Ternary Liquid Equilibria of the Water–Phosphoric Acid–Isoamyl Alcohol, Cyclohexanol, or Methyl Isobutyl Ketone Systems at 35°C.

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Liquid-liquid equilibria of the three ternary systems, water-phosphoric acid-isoamyl alcohol, or cyclohexanol, or methyl isobutyl ketone have been studied at 35°C. The tie-line data and plait points are determined. Isoamyl alcohol is a good solvent for phosphoric acid.

IN THE preceding paper (3), the liquid equilibria for the ternary systems, water-phosphoric acid-1-butanol or butyl acetate or methyl ethyl ketone have been studied. In this continuation of the work, the authors studied the equilibria of the three ternary systems, water-phosphoric acid-isoamyl alcohol or cyclohexanol or methyl isobutyl ketone at 35° C.

EXPERIMENTAL

Materials. Analar grade phosphoric acid (British Drug House Co., India) containing 88 weight % of phosphoric acid and not more than 0.1% impurities is used directly. Reagent grade cyclohexanol (E. Merck Co., Germany), reagent grade (B. D. H.) methyl isobutyl ketone, and reagent grade isoamyl alcohol are kept over anhydrous sodium sulfate for 24 hours, filtered, and distilled at atmospheric pressure in a Quickfit fractionating column. The physical properties of these materials are compared with the literature values in Table I. The refractive index is measured for sodium light with an Abbé precision refractometer calibrated to 0.001. The fourth decimal place is obtained by visual interpolation only.

The binodal curve data are determined at 35° C. for these three systems by the cloud point method and plotted in Figures 1, 2, and 3. The tie-line data are obtained by the analysis of the aqueous and organic phases for the phosphoric acid content (2) and plotted on Hand's (1) and Othmer-Tobias (4) coordinates in Figures 4 and 5. All these data are taken at $35^{\circ} \pm 0.01^{\circ}$ C. The plait point is determined by an empirical treatment of the tieline data (5). The distribution and the selectivity diagrams for these three systems are given in Figures 6 and 7.

The standard deviations for the binodal data and the tie-line data, obtained by an error analysis on the basis of phosphoric acid content, are 0.007, 0.08(aqueous phase), and 0.18(organic phase), respectively.

Table I. Physical Properties of Materials (6)

| | Normal Boiling Point, ° C. | | Density at 35° C., Grams per Ml. | | Refractive Index at 35° C. | | Viscosity at 35° C., Cp.ª | |
|--|-------------------------------|-------------------------|-------------------------------------|--------------------------------------|-------------------------------|--------------------------------------|---|-------------------------------|
| | Exptl. | Lit. | Exptl. | Lit. | Exptl. | Lit. | Exptl. | Lit. |
| Isoamyl alcohol Cyclohexanol Methyl isobutylketone | $132 \\ 161.5 \\ 116$ | $132 \\ 161.1 \\ 115.7$ | 0.7979 0.9378 0.7875 | $0.7981^{b}\ 0.9377^{b}\ 0.7871^{b}$ | $1.4008 \\ 1.4609 \\ 1.3882$ | $1.4011^{b}\ 1.4611^{b}\ 1.3883^{b}$ | $\begin{array}{c} 3.39\\ 25.42\\ \ldots\end{array}$ | 3.24° 25.5° |

^a Cp. = Centipoise. ^bObtained by using temperature correction.

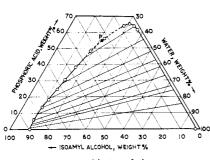


Figure 1. Equilibria of the system water-phosphoric acid-isoamyl alcohol at 35° C.

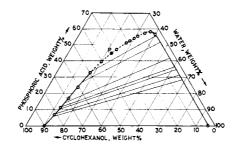
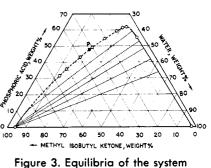


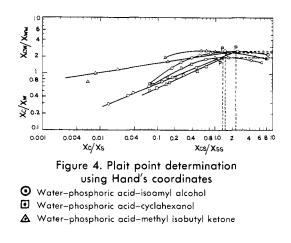
Figure 2. Equilibria of the system water-phosphoric acid-cyclohexanol at 35° C.



water–phosphoric acid–methyl isobutyl ketone at 35°C.

