$rmsd$ (%)
1-2	6503.78	-4954.61		1-2	12271.47	-261.00	
1-3	-170.08	-251.49	3.77	1-3	1829.37	330.66	3.70
2-3	-285.08	6106.41		2-3	14999.99	2183.03	

$${}^a a_{ij} = \left(\frac{u_{ij} - u_{ij}/R}{R} \right) \cdot b_{ij} = \left(\frac{g_{ij} - g_{ji}}{R} \right)$$

interaction parameters between each pair of components (Table 6), the experimental LLE results were used. The meaning of the parameters and equations are totally described in the current literature [33].

The quality of the correlation is measured by the root-mean square deviation ($rmsd$). From the difference between the experimental and calculated mass fractions, the $rmsd$ value can be computed via the following equation:

$$rmsd = \sqrt{\frac{\sum_{k=1}^n \sum_{j=1}^2 \sum_{i=1}^3 (w_i - \hat{w}_{ijk})^2}{6n}} \quad (3)$$

In this equation, n , w and \hat{w} are number of tie-lines, experimental mass fraction and calculated mass fraction, respectively, and i , j and k represent indices of components, phases and (1, 2, ..., n), orderly. The $rmsd$ values in the correlation by UNIQUAC and NRTL models for the system

studied at $T = (298.2, 308.2$ and $318.2)$ K are listed in Table 6. The correlated $rmsd$ values of UNIQUAC and NRTL models for the studied system at different temperatures of 298.2, 308.2 and 318.2 K are summarized in Table 6.

CONCLUSIONS

Experimental LLE data for the (water + HPO + 1-Nol) ternary system were determined at $T = 298.2, 308.2$ and 318.2 K and ambient pressure. The ternary system shows type-1 behavior of the LLE. The UNIQUAC and NRTL thermodynamic models were applied to correlate the experimental tie-line results and to calculate the phase compositions of the mixtures studied. In general, both models give good results for the investigated system.

The separation factor and distribution coefficient for the organic solvent were used in this work. The experimental results indicated that the separation factors for 1-Nol are

greater than one for the system reported in this work, showing the ability of the solvent to extract the acid from water.

