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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 magnetic 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

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Table I. Liquid-Liquid Equilibrium Composition Data (T = 25 °C)[a]

overall composition			water-rich phase			alcohol-rich phase			distribution coeff
A	B	C	A	B	C	A	B	C	alc/water
0.515	0.485	0.000	0.964	0.036	0.000	0.116	0.884	0.000	
0.461	0.481	0.058	0.877	0.049	0.074	0.157	0.787	0.056	0.757
0.431	0.439	0.130	0.802	0.046	0.152	0.192	0.696	0.112	0.737
0.423	0.390	0.187	0.735	0.061	0.204	0.238	0.588	0.174	0.853
0.378	0.386	0.236	0.632	0.100	0.266	0.312	0.464	0.224	0.836

[a] A = water; B = cyclohexanol; C = TMP. Composition in wt fraction.

Table II. Liquid-Liquid Equilibrium Composition Data (T = 35 °C)[a]

overall composition			water-rich phase			alcohol-rich phase			distribution coeff
A	B	C	A	B	C	A	B	C	alc/water
0.492	0.508	0.000	0.962	0.038	0.000	0.151	0.849	0.000	
0.486	0.483	0.031	0.923	0.045	0.032	0.160	0.814	0.026	0.813
0.450	0.466	0.084	0.865	0.046	0.089	0.171	0.746	0.083	0.933
0.434	0.434	0.132	0.809	0.054	0.137	0.211	0.661	0.128	0.934
0.418	0.391	0.191	0.720	0.072	0.208	0.259	0.559	0.182	0.875
0.393	0.375	0.232	0.650	0.100	0.250	0.313	0.463	0.224	0.896

[a] A = water; B = cyclohexanol; C = TMP. Composition in wt fraction.

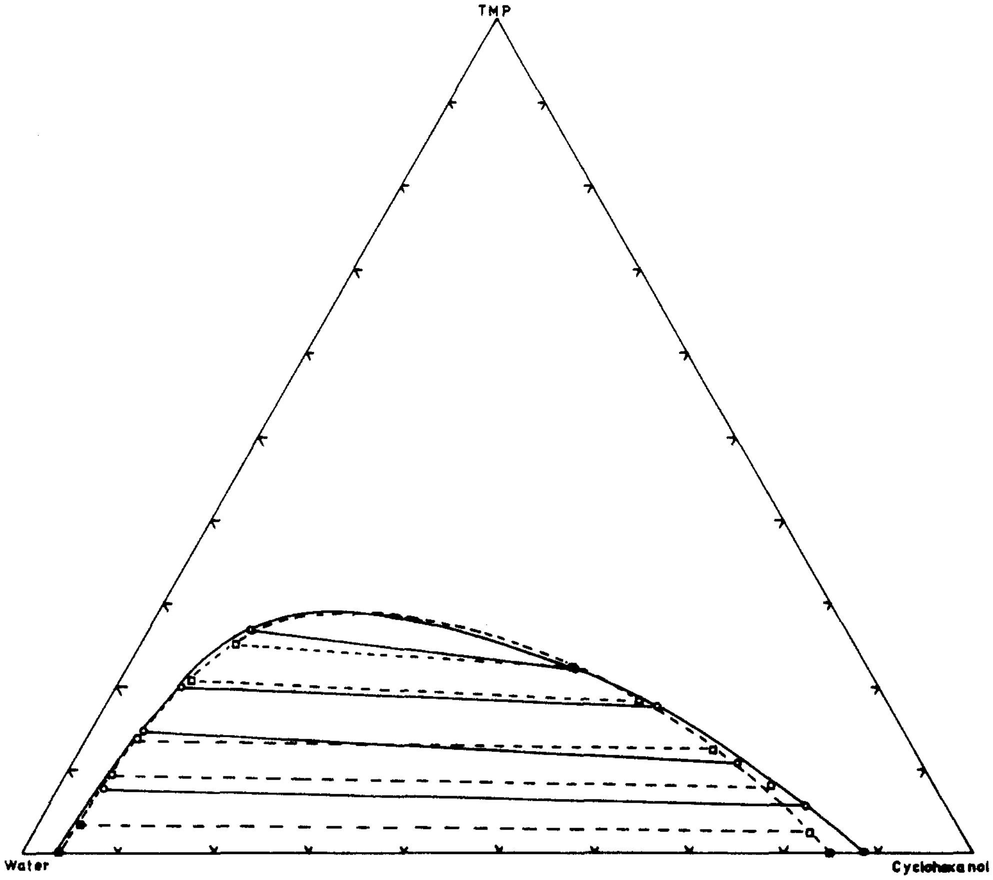

Figure 1. Liquid-liquid equilibria for the system water/cyclohexanol/trimethylolpropane: (—○—) 25 °C; (-□-) 35 °C. Composition in wt %.

liquid phase region were obtained. Tie lines were determined, and distribution coefficients were calculated. The results are given in Tables I and II. In Figure 1 the ternary diagrams at 25 and 35 °C are shown.

