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Liquid−Liquid Equilibria of the System Water/Phosphoric Acid/Diisopropyl Ether at (273.15, 283.15, and 293.15) K

Carlos H. Harrison† **and Pedro Roquero***

Facultad de Química, Universidad Nacional Autónoma de México, C. P. 04510, México D.F.

Liquid−liquid equilibrium for the ternary system water/phosphoric acid/diisopropyl ether was studied at the temperatures (273.15, 283.15, and 293.15) K. The concentration of each phase was determined by acidimetric titration, the Karl Fisher technique, and nuclear magnetic resonance. Phase diagrams with tie lines and plait points are reported; the latter are calculated by Hand's method. The behavior of the three-phase zone was also studied; results show that the size of this zone decreased as the temperature decreased.

Introduction

The production of wet phosphoric acid (WPA) from the phosphate rock is accompanied by the dissolving of most of the organic and inorganic impurities contained in the rock.[1] The liquid−liquid extraction technique has been used to obtain a highly purified phosphoric acid (PA). For this purpose diisopropyl ether (DIPE) and other solvents[2−7] have been used as extractant.

The Prayon process[8] and the process reported by Raz[9] are described using DIPE as extractant. However, these papers provide technical data of the process; information regarding the water/PA/DIPE phase equilibrium was not revealed, and the available information about the thermodynamics of this system is limited.[10]

Phase equilibria of the ternary system water/PA/DIPE have been studied before,[3,4] at (293.15, 298.15, and 313.15) K. These previous works report somewhat different results, with regard to the organic phase composition in the two-phase regions and to the mutual solubility of water and DIPE.

The objective of this work was to carry out a systematic study of the behavior of DIPE with temperature, allowing the characterization of the ternary phase diagram water/PA/DIPE at (273.15, 283.15, and 293.15) K.

Experimental Section

Chemicals. PA was supplied by Merck (Catalog No. 100564) with the nominal purity of 89 mass % H_3PO_4; the purity was found to be 88.53% through acidimetric titration with 1 N NaOH. DIPE with minimum purity 99.9 mass % was supplied by Merck (Catalog No. 100867). The content of water was found to be 0.008 mass % by the Karl Fisher method.

Bidistilled water was used throughout the experiment. The chemicals were used without further purification.

Apparatus. All weighing was carried out in a top pan balance accurate to ±0.01 g. Water content was measured with Orion F8 Karl Fisher equipment, and DIPE content was measured through nuclear magnetic resonance (NMR) at 300 MHz.[11,12]

Procedure. Tie lines were determined using the analysis method.[13] Samples were about 1 kg. The uncertainty of the technique in determining the composition of the tie lines was within ±0.01 mass fraction. The solubility curves were not obtained.

The conjugated phases were obtained by preparing mixtures whose compositions are in the immiscible region. The mixtures were stirred with a propeller mixer for at least 30 min in jacked cells with septum outlets. The mixtures were stirred for an additional 30 min to ensure the equilibrium of the system. The system was left without agitation for 2 h in order to obtain two or three transparent phases. A thermostat was used to control the temperature and to reach the temperature of study. Finally, one sample of each phase was withdrawn and the compositions were measured. Two syringes, placed in the cell during the period without agitation, were used to withdraw the samples of both organic phases in the three-phase zone. Concentration analyses of water and PA were carried out for the organic phase, and concentration analyses of DIPE and PA were carried out for the aqueous phase. The third component was calculated using eq 1:

$$w_1 + w_2 + w_3 = 1 \tag{1}$$

where w_1 is the mass fraction of water, w_2 is the mass fraction of diisopropyl ether, and w_3 is the mass fraction of phosphoric acid.

Results

Tables 1−3 show liquid−liquid equilibrium data for the system at (273.15, 283.15, and 293.15) K, respectively, where K_c is the distribution coefficient. Table 4 shows plait point compositions calculated by Hand's method.[13] Figures 1−3 show the tie lines and plait points for the system at (273.15, 283.15, and 293.15) K, respectively.

