

Measurement and Correlation of LLE Data for the Ternary System Water + Phosphoric Acid + 1-Undecanol at 303.2 K

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Experimental solubility curve and tie-line data were obtained for a ternary system of water, phosphoric acid, and 1-undecanol at $T = 303.2$ K and ambient pressure. The cloud point method was employed to determine the binodal curve data. The mass fraction compositions of each layer were explored by acid-base and the Karl Fisher titration methods accompanied by mass balance calculations. For the mentioned ternary system, a type-1 LLE behavior was observed. The reliability of the experimental compositions was verified using the Othmer-Tobias and Hand plots. The UNIQUAC and NRTL thermodynamic models were applied to correlate the equilibrium tie-line points. The experimental points were adequately regressed using the thermodynamic models. Distribution coefficients and separation factors were computed over the non-miscible region. For the separation process, separation factor should be greater than one. For the present system, this separation factor was suitable to apply separation treatment in all concentrations of phosphoric acid at the experiment temperature. The Katritzky parameters were utilized for LSER modeling of distribution coefficients of the target mixtures. The ternary system showed good fittings with the LSER model.

Keywords: Phosphoric acid, Liquid-liquid equilibrium, Thermodynamic model, LSER approach

INTRODUCTION

Phosphoric acid (PA) has a wide diversity of applications and the most common method of its production is wet process (in comparison with thermal and dry kiln process), but the manufactured acid is a dilute aqueous solution with various impurities. The pure PA is widely used in food industry, production of phosphate fertilizers and phosphate fuel cells [1-9]. Liquid-liquid extraction is an ordinary method for separating polar acids such as phosphoric acid, formic acid and lactic acid from aqueous solution [10-13].

Based on the literature, different solvents are used to extract phosphoric acid from dilute aqueous solutions, such as alcohols, esters, ketones and hydrocarbons [13-26].

Amongst the solvents investigated, alcohols have shown proper distribution coefficient and separation factor for extraction of PA from water. In this work, 1-undecanol or undecyl alcohol (UOH) was selected as a physical extractant for purification and liquid-liquid equilibrium measurements of PA from aqueous solutions. Suitable functional group, water immiscibility and high boiling point are the main characteristics of UOH as a top quality solvent for recovering PA from water. In addition, because of low toxicity of UOH, it could be applied in the food and the pharmaceutical industry. LLE data for systems consisting of 1-undecanol as a physical solvent have already been reported by some authors [27,28].

Current work contains valuable LLE data for the partitioning and extraction of phosphoric acid from water solutions, and, to the best of our knowledge, no such data have been published yet. Phase diagrams containing

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solubility curve and tie-line data were determined at 303.2 K. Distribution coefficients of phosphoric acid (D_2), water (D_1) and separation factors (S) of UOH were calculated to clarify the capacity of the solvent for separation of phosphoric acid from aqueous layer. The Othmer-Tobias [29] and Hand [30] correlation equations were employed to correlate and make certain reliability for the measured tie-line points. Also, the UNIQUAC method of Abrams and Prausnitz [31] and the NRTL model of Renon and Prausnitz [32] were applied as thermodynamic models to correlate the tie-line data as well. Finally, computed distribution coefficients of the studied system were fitted to the Katritzky [33] LSER model. In this model, Reichardt polarity, Kirkwood polarity and Lorenz and Lorentz polarizability functions were connected to the solute property.

EXPERIMENTAL

Materials

1-Undecanol and phosphoric acid were purchased from Merck and used without any further purification. The mass fraction purities of these materials were of 0.98 and 0.85, respectively. The purity of the acid was checked through acidimetric titration with 0.5 M NaOH. HPLC-grade water was used throughout all experiments.

Apparatus and Procedure

A Metrohm-870 KF Titrino plus Karl-Fisher titrator was used in the current work. The temperature of instruments was maintained with an accuracy of ± 0.1 K, verified by a Testo-735 digital thermometer. The mixtures were prepared by weighting via a Precisa electronic analytical balance (model LS120A) with an accuracy of ± 0.0002 g. Refractive index (n_D) of 1-undecanol at 303.2 K was measured with a thermostat DR301-95 KRUSS digital hand-held refractometer with the accuracy of ± 0.0001 .