REFERENCES

- [1] Becker, P., *Phosphates and phosphoric acid, raw materials, technology and economics of the wet process*. 2nd ed.; Marcel Dekker Inc.: New York, **1989**; p. 37-64.
- [2] Dorozhkin, S. V., Fundamentals of the wet-process phosphoric acid production. Kinetics and mechanism of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ surface crystallization and coating Formation. *Ind. Eng. Chem. Res.*, **1997**, *36*, 467-473, DOI: 10.1021/ie960219f.
- [3] McCullough, J. F.; Frederick, L. L., Purification of phosphoric acid with methanol and ammonia. *J. Agric. Food Chem.*, **1976**, *24*, 180-187 DOI: 10.1021/jf60203a050.
- [4] Dorozhkin, S. V., Fundamentals of the wet-process phosphoric acid production. Kinetics and Mechanism of the phosphate rock dissolution. *Ind. Eng. Chem. Res.*, **1996**, *35*, 4328-4335, DOI: 10.1021/ie960092u.
- [5] Marco, J. M.; Galan, M. I.; Costa, J., Liquid-liquid equilibria for the quaternary system water-phosphoric acid-1-hexanol-cyclohexanone at 25 °C. *J. Chem. Eng. Data*, **1988**, *33*, 211-214, DOI: 10.1021/je00052a043
- [6] Feki, M.; Fourati, M.; Chaabouni, M. M.; Ayedi, H. F., Purification of wet process phosphoric acid by solvent extraction liquid-liquid equilibrium at 25 and 40 °C of the system water-phosphoric acid-methylisobutylketone. *Can. J. Chem. Eng.*, **1994**, *72*, 939-944, DOI: 10.1002/cjce.5450720523.
- [7] Stenstrom, S.; Wingefors, S., On the modeling of multicomponent acid extraction with long-chain aliphatic amines. *Can. J. Chem. Eng.*, **1988**, *66*, 248-257, DOI: 10.1002/cjce.5450660209.
- [8] Dhouib-Sahnoun, R.; Feki, M.; Ayedi, H. F., Liquid-liquid equilibria of the ternary system water + phosphoric acid + tributyl phosphate at 298.15 K and 323.15 K. *J. Chem. Eng. Data*, **2002**, *47*, 861-866, DOI: 10.1021/je010293r.
- [9] Ruiz, F.; Galan, M. I.; Boluda, N., Quaternary liquid-liquid equilibrium: Water-phosphoric acid-1-butanol-2-butanone at 25 °C. *Fluid Phase Equilib.*, **1998**, *146*, 175-185, DOI: 10.1016/S0378-3812(98)00219-2.
- [10] Ruiz, F.; Marcilla, A.; Ma Ancheta, A.; Rico, C., Liquid-liquid equilibrium of the system water-phosphoric acid-di-n-propyl ether at 25 and 40 °C. influence of the isomer propyl-isopropyl ether on the appearance of three liquid phases at equilibrium. *Solvent Extr. Ion Exc.*, **1986**, *4*, 771-787, DOI: 10.1080/07366298608917892.
- [11] Ruiz, F.; Marcilla, A.; Ancheta, A. M.; Rico, C., Liquid-liquid equilibrium of the three liquid phases at equilibrium system water-phosphoric acid-diisopropyl ether at 25 and 40 °C. *Solvent Extr. Ion Exch.*, **1986**, *4*, 789-802, DOI: 10.1080/07366298608917893.
- [12] Ruiz, F.; Fernández, J.; Boluda, N., Variation of phosphoric acid diffusion coefficient with concentration. *AIChE J.*, **2004**, *41*, 185-189, DOI: 10.1002/aic.690410118.
- [13] Marcilla, A.; Ruiz, F.; Campos, J.; Asensio, M., Purification of wet process phosphoric acid by solvent extraction with dibutyl ether. Part I. Liquid-liquid equilibrium of the system water-phosphoric acid-dibutyl ether at 25 °C. *Solvent Extr. Ion Exch.*, **1989**, *7*, 211-221, DOI: 10.1080/07360298908962306.
- [14] Harrison, C. H.; Roquero, P., Liquid-liquid equilibria of the system water/phosphoric acid/diisopropyl ether at (273.15, 283.15 and 293.15) K. *J. Chem. Eng. Data*, **2004**, *49*, 218-220, DOI: 10.1021/je030158.
- [15] Gomez, A.; Ruiz, F.; Fernandez, J.; Torregrosa, E., Purification of phosphoric acid by extraction with 2-ethyl-1-hexanol: Equilibrium data and mass transfer coefficients. *Ind. Eng. Chem. Res.*, **2001**, *40*, 892-897, DOI: 10.1021/ie000065a.
- [16] Ghanadzadeh, H.; Ghanadzadeh, A.; Shekarsaraee, S.; Uslu, H., Liquid phase equilibria of the system (water + phosphoric acid + 1-octanol) at $T = (298.2, 308.2 \text{ and } 318.2)$ K. *Fluid Phase Equilib.*, **2012**, *316*, 109-116, DOI: 10.1016/j.fluid.2011.12.016.
- [17] Ghanadzadeh, H.; Ghanadzadeh, A.; Shekarsaraee, S.; Uslu, H., (Liquid + liquid) equilibrium data of (water + phosphoric acid + solvents) systems at $T = (308.2 \text{ and } 318.2)$ K. *J. Chem. Thermodyn.*, **2012**, *53*, 52-59, DOI: 10.1016/j.jct.2012.04.011.

