Liquid-Liquid Equilibrium Data of the Ternary Mixture of (Water + Phosphoric Acid + Heptyl Acetate) at 298.2 K and ≈ 102 kPa

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Solubility data and tie-line points were experimentally determined for a ternary system (water + phosphoric acid + Heptyl acetate) at $T = 298.2$ K and ambient pressure. The cloud point method was used to measure the immiscibility region. Type-1 liquid-liquid equilibrium (LLE) behavior was observed for the investigated system and the plait point data were calculated using the Treybal's method. The compositions of both aqueous and esteric layers were determined using acid-base titration, HPLC method and mass balance equation. The Othmer-Tobias and Hand equations were applied to show the reliability of tie-line data. Obtained tie-line points were then correlated using the UNIQUAC model, and the root-mean square deviation (RMSD) results showed that the measured points were satisfactorily regressed by the thermodynamic model. To evaluate the ability of the studied solvent for purification of phosphoric acid, distribution coefficients and separation factors were calculated over the biphasic area. Separation factors were greater than those in all investigated feeds of phosphoric acid for the studied system. Heptyl acetate showed the highest separation factors between all the investigated *n*-alkyl acetate esters.

Keywords: Phosphoric acid, Liquid-liquid equilibria, HPLC method, Plait point, Thermodynamic model

INTTRODUCTION

Phosphoric acid (PA) is one of the most important inorganic acids having many applications in different fields of science and technology. It is used in production of detergents, agricultural feeds, and phosphate fertilizers [1]. High purity PA is widely applied in many industrial process such as pharmaceutical, food and beverage industries. Phosphoric acid is mainly manufactured by the wet process method [2-4]; though, the dilute acid obtained is an aqueous solution with a variety of impurities. Liquid-liquid extraction has been applied for extraction of phosphoric acid [5-8] and other polar acids such as formic acid and lactic acid from water solution [9,10].

Different kinds of solvents like alcohols, esters, ketones and hydrocarbons have been applied for PA extraction from aqueous solutions [11-28]. Among the studied solvents, alcohols have had better the distribution coefficients of PA. Hydrocarbons have had very high separation factors; but very low distribution coefficients. Between the investigated solvents, esters have shown relatively good distribution coefficients and separation factors. Then, esters have optimum conditions for extraction of phosphoric acid. In this work, heptyl acetate (HA) was selected for purification of PA from water solution and liquid-liquid equilibrium studies were performed for the corresponding ternary systems. HA has useful properties such as suitable functional group, low water solubility and high boiling point that make it a high quality solvent for removing PA from aqueous solution. The liquid-liquid equilibrium (LLE) data for the system (water + acetic acid + heptyl acetate) has recently been reported by Oliveira *et al*. [29] at two different temperatures but the solvent has not been used for any other extraction process.

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This study reports worthy LLE data for separation and purification of phosphoric acid from aqueous solutions and to the best of our knowledge, no such data have been published before. Phase diagrams containing solubility, tie-line and plait point data were obtained at 298.2 K and ambient pressure. Distribution coefficients of water (D_1), phosphoric acid (D_2), D_1 and separation factors (S) of HA were computed to evaluate the capacity of the solvent for extraction of phosphoric acid from water layer. The Othmer-Tobias [30] and Hand [31] equations correlated the measured tie-lines and showed that the obtained data are reliable. The thermodynamic modeling and correlation of the measured tie-line points were done by UNIQUAC method of Abrams and Prausnitz [32].

The main aim of this study was to investigate the effect of increasing hydrophobicity on the extraction ability of some linear *n*-alkyl acetate esters. LLE data for (water + phosphoric acid + *n*-Propyl acetate, *n*-butyl acetate, *n*-pentyl (amyl) acetate and *n*-hexyl acetate) have already been reported by Ghanadzadeh *et al.* [26-28]. Investigating the effect of HA, as an extracting solvent, provides useful information to understand the effect of hydrophobicity increment on extraction properties of linear *n*-alkyl acetate esters. Since there is no VLE or LLE interaction parameter for the ternary system under study, the interaction parameters presented here could be very useful for prediction of LLE systems containing heptyl acetate-water or heptyl acetate-phosphoric acid pairs.

EXPERIMENTAL

Chemicals

Heptyl acetate and phosphoric acid were purchased from Sigma-Aldrich and Merck, respectively, and used without any farther purification. The mass fraction purities of these materials were of 0.98 for HA and 0.85 for PA. The purity of the acid was checked through acidimetric titration with 0.5 M NaOH. HPLC-grade water was used throughout the experiment. Reverse osmosis technology and Millipore filter papers (0.45 μm pore size) were used for producing water.

