

Breaking the Trimethyl Borate-Methanol Azeotrope with Supercritical Methane

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Supercritical methane is used to extract trimethyl borate (TMB) from methanol and to break the TMB-methanol azeotrope. The ability to extract TMB from methanol is a strong function of the operating pressure and is directly related to the phase behavior of the TMB-methane and methanol-methane systems and to the types of specific interactions that occur between TMB, methanol, and methane. In the TMB-methanol-methane system the interactions between methane and TMB are so strong that even as the TMB is depleted from the methanol-rich liquid phase its concentration in the methane-rich extract phase remains constant. Solubility isotherms, selectivity data, and distribution coefficient information are presented for the TMB-methane and TMB-methanol-methane systems at 0, 35, and 55 °C to pressure levels of 250 bar.

Introduction

A substantial number of studies were performed in the late 1970s and early 1980s on the application of supercritical fluid (SCF) extraction to the separation of mixtures normally processed by distillation, especially alcohol-water mixtures (Paulaitis et al., 1981; de Fillipi and Vivian, 1982; Moses et al., 1982; McHugh et al., 1983; Kuk and Montagna, 1983; Kander and Paulaitis, 1984; Diandreth and Paulaitis, 1984; Paulaitis et al., 1984). These studies showed that the selectivity values of the SCF solvent for the alcohol can be as high as 50-80 at ethanol concentrations of ~10 wt %, but the distribution coefficient of the alcohol, $(y/x)_{\text{alcohol}}$, is only on the order of 0.1 (weight basis) in this region. With such a low distribution coefficient supercritical solvent-to-feed ratios of 10 or more are needed to extract ethanol from water. Furthermore, in none of these studies was it found possible to surpass the alcohol-water azeotropic concentration.

In this paper we report on the ability of supercritical methane to extract trimethyl borate (TMB) from methanol and to break the TMB-methanol azeotrope (70 wt % TMB). TMB-methanol azeotropic solutions result from the synthesis process for producing TMB. The resultant TMB-methanol solution must be processed in a three column distillation sequence or by some combination of extraction and distillation. The TMB-methanol system forms a weak, Lewis acid-base complex which occurs when the oxygen on the methanol donates a pair of electrons to the unfilled orbital of boron. Ionic compounds dissolved in TMB-methanol mixtures generally exist as ion pairs, indicating that these mixtures are weak hydrogen bond acceptors although they are strong hydrogen bond donors (Kreevoy and Kantner, 1977).

To extract TMB from TMB-methanol mixtures, it is necessary to find a solvent that is relatively immiscible in methanol yet is miscible with TMB at the same conditions. TMB is very soluble in benzene, hexane, heptane, nonane, and carbon tetrachloride, indicating that it exhibits very lipophilic characteristics (Plank and Christopher, 1976; Niswonger et al., 1985; Schmidt et al., 1985; Munster et al., 1984). Hence, TMB should be soluble in the more common supercritical fluid solvents such as ethane and carbon dioxide. Methanol is moderately miscible with xenon, ethane, ethylene, and carbon dioxide since a single phase is obtained at pressures of less than ~200 bar at

temperatures between the respective critical temperatures of the binary components (Brunner, 1985). It should be noted that the ethane-methanol, ethylene-methanol, and xenon-methanol systems do not have continuous critical-mixture curves and that they have small three-phase, liquid-liquid-vapor regions near the critical points of ethane, ethylene, and xenon (Brunner, 1985). The carbon dioxide-methanol system does have a continuous critical-mixture curve (Robinson et al., 1985; Brunner, 1985).