The cloud-point method was employed to determine the solubility data of the investigated system [34]. An equilibrium glass cell (10 ml) was used to measure the cloud point data. This cell was equipped with a magnetic stirrer and thermostated water jacket to keep the temperature of the mixture constant. UOH and water were introduced into the cell using a Brand Transferpette

micropipette with an accuracy of ± 0.001 ml. The titration endpoint was visually verified by observing the transformation of system from a homogeneous to a heterogeneous state. The visual titrations were repeated at least three times. The averages of these readings were selected for the cloud point data. The standard uncertainty in composition of the solubility data was estimated to be better than ± 0.0039 . The binodal curve data of the studied system are tabulated in Table 1.

The tie-line measurements of the ternary system (water + phosphoric acid + 1-undecanol) were performed at $T = 303.2$ K. The ternary mixtures of known mass fractions of water, PA, and UOH were first prepared in an equilibrium glass cell (20 ml). The mixtures were strongly stirred by a magnetic stirrer for 2 h, and then settled for 2 h until the two phases were separated from each other. Prelude tests verified that these times are enough to reach the equilibrium. The samples of both alcoholic-rich and water-rich phases were removed by a glass syringe from upper and lower layers of the cell, respectively.

The acid mass fractions in both phases (w_{21} for water phase and w_{23} for organic phase) were measured by acid-base titration. The mass contents of water in the organic (w_{13}) and aqueous (w_{11}) phases were obtained using Karl-Fisher measurements [35]. The content of 1-undecanol in each phase (*i.e.* w_{31} and w_{33} for aqueous and alcohol phases, orderly) was calculated using the equation of $\sum w_i = 1$. The estimated standard uncertainty of all measured mass fractions was better than ± 0.0042 .

RESULTS AND DISCUSSION

Experimental LLE Results

The experimental tie-lines of the ternary system (water + phosphoric acid + 1-undecanol) were obtained at $T = 303.2$ K and atmospheric pressure. The equilibrium data and LLE phase diagram of the ternary system at the studied temperature are presented in Table 2 and Fig. 1, respectively. It could be seen from Fig. 1 that the system exhibits a type-1 behavior. This behavior is observed because there is just one liquid pair with partial miscibility (water + UOH) and the two other pairs ((water + PA) and (PA + UOH)) are unlimitedly miscible. Since the mutual

Table 1. Solubility Curve Data in Mass Fractions (w_i) for (Water + Phosphoric Acid + 1-Undecanol) at $T = 303.2$ K^a

w_1	w_2	w_3	w_1	w_2	w_3
Left side of diagram			Right side of diagram		
0.0230 ^b	0.0000	0.9770 ^b	0.1077	0.8061	0.0862
0.0279	0.0380	0.9341	0.1145	0.8238	0.0617
0.0319	0.0678	0.9003	0.1315	0.8313	0.0372
0.0329	0.0882	0.8789	0.1567	0.8301	0.0132
0.0359	0.1192	0.8449	0.1692	0.8226	0.0082
0.0381	0.1425	0.8194	0.1795	0.8125	0.0080
0.0389	0.1812	0.7799	0.2029	0.7902	0.0069
0.0393	0.2117	0.7490	0.2225	0.7707	0.0068
0.0379	0.2413	0.7208	0.2468	0.7470	0.0062
0.0399	0.3096	0.6505	0.2969	0.6980	0.0051
0.0427	0.3455	0.6118	0.3327	0.6630	0.0043
0.0460	0.4027	0.5513	0.3898	0.6064	0.0038
0.0493	0.4485	0.5022	0.4206	0.5759	0.0035
0.0527	0.4917	0.4556	0.5978	0.3999	0.0023
0.0556	0.5440	0.4004	0.7131	0.2847	0.0022
0.0621	0.6083	0.3296	0.8503	0.1481	0.0016
0.0686	0.6611	0.2703	0.9401	0.0591	0.0008
0.0729	0.6946	0.2325	0.9993 ^b	0.0000	0.0007 ^b
0.0846	0.7463	0.1691	-	-	-
0.0985	0.7810	0.1205	-	-	-

