

Two-Phase and Three-Phase Liquid-Liquid Equilibrium for Bis(2-methylpropyl) Ether + Phosphoric Acid + Water

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Solubility and tie line data have been measured for bis(2-methylpropyl) ether + phosphoric acid + water at 25, 51, and 60 °C. This system presents a three-phase region at temperatures greater than 49.5 °C. The extension of the two-phase region, as well as that of the three-phase region, increases with temperature (i.e., decreasing solubility). The behavior of this system has been compared to those of dipropyl ethers (bis(1-methylethyl) ether, dipropyl ether, and 1-methylethyl propyl ether), showing the influence of chain branching on the appearance of the three-phase region.

Introduction

A prime focus of our work is the study of liquid-liquid equilibrium of systems containing phosphoric acid (1-5) in connection with the wet process phosphoric acid purification (6-10). During this research, several systems have been shown to have three liquid phases at equilibrium (2, 3). This phenomenon has been observed for the system bis(1-methylethyl) ether + phosphoric acid + water (10).

In previous papers (2, 3) we showed the importance of the branching in the appearance of three-phase liquid-liquid equilibria. The objective of this work is the study of equilibrium in bis(2-methylpropyl) ether + phosphoric acid + water at different temperatures and comparison of the results to those with propyl ethers, in order to determine the influence of the structure of the solvent on the appearance of the three-phase region.

Materials

Bis(2-methylpropyl) ether was supplied by Aldrich Chemie (isobutyl ether, 99+%). The solvent was used as supplied, and the amount of volatile impurities (<1%) was confirmed by gas chromatography. Orthophosphoric acid (Merck, 99+%, p.a. grade) was used as supplied and titrated previously to the preparation of any mixture. The water used was bidistilled.

Procedure

A goldbrand ASTM calibrated mercury thermometer with an accuracy of better than ± 0.1 °C was used to measure the temperature. A thermostatic bath equipped with a Tectron 100 temperature controller with nominal temperature fluctuations lower than ± 0.05 °C was used.

The binodal curves were determined by the cloud point method (11). Mixtures of different compositions located in the heterogeneous region were titrated (titrated mixtures) with mixtures of other compositions located in the homogeneous region (titrating mixtures), at constant temperature, until the turbidity disappeared. The masses of titrated and titrating mixtures were measured. In order to minimize the errors, the relative position of titrated and titrating mixtures was selected as close as possible to the normal position of the binodal curve and at approximately the same distance from this curve. The amounts of titrated and titrating mixtures were always around 5 g, and their respective masses were determined to ± 0.001 g. Several points were triplicated, and the deviations observed (i.e., σ_{n-1}/\bar{x} , variation coefficient) for each composition were lower than 0.001. Tie lines and binary

Table 1. Binodal Curves for Bis(2-methyl propyl) Ether (1) + Phosphoric Acid (2) + Water (3)*