To obtain quickly an estimate of the distribution coefficient for TMB in carbon dioxide, ethane, and ethylene, we performed rapid screening experiments with a dynamic flow apparatus at temperatures ranging from 0 to 55 °C at a number of pressures. From this preliminary study we found that carbon dioxide does not discriminate between TMB and methanol even at moderate pressures since it dissolves both of these components to a very high level. Both ethane and ethylene also fail to separate TMB from methanol. Further screening experiments were performed using methane with the expectation that methane would not be as strong a supercritical solvent as ethane, ethylene, or carbon dioxide since its polarizability and density are significantly less than that of these solvents at 0 °C and 150 bar. In these preliminary tests methane exhibited a high selectivity for TMB relative to methanol. It is not surprising that methanol is not extracted with methane since literature data show that methane and methanol are not very miscible (Francesconi et al., 1981; Brunner, 1985). Figure 1 shows a portion of the pressure-temperature (P - T) trace of the critical-mixture curves for the methane-methanol, ethane-methanol, ethylene-methanol, and carbon dioxide-methanol systems. Pressures in excess of ~2500 bar are needed at around room temperature to obtain a single phase with the methane-methanol system while only ~150 bar are needed to obtain a single phase with ethane, ethylene, xenon, or carbon dioxide (Robinson et al., 1985; Brunner, 1985). The P - T data shown in Figure 1 suggest that the solvent power of methane, the weakest of the supercritical solvents shown in this figure, can be "fine-tuned" using pressure while the other solvents are already too "strong" even at relatively low pressures. It should be noted that at temperatures below about -25 °C the critical-mixture curve for ethane-methanol rises steeply in a manner similar to that of methane-methanol system. However, operation at -25 °C is probably not practical since the concentration of methanol in the ethane-rich phase is more than likely quite small. Unfortunately, to our knowledge there are no available data on the TMB-gas

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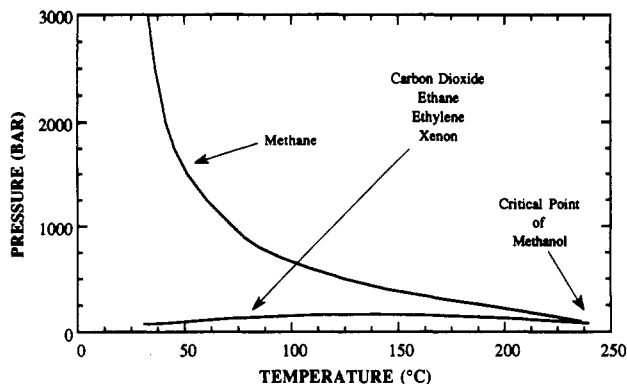


Figure 1. Portions of the pressure-temperature (P - T) trace of the critical-mixture curves for binary mixtures of methanol with methane, ethane, ethylene, xenon, and carbon dioxide (Francesconi et al., 1981; Brunner, 1985). The P - T trace for the ethane, ethylene, xenon, and carbon dioxide systems essentially superpose in the region shown in the graph.

systems of interest in this study to help guide the choice of an effective supercritical solvent.

In this paper we present phase behavior information on the TMB-methanol-methane system which is used to more fully determine the potential of methane to extract TMB from methanol and to break the TMB-methanol azeotrope. One objective of this study is to obtain solubility isotherms for the TMB-methane system at 35 and 55 °C. The behavior of the ternary TMB-methanol-methane system also is obtained at 35 °C and 152 bar, conditions similar to those used in preliminary screening study. The phase-behavior data are modeled by use of the Peng-Robinson equation of state with one adjustable mixture parameter for each binary pair. Further extraction studies are performed using methane to determine the distribution coefficient of TMB in methane at 0 °C and 152 bar.

Experimental Section

Two types of experimental techniques are used in this study. The synthetic method is used with a view cell apparatus to obtain equilibrium solubility isotherms and ternary information. A dynamic flow technique is used to obtain selectivity and extraction information. Each of these techniques is described extensively elsewhere (Krukoni and Kurnik, 1985; Occhiogrosso et al., 1986; Dhalewadikar et al., 1987; Seckner et al., 1988); only the highlights of the experimental procedures are given here.

A view cell apparatus is used to obtain dew, bubble, and critical points using the synthetic method. With this view cell it is possible to detect visually the number of equilibrium phases and to adjust the volume of the mixture by displacing a movable piston in the cell. The cell is initially loaded to within ± 0.002 g with either TMB-methanol mixture. Methane is used to purge the residual air from the cell and is then transferred into the cell gravimetrically to within ± 0.002 g with the use of a high-pressure bomb. Care is taken to ensure that no water is introduced into the system as TMB readily hydrolyzes with water to form boric acid. The contents of the cell are maintained to within ± 0.1 °C as measured with a Pt-resistance device connected to a digital multimeter and are mixed by a glass-encased stirring bar activated by a magnet located below the cell. System pressure is measured with a Heise gauge accurate to within ± 0.69 bar.

