Liquid-Liquid Equilibrium in Ternary System Consisting of Isoprene, Cyclopentadiene and *N*-methylpyrrolidone*

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Summary: As a part of a study on C_5 -hydrocarbons, this paper deals with the liquid-liquid equilibrium in a ternary system consisting of isoprene, cyclopentadiene and (aqueous) *N*-methylpyrrolidone.

The experiments were carried out using four solvents; (anhydrous *N*-methylpyrrolidone and aqueous solutions), (12.7, 19.6, and 32.7 wt% water). Temperatures were 2.0 (± 0.3)°C and -8 (± 0.3)°C.

When the water-free *N*-methylpyrrolidone was used as solvent, both isoprene and cyclopentadiene were miscible in all proportions, but when the three aqueous solvents were used, isoprene and cyclopentadiene were partially miscible with solvent to form two liquid phases.

From the results obtained, it was confirmed that it was favourable for the extraction of cyclopentadiene to employ solvent containing much water, however, the considerable decrease of the solubilities of isoprene and cyclopentadiene in the solvent-rich phase also took place, and it would seem that the lower temperature is more favourable for extraction.

1 Introduction

Recently, the use of the C_5 -hydrocarbons fraction in the petrochemical industry have attracted much attention.

Among such usages, isoprene is important as monomer for cispolyisoprene rubber.

In the presence of cyclopentadiene, it is very difficult to prepare pure isoprene, since their boiling points are very close.

Recently, *N*-methylpyrrolidone has been considered a useful solvent for this system, there are, however only few fundamental data in the literature^{1)~3)}.

This work was carried out in order to obtain some information on the liquid-liquid equilibrium in the ternary consisting of isoprene, cyclopentadiene and *N*-methylpyrrolidone.

2 Experimental

2.1 Materials

The materials used in this study were prepared in the following manner:^{4)~6)}

Isoprene was purified by distillation of commercial grade in order to eliminate its dimer

and polymer, the fraction boiling from b.p. 34.0°C to 34.5°C was recovered.

Cyclopentadiene was prepared by decomposition of dicyclopentadiene obtained by distillation of commercial grade at about 16 mmHg (b.p. 43.0~44.0°C). It was stored in a dry-ice bath until the experiments were started, because of its rapid redimerization at room temperature.

N-methylpyrrolidone was also prepared by distillation of the commercial reagent at about 15 mmHg (b.p. 86~88°C).

Ethylbenzene and cyclohexane for the gas chromatograph analysis were purified by conventional methods.

2.2 Procedure

The sample mixtures, 30~40 ml, were admitted to a 80 ml round bottomed flask which was immersed in a thermostat controlled at the given temperature, stirred for half an hour and then allowed to stand for the same length of time. These time interval had been confirmed by prior experiments carried out for 5, 10, 20, 30 and 60 minutes, to be adequate to obtain equilibrium.

After settling of the mixture, 2 or 4 ml of the lower (heavy) layer and 1 ml of the upper (light) layer were sampled and analyzed for concentrations of isoprene and cyclopentadiene by respectively gas chromatograph analysis. The concentration of the solvent (*N*-methylpyrrolidone) was determined by gas chromatograph analysis.

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done) was determined by calculation. For the gas chromatograph analysis, silicone DC 550 was used as the packing materials⁶⁾, hydrogen as the carrier gas, cyclohexane as the standard reagent and ethylbenzene as the diluent. The temperatures of the column and the detector employed were 80°C.

The experiments were carried out using four

solvents; (anhydrous *N*-methylpyrrolidone and aqueous solutions), (12.7, 19.6, and 32.7 wt% of water); and at temperatures of 2.0 (± 0.3)°C and $-8.0(\pm 0.3)$ °C.

3 Discussion of Results

When the water-free *N*-methylpyrrolidone was used as a solvent, both isoprene and cyclo-