A three-phase zone was found at the three different temperatures. In Figure 4, compositions for the three phases at equilibrium in this zone are shown, together with the results of Lozano et al.[4] at 293.15 K and with those of Ruiz et al.[3] at (298.15 and 313.15) K.

Discussion

Figures 1−3 reveal three two-phase zones and one three-phase zone. These ternary diagrams satisfy Schreinemak-

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* To whom correspondence should be addressed. Fax: (5255)-55-501-572. E-mail: p_roquero@entropiahumana.com.

† Current address: Chemical Engineering Department, UMIST, Sackville Street, Manchester M60 1QD, U.K.

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Table 1. Experimental Compositions of the System Water (1)/Diisopropyl Ether (2)/Phosphoric Acid (3) Tie Lines at 273.15 K

aqueous phase			organic phase			
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$	K_c
99.25	0.745	0.00	0.56	99.44	0.00	
70.82	0.60	28.58	0.25	99.36	0.39	0.0136
47.82	0.74	51.44	0.31	98.93	0.76	0.0148
31.85	1.53	67.02	6.57	53.74	39.69	0.5922
30.75	1.06	68.19	8.43	49.05	42.52	0.6236
28.93	1.82	69.25	8.60	45.92	45.48	0.6568
25.55	2.76	71.69	8.90	40.76	50.34	0.7022
22.08	4.10	73.82	8.95	37.23	53.82	0.7291
21.00	4.26	74.74	9.68	34.74	55.58	0.7436
19.04	5.13	75.83	9.42	32.28	58.30	0.7688

Three-Phase Zone

aqueous phase			heavy organic phase			light organic phase		
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$
32.17	1.13	66.70	6.69	61.78	31.53	1.60	88.87	9.53

Lateral Two-Phase Zone

$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$
4.99	61.49	33.52	1.33	91.96	6.71

Table 2. Experimental Compositions of the System Water (1)/Diisopropyl Ether (2)/Phosphoric Acid (3) Tie Lines at 283.15 K

aqueous phase			organic phase			
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$	K_c
99.21	0.793	0.00	0.58	99.42	0.00	
71.65	0.67	27.68	0.27	99.34	0.33	0.0119
40.08	1.08	58.84	0.36	98.88	0.45	0.0076
28.83	1.86	69.31	7.98	48.66	43.36	0.6256
26.20	2.27	71.53	8.84	42.16	49.00	0.6850
25.17	2.73	72.10	9.41	38.92	51.67	0.7166
19.85	5.15	75.00	9.89	35.26	54.85	0.7313
18.90	5.51	75.59	10.40	31.87	57.73	0.7637

Three-Phase Zone

aqueous phase			heavy organic phase			light organic phase		
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$
30.17	1.20	68.63	7.45	57.08	35.47	1.01	91.64	7.35

Lateral Two-Phase Zone

$100\ w_1$	$100\ w_2$	$100\ w_3$	$100\ w_1$	$100\ w_2$	$100\ w_3$
4.85	58.88	36.27	0.91	94.26	4.83

Table 3. Experimental Compositions of the System Water (1)/Diisopropyl Ether (2)/Phosphoric Acid (3) Tie Lines at 293.15 K

aqueous phase			organic phase			
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$	K_c
99.13	0.872	0.00	0.821	99.18	0.00	
71.98	0.42	27.6	0.69	99.08	0.23	0.0083
39.62	0.35	60.03	0.87	98.71	0.42	0.0070
28.21	1.80	69.99	0.93	97.94	3.1	0.0443
24.74	2.88	72.38	8.75	42.85	48.40	0.6687
22.71	4.17	73.12	9.69	38.58	51.73	0.7075
20.88	5.14	73.98	10.14	36.76	53.1	0.7178
18.84	6.32	74.84	10.20	33.51	56.29	0.7521

Three-Phase Zone

aqueous phase			heavy organic phase			light organic phase		
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$
26.89	2.55	70.61	7.18	51.72	41.10	0.96	93.50	5.54