For the experiments with TMB-methane mixtures dew, bubble, and mixture-critical points are obtained in the following manner. At a fixed temperature the mixture in the cell is compressed to a single phase. The pressure is

then slowly decreased until a second phase appears. The appearance of a fine mist indicates a dew point while a small vapor bubble indicates a bubble point. In either case, the composition of the major phase present is equal to the composition of the overall solution since the small amount of mass in the precipitated phase can be neglected. A mixture-critical point is obtained if critical opalescence is observed during the transition process and if two phases of equal volume are present when the mixture phase separates.

Most of the data reported for the ternary TMB-methanol-methane system are obtained by sampling each phase once the desired operating pressure and temperature are maintained long enough for equilibrium. Each phase is separately displaced into high-pressure sampling bombs by moving the piston forward. The pressure is normally maintained constant to within ± 1.7 bar during sampling. The loaded sample bomb is weighed to within ± 0.002 g and then cooled in a dry ice-acetone bath. At dry ice-acetone conditions the methane is slowly vented from the bomb. The bomb is then reweighed and the amount of methane in the sample is readily determined. The TMB-methanol mixture remaining in the bomb is analyzed using both refractive index measurements and a titration technique (Schmidt et al., 1985). The error in the weight fractions is estimated to be within $\pm 2.0\%$. In most cases it was only possible to obtain an accurate determination of the amount of methane in the gas-phase sample since the amount of methanol and TMB in the sample was quite low. However, by visually determining the binodal curve near the pure methanol apex of the triangular diagram, it is possible to obtain reasonable estimates of the composition of the gas phase.

A dynamic, flow-through apparatus is also used to obtain distribution coefficient information. A measured amount of TMB-methanol azeotropic solution (70 wt % TMB) is charged to a high pressure extraction column (1.8 cm i.d. \times 30 cm long). A check valve at the bottom of the column prevents the liquid from draining from the column, and glass wool is packed into the top of the column to remove any entrained solution in the methane-rich extract stream. Virtually pulse-free flow rates of 20 standard L of methane/min are obtained with a diaphragm compressor-surge tank setup which is controlled with a back-pressure regulator that recycles the bulk of the compressed gas back to the suction side of the pump. With this arrangement the operating pressure is maintained constant to within ± 2.0 bar. The gas from the surge tank is heated and delivered to the extraction column which is maintained at a constant temperature to within ± 0.5 °C as determined with an iron-constantan thermocouple positioned in the inlet of the extractor. The loaded methane-rich gas phase exiting the column is expanded through a heated, flow-regulating, pressure let-down valve. The liquid solute precipitates from the low-pressure methane into a preweighed U-tube situated in a dry ice-acetone bath. Glass-wool filters at the exit of the U-tube trap any fine mist entrained in the methane. The gaseous methane is routed to a dry-test meter to monitor the total volume of methane passed through the extractor. The liquid sample in the U-tube is weighed and subsequently analyzed according to a titration technique (Schmidt et al., 1985).

Materials

The methanol (HPLC grade, 99.9% purity), TMB (99.9% pure), and TMB-methanol azeotropic solution were obtained from Aldrich Chemical Company. Methane (research grade, 99.9% minimum purity) was obtained from Linde Corporation.