25 °C			51 °C			60 °C		
100w ₁	100w ₂	100w ₃	100w ₁	100w ₂	100w ₃	100w ₁	100w ₂	100w ₃
0.16	0	99.8	0.16	0	99.8	0.15	0	99.9
0.16	7.71	92.1	0.16	8.03	91.8	0.15	5.09	94.8
0.16	15.2	84.6	0.16	20.4	79.4	0.15	15.4	84.4
0.16	25.4	74.5	0.16	32.2	67.7	0.15	37.2	62.6
0.17	37.4	62.4	0.16	39.2	60.6	0.16	43.0	56.8
0.17	43.3	56.6	0.16	44.1	55.8	0.16	52.2	47.7
0.17	51.0	48.8	0.16	52.2	47.7	0.16	65.3	34.6
0.17	63.3	36.6	0.16	61.1	38.8	0.16	75.1	24.7
0.17	71.3	28.6	0.16	68.4	31.4	0.19	85.9	13.9
0.18	83.1	16.7	0.17	74.1	25.8	0.42	89.0	10.6
0.27	87.4	12.3	0.18	84.2	15.7	0.97	92.1	6.98
0.82	91.9	7.28	0.29	88.3	11.5	1.93	93.0	5.05
3.25	92.1	4.65	0.91	91.8	7.34	6.22	90.2	3.63
5.64	90.3	4.05	4.53	91.4	4.05	11.7	85.1	3.17
11.3	85.2	3.48	9.51	87.0	3.46	27.5	70.3	2.20
16.4	80.3	3.30	19.7	77.5	2.83	36.1	61.9	1.95
21.1	75.9	2.95	33.6	64.2	2.21	45.9	52.6	1.47
28.9	68.5	2.66	47.3	51.1	1.68	59.8	39.1	1.05
34.9	62.8	2.36	56.6	42.1	1.35	71.3	27.9	0.75
42.9	55.0	2.10	68.8	30.2	0.98	83.2	16.3	0.52
52.1	46.2	1.68	84.0	15.4	0.59	91.8	7.81	0.35
54.6	43.8	1.64	91.7	7.91	0.40	99.7	0	0.30
63.4	35.3	1.32	99.7	0	0.31			
72.1	26.9	1.03						
81.8	17.4	0.77						
90.3	9.21	0.54						
99.7	0	0.32						

* Compositions in mass fraction w .

solubility were measured by analyzing the phosphoric acid content in the conjugated phases, which were obtained from the mixtures of known composition, prepared within the heterogeneous region (and approximately around the midpoint of the tie lines). Phosphoric acid concentrations were obtained by potentiometric titration with NaOH of a known concentration (measured by using potassium hydrogen phthalate, ACS primary standard). The estimated precision of these determinations was ± 0.005 mass fraction. The amounts of solvent and water were deduced from the phosphoric acid concentration and the binodal curve. The phosphoric acid used for the preparation of any mixture was previously titrated with NaOH of a known concentration. Triplicated determinations of several tie lines showed variation coefficients of less than 0.005. Results for the phosphoric acid concentration are averages of two titrations.

Furthermore, the data of the composition of each tie line and the composition of the initial mixtures permit the amount

Table 2. Initial Mixtures for the Determination of the Tie Lines for Bis(2-methylpropyl) Ether (1) + Phosphoric Acid (2) + Water (3)^a

25 °C			51 °C			60 °C		
100w ₁	100w ₂	100w ₃	100w ₁	100w ₂	100w ₃	100w ₁	100w ₂	100w ₃
49.2	42.8	8.09	51.9	41.7	6.41	44.8	49.5	5.73
47.1	44.6	8.24	50.7	43.6	5.66	44.2	50.3	5.52
43.3	48.8	7.95	47.6	46.9	5.57	47.0	48.3	4.70
40.3	52.1	7.66	43.0	51.6	5.42	69.1	30.0	0.92
35.9	56.4	7.66	41.8	53.2	4.99	21.7	73.1	5.26
31.8	61.3	6.91	76.9	22.4	0.76	19.1	76.4	4.59
29.1	64.3	6.57	36.2	58.6	5.13	16.2	79.4	4.35
25.7	67.7	6.52	34.7	60.7	4.59	14.2	81.6	4.10
24.5	69.8	5.70	29.8	65.9	4.33	13.1	83.0	3.88
18.9	75.9	5.18	25.4	70.1	4.52			
14.3	80.6	5.02	22.7	73.0	4.28			
			18.5	77.2	4.38			
			14.5	81.1	4.44			

^a Compositions in mass fraction *w*.**Table 3. Tie Line Results for Bis(2-methylpropyl) Ether (1) + Phosphoric Acid (2) + Water (3)^a**