Instruments

With an accuracy of ±0.1 K, verified by a digital thermometer (Testo-735), the temperature of the instruments was kept constant. The mixtures weighing was performed using a Precisa electronic analytical balance (model LS120A) with an accuracy of ±0. 2 mg. A Young Lin high performance liquid chromatography (HPLC), model YL Acme 9000, powered by UV visible detector (UV-Vis), was applied to determine the content of heptyl acetate in both the aqueous and organic solutions.

Solubility Measurements

For determination of the solubility curve data, the cloud point method was applied [33]. A glass cell with volume of 10 ml was employed to obtain the cloud point data. The mixtures in the cell containing water and PA or HA and PA were magnetically stirred while a water jacket kept the temperature of the mixtures constant. The third component (HA or water) was poured into the cell using a Brand Transferpette micropipette with an accuracy of ±0.001 ml. The endpoint of the titration was determined visually. The appearance of the system changed from a clear to a turbid state. Every titration was repeated three times and the average of the records was chosen for the cloud point data. The standard uncertainty in mass fractions of the solubility data was estimated to be better than ±0.0048.

Tie-line Determination

The tie-line measurements of the ternary system (water + phosphoric acid + heptyl acetate) were performed at *T* = 298.2 K and about 102 kPa. The mixtures of three components containing water, PA, and HA were first poured in a glass cell (20 ml). Every mixture was powerfully stirred for 2 h, and then stayed relax for 2 h until the two layers were divided from each other. Based on the Prologue tests, these times are sufficient to achieve the equilibrium. The samples of both esteric-rich and water-rich phases were separated by a glass syringe from aqueous (lower) and organic (upper) layers.

The weight fractions of phosphoric acid in the lower and upper layers (w_{21} for water layer and w_{23} for esteric layer) were determined by acid-base titration. Analysis of the heptyl acetate in both phases; *i.e.*, the mass fraction of the solvent in aqueous (w_{13}) and organic (w_{33}) phases, respectively, was performed using reverse-phase high performance liquid chromatography (RP-HPLC) method.
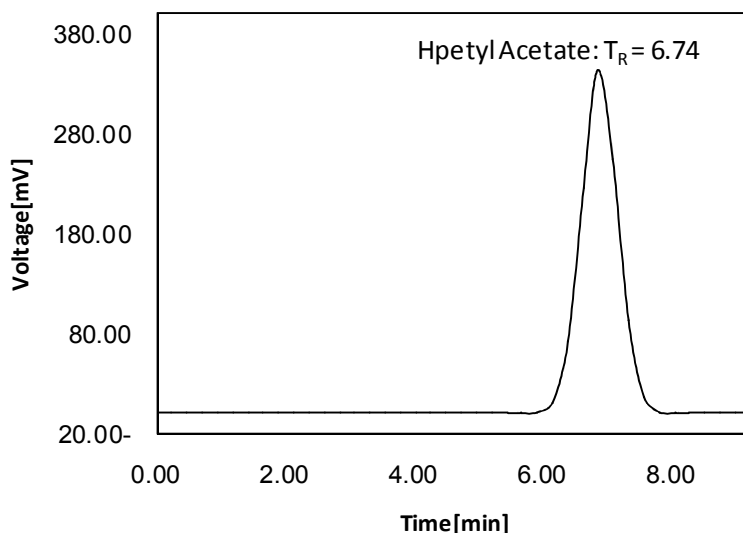
Fig. 1. HPLC chromatogram of standard solution containing heptyl acetate at $T = 298.2$ K. 5% (v/v) methanolic solution of heptyl acetate was prepared by diluting 5 ml of pure component to 100 ml with methanol.