Table I. Pressure-Composition Data for the Trimethyl Borate (TMB)-Methane System at 35 and 55 °C

TMB concn, wt %	press., bar	TMB concn, wt %	press., bar
$T = 35.0\text{ }^{\circ}\text{C}$			
9.4	143.2	54.4	211.6
24.5	210.8	57.9	211.0
32.5	222.1	64.6	191.7
41.2	224.1	76.1	139.8
42.1	227.8	86.3	93.2
44.7	226.5	94.7	36.9
$T = 55\text{ }^{\circ}\text{C}$			
29.1	230.4	73.7	166.5
33.3	224.4	77.5	148.6
37.3	223.8	77.7	149.2
43.9	222.5	82.6	119.9
52.1	219.2	89.9	82.3
59.7	211.7	90.6	74.8
61.7	208.6	92.2	63.0
66.3	193.6		

Results and Discussion

Table I lists the experimental pressure-temperature-composition data for the TMB-methane system at 35 and 55 °C. Since there is very little difference in the P - x behavior of this system at these two temperatures, only the solubility isotherm at 35 °C is shown in Figure 2 to avoid cluttering the graph. The pressures for each bubble and dew point generally were reproducible to within ± 0.3 bar. Also shown in Figure 2 is the 35 °C solubility isotherm for the methanol-methane system obtained by Francesconi et al. (1981). Notice that modest pressures of ~ 225 bar are needed to obtain a single phase with the TMB-methane system at any concentration while, at the same temperature and concentration, up to ~ 2500 bar can be needed with the methanol-methane system. The extremely high pressure needed to dissolve methanol in methane is probably a result of the strong hydrogen bonding that occurs between methanol molecules in the liquid phase (Prausnitz, 1969; Franck and Duel, 1978). It should be noted that the density of methane at 35 °C and ~ 2500 bar comes to within a factor of about 2 of the density of liquid methanol before complete miscibility is obtained (Diguët et al., 1987). This suggests that methane and methanol must be packed closely together to allow the weak forces of attraction between methane and methanol to have an effect. Only modest pressures are needed to solubilize TMB in methane since TMB primarily interacts through dispersion forces that are much less than the specific chemical interactions found with methanol and, thus, are more compatible with nonpolar methane. The differences in binary phase behavior of methane with TMB

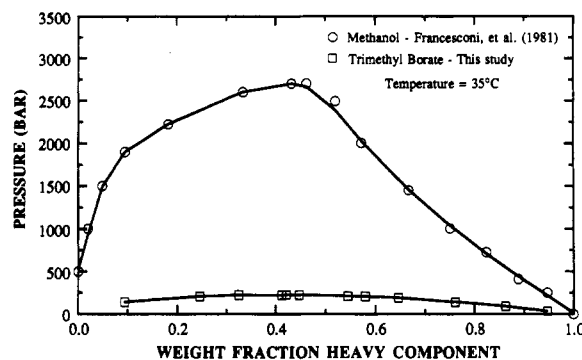


Figure 2. Comparison of the 35 °C solubility isotherm of methanol in methane (Francesconi et al., 1981) with that of trimethyl borate in methane.

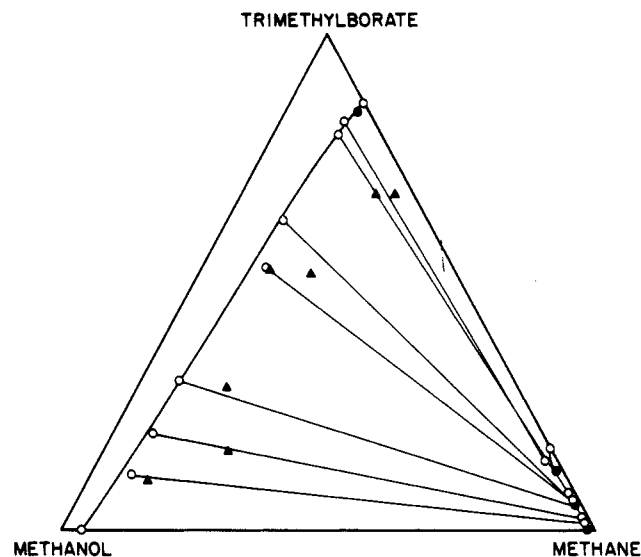


Figure 3. Ternary trimethyl borate-methanol-methane weight percent data obtained in this study at 35 °C and 152 bar. The open symbols are analyzed samples, the triangles are loadings, and the closed circles are visually determined phase boundaries.

and with methanol suggests that it may be feasible to extract readily TMB from methanol. However, it is necessary to determine ternary phase behavior information since it is known that TMB and methanol form a weak acceptor-donor complex that may preclude the efficient extraction of TMB from these mixtures (Kreevoy and Kantner, 1977).