Table 1 Liquid-Liquid Equilibrium Data at -8°C

	32.7 wt% of Water				19.6 wt% of Water				12.7 wt% of Water			
	<i>x</i>	<i>y</i>	<i>K</i>	β	<i>x</i>	<i>y</i>	<i>K</i>	β	<i>x</i>	<i>y</i>	<i>K</i>	β
Isoprene	94.8	1.2			88.9	4.6			74.0	12.0		
Cyclopentadiene												
Solvent	5.2	98.8			11.1	95.4			26.0	88.0		
Isoprene	73.5	0.8	0.011		81.7	4.1	0.050		65.8	10.9	0.16	
Cyclopentadiene	16.8	0.5	0.030	2.8	6.2	0.8	0.129	2.6	6.2	1.9	0.31	1.9
Solvent	9.7	98.7			12.1	95.1			28.0	87.2		
Isoprene	44.6	0.5	0.011		72.7	3.7	0.051		55.0	9.4	0.17	
Cyclopentadiene	38.0	1.1	0.035	3.2	12.7	1.4	0.110	2.2	13.3	3.9	0.29	1.7
Solvent	17.4	98.4			14.6	94.9			31.7	86.7		
Isoprene	25.4	0.3	0.012		51.9	2.9	0.056		37.2	7.4	0.20	
Cyclopentadiene	50.7	1.7	0.036	3.0	26.3	2.8	0.109	1.9	25.2	7.5	0.30	1.5
Solvent	23.9	98.0			21.8	94.3			37.6	85.1		
Isoprene	9.9	0.2	0.020		34.5	2.1	0.061		21.4	5.4	0.25	
Cyclopentadiene	61.1	2.2	0.036	1.8	36.7	4.3	0.117	1.9	35.7	12.4	0.35	
Solvent	29.0	97.6			28.8	93.6			42.9	82.2		
Isoprene					14.4	1.1	0.076		8.1	3.1	0.38	
Cyclopentadiene	67.3	3.3			47.2	6.7	0.142	1.9	43.5	18.7	0.43	1.1
Solvent	32.7	96.7			38.4	92.2			48.4	78.2		
Isoprene												
Cyclopentadiene					55.0	9.6						
Solvent					45.0	90.4						

x: Concentration (wt%) in the upper phase

y: Concentration (wt%) in the lower phase

K: ($=y/x$) the partition coefficient

β : The selectivity

Table 2 Liquid-Liquid Equilibrium Data at $+2^\circ\text{C}$

	32.7 wt% of Water				19.6 wt% of Water				12.7 wt% of Water			
	<i>x</i>	<i>y</i>	<i>K</i>	β	<i>x</i>	<i>y</i>	<i>K</i>	β	<i>x</i>	<i>y</i>	<i>K</i>	β
Isoprene	93.1	1.5			82.5	5.2			71.6	12.9		
Cyclopentadiene												
Solvent	6.9	98.5			17.5	94.8			28.4	87.1		
Isoprene	72.2	1.0	0.014		75.5	4.5	0.060		63.6	11.9	0.19	
Cyclopentadiene	16.5	0.6	0.036	2.6	6.1	0.9	0.148	2.5	6.0	2.2	0.37	1.9
Solvent	11.3	98.4			18.4	94.6			30.4	85.9		
Isoprene	51.6	0.7	0.014		68.7	4.1	0.060		53.2	11.2	0.21	
Cyclopentadiene	31.6	1.2	0.038	2.7	11.9	1.7	0.143	2.4	12.7	4.3	0.34	1.6
Solvent	16.8	98.1			19.4	94.2			34.1	84.5		
Isoprene	25.5	0.4	0.016		56.8	3.3	0.058		35.0	9.4	0.27	
Cyclopentadiene	49.8	2.2	0.044	2.8	27.3	3.0	0.110	1.9	25.1	9.3	0.37	1.4
Solvent	24.7	97.4			25.9	93.7			39.9	81.3		
Isoprene	7.3	0.2	0.027		33.5	2.5	0.075		20.3	6.9	0.34	
Cyclopentadiene	60.8	2.8	0.046	1.7	35.9	4.7	0.131	1.8	35.3	15.0	0.42	1.2
Solvent	31.9	97.0			30.6	92.8			44.4	78.1		
Isoprene					15.1	1.4	0.093		7.9	3.8	0.48	
Cyclopentadiene	66.2	3.5			47.2	6.9	0.146	1.6	42.7	21.2	0.50	1.0
Solvent	33.8	96.5			37.7	91.7			49.4	75.0		
Isoprene												
Cyclopentadiene					53.7	10.0			48.8	26.1		
Solvent					46.3	90.0			51.2	73.9		

pentadiene were miscible in all proportions, and hence no separation coefficient could be obtained.

In these cases where the three aqueous solvents are employed, isoprene and cyclopentadiene were partially miscible with solvent to form two liquid phases, the upper one being the isoprene or cyclopentadiene-rich phases and the lower one the solvent-rich phase.

The liquid-liquid equilibrium data obtained for these systems are shown in Table 1~2, and Fig. 1~4 represented by triangular diagrams.

In these figures, the left and right solid curves indicate the equilibrium composition of the upper

and lower phases respectively, and the dotted lines represent the tie-lines.