Pure methanol (HPLC grade, Romil, England) was used to prepare internal standard. The column [Teknokroma Brisa C18 (15 cm × 4.6 mm, i.d.5 μm)] temperature was held constant at $T = 298.2$ K. Mobile phase was a mixture of HPLC grade water, methanol, and acetonitrile (50, 30, 20 v/v/v), and the pH of mobile phase was kept constant at 3 with orthophosphoric acid (85% mass purity) and the flow rate was 1 ml min[1]. Detection wavelength was set at 210 nm. Furthermore, the injection volume of the samples was 10 μl. Figure 1 shows HPLC chromatogram of the standard solution containing heptyl acetate. The content of water in each layer (w_{11} and w_{13} for aqueous and ester phases, respectively) was determined via the following equation. The estimated standard uncertainty of all measured mass fractions was better than ± 0.003.

$$\sum w_i = 1 \tag{1}$$

RESULTS AND DISCUSSION

LLE Results

The solubility data obtained and tie-line points of the ternary system (water + phosphoric acid + heptyl acetate)

were measured at $T = 298.2$ K and ambient pressure, and the equilibrium data are inserted in Tables 1 and 2, respectively. Phase diagram of the studied system containing tie-line endpoints, cloud point data, UNIQUAC and plait point results is presented in Fig. 2. As can be seen from Fig. 2, the system shows type-1 behavior for the reason that heptyl acetate-water is the only pair with partial miscibility. The solubilities of water in heptyl acetate and heptyl acetate in water is very low and then, biphasic region is so wide. This makes heptyl acetate a suitable solvent for extraction and purification process. The solubility of water in heptyl acetate is about five times larger than the solubility of heptyl acetate in water. Low solubility of the solvent in water causes lower environmental problems and contaminations.

The Othmer-Tobias (Eq. (2)) [30] and the Hand (Eq. (3)) [31] equations correlated the obtained tie-lines to evaluate the consistency and reliability of the measured points. The parameters A, B, A' and B' could be obtained by plotting the related equations. Figure 3 shows the results of the equations mentioned and contains the regression parameters and R square factors. As can be seen from the figure, both the plots are linear (R squares should be larger than 0.98 up to 1), indicating the obtained tie-lines are

Table 1. Solubility Curve Data in Mass Fractions (w_i) for [Water (1) + Phosphoric Acid (2) + Heptyl Acetate (3)] at $T = 298.2$ K[a]

w_1	w_2	w_3	w_1	w_2	w_3
Right side of diagram			Left side of diagram		
0.9992	0.0000	0.0008	0.0849	0.8171	0.0980
0.9488	0.0501	0.0011	0.0694	0.7540	0.1766
0.8995	0.0992	0.0013	0.0567	0.6806	0.2627
0.8518	0.1467	0.0015	0.0511	0.5910	0.3579
0.8129	0.1864	0.0007	0.0428	0.4961	0.4611
0.7960	0.2023	0.0017	0.0364	0.4200	0.5436
0.7611	0.2371	0.0018	0.0278	0.3141	0.6581
0.7014	0.2965	0.0021	0.0181	0.2107	0.7712
0.6429	0.3548	0.0023	0.0162	0.1694	0.8144
0.5965	0.4011	0.0024	0.0114	0.1168	0.8718
0.5244	0.4725	0.0031	0.0094	0.0671	0.9235
0.4774	0.5193	0.0033	0.0082	0.0504	0.9414
0.4090	0.5872	0.0038	0.0067	0.0279	0.9654
0.2848	0.7113	0.0039	0.0049	0.0094	0.9857
0.2069	0.7852	0.0079	0.0039	0.0000	0.9961
0.1712	0.8182	0.0106	-	-	-
0.1387	0.8363	0.0106	0.046[b]	0.531[b]	0.423[b]
0.1024	0.8508	0.0468	-	-	-

[a]Standard uncertainties, u, are $u(T) = 0.1$ K, $u(P) = 0.5$ kPa and $u(w) = 0.0048$. [b]Plait point data obtained by calculations.

trustable and consistent.

$$\ln\left(\frac{1 - w_{33}}{w_{33}}\right) = A + B\ln\left(\frac{1 - w_{11}}{w_{11}}\right) \tag{2}$$

$$\ln\left(\frac{w_{21}}{w_{11}}\right) = A' + B'\ln\left(\frac{w_{23}}{w_{33}}\right) \tag{3}$$

Distribution coefficients of water (D_1) and PA (D_2) and

separation factors (S) are common parameters for evaluation of solvent extraction ability (Eqs. (4) to (6)).