Shown in Figure 3 and listed in Table II are ternary TMB-methanol-methane data at 35 °C and 152 bar, conditions very similar to those used in the screening

Table II. Tie-Line Data for the Methanol-TMB-Methane System at 35 °C and 152 bar^a

loading, wt %			vapor phase, wt %			liquid phase, wt %		
CH ₄	TMB	CH ₃ OH	CH ₄	TMB	CH ₃ OH	CH ₄	TMB	CH ₃ OH
			0.836	0.164	0.000	0.136	0.864	0.000
			0.988	0.000	0.012	0.955	0.000	0.045
0.287	0.679	0.035	0.838	0.141	0.021	0.188	0.827	0.055
0.210	0.517	0.273	0.932	0.058*	0.010*	0.103	0.628	0.269
0.252	0.678	0.070	0.914	0.076*	0.010*	0.120	0.801	0.079
0.112	0.098	0.790	0.975 [†]	0.015 [†]	0.010 [†]	0.076	0.111	0.813
0.233	0.157	0.610	0.965 [†]	0.025 [†]	0.010 [†]	0.075	0.195	0.729
0.134	0.845	0.021				0.134	0.845	0.021
0.167	0.286	0.547	0.940	0.050*	0.010*	0.071	0.302	0.628
0.129	0.525	0.346	0.930 [†]	0.060 [†]	0.010 [†]	0.119	0.532	0.350
0.873	0.117	0.012	0.871	0.117	0.012			
0.940	0.051	0.009	0.940	0.051	0.009			

^aThe vapor-phase data points with an asterisk are estimates based on the measured weight percent of methane in the vapor-phase sample and the intersection of the experimental binodal curve near pure methane. The vapor-phase data points with a double dagger are estimates based on the tie lines drawn through the liquid-phase point, the loading, and the binodal curve near pure methane.

Table III. Sequential Extraction Data for the TMB-Methanol System with Methane at 0 °C and 152 bar Using the Dynamic, Flow Technique^a

fraction	liquid extract collected, g	methane from degassed extract, g	wt % TMB extract ^b	wt % TMB in column ^b	TMB-DC
charge	20.71			70.0	
1	1.56	14.28	96.2	67.9	1.4
2	2.95	28.56	93.7	63.2	1.5
3	2.72	28.57	96.5	56.5	1.7
4	3.79	42.85	94.5	41.7	2.1
5	2.95	35.71	95.7	18.1	3.6
6 ^c	6.74	55.40	14.8	~0	

^aThe weight percent of TMB in the column is calculated to within $\pm 5\%$ on a methane-free basis from a mass balance. TMB-DC is the weight fraction distribution coefficient of trimethyl borate on a methane-free basis. ^bMethane-free basis. ^cFor this fraction CO₂ was used and the column was depleted completely of liquid solution.

study. There are several features of this diagram which indicate that methane is the supercritical fluid solvent of choice for the separation of TMB from methanol. From the shape of the two-phase region and the slopes of the tie lines it is apparent that greater than 70 wt % TMB (solvent-free basis) can be obtained in the methane-rich extract phase if the TMB-methanol azeotropic mixture is extracted with methane. Not only is the loading of TMB in the methane-rich phase quite high, ~ 12 wt %, it remains essentially constant as the concentration of TMB decreases in the liquid phase. As mentioned earlier, the methanol that is complexed to TMB also hydrogen bonds to other methanol molecules. Intermolecular interactions between methane and methanol are not strong enough to compete with the hydrogen bonding that occurs between methanol molecules so that methanol remains essentially insoluble at this low pressure. Even large amounts of methane dissolved in methanol do little to disrupt the hydrogen bonding (Diguët et al., 1987). It is interesting that the presence of relatively large amounts of TMB in the methane-rich gas phase has little effect on the solubility of methanol in this phase even though TMB and methanol form a weak complex. This lack of "entrainer" effect was surprising.