Lateral Two-Phase Zone

$100\ w_1$	$100\ w_2$	$100\ w_3$	$100\ w_1$	$100\ w_2$	$100\ w_3$
4.41	55.75	39.84	0.94	95.09	3.97

ers' rule.[14] There are no degrees of freedom inside the three-phase zone, as indicated by the phase rule.[15]

Table 4. Plait Points of the System Water (1)/Diisopropyl Ether (2)/Phosphoric Acid (3)

T/K	$100w_1$	$100w_2$	$100w_3$
273.15	10.69	19.64	69.67
283.15	11.89	21.54	66.57
293.15	12.79	23.84	63.37

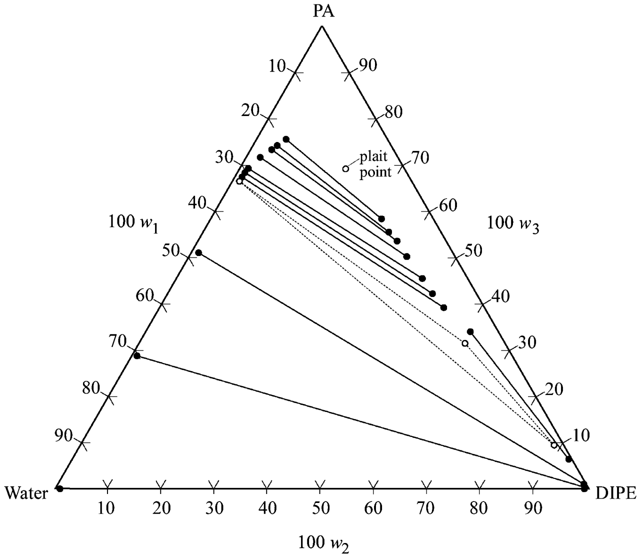

Figure 1. Tie lines of the system water (1)/diisopropyl ether (2)/ phosphoric acid (3) at 273.15 K.

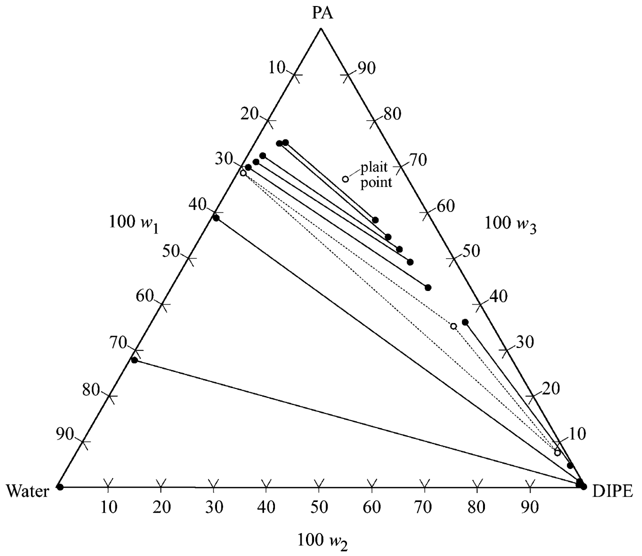

Figure 2. Tie lines of the system water (1)/diisopropyl ether (2)/ phosphoric acid (3) at 283.15 K.

The source of the lateral two-phase zone is a second binodal curve, and the tie line on this lateral zone is approximately parallel to the tie line joining the compositions of the heavy organic phase and the light organic phase, in the three-phase zone. Hence, recovery of PA in the lateral two-phase zone is very low.

In the three-phase zone and in the lateral two-phase zone, the compositions of the organic phases approach each other as the temperature decreases. A correlation of the three-phase zone compositions versus temperature shows that the temperature where both compositions would be the same (where the three-phase zone disappears)[16] is 243.15 K.

The surface area of the upper two-phase zone (above the three-phase zone in Figures 1−3) decreases as temperature increases, showing that mutual solubility increases with temperature in this zone.