^aStandard uncertainties u are $u(T) = 0.1$ K, $u(P) = 0.5$ kPa and $u(w) = 0.0039$. ^bMutual solubilities.

solubilities of UOH in water and water in UOH are very low, the area of the two-phase region is very wide and could be an important reason for ability of UOH as a proper solvent in extraction process. The solubility of water in UOH is 23.5 g_{water}/1000 g_{UOH} and that of UOH in water is 0.7 g_{UOH}/1000 g_{water} at 303.2 K.

To investigate the quality, reliability, and consistency of measured tie-lines, the Othmer-Tobias (Eq. (1)) [29] and the Hand (Eq. (2)) [30] correlation equations were applied,

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

Table 2. Experimental Tie-line Data in Mass Fraction and Separation Factors (S) and Distribution Coefficients of PA (D_2) and Water (D_1) for (Water + Phosphoric Acid + 1-Undecanol) at $T = 303.2$ K^a

w_{11}	w_{21}	w_{13}	w_{21}	D_1	D_2	S
Aqueous phase		Organic phase				
0.8314	0.1669	0.0236	0.0052	0.028	0.031	1.098
0.7830	0.2152	0.0246	0.0138	0.031	0.064	2.041
0.6990	0.2988	0.0264	0.0234	0.038	0.078	2.074
0.6231	0.3746	0.0296	0.0505	0.048	0.135	2.838
0.5664	0.4307	0.0321	0.0735	0.057	0.171	3.011
0.5145	0.4823	0.0353	0.1178	0.069	0.244	3.560
0.4460	0.5506	0.0384	0.1532	0.086	0.278	3.232
0.3983	0.598	0.0384	0.1765	0.096	0.295	3.061

^aStandard uncertainties u are $u(T) = 0.1$ K, $u(P) = 0.5$ kPa, $u(w) = 0.0042$.

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

where A , B , A' , and B' are the parameters of the Othmer-Tobias and Hand equations, respectively. The Othmer-Tobias, and Hand plots, and the corresponding parameters are summarized in Fig. 2. The proximity of R square factor to 1 shows the linearity of the plots and degree of consistency and the quality of the obtained tie-lines in this study.

In order to study the efficiency of the heavy alcohol solvent (UOH) for separation of the acid, distribution coefficients of water ($D_1 = w_{13}/w_{11}$) and PA ($D_2 = w_{23}/w_{21}$) and separation factors ($S = D_2/D_1$) were computed using the measured tie-line data and are given in Table 2. The plots of calculated separation factors and distribution coefficients of PA as a function of the mass fraction of the acid in aqueous phase are presented in Fig. 3. It can be seen that all separation factors in the investigated range of acid concentration are larger than 1, indicating that PA could be successfully extracted from the water by 1-undecanol.

Correlation Models

The measured tie-line data were correlated using the universal quasi-chemical (UNIQUAC) method of Abrams and Prausnitz [31] and the nonrandom two-liquid (NRTL) model of Renon and Prausnitz [32]. The correlated data of the ternary system are given in Table 3. The UNIQUAC structural parameters r (the number of segments per molecules) and q (the relative surface area per 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 [36]. The calculated values of r and q used for this ternary system are mentioned in Table 3. In this study, the value of the non-randomness (α) applied for NRTL modeling was fixed at 0.2. The values 0.1 and 0.3 were also tested for NRTL correlation, however, 0.2 was found to be the best estimation.