Since the binodal curves intersect the TMB-methane axis, it is possible to obtain pure TMB by using a countercurrent extraction process with reflux. If the system pressure is increased above the TMB-methane critical pressure at 35 °C, a closed-dome, two-phase region would exist and it would not be possible to obtain pure TMB with a countercurrent process.

Table III lists the extraction data obtained with the flow apparatus at 0 °C and 150 bar, and Figure 4 shows the plot of this data. The data presented in this figure are not strictly equilibrium data at the flow rates used for the extraction, although it is estimated that the solution exiting the column comes to within $\sim 80\%$ of its equilibrium value. The extraction data at 0 °C and 150 bar are compared with the equilibrium data obtained at 35 °C and 152 bar since this small temperature difference will have little effect on the physical properties of pure methane or methanol or on the equilibrium concentrations of the liquid and vapor phases of the methane-methanol system (Francesconi et al., 1981). Figure 4 shows that the concentration of TMB in the extract phase remains essentially constant as the extraction proceeds, consistent with the trends in the equilibrium data shown in Figure 3. The concentration curve exhibits the characteristics found when extracting a single component (i.e., in the dynamic measurement of solubility of a pure liquid or solid at a fixed temperature and pressure the concentration in the extract phase ini-

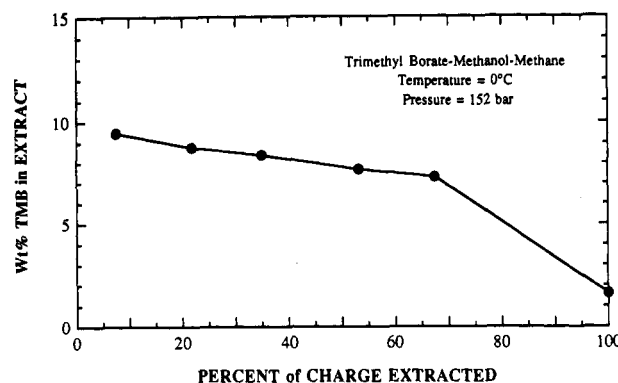


Figure 4. Performance of the dynamic extraction of the trimethyl borate-methanol azeotropic mixture using supercritical methane.

tially remains constant but then drops off rapidly once the material in the column becomes depleted). The distribution data for TMB tabulated in Table III show that the distribution coefficient increases as the extraction proceeds. The distribution coefficient for TMB is also about an order of magnitude higher than that found with ethanol extracted from water using a supercritical fluid solvent.

Using geometrical considerations inherent with ternary-phase diagrams, it is possible to show that any liquid-mixture azeotrope can be broken if the system has binodal curves similar to those exhibited by the TMB-methanol-methane system in Figure 3. For example, it would be possible to break the ethanol-water azeotrope with a supercritical fluid if the system is processed at a low pressure such that the ethanol-SCF axis is intersected by the binodal curves. Since the mutual miscibility of water and hydrocarbons or CO₂ is relatively insensitive to pressure at around room temperature, the operating pressure for a supercritical extraction process must be lower than that needed to obtain a single phase with the ethanol-SCF binary system. Only modest pressures are needed at around room temperature to obtain a single phase for ethanol with ethylene (Paulaitis et al., 1981; Ohgaki et al., 1983), ethane (McHugh et al., 1983), and carbon dioxide (Francis, 1954; Paulaitis et al., 1981), and therefore, the extraction pressure used with the ethanol-water-SCF system must be very low to avoid a closed, two-phase dome. Obviously a low operating pressure limits the practical application of using a supercritical fluid solvent to break the ethanol-water azeotrope since the amount of ethanol in the SCF-rich phase would be prohibitively low. This solubility behavior is in marked contrast with the TMB-methanol-methane system, which has a high solubility of TMB at pressures below 175 bar while maintaining a very low solubility of methanol at this modest pressure. Even the presence of large amounts of TMB in the methane-rich gas phase has little effect on the solubility of methanol in this phase.