100w ₁ ^{or}	100w ₂ ^{or}	100w ₃ ^{or}	100w ₁ ^{aq}	100w ₂ ^{aq}	100w ₃ ^{aq}
25 °C					
99.5	0.17	0.33	0.19	84.0	15.8
98.6	1.05	0.35	0.20	84.2	15.6
94.6	4.94	0.43	0.20	85.4	14.4
86.9	12.4	0.65	0.21	86.3	13.5
79.6	19.6	0.83	0.24	86.8	13.0
67.3	31.5	1.17	0.28	87.5	12.2
59.3	39.3	1.45	0.33	88.0	11.7
52.1	46.2	1.73	0.40	88.7	11.0
46.6	51.5	1.90	0.52	89.8	9.73
35.0	62.6	2.41	0.71	91.0	8.26
27.0	70.3	2.75	0.79	91.9	7.36
51 °C					
99.6	0.09	0.30	0.23	87.3	12.5
99.0	0.70	0.31	0.27	88.3	11.4
96.4	3.27	0.32	0.29	88.7	11.0
88.9	10.6	0.48	0.35	89.5	10.2
84.7	14.7	0.54	0.46	90.1	9.43
84.7	14.7	0.54	69.5	29.6	0.90
69.5	29.6	0.90	0.46	90.1	9.43
63.5	35.4	1.11	0.60	90.5	8.95
51.7	46.9	1.45	0.72	91.0	8.26
46.3	52.1	1.69	0.75	91.2	8.03
39.8	58.3	1.93	0.82	91.7	7.44
32.8	64.9	2.27	0.85	92.1	7.04
26.1	71.3	2.61	1.02	92.5	6.47
60 °C					
99.4	0.30	0.30	0.31	89.7	9.99
98.2	1.51	0.31	0.37	90.2	9.43
97.1	2.60	0.31	0.54	90.5	8.94
97.1	2.60	0.31	42.0	56.3	1.72
42.0	56.3	1.72	0.54	90.5	8.94
35.8	62.3	1.93	0.85	91.6	7.55
30.4	67.4	2.13	0.96	92.4	6.63
25.9	71.8	2.29	1.12	92.6	6.25
22.2	75.3	2.51	1.47	92.9	5.68

^a Compositions in mass fraction *w*.

of organic and aqueous phases for each experiment to be evaluated, by solving the material balances for the three components. Experiments for determining the tie lines which lead to variation coefficients for the three amounts of the organic (or aqueous) phases higher than 1 mass % were rejected.

Results

All concentrations are determined as mass percentages and named as follows: w_i^f , where *f* stands for the phase (i.e., organic, *f* = or, and aqueous, *f* = aq, or light, *f* = l, and heavy, *f* = h) and *i* for the component.

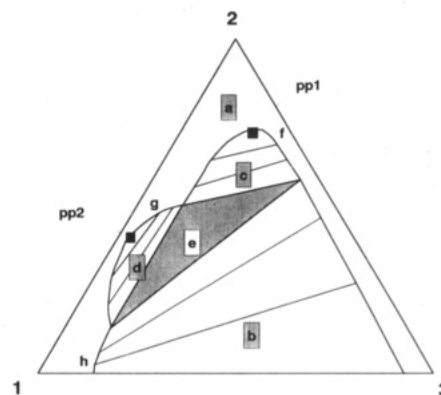


Figure 1. Equilateral triangle representation of a system showing three-phase equilibria as the system under study: (a) homogeneous region, (b–d) two-phase regions, (e) three-phase region, (pp1) plait point corresponding to zone c, (pp2) plait point corresponding to zone d.

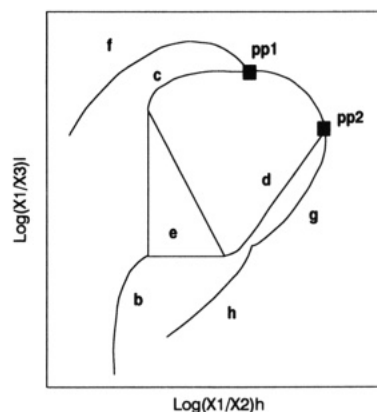


Figure 2. Hand's representation of a system such as that shown in Figure 1: (a) homogeneous region. (b–d) two-phase regions (e) three-phase region, (pp1) plait point corresponding to zone c, (pp2) plait point corresponding to zone d.