To optimize the thermodynamic models and obtaining binary interaction parameters, the objective function introduced by Sorensen [37] was employed. This function is the summation of the squares of the differences between the experimental and correlated tie-lined. The dissimilarity of

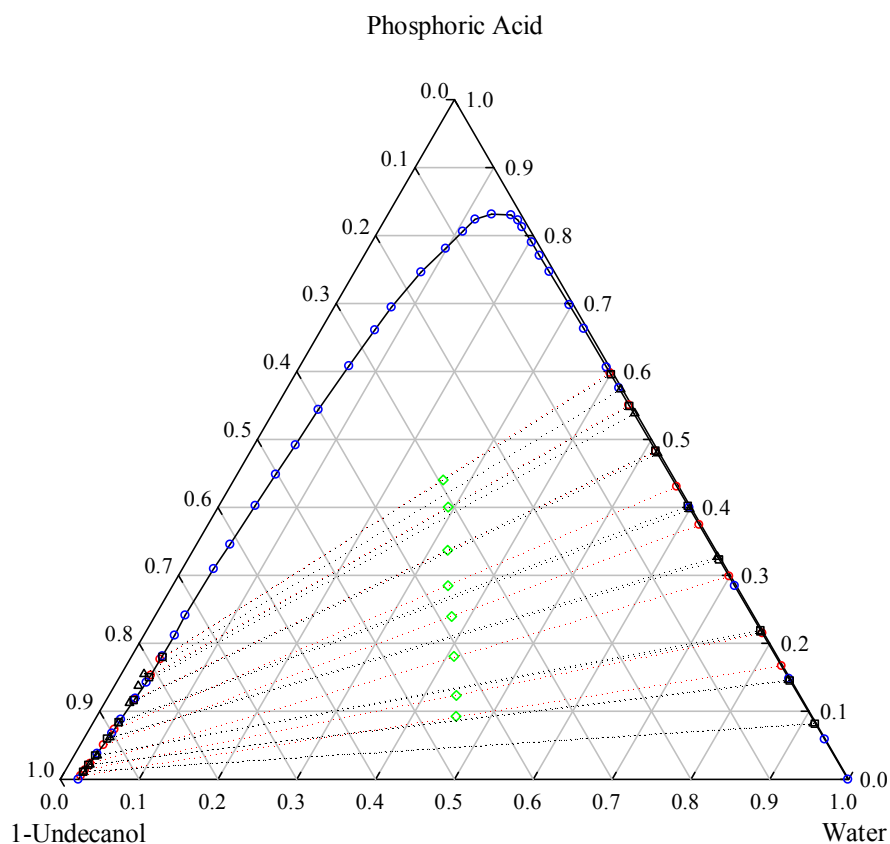


Fig. 1. Ternary phase diagram for LLE of [water (1) + phosphoric acid (2) + 1-undecanol (3)] at $T = 303.2$ K; (\circ) experimental cloud points, (\diamond) ternary mixtures feeds, (\circ) experimental tie-lines, (\square) UNIQUAC calculated points, and (Δ) NRTL calculated points ($\alpha = 0.2$).

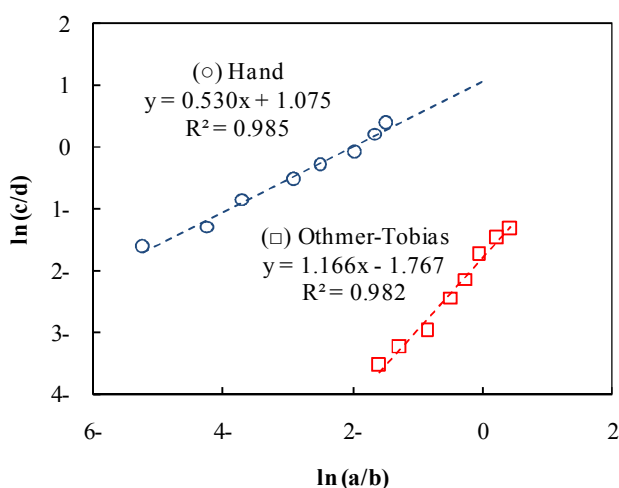


Fig. 2. The Othmer-Tobias and Hand plots of the [water (1) + phosphoric acid (2) + 1-undecanol (3)] ternary system at 303.2 K; (\circ) hand plot, (\square) othmer-tobias plot; $(a/b) = w_{23}/w_{33}$ or $1 - w_{11}/w_{11}$ and $(c/d) = w_{21}/w_{11}$ or $1 - w_{33}/w_{33}$ for hand and othmer-Tobias equations, respectively.