Data Reduction

The phase-equilibrium data obtained in this study are modeled with the Peng-Robinson equation of state (Peng and Robinson, 1976) to determine whether a cubic equation of state can be used to represent the phase-behavior characteristics found with this ternary system. No attempt is made to quantify the local composition expected with hydrogen-bonded methanol associates or with TMB-methanol complexes. With the use of correlations given by Christopher (1960) the critical properties of TMB are estimated to be 238 °C and 34 bar and the acentric factor is 0.270. These critical properties are in qualitative agreement with our experimental observation that critical opalescence was not observed for pure TMB to tempera-

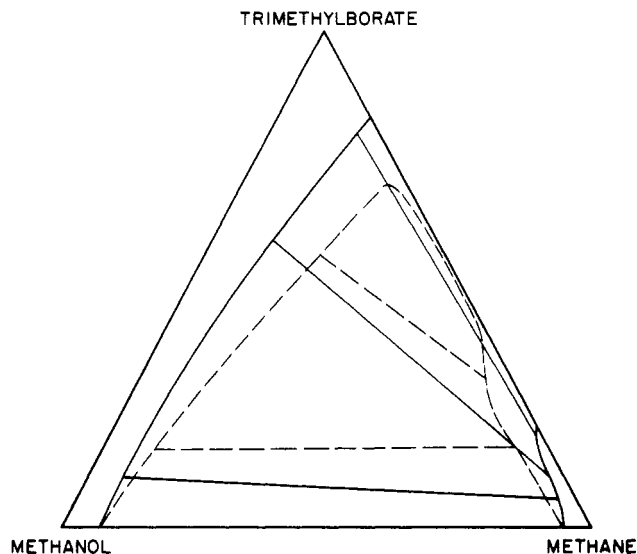


Figure 5. Comparison of calculated and experimental data on a weight percent basis for the ternary trimethyl borate-methanol-methane system at 35 °C. The solid lines represent calculations at 152 bar, and the dashed lines represent calculations at 250 bar.

tures of 215 °C, the limit of our experimental apparatus. Pure component values for methanol and methane are obtained from Reid et al. (1987).

Regardless of the value of k_{ij} , it is possible to only obtain a modest fit of the phase behavior of the TMB-methane system at 35 °C. A value of 0.005 for k_{ij} resulted in good agreement with the observed and calculated mixture-critical pressure although the calculated phase envelope is shifted to slightly higher TMB concentrations. Likewise, it was not possible to get a good fit of the methanol-methane system at 35 °C over the entire composition range. However, the mixture-critical pressure for the methanol-methane system is matched at 35 °C with a k_{ij} of 0.0025. Figure 5 shows that a reasonable fit of the ternary TMB-methanol-methane system at 35 °C and 152 bar is obtained with k_{ij} values of 0 for TMB-methanol, 0.005 for TMB-methane, and 0.0025 for methanol-methane. Further attempts at refining the fit of the calculated tie lines are not warranted since we only have a crude estimate of the critical properties of TMB. The calculated results at a pressure of 250 bar show that a closed-dome, two-phase region is predicted in qualitative agreement with our phase-behavior studies.

Calculations were also performed on the TMB-methanol-carbon dioxide system. k_{ij} values of 0 were used for the TMB-methanol and TMB-methane binaries, and a value of 0.077 was used for the methanol-carbon dioxide binary. The calculated results indicate that TMB-methanol-carbon dioxide mixtures would exist as a single phase at 35 °C and 152 bar. This result is consistent with the experimental observation that virtually no selectivity is obtained when supercritical carbon dioxide is used. Using a straightforward equation of state, it is possible to obtain a reasonable estimate of the separability of TMB from methanol, thus potentially streamlining the efforts needed for difficult experimental studies on the ternary system.