- [18] Ghanadzadeh, H.; Ghanadzadeh, A.; Shekarsaraee, S., Experimental study of phase equilibria in aqueous mixtures of phosphoric acid with isoamyl acetate and methyl isoamyl ketone at $T = (298.2, 308.2 \text{ and } 318.2)$ K. *Fluid Phase Equilib.*, **2013**, *337*, 32-38, DOI: 10.1016/j.fluid.2012.09.038.
- [19] Ghanadzadeh, H.; Ghanadzadeh, A.; Shekarsaraee, S., Solubility and tie line data of the water-phosphoric acid-solvents at $T = 303.2, 313.2 \text{ and } 323.2$ K: An experimental and correlational study. *Thermochim. Acta*, **2013**, *558*, 36-45, DOI: 10.1016/j.tca.2013.02.006.
- [20] Kirbaslar, S. I.; Sahin, S.; Bilgin, M., (Liquid + liquid) equilibria of (water + propionic acid + alcohol) ternary systems. *J. Chem. Thermodyn.*, **2006**, *38*, 1503-1509, DOI: 10.1016/j.jct.2006.05.001.
- [21] Sahin, S.; Kirbaslar, S. I.; Bilgin, M., (Liquid + liquid) equilibria of (water + lactic acid + alcohol) ternary systems. *J. Chem. Thermodyn.*, **2009**, *41*, 97-102, DOI: 10.1016/j.jct.2008.07.014.
- [22] Abrams, D. S.; Prausnitz, J. M., Statistical thermodynamics of liquid mixtures: a new expression for the excess Gibbs energy of partly or completely miscible systems. *AIChE J.*, **1975**, *21*, 116-128, DOI: 10.1002/aic.690210115.
- [23] Renon, H.; Prausnitz, J. M., Local compositions in thermodynamic excess functions for liquid mixtures. *AIChEJ.*, **1968**, *14*, 135-144, DOI: 10.1002/aic.690140124.
- [24] Peschke, N.; Sandler, S. I., Liquid-liquid equilibria of fuel oxygenate + water + hydrocarbon mixtures. *J. Chem. Eng. Data*, **1995**, *40*, 315-320, DOI: 10.1021/je00017a069.
- [25] Li, H.; Tamura, K., Ternary liquid-liquid equilibria for (water + terpene + 1-propanol or 1-butanol) systems at the temperature 298.15 K. *Fluid Phase Equilib.*, **2008**, *263*, 223-230, DOI: 10.1016/j.fluid.2007.10.014.
- [26] Merzougui, A.; Hasseine, A.; Kabouche, A.; Korichi, M., LLE for the extraction of alcohol from aqueous solutions with diethyl ether and dichloromethane at 293.15 K, parameter estimation using a hybrid genetic based approach. *Fluid Phase Equilib.*, **2011**, *309*, 161-167, DOI: 10.1016/j.fluid.2011.07.011.
- [27] Othmer, D.; Tobias, P., Liquid-liquid extraction data-The line correlation. *Ind. Eng. Chem.*, **1942**, *34*, 693-696, DOI: 10.1021/ie50390a600.
- [28] Brandani, V.; Chianese, A.; Rossi, M., Ternary liquid-liquid equilibrium data for the water-ethanol-benzene system. *J. Chem. Eng. Data*, **1985**, *30*, 27-29, DOI: 10.1021/je00039a009.
- [29] Bondi, A., Van der waals volumes and radii. *J. Phys. Chem.*, **1964**, *68*, 441-451, DOI: 10.1021/j100785a001.
- [30] Bondi, A., *Physical Properties of Molecular Crystals Liquids and Glasses*. John Wiley and Sons Inc.: New York, **1968**, p. 114-129.
- [31] Sorensen, J. M., Technical University of Denmark, Lyngby, Denmark, Ph.D. Thesis 1980.
- [32] Banerjee, T.; Singh, M. K.; Sahoo, R. K.; Khanna, A., Volume, surface and UNIQUAC interaction parameters for imidazolium based ionic liquids via Polarizable Continuum Model. *Fluid Phase Equilib.*, **2005**, *234*, 64-76, DOI: 10.1016/j.fluid.2005.05.017.