the pressure approaches the solvent critical point. Therefore, in this exercise, the fugacity coefficients calculated by using a modified Redlich–Kwong equation of state (7) consistent with the vapor–liquid equilibria data of this study were used to yield values of the Henry's law constant more consistent with the criteria set forth by Renon et al. (2).

Acknowledgment

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Ternary Equilibrium for the System Water/Methyl Isobutyl Ketone/2-Ethyl-2-(hydroxymethyl)-1,3-propanediol

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Liquid–liquid equilibrium has been determined for the ternary system water/methyl isobutyl ketone/2-ethyl-2-(hydroxymethyl)-1,3-propanediol at 25 and 70 °C. The latter compound is known commercially as trimethylolpropane.

Cyclohexanol (7) has been tested as a solvent for extracting 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (TMP), but the two liquid phase region for this system is not very large. It is the purpose of the present paper to show the behavior of another solvent in the extraction of TMP.

Experimental Procedure

The water was purified by distilling it in the presence of potassium permanganate. The methyl isobutyl ketone was supplied by Merck as a spectroscopic reagent. The TMP was purified by extracting impurities with methyl isobutyl ketone followed by drying at 100 °C for 24 h. The melting point for the final TMP was 57–57.5 °C.

The experiments were carried out in a small glass stirring vessel of 100-mL volume, provided with a circulating jacket. The circulating-water temperature was controlled by a recirculating bath. A PTFE-covered magnetic bar was used for stirring.

The points on the binodal curve were first obtained by using the titration method. Tie lines were obtained secondly by preparing overall mixtures of the three components, which would yield an overall composition within the two liquid phase region, stirring them for 4 h, and allowing the mixture to settle for 6 h.

Table I. Liquid-Liquid Equilibrium Composition Data ($T = 25\ °C$)

binodal curve (wt fraction)		
water	TMP	MIBK
0.981		0.019
0.877	0.097	0.026
0.779	0.195	0.026
0.675	0.290	0.035
0.568	0.380	0.052
0.467	0.464	0.069
0.358	0.536	0.106
0.253	0.584	0.163
0.166	0.585	0.249
0.081	0.495	0.424
0.046	0.382	0.572
0.033	0.291	0.676
0.028	0.195	0.777
0.029	0.097	0.874
0.021		0.979

tie lines (wt fraction)						distribution coeff, ketone/water
water-rich phase			ketone-rich phase			
water	TMP	MIBK	water	TMP	MIBK	water
0.869	0.110	0.021	0.021	0.008	0.971	0.071
0.573	0.378	0.049	0.019	0.037	0.944	0.097
0.477	0.458	0.065	0.022	0.048	0.930	0.105
0.282	0.574	0.144	0.022	0.078	0.900	0.136
0.168	0.582	0.250	0.025	0.122	0.853	0.210
0.119	0.556	0.325	0.024	0.186	0.790	0.335
0.073	0.487	0.440	0.027	0.227	0.746	0.466
0.034	0.316	0.650	0.028	0.247	0.725	0.782