Fig. 1~4 show that the solubility of the solvent in the upper (isoprene or cyclopentadiene-rich) phases is considerably larger than that of isoprene or cyclopentadiene in the lower (solvent-rich) phase. Thus, in the case of *N*-methylpyrrolidone containing 32.7 wt% of water, the former is 10~30 wt%, while the latter is several wt%. These features may be explained by assuming that *N*-methylpyrrolidone is exported into the isoprene and cyclopentadiene mixture from the solvent, the remaining solvent consisting of higher proportion of water than that

Fig. 1 Liquid-Liquid Equilibrium in Ternary System Consisting of Isoprene, Cyclopentadiene and *N*-methylpyrrolidone

Fig. 3 Liquid-Liquid Equilibrium in Ternary System Consisting of Isoprene, Cyclopentadiene and *N*-methylpyrrolidone

Fig. 2 Liquid-Liquid Equilibrium in Ternary System Consisting of Isoprene, Cyclopentadiene and *N*-methylpyrrolidone

Fig. 4 Liquid-Liquid Equilibrium in Ternary System Consisting of Isoprene, Cyclopentadiene and *N*-methylpyrrolidone

Table 3 The Saturated Solubilities of Isoprene and Cyclopentadiene for Three Solvents; columns 5~7 are the relative ratios based on column 2.

		32.7 wt% of Water	19.6 wt% of Water	12.7 wt% of Water	32.7 wt% of Water	19.6 wt% of Water	12.7 wt% of Water
2°C	{ Isoprene Cyclopentadiene	1.5 3.5	5.2 10.0	12.9 26.1	1.0 1.0	3.5 2.9	8.6 7.5
-8°C	{ Isoprene Cyclopentadiene	1.2 3.3	4.6 9.6	12.0 25.9	1.0 1.0	3.8 2.9	10.0 7.8

of the original solvent.

Fig. 1~4 also show that, depending upon the solvent employed the solubilities of the C₅-hydrocarbon mixture vary considerably. This can be explained by considering that, as mentioned above, C₅-hydrocarbon mixture is miscible in all proportions with the water-free *N*-methylpyrrolidone, while for the solvents containing water it is only partially miscible, thus, its solubilities are dependent upon the water content of the solvent.

Table 3 shows the saturated solubilities of isoprene and cyclopentadiene estimated from results obtained for three different solvents. From Table 3, the effect of the water content upon the solubility of isoprene is larger than that for cyclopentadiene. Consequently, it is advantageous for the extraction of cyclopentadiene to employ the solvent containing a large amounts of water. The above deduction can be additionally confirmed by comparison with the selectivity β for different solvents, which is defined as,

$$\beta = \frac{K_B}{K_A} = \frac{x_A y_B}{x_B y_A}$$

where x and y are the concentrations (wt%) in the upper and lower phases respectively, K ($=y/x$) is the partition coefficient, and the subscripts A and B indicate isoprene and cyclopentadiene respectively.

The β values calculated for two different compositions are shown in Table 4. The latter shows that the increase of water content in the solvent causes slight increase in the selectivity and ratio of cyclopentadiene to isoprene in the solvent-rich phase.

In this case, however, it should be noticed that the substantial decrease of the solubilities of isoprene and cyclopentadiene in the solvent-rich phase also takes place with increasing water

Table 4 The β Values Calculated for Two Different Compositions

	A, B	12.7 wt% of Water		19.6 wt% of Water		32.7 wt% of Water	
		C. P I. P	β	C. P* I. P	β	C. P* I. P	β
2°C	A	$\frac{18}{100}$	1.8	$\frac{28}{100}$	2.2	$\frac{40}{100}$	2.5
	B	$\frac{33}{100}$	1.4	$\frac{47}{100}$	2.1	$\frac{59}{100}$	2.6
-8°C	A	$\frac{18}{100}$	1.8	$\frac{29}{100}$	2.4	$\frac{38}{100}$	2.6
	B	$\frac{33}{100}$	1.7	$\frac{51}{100}$	2.2	$\frac{65}{100}$	2.8

Composition

A, Isoprene (I. P)34 wt%
Cyclopentadiene (C. P) 6 wt%
Solvent60 wt%
B, Isoprene (I. P)30 wt%
Cyclopentadiene (C. P)10 wt%
Solvent60 wt%
C. P*
I. P, In the solvent-rich phase

content.

As for the temperature effect, although only two different temperatures were employed in this study, it appears from Table 3 and 4 that the lower temperature is more favourable. There are, however, obvious lower limits in the temperature, namely the freezing points of water (0°C) and *N*-methylpyrrolidone (-17°C).

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