Table 3. The UNIQUAC Structural Parameters (r and q) for Pure Components and Calculated UNIQUAC and NRTL ($\alpha = 0.2$) Tie-line Data in Mass Fraction for (Water + Phosphoric Acid + 1-undecanol) at $T = 303.2$ K.

NRTL		UNIQUAC ^a		NRTL		UNIQUAC	
W_{11}	W_{21}	W_{11}	W_{21}	W_{13}	W_{23}	W_{13}	W_{23}
0.9143	0.0822	0.9163	0.0818	0.0235	0.0112	0.0237	0.0111
0.8505	0.1462	0.8525	0.1455	0.0268	0.0217	0.0250	0.0213
0.7809	0.2160	0.7785	0.2193	0.0295	0.0352	0.0268	0.0352
0.6699	0.3274	0.6740	0.3235	0.0321	0.0619	0.0295	0.0598
0.6000	0.3974	0.5947	0.4024	0.0326	0.0828	0.0321	0.0842
0.5180	0.4797	0.5131	0.4836	0.0318	0.1123	0.0350	0.1165
0.4594	0.5385	0.4473	0.5492	0.0304	0.1375	0.0376	0.1503
0.4243	0.5737	0.4004	0.5959	0.0291	0.1547	0.0396	0.1802

^aThe UNIQUAC structural parameters r (and q) of water: 0.920 (1.400), phosphoric acid: 3.000 (4.000) and 1-undecanol: 8.645 (7.448).

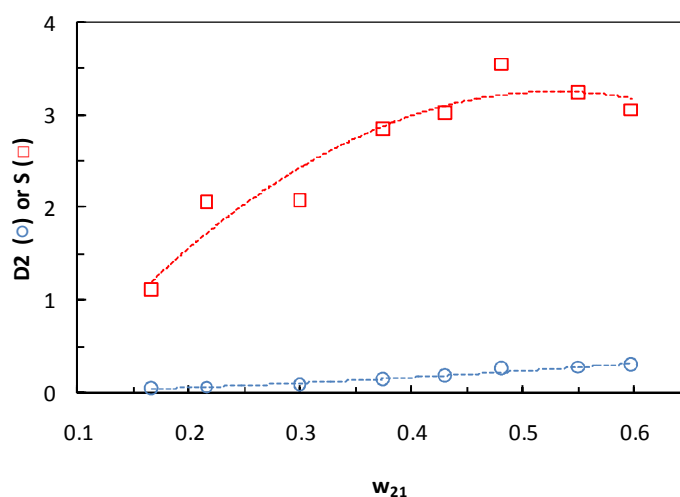


Fig. 3. Plot of the separation factor (S) and distribution coefficient of PA (D_2) as a function of mass fraction of acid in the aqueous phase; (\square) separation factor, and (\circ) distribution coefficient.

experimental and correlated data could be seen in Fig. 1. Through the correlation process, the optimum UNIQUAC

and NRTL binary interaction parameters between each pair of components were obtained and inserted in Table 4.

