Mutual Solubilities of Some Hydrocarbon Oils and Liquid Ammonia. I. Solubility Data

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Liquid ammonia has good solvency and selectivity for the extraction of aromatic hydrocarbons[1,2], olefinic hydrocarbons[1,2] or phenols[3] from hydrocarbon mixtures, and there is a possibility of the use of liquid ammonia as a solvent for the separation of hydrocarbons. It is desirable to have at hand accurate liquid-equilibrium data in order that the relative value of various solvents can be compared. However, relatively few ternary systems containing liquid ammonia have been investigated. Moreover, even for the binary systems, only a few solubility data of hydrocarbon oils and liquid ammonia have been reported[2,4-6]. When data on the mutual solubilities are available, it is possible to predict the equilibrium relations for the ternary system from the mutual solubilities between solvent and each of two components[7].

The paucity of information about the liquid equilibrium data for hydrocarbons and liquid ammonia prompted the author to obtain the knowledge of quantitative solubility relations. This paper includes solubility data for the representative compounds of olefins and saturated hydrocarbons at around room temperature, and those for aromatics at the temperatures near the critical solution temperature. As representative compounds of hydrocarbons, those in the C_7 to C_9 range for aromatics and in the C_6 to C_8 range for olefins and saturated hydrocarbons were mainly selected.

Experimental Procedure and Materials

Solubilities were determined by the same method as described in the previous paper[8,9]. Cloud points could be determined to within ±0.05°C or better by using the thermometer which was graduated in tenths of a degree and corrected by the P. T. R. thermometer. Mutual solubilities at the temperatures far from the critical solution temperature were obtained by determining the composition of the two liquid phases in equilibrium at a given temperature (±0.05°C). About five grams (±0.0005 g) of each of the separate phases were used for the analysis at each time, and the concentration of ammonia was determined by titrating with 0.5 N sodium hydroxide solution the excess of sulfuric acid which absorbed all ammonia in the liquid phase. The determination was repeated several times for each phase at a given temperature, and averaged. The average error was less than 0.1% with a maximum error of 0.4%.

Except for some of the materials, which were commercially available products purified by the ordinary methods, many hydrocarbons used for the determination were synthesized and carefully purified. In Table 1, their physical constants are listed together with the values in the literature[10].

n-Hexane and *n*-octane were synthesized from corresponding alkyl bromides according to Wurtz's method. Propylbenzene was prepared from bromobenzene and propyl bromide by Fittig reaction. *iso*-Propylbenzene was synthesized according to H. Meyer et al[13]. *o*-Xylene was prepared by the condensation of *o*-bromotoluene, which was synthesized by means of Sandmeyer reaction from acet-*o*-toluide of melting point 110°C as a starting material and methyl iodide using metallic sodium and purified by careful distillation. *m*-Xylene was obtained by decomposing *m*-xylene sulfonate of melting point 60°C which was prepared and purified from a commercial product by removing the *p*-isomer according to Clark et al.[15] after the sulfonation and the decomposition were repeated. *p*-Xylene was prepared by reducing *p*-chloromethyltoluene obtained by chloro-