Table 1 shows the results of the binodal curve obtained by the cloud point method at 25, 51, and 60 °C. Table 2 shows the initial mixtures of bis(2-methylpropyl) ether (1) + phosphoric acid (2) + water (3) used for the determination of the tie lines. All the mixtures were prepared within the heterogeneous region defined by the binodal curve previously obtained. After phase separation, the phosphoric acid concentration was determined in both phases. Table 3 shows the w_2^f obtained by potentiometric titration, as well as w_1^f and w_3^f deduced from w_2^f and the binodal curve at 25, 51, and 60 °C.

Figure 1 shows a model of the behavior of a system, such as that of the present work (i.e., showing three phases at equilibrium), in a triangular representation. Five regions can be observed: one homogeneous region (a), three two-phase regions (b–d), and one three-phase region (e). Figure 2 shows a sketch of how the Hand representation of such a system should be, indicating the relationship among the different regions. Figure 3 shows how the distribution curve for a system such as that shown in Figure 1 should be. In order to build Figure 2, it was necessary to plot the data corresponding to the heavy phases on the horizontal axis and those corresponding to the light phases on the ordinate axis. In the case of Figure 3, heavy phases are on the vertical axis. Obviously three branches must appear, each one corresponding to each two-phase region, and the three phases at equilibrium define a triangle. In each representation, the vertices of these triangles are the origins of the three named branches.

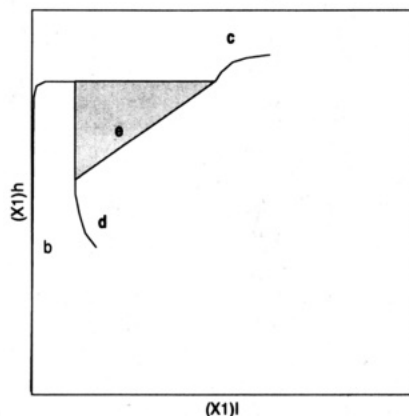


Figure 3. Distribution curve for a system such as that shown in Figure 1: (a) homogeneous region, (b-d) two-phase regions, (e) three-phase region.

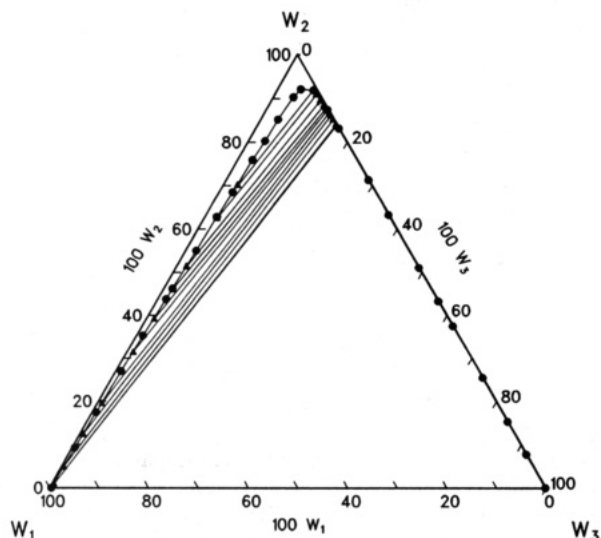


Figure 4. Solubility curve and tie lines for bis(2-methylpropyl) ether (1) + phosphoric acid (2) + water (3) at 25 °C: (▲) tie lines, (●) solubility points.