The compositions of the three-phase zone are shown in Figure 4. The results at 293.15 K (Lozano et al.[4] and this

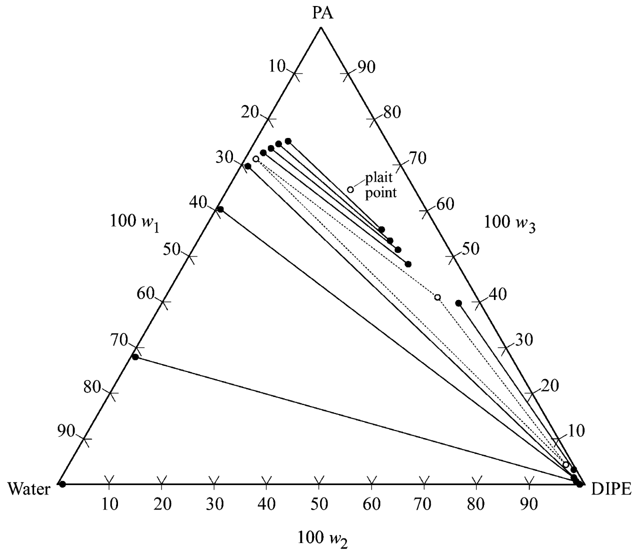

Figure 3. Tie lines of the system water (1)/diisopropyl ether (2)/ phosphoric acid (3) at 293.15 K.

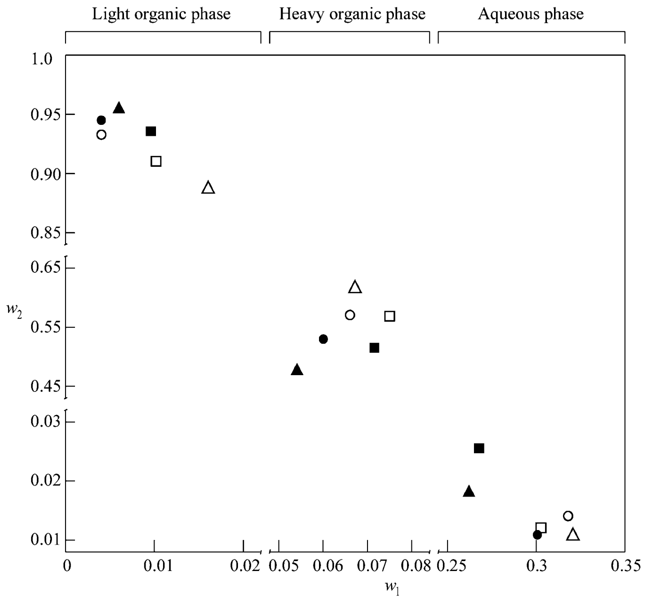

Figure 4. Equilibrium compositions in the three-phase zone: ○, Lozano et al.[4] at 293.25 K; ●, Ruiz et al.[3] at 298.15 K; ▲, Ruiz et al.[3] at 313.15 K; △, this work at 273.15; □, this work at 283.15; ■, this work at 293.15 K.

work) present the most important difference for the DIPE concentration in the heavy organic phase, corresponding to an uncertainty of 5.7%. Comparison of results at the extreme temperatures (Ruiz et al.[3] at 313.15 K and this work at 273.15 K) reveals that the concentration of PA in the light organic phase decreases by 5.83 mass %, as temperature increases from 273.15 K to 313.15 K, while the PA concentration in the heavy organic phase increases by 14.87 mass % as temperature increases in the same interval.

DIPE has a disadvantage as extractant in the lowest two-phase zone (below the three-phase zone in Figures 1−3): the extraction of PA is low, and the distribution coefficients are less than 0.15. Therefore, the minimum content of phosphoric acid in a feed stream should be 67 mass %, so as to ensure a good extraction of PA and to have distribution coefficients higher than 0.59.

Conclusions

Liquid−liquid equilibrium data of the system water/PA/ DIPE were experimentally determined at (273.15, 283.15, and 293.15) K. Three two-phase zones and one three-phase zone were found at the three temperatures. Data obtained at 293.15 K are within an error of 5.7% when compared with those of Lozano et al.[4]

DIPE shows good extraction performance at high PA concentrations (more than 67%). The size of the three-phase zone decreases with temperature and is expected to disappear at 243.15 K.

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