Conclusions

It is evident from Figure 1 that the two liquid phase region is not very large for the present system. Hence aqueous solutions with a composition higher than 35 wt.% of TMP cannot be extracted. Furthermore, at 25 °C the tie lines favor the aqueous phase, while at 35 °C the distribution coefficients are close to unity. Comparing the distribution coefficients at 25 and 35 °C, one would expect that an increase in temperature will make distribution coefficients larger than one, and this would help to extract TMP.

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method used in the present work.

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Partial Miscibility Behavior of the Methane–Ethane–*n*-Octane System

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The phase behavior of the ternary system methane–ethane–*n*-octane was studied in the region of immiscibility. Two liquid phases and a vapor phase (L_1–L_2–V) were found to exist in this system in a region extending from 197.8 K and 43.3 atm to ~222 K and 69 atm. Pressure and liquid-phase composition and liquid-phase molar volume data for both of the coexisting liquid phases were measured and are presented as a function of temperature. The immiscibility area was found to be bounded by loci of K points (L_1–L_2 = V), Q points (S–L_1–L_2–V), and LCST points (L_1 = L_2–V).

This study of the methane–ethane–*n*-octane system was undertaken to investigate liquid–liquid–vapor (L–L–V) phenomena that can occur in liquified natural gas (LNG) and natural gas liquid systems. This information is expected to serve as fundamental data with which to evaluate correlations purporting to describe L–L–V behavior in the design of LNG systems.

There are a limited number of binary liquid–liquid–vapor phase equilibria data available for systems rich in methane and ethane relevant to LNG systems. A L–L–V locus has been observed in the system methane–hexane (*1*) and methane–toluene (*2*). Each of these loci terminates at both ends with critical points (L–L = V and L = L–V). A L–L–V locus is observed in the system methane–*n*-heptane (*3*) terminated by a L–L = V critical point and a Q (S–L–L–V) point. Solutes beginning with *n*-octane and higher form crystals before they can become immiscible with methane (*4*).

With ethane as the solvent, solutes beginning with *n*-C_{19} and higher demonstrate L–L–V behavior (*5–7*). With propane, only very long-chain hydrocarbons (*n*-C_{37} and higher) will demonstrate L–L–V behavior (*8*).

Very few L–L–V data exist for ternary or more complex systems relevant to LNG systems. A few observations of L–L–V behavior were made during S–L–V studies (*9*, *10*), but many data were taken.

Experimental Section

Materials and Analyses. The methane used in this study was Linde "Ultra Pure" grade stated to be 99.97 mol % pure. The ethane was a Matheson CP grade gas stated to be 99 mol % pure. The methane was used without further purification. However, the ethane was prepared for use by flashing it from the cylinder at room temperature to a 3000-mL storage reservoir maintained at 273.16 K. The vapor phase was then vented from the reservoir to remove the impurities remaining in the vapor phase after liquefaction from the cylinder. The ethane was further purified through activated carbon before use.

Dew-point bubble-point experiments were carried out for both pure gases. For example at 185.06 K, methane exhibited a difference between dew-point and bubble-point pressures of less than 0.20 atm. The ethane had dew-point and bubble-point pressures which differed by 0.24 atm at 273.16 K. The vapor pressures at 50 vol % liquid agreed well with recent literature values for both gases, and the critical temperature and pressure of the ethane was within 0.2 K and 0.1 atm of those given by the National Bureau of Standards (*11*).

The *n*-octane was purchased from the Humphrey-Wilkinson Chemical Co. It had a stated purity of 99 mol %. The measured air-saturated freezing point agreed to within 0.2 K of current literature values. The *n*-octane was used without further purification.

Apparatus and Procedure. The apparatus used in this study was the same as that used by Kohn and others in cryoscopic studies (*9*, *12*, *13*). Briefly, the procedure involved charging and carefully weighing an amount of *n*-octane in a 10-mL glass cell. This glass cell had previously been calibrated for visual volumetric readings. The cell was then placed in a thermostated liquid bath and chilled until the octane froze. The air in the cell was then removed with a vacuum pump. Separately, ethane and then methane were added to the cell from reservoirs maintained at a convenient pressure by a manually operated syringe-type pump. The *n*-octane was melted by the solvents while being mixed in the cell with a steel ball actuated by an external magnet. The use of separate addition systems for methane and ethane gave improved experimental flexibility.

To obtain a Q point (S–L_1–L_2–V), we lowered the temperature until crystals formed and then raised it until only a trace of crystals remained. It was possible to detect visually as little as a few tenths of a milligram of solid octane in the cell. This was regarded as an equilibrium crystal point (Q point) if two liquid phases were present. By judiciously selecting the amounts of *n*-octane, ethane, and methane added to the cell, we made one of the liquid phases occupy at least 60% (usually more than 80%) of the cell volume. The concentration of ethane in the vapor phase was estimated with the aid of existing literature on methane–ethane vapor–liquid equilibria (*14*). An insignificant amount of octane was assumed to be in the vapor space.

Type-K data points (L_1–L_2 = V) were obtained by increasing the temperature until a sizable L_2 phase (the *n*-octane lean phase) went critical with the vapor phase. This was accompanied with the usual opalescence as the L_2 phase became identical with the vapor phase. For data points where the solute

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