Table 4. Correlated Results from the UNIQUAC and NRTL ($\alpha = 0.2$) 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

	$(a_{ij}/K)^a$	a_{ij}/K	rmsd (%) ^c	$(b_{ij}/K)^b$	b_{ij}/K	rmsd (%)
1-2	289.12	62.45		407.15	16682.94	
1-3	-65.96	-425.34	3.05	2184.32	148.46	3.19
2-3	-823.37	264.56		17169.66	3618.10	

^a $a_{ij} = \frac{(u_{ij} - u_{ji})}{R}$ for UNIQUAC model
^b $a_{ij} = \frac{(g_{ij} - g_{ji})}{R}$ for NRTL model

Table 5. The Katritzky Experimental Parameters for 1-Undecanol and Estimated Parameters of the LSER Equation Obtained by the Linear Regression

Parameters	Values
$\log D_2^0$	1.285
a	-4.786
b	-2.509
c	-6.323
ε	6.650
$\left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right)$	0.395
n_D	1.4356
$\left(\frac{n^2 - 1}{2n^2 + 1}\right)$	0.207
E_T^N	0.522

The root-mean square deviation (rmsd) was applied to explore the quality of the correlated data and validity of the obtained interaction parameters. The following equation shows how rmsd could be calculated from the difference between the experimental and correlated mass fractions,

$$rmsd = \sqrt{\frac{\sum_{k=1}^n \sum_{j=1}^2 \sum_{i=1}^3 (w_{ijk}^{exp} - w_{ijk}^{cal})^2}{6n}} \quad (3)$$

where n is the number of tie-lines and w_{ijk}^{exp} and w_{ijk}^{cal} point

to the experimental and correlated mass fractions. The subscript *i*, *j* and *k* are indices of components, phases and tie-lines (*k* = 1, 2, . . . , *n*), respectively. The rmsd values of UNIQUAC and NRTL models for the investigated system at *T* = 303.2 K are listed in Table 4. Based on the rmsd values, both thermodynamic models have shown proper fitting with experimental data, though UNIQUAC model resulted in slightly better estimations.

LSER Modeling

To correlate the distribution coefficients of PA (*D*₂), the Katritzky LSER model [33] was applied. LSER is an abbreviation for linear solvation energy relationship [33] providing a linear equation to connect a solute property (in this work *D*₂) to solvent properties like below:

$$\log D_2 = \log D_2^0 + a \left(\frac{\varepsilon - 1}{2\varepsilon + 1} \right) + b \left(\frac{n^2 - 1}{2n^2 + 1} \right) + cE_T^N \quad (6)$$

Katritzky merged three parameters to each other. Reichardt polarity function (E_T^N), dielectric constant (ε) (as Kirkwood polarity function) and refractive index (*n*) function that represent polarity parameters of solvent. The coefficients *a*, *b* and *c* show the relative susceptibilities of the investigated property ($\log D_2$) to the selected solvent parameters. The $\log D_2^0$ term specifies the property where there is no interaction with the solvent. The Katritzky equation shows the effects of solvent dipolarity, polarizability, and specific interactions (such as hydrogen bonding, π - π interaction). The refractive index (*n*) of 1-undecanol at 303.2 K was measured by the authors, and the relative permittivity (ε) and E_T^N values of the solvent were taken from references [33,38]. All the data obtained are summarized in Table 5.

The distribution coefficients achieved by experimental tie-lines were regressed by the Excel Solver pack. The comparison of experimental and correlated data for the distribution coefficients is given in Table 6. The Katritzky LSER model values showed a good regression compared to experimental data. The values of LSER model parameters are presented in Table 5. The results show that specific interaction term is the most effective parameter for extraction of PA from water, though polarity and polarizability have important effects on the separation

process.

CONCLUSIONS

Experimental LLE data for a ternary system of water, PA, and UOH were obtained at *T* = 303.2 K and ambient pressure. The ternary system shows type-1 behavior of the LLE. The UNIQUAC and NRTL models were used to correlate the experimental tie-line data and to calculate the phase compositions of the investigated mixtures. Both models gave good results for the target system. The separation factors and distribution coefficients for the alcoholic solvent applied in this work were determined. The experimental results showed that the separation factors for UOH are larger than those for the range of acid concentration used in this work, indicating the ability of the solvent to purify the acid from water. Finally, Katritzky LSER model was used to correlate the distribution coefficients and this model fitted properly with the experimental partition function.

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