Conclusions

The TMB-methanol azeotrope can be broken at its azeotropic concentration by using supercritical methane at very mild temperatures and pressures. Operating countercurrently with reflux, it is possible to obtain essentially pure TMB since the binodal curve intersects the TMB-methane axis. The relative strength in the inter-

molecular forces in operation in the binary systems, TMB-methanol, TMB-methane, and methanol-methane, and in the ternary TMB-methanol-methane system, can be interpreted with information on the types of phase behavior exhibited by each of these binary mixtures and the physicochemical properties of each component. TMB, a lipophilic substance, dissolves quite readily in nonpolar methane at moderate pressures. However, intermolecular interactions between methane and methanol are not strong enough to compete with the hydrogen bonding found with liquid methanol at 35 °C until high methane densities are obtained at very high operating pressures. Radically different binary phase behavior is found for the methane-TMB and the methane-methanol systems, suggesting that TMB can be extracted from methanol. To verify this conjecture, experimental information was obtained on the TMB-methanol-methane system to ascertain whether the weak TMB-methanol complex can be broken by nonpolar methane. Interestingly, carbon dioxide, ethane, and ethylene, which are all much better supercritical solvents than methane, dissolve both methanol and TMB to such a large extent that they are not selective for either component. With methane, however, the interactions between methane and TMB are strong enough to maintain a constant concentration of TMB in the extract phase as TMB is removed from the methanol-rich liquid phase. This means that the distribution coefficient for TMB increases as the concentration in the liquid phase decreases. We know of no other system that exhibits this type of distribution coefficient behavior.

Using a cubic equation of state to model the phase behavior without accounting for local composition effects associated with complexes formed between methanol molecules and the TMB and methanol gives qualitative agreement with experimental results, suggesting that it is possible to screen potential solvents by calculating the ternary-phase behavior.

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Registry No. TMB, 121-43-7; CH₃OH, 67-56-1; CH₄, 74-82-8.

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Longitudinal Holdup Distribution of Gas and Dispersed Liquid in Bubble Columns with Two Immiscible Liquids

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The longitudinal distribution of the fractional gas holdup and the volume fraction of a dispersed liquid (droplet) was measured in bubble columns with two immiscible liquids. The columns were operated batchwise with respect to both liquids, over a wide range of relevant physical properties and average volume fraction of the dispersed liquid. The average gas holdups could be correlated by a previous empirical expression for a single liquid phase, when it was applied to the individual liquid phases, allowing for their volume fraction. The observed longitudinal distribution of the volume fraction of the dispersed liquid was analyzed by means of the dispersion model, allowing for the slip velocity caused by the density difference between both liquid phases. The data were empirically correlated in terms of the Peclet number based on the slip velocity, as a function of the relevant system parameters.

Mass-transfer or chemical reactions for gas-liquid-liquid systems may be encountered in gas absorption, gas-liquid reactions, and fermentation, often with a heterogeneous liquid catalyst or an extracting solvent, liquid-liquid extraction, or liquid-liquid reactions with gas agitation. Some examples can be cited: absorption of SO₂ into aqueous emulsion of xylydine in water (Kohl and Riesenfeld, 1985); purification of crude naphthalene with H₂SO₄ accompanied by air sparging (Doraiswamy and Sharma, 1984); air oxidation of hydrocarbon in aqueous emulsion; fermentation of hydrocarbons, in which a substrate, hydrocarbon, is dispersed in an aqueous culture medium with air bubbling; and extractive fermentation of useful species, such as alcohols and steroids, which are produced in the aqueous phase by the metabolism of the relevant microorganisms and are extracted in situ into the coexisting organic phase of an extractant, shifting the reaction fa-

vorably. A few examples of more complicated systems containing solid particles are air oxidation of substituted benzyl alcohol catalyzed by palladium catalyst in the presence of aqueous phase, which gives rise to the favorable formation of aldehyde (Ma, King, 1982), and competitive liquid-phase hydrogenation of cyclohexanone and cyclohexene catalyzed by Ru catalyst in the presence of water (Koopman et al., 1981).

Over any other conventional gas-liquid or liquid-liquid contactors, bubble columns have many advantages. They are of simple configuration without moving parts and require no seal, need little space and maintenance, can easily and widely adjust the resistance time of the liquid phases, and allow comparatively large liquid-phase volumetric mass-transfer coefficients or interfacial area to be achieved with relatively low energy consumption.

Therefore, bubble columns may be expected to be capable of being used successfully also for gas-liquid-liquid systems. However, relatively few studies have been per-

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