$$D_1 = \frac{w_{13}}{w_{11}} \tag{4}$$

$$D_2 = \frac{w_{23}}{w_{21}} \tag{5}$$

Table 2. Experimental Tie-line Data in Mmass Fractions, Separation Factors (S) and Distribution Coefficients of PA (D_2) and Water (D_1) for (Water + Phosphoric Acid + Heptyl Acetate) at $T = 298.2$ K[a]

w_{11}	w_{21}	w_{13}	w_{23}	D_1	D_2	S
Aqueous phase		Organic phase				
0.843	0.156	0.003	0.007	0.004	0.045	12.61
0.728	0.271	0.003	0.014	0.004	0.052	12.54
0.649	0.349	0.004	0.022	0.006	0.063	10.23
0.581	0.417	0.005	0.031	0.009	0.074	8.64
0.533	0.465	0.006	0.04	0.011	0.086	7.64
0.441	0.556	0.006	0.048	0.014	0.086	6.35

[a]Standard uncertainties, u, are u(T) = 0.1 K, u(P) = 0.5 kPa, u(w_{PA}) = 0.003 and u(w_{HA}) = 0.002.
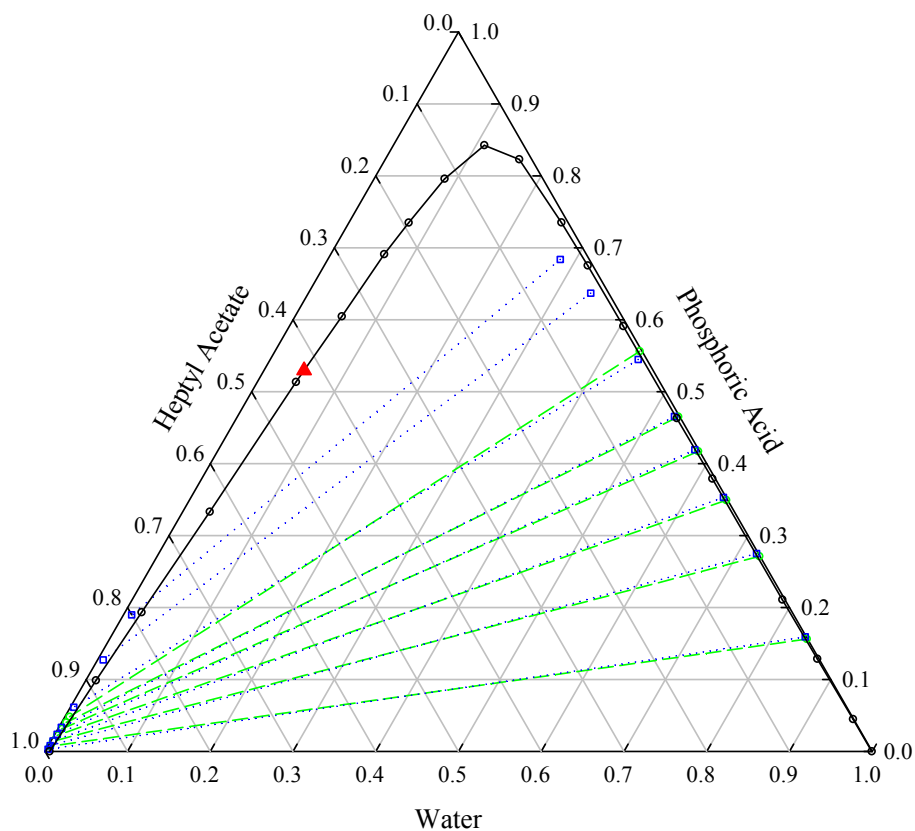
Fig. 2. Ternary phase diagram for LLE of (water + phosphoric acid + heptyl acetate) at T = 298.2 K; (○) experimental cloud points, (○) experimental tie-lines, (□) UNIQUAC calculated points, (▲) Calculated plait point.
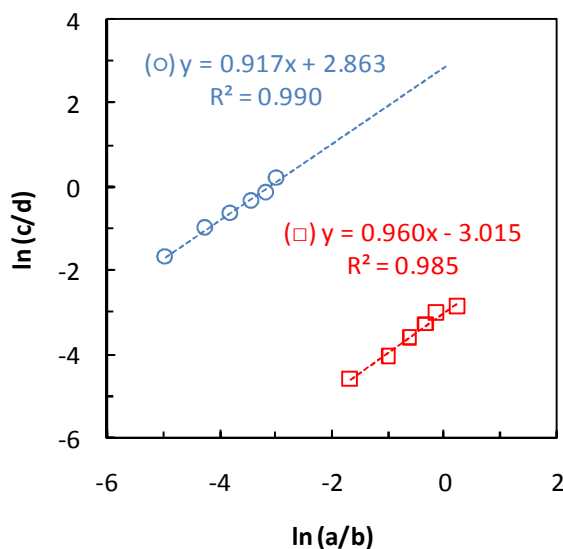
Fig. 3. The Othmer-Tobias and the Hand plots of the (water + phosphoric acid + heptyl acetate) ternary system at 298.2 K. The symbols are (○) Hand plot, (□) Othmer-Tobias plot, $(a/b) = w_{23}/w_{33}$ or $(1-w_{11})/w_{11}$ and $(c/d) = w_{21}/w_{11}$ or $(1-w_{33})/w_{33}$ for Hand and Othmer-Tobias equations, respectively.