At the end of each experiment, samples were taken from both phases and weighed, and then both water and solvent were
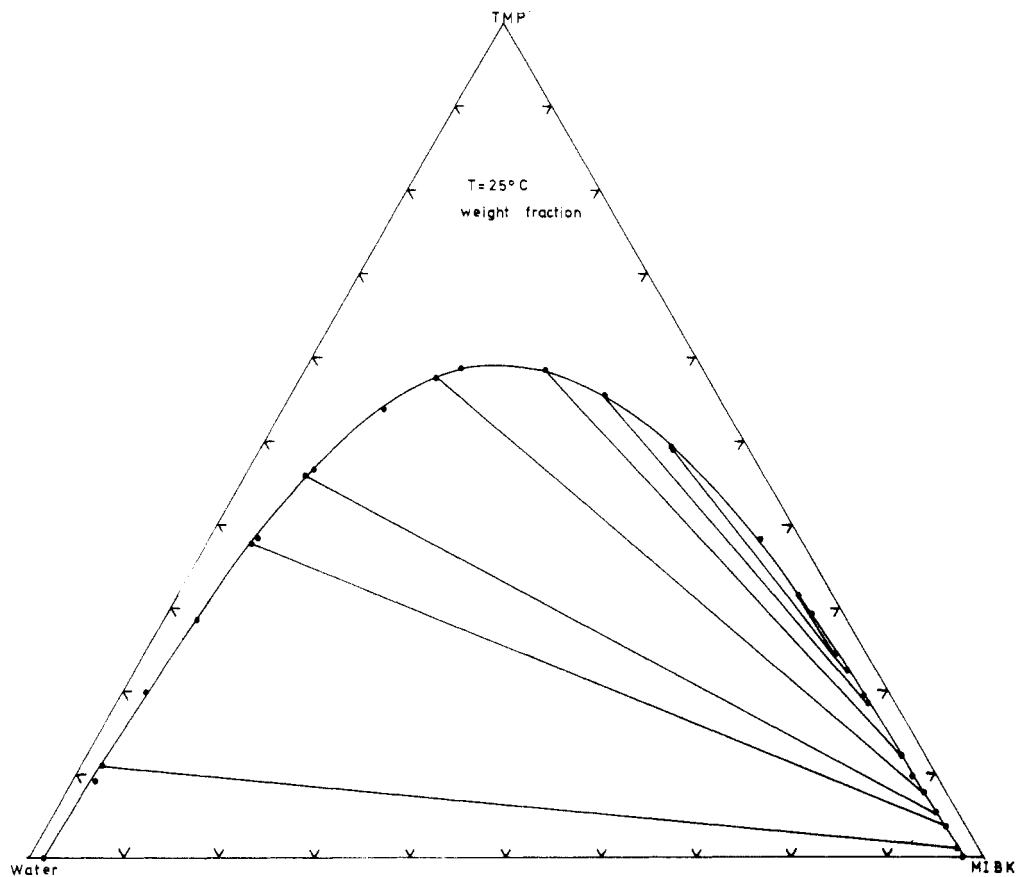
Figure 1. Two liquid phase region at 25 °C for the system water/methyl isobutyl ketone/trimethylolpropane.
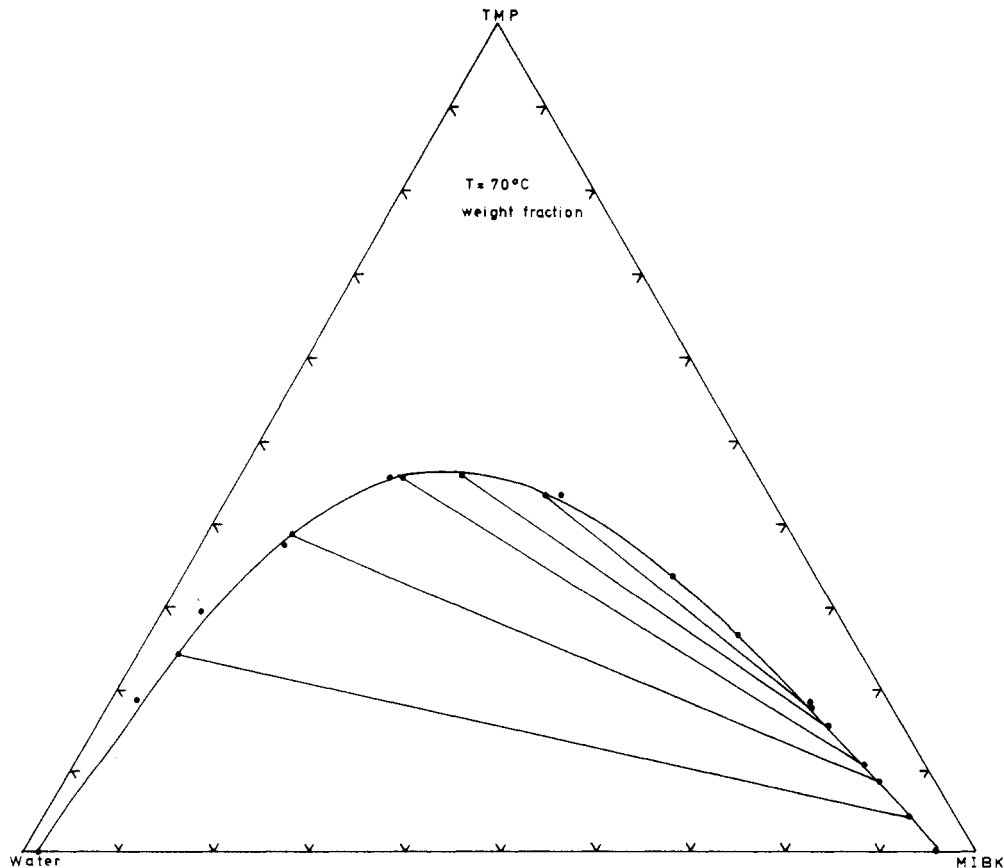

Figure 2. Two liquid phase region at 70 °C for the system water/methyl isobutyl ketone/trimethylolpropane.

