HIGH PRESSURE VAPOR-LIQUID-LIQUID EQUILIBRIA FOR THE ETHYLENE-MEK-WATER SYSTEM*

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For the separation of mixtures numerous separation processes are used in industry, e.g. distillation, extraction, and crystallization. Distillation, however, requires heating of the mixture, which is not suitable for a heat-sensitive mixture. Extraction is effective for such a mixture, but usually requires an auxiliary operation like distillation for the recovery of solvent. The solvent power of compressed gases has been known since the first qualitative observation on the extraction of materials by supercritical gases was made by Hannay³⁾ in 1880.

Although vapor-phase extraction with compressed gas is an attractive separation method, it is only in recent years that interest has revived, and relatively little work has been done on high-pressure vapor-liquid equilibria with supercritical gas^{1,2)}. The purpose of this work is to obtain phase equilibrium data for the ternary ethylene-methyl ethyl ketone-water system and to examine the solvent effect of ethylene at temperatures near its critical temperature and at high pressures.

Experimental Apparatus and Method

The method for high pressure vapor-liquid equilibrium determinations has been reviewed in detail by numerous authors⁴⁾. The most common method, referred to as the vapor circulation method, consists of an equilibrium cell and a circulation pump. The experimental apparatus was a modification of that used previously⁷⁾. The equilibrium cell was a transparent-type Jerguson gauge with a stainless steel liquid chamber holding about 90 ml.

The samples were analyzed by a Shimadzu GC-1C gas chromatograph in conjunction with an Infotronics Integrator Model CRS-104. PEG 6000 (1.6 m) and Porapak Q (1.6 m) were used as the column packing materials and hydrogen was used as the carrier gas. Purities of materials used were, for ethylene: 99.95 mol%, methyl ethyl ketone: 99.6 mol%,

and water: distilled water.

Results and Discussion

Vapor-liquid-liquid equilibrium data for the system studied are shown in **Table 1**. The experiment was done at four isothermal conditions (10.8, 14.8, 20.0 and 25.0°C) and at pressures up to about 50 atm. As equilibrium compositions in vapor were essentially pure ethylene, these are not shown in this table. Concentrations of water in vapor were so small that these were not detected in gas chromatographic analysis. Concentrations of methyl ethyl ketone (MEK) in vapor were at most 1 mole percent, and the higher the temperature and pressure, the lower the concentration of MEK in vapor tended to become. Although MEK is partially miscible with water in the absence of ethylene, the immiscibility was enhanced by increasing system pressure or increasing ethylene solubility.

It has been known that the miscibility gap in liquid-liquid equilibria for the MEK-water system narrows and finally disappears as the pressure is increased isothermally⁸⁾. Liquid-liquid equilibria were also measured for the nitrogen-MEK-water system. Pressures up to 40 atm did not affect the liquid-liquid equilibrium for the system, because solubility of nitrogen was very small. These results indicate that the width of the miscibility gap in the system with ethylene does not result from mere pressure rise, but results from the solvent effect of ethylene in the liquid phase.

Degree of separation was expressed by the separation factor α , defined as

$$\alpha = (x_M^I/x_W^I)/(x_M^{II}/x_W^{II})$$

where x_M^I and x_W^I are the mole fraction of MEK and water in MEK-rich phase and x_M^{II} and x_W^{II} are the mole fraction of MEK and water in water-rich phase (all on an ethylene-free basis). The separation factor of the system is plotted in **Fig. 1** as a function of pressure. Due to the difficulty of analyzing low concentrations of x_M^I and x_W^I , the values of the separation factor fluctuate considerably. The general trend is that the separation factor increases with decreasing temperature and increasing pressure. In other words,

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Table 1 Experimental equilibrium data
Composition [Mole percent]

Temp. [°C]	Pressure [atm]	Top liquid layer			Bottom liquid layer		
		Ethylene	MEK	Water	Ethylene	MEK	Water
8.0	15.0	18.36	71.50	10.14	0.22	7.05	92.73
10.8	10.0	13.22	70.68	16.10	0.21	7.22	92.57
10.8	20.0	26.47	65.26	8.27	0.30	5.82	93.88
10.8	48.5	98.10	1.90	0	0.26	2.62	97.12
14.8	10.0	10.46	71.94	17.60	0.20	7.87	91.93
14.8	20.0	23.99	66.71	9.30	0.26	6.00	93.74
14.8	30.0	40.02	53.23	6.75	0.30	4.26	95.44
14.8	35.0	52.52	45.14	2.34	0.21	3.72	96.07
14.8	40.0	62.61	35.40	1.99	0.41	3.81	95.78
14.8	45.0	74.03	25.97	0	0.47	3.59	95.94
15.0	51.0	91.15	5.99	2.86	0.30	3.23	96.47
20.0	10.0	8.80	70.39	20.81	0.15	7.07	92.78
20.0	20.0	18.72	68.38	12.90	0.21	5.92	93.87
20.0	30.0	36.66	56.73	6.61	0.35	4.90	94.75
20.0	35.0	44.08	50.69	5.23	0.39	4.41	95.20
20.0	40.0	55.78	39.69	4.53	0.38	3.98	95.64
20.0	45.0	52.25	44.80	2.95	0.41	3.49	96.10
20.0	50.0	75.76	22.65	1.59	0.39	3.04	96.57
25.0	20.0	20.16	64.63	15.21	0.27	6.13	93.60
25.0	35.0	36.76	54.42	8.82	0.30	4.06	95.64
25.0	40.0	47.93	47.42	4.65	0.33	3.65	96.02
25.0	45.0	51.97	43.86	4.17	0.33	3.62	96.05
25.0	51.7	71.52	26.90	1.58	0.36	3.35	96.29

Fig. 1 Separation factor as a function of pressure

lower temperature and higher pressure are desirable for the separation. However, these conditions are limited due to the formation of ethylene hydrate. In **Table 2** formation pressures of ethylene hydrate are shown for the ethylene-MEK-water system in the two-liquid region. From these data the formation pressures rise due to the presence of MEK. Hydrate formation is desirable from the standpoint of separation factor. With respect to this, the removal of water from an aqueous solution by hydrate formation is reported in the literature⁶⁾.

Conclusion

Vapor-liquid-liquid equilibria for the ethylene-MEK-water and nitrogen-MEK-water system have been described. In the system with nitrogen pressures up to 40 atm did not affect the liquid-liquid

Table 2 Formation pressure of ethylene hydrate for ethylene-MEK-water system in two-liquid region

Temp. [°C]	Pres. [atm]	Temp. [°C]	Pres. [atm]
2.5	11.60	12.0	31.00
4.6	13.05	13.0	33.20
6.0	15.40	14.0	38.75
8.1	18.85	15.0	48.50
10.0	23.25	10.8	21.50*
11.0	26.10		

* This value is in one-liquid region: MEK, 2.35 mol%, Water, 97.65 mol%

equilibria. On the other hand, in the system with ethylene the immiscibility in liquid phase was enhanced by increasing pressure and decreasing temperature until an ethylene hydrate was formed. The formation pressures of the ethylene hydrate were also reported for the ethylene-MEK-water system in the two-liquid region.

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