$$S = \frac{D_2}{D_1} \tag{6}$$

These parameters should be experimentally calculated. The calculated data are given in Table 2 and the plots of calculated separation factors and distribution coefficients of PA as a function of the mass fraction of the acid in aqueous phase for all studied linear *n*-alkyl acetate esters [26-28] accompanied with heptyl acetate are presented in Fig. 4. The figure shows that the entire separation factors are greater than unity, indicating that the extraction of PA from aqueous solution is possible with every *n*-alkyl acetate ester, though, heptyl acetate has the largest separation factors.

The larger separation factors of a solvent indicate the higher purity of the extracted material by that solvent, and the larger distribution coefficients of a solvent indicates the lower solvent consumption. The use of a solvent for purification process depends on what purity is required or how much the solvent is available for purification. In this study, heptyl acetate has the highest separation factors, causing the production of PA with the highest purity in comparison with the other esteric solvents, but the lowest distribution coefficients, causing the highest consumption of

the solvent for the separation process.

The effect of hydrophobicity on distribution coefficients and separation factors could be clearly seen in Fig. 4. Increasing the hydrophobicity decreases the distribution coefficients and increases the separation factors. Then, heptyl acetate has the lowest distribution coefficients and the highest separation factors because it has the longest alkyl chain.

Each type-1 Ternary system has a plait point. The plait point data in this work were determined by Treybal's method [34] on Hand's coordinates, Table 1. For calculating the plait point, cloud point data and tie line points should be drawn in a plot and extrapolation of tie-lines gives the plait point data. Plot of Hand's coordinates is shown in Fig. 5.

Correlation Model

Measured equilibrium data can be correlated by UNIQUAC model of Abrams and Prausnitz [32]. At the equilibrium point of two immiscible liquid mixtures, the composition of the two layers (*e.g.*, aqueous and organic phases) can be calculated by using the following equations.

$$(\gamma_i x_i)^1 = (\gamma_i x_i)^2 \tag{7}$$
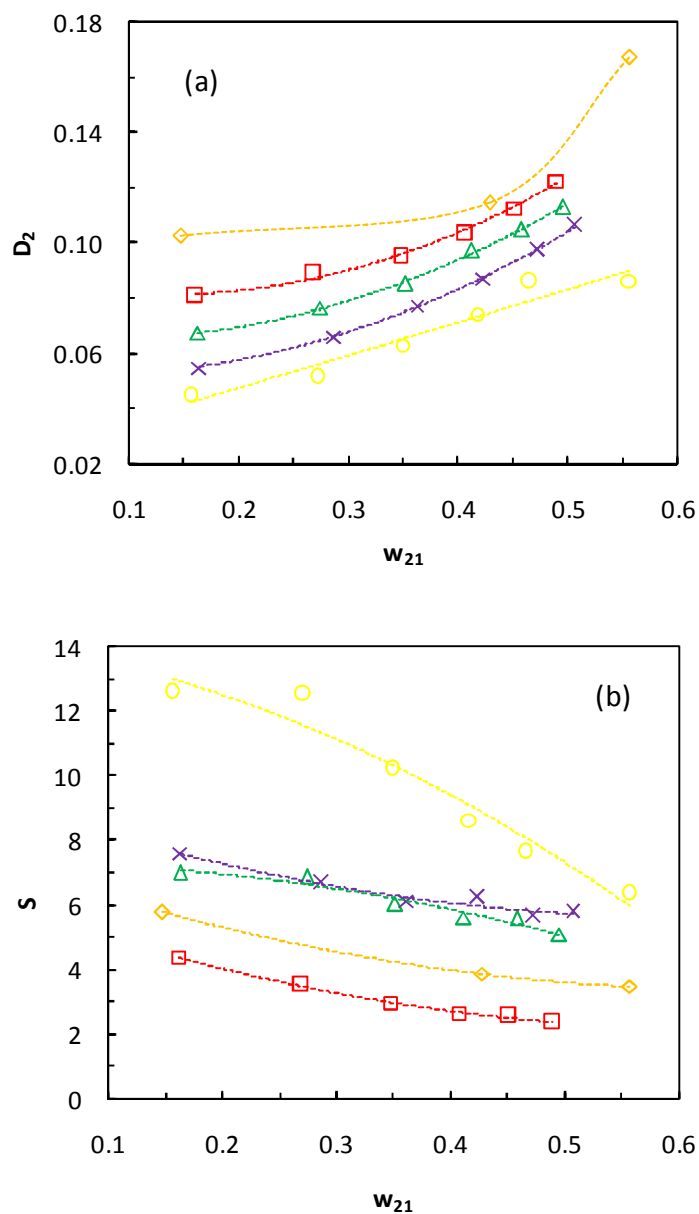
Fig. 4. Plot of distribution coefficients of PA (a) and separation factors (b) as a function of mass fraction of the acid in the aqueous phase for the systems {water + phosphoric acid + [(□) *n*-propyl acetate, (◊) *n*-butyl acetate, (△) *n*-amyl acetate, (×) *n*-hexyl acetate and (○) *n*-heptyl acetate]}.