Table II. Binodal Data at 35° C.

| Data in wt. % | | | | | | |
|--|---|---|--|--|--|--|
| Water | Phosphoric Acid | Solvent | | | | |
| | | Isoamyl Alcohol | | | | |
| $\begin{array}{c} 10.24\\ 9.14\\ 10.43\\ 11.20\\ 12.76\\ 13.95\\ 15.75\\ 18.38\\ 21.86\\ 22.10\\ 28.38\\ 30.60\\ 30.23\\ 36.92\\ 97.90\end{array}$ | $\begin{array}{c} 0.00\\ 6.02\\ 13.24\\ 18.06\\ 24.43\\ 30.06\\ 38.15\\ 48.56\\ 56.13\\ 55.54\\ 63.98\\ 65.33\\ 67.25\\ 61.27\\ 0.00\\ \end{array}$ | $\begin{array}{c} 89.76\\ 84.84\\ 76.33\\ 70.74\\ 62.81\\ 55.99\\ 46.10\\ 33.06\\ 22.01\\ 22.36\\ 7.64\\ 4.07\\ 2.52\\ 1.81\\ 2.10\\ \end{array}$ | | | | |
| | | Cyclo- hexanol | | | | |
| $\begin{array}{c} 9.86 \\ 11.93 \\ 12.77 \\ 13.97 \\ 16.06 \\ 17.79 \\ 20.16 \\ 24.18 \\ 27.55 \\ 28.68 \\ 30.17 \\ 31.45 \\ 34.59 \\ 36.50 \\ 39.72 \\ 96.55 \end{array}$ | $\begin{array}{c} 0.00\\ 6.33\\ 11.20\\ 17.18\\ 23.26\\ 32.99\\ 39.51\\ 47.28\\ 51.05\\ 52.18\\ 53.95\\ 55.21\\ 56.57\\ 58.19\\ 56.94\\ 0.00\\ \end{array}$ | $\begin{array}{c} 90.14\\ 81.74\\ 76.03\\ 68.85\\ 60.68\\ 49.22\\ 40.33\\ 28.54\\ 21.40\\ 19.14\\ 15.88\\ 13.34\\ 8.84\\ 5.31\\ 3.34\\ 3.45\end{array}$ | | | | |
| | | Methyl Isobutyl Ketone | | | | |
| $\begin{array}{c} 3.53 \\ 5.70 \\ 12.21 \\ 13.88 \\ 17.22 \\ 20.73 \\ 24.62 \\ 28.70 \\ 30.95 \\ 32.28 \\ 41.20 \\ 97.96 \end{array}$ | $\begin{array}{c} 0.00\\ 10.85\\ 31.52\\ 35.24\\ 42.99\\ 49.26\\ 54.66\\ 59.34\\ 61.32\\ 61.94\\ 55.42\\ 0.00\\ \end{array}$ | $\begin{array}{c} 96.47\\ 83.45\\ 56.27\\ 50.88\\ 39.79\\ 30.01\\ 20.72\\ 11.96\\ 7.73\\ 5.78\\ 3.38\\ 2.04 \end{array}$ | | | | |



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Table III. Tie-Line Data at 35° C.