Table II. Liquid-Liquid Equilibrium
Composition Data (T = 70 °C)

binodal curve (wt fraction)		
water	TMP	MIBK
0.983		0.017
0.788	0.188	0.024
0.663	0.299	0.038
0.538	0.378	0.084
0.385	0.458	0.157
0.217	0.435	0.348
0.150	0.340	0.510
0.119	0.264	0.617
0.081	0.183	0.736
0.040		0.960

tie lines (wt fraction)						distribution coeff, ketone/water
water-rich phase			ketone-rich phase			
water	TMP	MIBK	water	TMP	MIBK	
0.716	0.242	0.042	0.048	0.042	0.910	0.174
0.529	0.385	0.086	0.060	0.084	0.856	0.218
0.371	0.455	0.174	0.064	0.106	0.830	0.233
0.312	0.469	0.219	0.081	0.154	0.765	0.328
0.231	0.439	0.330	0.086	0.174	0.740	0.396

evaporated to dryness at 100 °C. Using these data and the binodal curve, we obtained the tie lines. The error in the determination of the equilibrium diagram was within 5%.

Results

Experimental data for the equilibrium of the ternary system

water/methyl isobutyl ketone/TMP in the two liquid phase region were obtained. The binodal curve as well as the tie lines were determined, and the distribution coefficients were calculated. The results are presented in Tables I and II. In Figures 1 and 2 the ternary diagrams at 25 and 70 °C are shown, respectively.

Conclusions

The two liquid phase region for this system is larger than the one for the cyclohexanol as a solvent (1), even at 70 °C. Nevertheless, the distribution coefficients for the present system are less than those for the cyclohexanol system. Clearly the ketone does not offer a great advantage over cyclohexanol, but it has to be taken into account that TMP is normally present with a formate salt in commercial process solutions, and this will tend to increase the distribution coefficient and enlarge the two liquid phase region.

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Ternary Equilibrium for the System Water/Cyclohexanol/2-Ethyl-2-(hydroxymethyl)-1,3-propanediol

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Liquid-liquid equilibrium at 25 and 35 °C has been determined for the ternary system water/cyclohexanol/2-ethyl-2-(hydroxymethyl)-1,3-propanediol. The latter is known commercially as trimethylolpropane.

The ability of cyclohexanol to extract trimethylolpropane from water was determined at two temperatures for the purpose of exploring its capability to serve as a commercial process solvent.

Experimental Procedure

The water was purified by distilling it in the presence of potassium permanganate. Cyclohexanol was fractionally distilled in the presence of calcium oxide. The melting point obtained was 25.1 °C, and a chromatographic analysis showed a purity of 99.9%. The 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (TMP) was purified by extracting impurities with methyl isobutyl ketone followed by drying at 100 °C for 36 h. The melting point for the final TMP was 57-57.5 °C.

The experiments were carried out in a small glass stirring vessel of 100-mL volume, provided with a cooling jacket. The cooling-water temperature was controlled by means of a recirculating constant-temperature bath. A PTFE-covered mag-

netic bar was used for stirring.

To determine the time needed for the mixture to reach equilibrium, we measured the refractive index of one of the phases as a function of time; the minimum contact time to achieve equilibrium was 2 h. Nevertheless, stirring was kept for 4 h, and the mixture was allowed to settle for 6 h more.

Equilibrium data were obtained by preparing mixtures of known overall composition, stirring for 4 h, and settling for 6 h at constant temperature (25 and 35 °C, ±0.1 °C).

At the end of each experiment, samples were taken from both phases and were analyzed by means of nuclear magnetic resonance (NMR) (1). This analytical method allowed us to measure the proton contribution of each functional group in the molecules present, and from there the mass fraction of each component in the phase was determined. The accuracy of the analytical method was tested by comparing the binary equilibrium for the system water/cyclohexanol, whose data were taken from the literature; the error was within 2%. Determination of the composition in a ternary mixture at equilibrium using the NMR method has been successfully used elsewhere (2, 3).

Results

In the present work, experimental data for the composition at equilibrium of the system water/cyclohexanol/TMP at the two