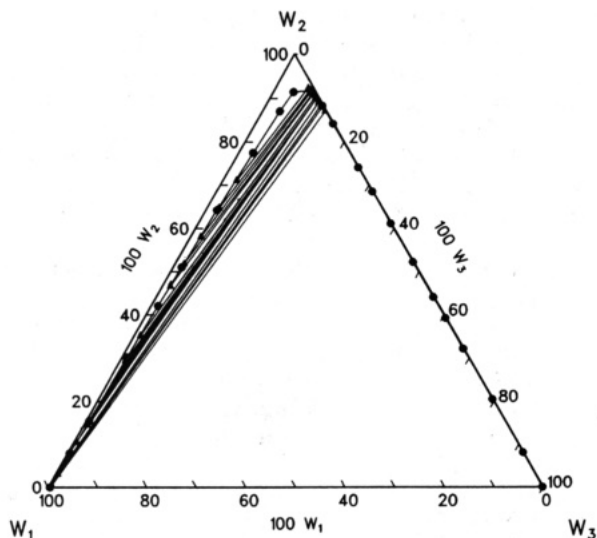


Figure 5. Solubility curve and tie lines for bis(2-methylpropyl) ether (1) + phosphoric acid (2) + water (3) at 51 °C, showing the three-phase region (shaded zone): (▲) tie lines, (●) solubility points.

Figures 4–6 show the binodal curve and the tie lines for the system bis(2-methylpropyl) ether + phosphoric acid + water at 25, 51, and 60 °C. The reliability of these results can be

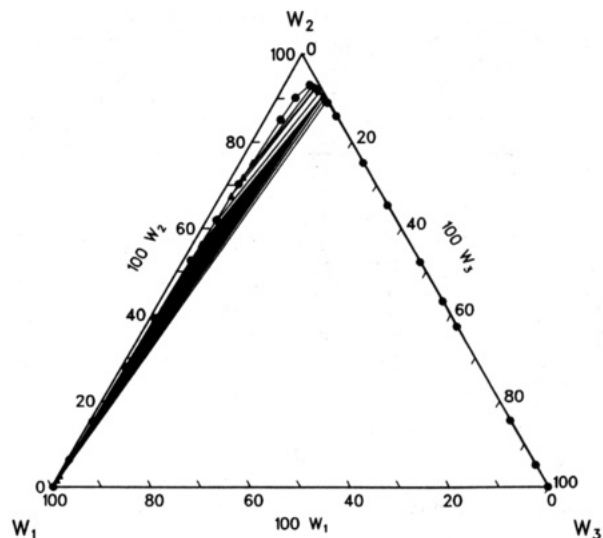


Figure 6. Solubility curve and tie lines for bis(2-methylpropyl) ether (1) + phosphoric acid (2) + water (3) at 60 °C, showing the three-phase region (shaded zone): (▲) tie lines, (●) solubility points.

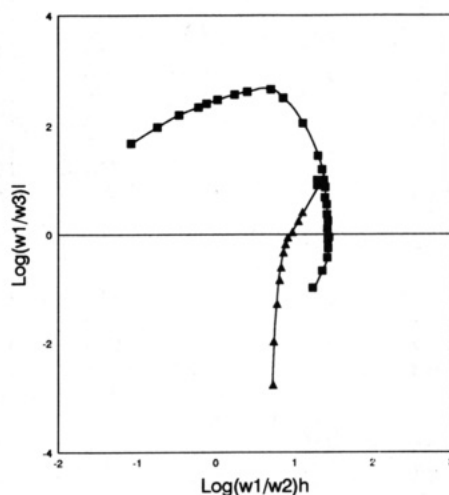


Figure 7. Solubility curve and tie lines for bis(2-methylpropyl) ether (1) + phosphoric acid (2) + water (3) at 25 °C in Hand's coordinates: (▲) tie lines, (■) solubility points.

Table 4. Plait Point Compositions in Mass Fraction w for Bis(2-methylpropyl) Ether (1) + Phosphoric Acid (2) + Water (3)

$100w_1$	$100w_2$	$100w_3$	$T/^\circ\text{C}$
7.5	88.6	3.9	25
4.5	91.4	4.1	51
8.9	87.7	3.4	60

ascertained by the plots of Hand (12), as shown in Figures 7–9, respectively. Plait point composition (mass %), obtained from the intersection of the straight final part corresponding to the tie lines with the curve corresponding to the binodal data (12), are shown in Table 4. The precision of these values depends on the distance of the required extrapolation, and these values must be considered as approximate.