$$\sum x_i^1 = \sum x_i^2 = 1 \tag{8}$$

where γ_i^1 and γ_i^2 are the activity coefficients of component

i in layer 1 and layer 2. Mole fractions of each layer have been expressed by X_i^1 and X_i^2 for the related component. Equations (7) and (8) should be solved in the two liquid layers by using an iterative progress.
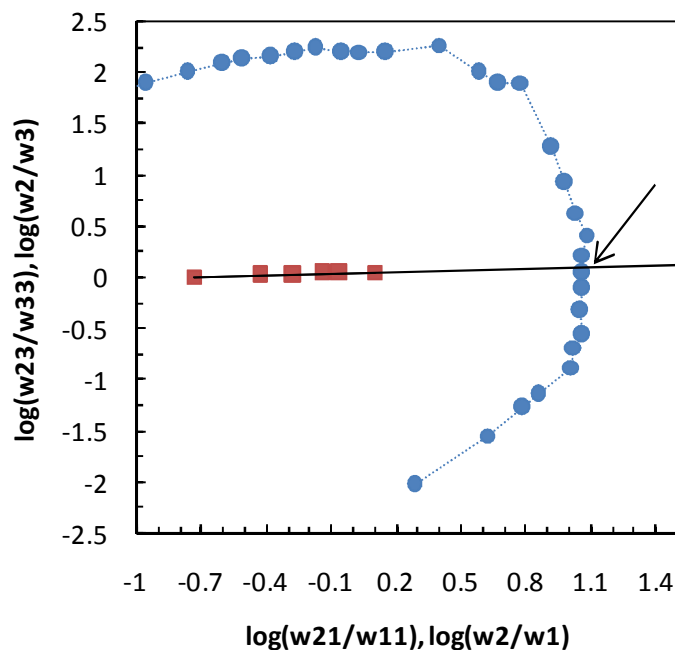
Fig. 5. Hand's coordinates for plait point calculation. (●) Obtained from cloud point data and (■) obtained from tie line data.

The UNIQUAC model (universal quasi-chemical model) for excess Gibbs energy (G^E) is presented as [32]:

$$\frac{G^E}{RT} = \sum_{i=1}^{3} x_i \ln\left(\frac{\Phi_i}{x_i}\right) + 5\sum_{i=1}^{3} q_i x_i \ln\left(\frac{\theta_i}{\Phi_i}\right) - \sum_{i=1}^{3} q_i x_i \ln\left(\sum_{j=1}^{n} \theta_j \tau_{ji}\right)$$

(9)

In this model, the logarithm of the activity coefficient is supposed to be the summation of two contributions:

$$\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^r$$

(10)

The combinational (γ_i^c) and residual elements (γ_i^r) of the activity coefficient can be expressed in the following equations:

$$\ln \gamma_i^c = \ln\left(\frac{\Phi_i}{x_i}\right) + \frac{z}{2} q_i \ln\left(\frac{\theta_i}{\Phi_i}\right) + \iota_i - \frac{\phi_i}{x_i}\sum_{j=1}^{c} x_j \iota_j$$