Data in wt. %

| Solvent Layer | | | Water Layer | | | |
|-----------------|-----------|---------|---------------------------------------|--------|--------------------|--|
| Phosphoric | | | Phosphoric | | | |
| Water | acid | Solvent | Water | acid | Solvent | |
| Isoamyl Alcohol | | | | | Isoamyl Alcohol | |
| 10.36 | 1.24 | 88.40 | 82.60 | 15.68 | 1.72 | |
| 9.84 | 2.66 | 87.50 | 74.10 | 24.07 | 1.83 | |
| 10.03 | 3.27 | 86.70 | 72.00 | 26.27 | 1.73 | |
| 9.13 | 5.87 | 85.00 | 65.10 | 32.91 | 1.99 | |
| 9.48 | 9.52 | 81.00 | 60.00 | 38.23 | 1.77 | |
| 9.99 | 13.81 | 76.20 | 56.00 | 42.60 | 1.40 | |
| 11.50 | 19.50 | 69.00 | 50.20 | 47.83 | 1.97 | |
| 13.02 | 28.48 | 58.50 | 43.00 | 55.10 | 1.90 | |
| 17.17 | 44.33 | 38.50 | 34.00 | 63.85 | 2.15 | |
| | Plai | 55. | 23% water 25% phosph 52% isoamy | | | |
| С | YCLOHEXAN | OL | | | Cyclo- hexanol | |
| 11.32 | 6.18 | 82.50 | 68,50 | 28.47 | 3.03 | |
| 11.84 | 7.66 | 80.50 | 65.70 | 31.25 | 3.05 | |
| 12.31 | 10.89 | 76.80 | 62.00 | 34.97 | 3.03 | |
| 12.86 | 11.94 | 75.20 | 60,60 | 36.35 | 3.05 | |
| 10.00 | | | | - 5100 | 5100 | |

13.30

16.42

17.92

14.70

27.28

33.68

Plait Point 22.67% water 44.42% phosphoric acid 32.91% cyclohexanol

55.00

45.50

40.90

41.99

51.40

55.86

3.01

3.10

3.24

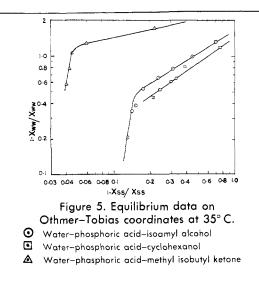
72.00

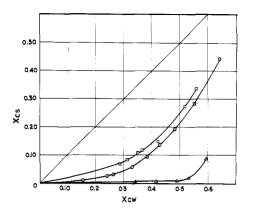
56.30

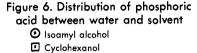
48.40

| Methyl Isobutyl Ketone |
|------------------------------|
| 2.94 |
| 2.90 |
| 3.04 |
| 3.16 |
| 3.78 |
| |

Plait Point 20.19% water 47.86% phosphoric acid 31.95% methyl isobutyl ketone







▲ Methyl isobutyl ketone

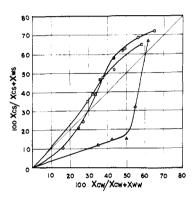


Figure 7. Selectivity diagrams

- Water-phosphoric acid-isoamyl alcohol
- Water-phosphoric acid-cyclohexanol
- ▲ Water-phosphoric acid-methyl isobutyl ketone

DISCUSSION

Figures 6 and 7 show that the distribution coefficient of phosphoric acid between water and methyl isobutyl ketone and the selectivity of the latter for the solute are low compared with those of isoamyl alcohol and cyclohexanol. So these disadvantages curtail the usefulness of this solvent.

At low initial concentrations of phosphoric acid, cyclohexanol has a higher distribution coefficient and selectivity than isoamyl alcohol, but, at higher initial concentrations, the distribution coefficients and selectivity values are nearly the same for cyclohexanol and isoamyl alcohol. The viscosity of cyclohexanol is about eight times that of isoamyl alcohol. Hence, isoamyl alcohol is a good solvent for phosphoric acid because of its higher capacity for the solute, low viscosity, and low boiling point.

NOMENCLATURE

- X_{cw} = weight fraction of solute in water-rich phase
- weight fraction of water in water-rich phase = $\begin{array}{rcl} X_{uw} & = \\ X_{cs} & = \\ X_{ss} & = \\ X_{c} & = \\ X_{u} & = \\ X_{s} & = \end{array}$
- weight fraction of solute in solvent-rich phase
- weight fraction of solvent in solvent-rich phase
- weight fraction of solute
- = weight fraction of water
- weight fraction of solvent

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