Unlike systems with bis(1-methyl ethyl) ether and 1-methylethyl propyl ether (2, 3), it was impossible to obtain tie line values within the two-phase region which must be located at the left of the two organic phases in equilibrium with the aqueous phase, determining the three-phase region (region d in Figure 1). This shows that this region must be very small in this system.

In order to determine the temperature at which the three-phase region appears, a set of mixtures was prepared covering

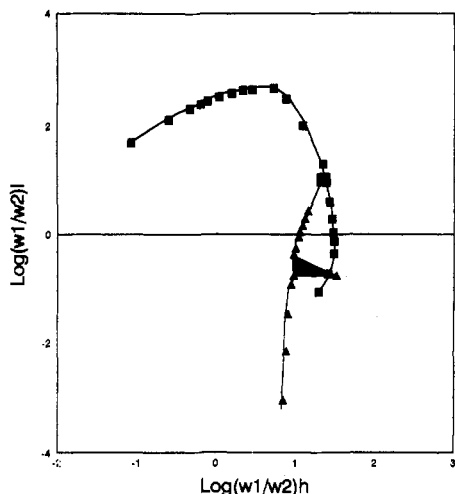


Figure 8. Solubility curve and tie lines for bis(2-methylpropyl) ether (1) + phosphoric acid (2) + water (3) at 51 °C in Hand's coordinates, showing the three-phase region (shaded zone): (▲) tie lines, (■) solubility points.

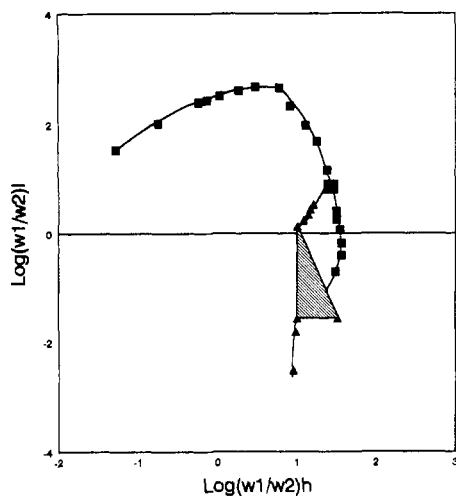


Figure 9. Solubility curve and the lines for bis(2-methylpropyl) ether (1) + phosphoric acid (2) + water (3) at 60 °C in Hand's coordinates, showing the three-phase region (shaded zone): (▲) tie lines, (■) solubility points.

the region of probable appearance of this phenomenon, and at small composition intervals. These samples were allowed to settle at different temperatures. By observing the number of phases present at equilibrium, we could deduce that the temperature at which this phenomenon appears is around 49.5 °C. These experiments were carried out also with dibutyl ether, and no evidence of three-phase equilibria was observed in the range of temperature studied (up to 70 °C).

Discussion

Figures 4–6 show the binodal curves and the tie line results for this system at the three temperatures studied. A slight variation of the binodal region with temperature can be observed. Figure 10 shows the distribution curves (w_2^{aq} plotted against w_2^{or}) for this system at the three temperatures. The unusual feature is the apparition of the three liquid phases at equilibrium at 51 and 60 °C, and the marked increase in the amplitude of this zone with an increase in temperature. In the two-phase region the three curves are very similar, with a slight decrease in the solubility in the organic phase when increasing the temperature (i.e., higher w_2^{aq} for a given w_2^{or}).