(11)

$$\ln \gamma_i^r = q_i\left[1 - \ln\left(\sum_{j=1}^{c} \theta_j \tau_{ji}\right) - \sum_{j=1}^{c}\left(\frac{\theta_j \tau_{ij}}{\sum_{k=1}^{c} \theta_k \tau_{kj}}\right)\right]$$

(12)

Adjustable parameter of the UNIQUAC equation is τ_{ij}. The parameter Φ_i (segment fraction) and θ_i (area fraction) are presented by Eqs. (13) and (14):

$$\Phi_i = \frac{x_i r_i}{\sum_{i=1}^{c} x_i r_i} \quad \theta_i = \frac{x_i q_i}{\sum_{i=1}^{c} x_i q_i}$$

(13)

$$\tau_{ij} = \left(-\frac{\Delta u_{ij}}{RT}\right) = \exp\left(-\frac{a_{ij}}{T}\right)$$

(14)

The parameter u_{ij} characterizes the interaction energy between compounds i and j. In Eqs. (13) and (14), a_{ij} and a_{ji} are expressed in K and imply the binary interactions between i - j pair of molecules.

In this study, the obtained tie-line points were correlated using the universal quasi-chemical (UNIQUAC) method of

Table 3. The UNIQUAC Structural Parameters (r and q) for Pure Components and Calculated UNIQUAC Tie-line Data in Mass Fraction for (Water + Phosphoric Acid + Heptyl Acetate) at T = 298.2 K. Data in Orange are Predicted Using the Obtained Iinteraction Parameters[a]

w_{11}	w_{21}	w_{31}	w_{13}	w_{23}	w_{33}	D_1	D_2	S
0.839	0.159	0.001	0.002	0.003	0.995	0.003	0.019	6.31
0.723	0.275	0.002	0.003	0.008	0.989	0.004	0.029	8.08
0.644	0.353	0.003	0.003	0.014	0.983	0.004	0.041	9.52
0.576	0.419	0.005	0.003	0.024	0.973	0.005	0.056	10.77
0.528	0.465	0.006	0.003	0.033	0.963	0.006	0.072	11.44
0.445	0.545	0.011	0.004	0.061	0.934	0.010	0.112	11.77
0.341	0.637	0.022	0.007	0.127	0.866	0.020	0.200	9.86
0.281	0.684	0.035	0.010	0.190	0.800	0.036	0.277	7.80

[a]The UNIQUAC structural parameters r (and q) of water: 0.920 (1.400), phosphoric acid: 3.000 (4.000) and heptyl acetate: 6.850 (5.816).

Table 4. Correlated Results from the UNIQUAC Model and the Corresponding Binary Interaction Parameters (a_{ij} and a_{ji}) for the Ternary System [Water (1) + Phosphoric Acid (2) + Heptyl Acetate (3)][a]

	$\dfrac{a_{ij}}{K}$	$\dfrac{a_{ji}}{K}$	rmsd (%)[b]			
			Mass fractions	D_1	D_2	S
1-2	1027.76	-66.40				
1-3	-118.90	-811.41	0.50	0.31	2.20	425.16
2-3	-52.92	698.94				

[a] $a_{ij} = \dfrac{(u_{ij} - u_{jj})}{R}$.

Abrams and Prausnitz [32]. The correlated points of the investigated system are inserted in Table 3. The structural parameters r (the number of segments per molecules) and q (the relative surface area per molecules) in UNIQUAC model were calculated using the Bondi method [35], and are inserted in Table 3. For optimizing the coefficient model and calculating binary interaction parameters, the objective function (OF) defined by Sorensen [36] was used.

The UNIQUAC correlated data are inserted in Fig. 2. Binary interaction parameters for W-PA, PA-W, W-HA, HA-W, PA-HA and HA-PA were calculated and are given in Table 4. The lower and upper ranges for calculations of interaction parameters were -1100 and 1100, respectively. Different ranges from -100 to 100 up to -1500 to 1500 were
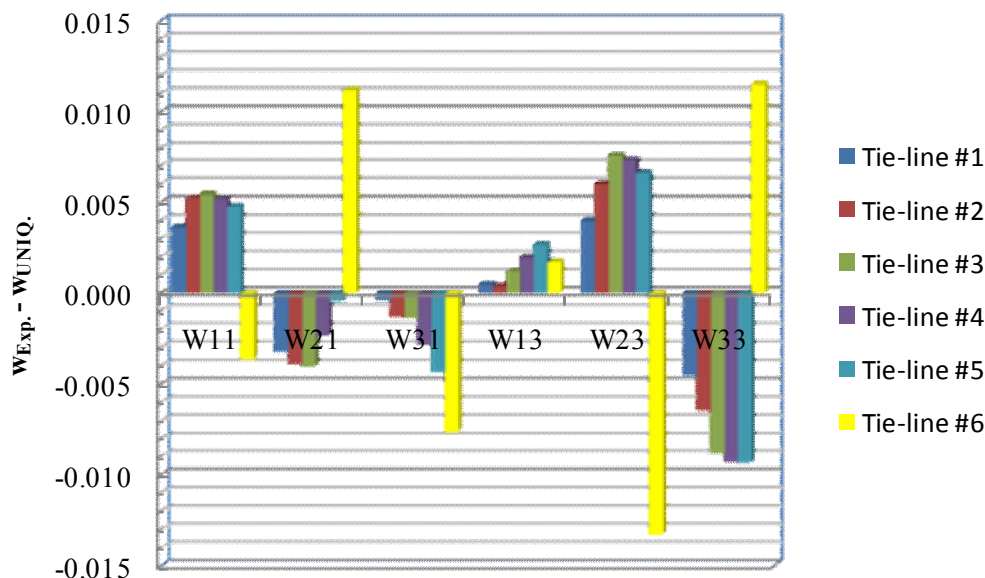
Fig. 6. Residuals of the experimental and UNIQUAC calculated data for all mass fractions of all tie-lines.

tested. Best results were obtained in the range of -1100-1100. The obtained binary interaction parameters were then used for prediction of two other tie-line points. The nearness of the predicted data with experimental cloud points are shown in Fig. 1. As can be seen, the predicted data have a good accordance with experimental points.

The root-mean square deviation (rmsd) was used to investigate the excellence of the correlation process and validation of calculated interaction parameters (Eq. (15)). In the equation, n is the number of data, w_{ijk}^{exp} is experimental tie-lines and w_{ijk}^{cal} is correlated points. The subscripts i, j and k present components, phases and tie-lines (k = 1,2,. . ., n), respectively. The root-mean square deviation (RMSD) values of calculated weight fractions, distribution coefficients (D_1 and D_2) and separation factors for the investigated system at $T = 298.2$ K are listed in Table 4. The RMSD values show that the thermodynamic model has properly fitted the experimental data but the trend of experimental data has not been fitted well. The RMSD values of separation factors are very high while the RMSD values of distribution coefficients are reasonable. Then, the interaction parameters are trustable for prediction of mass

fractions and distribution coefficients but not for separation factors. While in many studies, the RMSD value of mass fractions is only reported, here, we show that this value alone is not enough for a comprehensive judgment.

Finally, the differences between the experimental and predicted data are graphically presented in Fig. 6. As can be seen from the figure, the most deviations are related to mass fractions of the tie-line #6 (yellow columns). In this tie-line, phosphoric acid concentration is very high and thermodynamic models usually show large deviations. Figure 6 shows that correlations limits to tie-line #6 and in higher concentrations of PA, correlations show the large deviations.

CONCLUSIONS

Experimental tie-line data for the system (water + phosphoric acid + heptyl acetate) were measured at $T = 298.2$ K and ambient pressure. The ternary system exhibits type-1 behavior of the LLE. Plait point data were calculated using Treybal's method and laid on the left side of the phase diagram. The UNIQUAC model was applied to correlate the experimental endpoints and to calculate the

mass fractions of the investigated mixtures. The model gave good results for the studied system and the binary interaction parameters obtained were used to predict more tie-line data. The predicted points were close to cloud point data. The separation factors and distribution coefficients for the studied esteric solvent were computed. The experimental results showed that the separation factors for heptyl acetate are greater than unity for the investigated system which shows the efficiency of the solvent for removal of the acid from water. The comparison of the distribution coefficients and separation factors of the studied solvent with other *n*-alkyl acetate esters showed that increasing the hydrophobicity of the esteric solvents decreases the distribution coefficients and increases the separation factors. Then, heptyl acetate has the highest separation factor among the *n*-alkyl esteric solvents studied.

$$RMSDrmsd = \sqrt{\frac{\sum_{k=1}^{n}\sum_{j=1}^{2}\sum_{i=1}^{3}\left(w_{ijk}^{exp} - w_{ijk}^{cal}\right)^2}{6n}} \qquad (15)$$

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