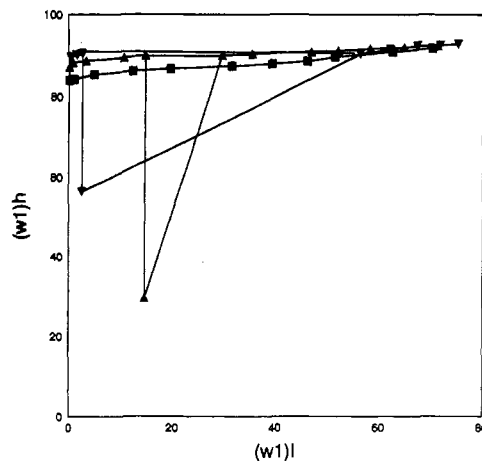


Figure 10. Distribution curves for bis(2-methylpropyl) ether (1) + phosphoric acid (2) + water (3): (■) 25 °C, (▲) 51 °C, (▼) 60 °C.

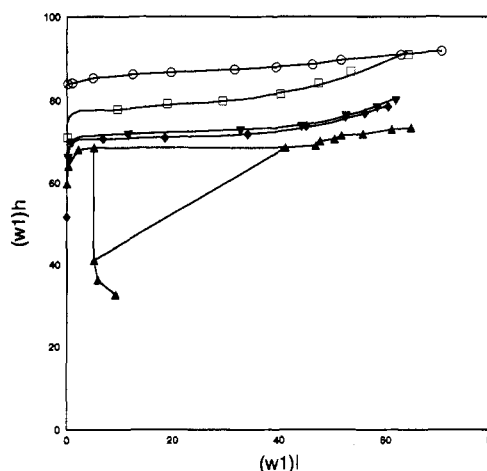


Figure 11. Distribution curves for ternary systems for the type ether (1) + phosphoric acid (2) + water (3) at 25 °C: (●) bis(2-methylpropyl) ether, (■) dibutyl ether, (▲) bis(1-methylethyl) ether, (◆) dipropyl ether, (▼) dipropyl ether with around 6% of the isomer 1-methylethyl propyl ether as supplied by Merck.

Figure 11 shows the distribution curves of this system compared to other ethers studied at 25 °C previously (dibutyl ether (S), bis(1-methylethyl) ether (2), dipropyl ether, and dipropyl ether with around 6% of the isomer 1-methylethyl propyl ether as supplied by Merck (3)). There is a lower solubility of phosphoric acid in dipropyl ether than in bis(1-methylethyl) ether in the aqueous phase (i.e., the distribution curve for dipropyl ether lies above that of bis(1-methylethyl) ether). In the case of butyl ethers, however, the behavior is the opposite, as dibutyl ether dissolves more phosphoric acid in the organic phase.

Concerning the three liquid phases at equilibrium, it can be concluded that bis(1-methylethyl) ether shows a wider three-phase region than dipropyl ether with 6% of the isomer 1-methylethyl propyl ether, and this shows a wider region than bis(2-methylpropyl) ether. Furthermore, the temperature at which this feature appears is lower for bis(1-methylethyl) ether than for dipropyl ether with 6% of the isomer 1-methylethyl propyl ether and bis(1-methylpropyl) ether. It can be concluded that the branched methyl group adjacent to an ether oxygen is more incompatible with phosphoric acid and water than the propyl group, and that the isobutyl group is more compatible with phosphoric acid and water than the isopropyl group. The systems with bis(1-methylether) ether, dipropyl ether with 6% of the isomer

1-methylethyl propyl ether, and bis(2-methylpropyl) ether with water and phosphoric acid have been studied, and the three liquid phase phenomenon shows a maximum for bis-(1-methylethyl) ether (two branched methyl groups next to the oxygen), followed by dipropyl ether with 6% of the isomer 1-methylethyl propyl ether (only 6% of the branched isomer), and a minimum for bis(2-methylpropyl) ether (two branched methyl groups separated by one methylene group from the oxygen). From these results it is concluded that the branched methyl group next to the oxygen is the most effective in producing this effect. Work will be continued with ethers of different structures and chain branching in order to obtain a better understanding of this phenomenon.

Registry Numbers Supplied by Author. Phosphoric acid, 7664-38-2; bis(2-methylpropyl) ether, 628-55-7; dibutylether, 142-96-1, bis(1-methylethyl) ether, 108-20-3; dipropyl ether 111-43-3.

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