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TABLE I

PHYSICAL PROPERTIES OF HYDROCARBONS USED FOR THE DETERMINATIONS

Name	b. p., °C		d_4^{20}		n_D^{20}		Remarks
	Obs.	Lit.[10]	Obs.	Lit.[10]	Obs.	Lit.[10]	
n-Hexane	68.7	68.740	0.6594	0.65937	1.3749	1.37486	a
n-Heptane	98.3	98.427	0.6838	0.68376	1.3878	1.38764	b[8,9]
n-Octane	125.4	125.665	0.7026	0.70252	1.3976	1.39743	a
2, 2, 4-Trimethylpentane	99.2	99.238	0.6919	0.69192	1.3916	1.39145	b
n-Cetane	286.6	286.793	0.7749	0.77344	1.4350	1.43453	c, m. p. 17.2 Lit. 18.165
Cyclohexane	80.5–81.0	80.738	0.7788	0.77855	1.4263	1.42623	d[11], m. p. 6.32 Lit. 6.554
Methylcyclohexane	100.9	100.934	0.7686	0.76939	1.4231	1.42312	c
Decalin *cis*	189–190	195.69	0.8859	0.8965	1.4750	1.4810	c[12]
trans		187.25		0.8699		1.4695	
Cyclohexene	82.8	82.979	0.8096	0.81096	1.4465	1.44654	c, Br. No. 194.6 Theor. 194.58
1-Octene	122.6	121.280	0.7161	0.71492	1.4086	1.40870	a[11], Br. No. 142.2 Theor. 142.7
Styrene	48/24.1	145.2	0.9059	0.90600	1.5468	1.54682	c[1], Br. No. 151.2 Theor. 153.5
Toluene	110.5	110.625	0.8660	0.86694	1.4961	1.49693	c[8,9]
Ethylbenzene	136.0	136.186	0.8670	0.86702	1.4959	1.49588	a[1]
o-Xylene	144.2	144.414	0.8805	0.88020	1.5045	1.50545	a, m. p. −25.3 Lit. −25.182
m-Xylene	139.1	139.103	0.8636	0.86417	1.4971	1.49722	d, m. p. −47.9 Lit. −47.872
p-Xylene	138.4	138.351	0.8605	0.86105	1.4957	1.49582	a, m. p. 13.2 Lit. 13.263
Propylbenzene	159.2	159.217	0.8619	0.86204	1.4920	1.49202	a
iso-Propylbenzene	152.4	152.392	0.8618	0.86179	1.4912	1.49145	a[13]
Mesitylene	164.7	164.715	0.8647	0.86518	1.4993	1.49937	a[14]
1-Methylnaphthalene	244.4	244.642	1.0200	1.02015	1.6174	1.6174	a
Tetralin	207	207.57	0.9702	0.9702	1.5414	1.54135	d[12]

a) This material was synthesized.
b) This material is the reference fuel for Octane Number determination.
c) Commercially available product was purified according to the ordinary method.
d) Commercially available product was purified according to the description in the literature.

methylation of toluene, and purified by the conversion in to the sulfonate which melted at 86°C after three recrystallizations from water.

Mesitylene was synthesized by sulfuric acid condensation of acetone[14]. 1-Methylnaphthalene was synthesized by the reduction of 1-chloromethylnaphthalene which was obtained by the chloromethylation of naphthalene, and purified by applying chromatographic cleavage of the picrate whose melting point was 141—141.5°C. Methods of purifying for the other materials have been described in the previous paper[8,11,12].

Results

Mutual solubility data of liquid ammonia and paraffins, naphthenes and olefins are given in Table II.

Values for *n*-heptane[9], cyclohexane[1], decalin[12] and purified commercial hexane which is used for the extraction of vegetable oils[1,11] are also given in Table II for convenience of comparison.

As will be clear from Table II, it is observed for liquid ammonia-saturated hydrocarbons systems that within the experimental range, naphthenic hydrocarbons are more soluble in liquid ammonia at a given temperature than paraffins which have the same number of carbon atoms, whereas the quantities of ammonia dissolved in hydrocarbon rich phase are greater in paraffins; it is also observed that solubilities decrease as the molecular weight increases. For binary systems of aliphatic hydrocarbons and liquid ammonia, it is observed that logarithms of solubilities of paraffins in each phase are almost proportional to those of vapor pressures of these hydrocarbons at a given temperature, and that their solubilities are small compared with those of olefins.

The experimental data for aromatic

TABLE II

MUTUAL SOLUBILITY DATA FOR PARAFFINS, NAPHTHENES AND OLEFINS WITH LIQUID AMMONIA, Wt. % OF NH_3

Material	Phase	Temperature, °C					
		30	20	10	0	−7.5	−15
Purified Hexane Used for Vegetable Oil Extraction	Upper		94.4				
	Lower		6.1				
n-Hexane	Upper		$94\cdot9_4$		97.4_1		
	Lower		5.7_8		3.0_2		
n-Heptane	Upper		96.9_2		98.1_6	98.4_9	98.8_0
	Lower		4.8_5		2.7_3	2.2_3	1.7_1
n-Octane	Upper		97.7_5		98.5_6		
	Lower		4.1_3		2.2_9		
2, 2, 4-Trimethylpentane	Upper		96.8_9		98.5_1		
	Lower		5.0_8		2.7_3		
n-Cetane	Upper	98.5_7	99.4_4				
	Lower	3.0_8	2.4_3				
Cyclohexane	Upper		94.2_2		96.7_8		
	Lower		3.9_9		2.1_2		
Methylcyclohexane	Upper		94.7_2		97.8_8		
	Lower		4.1_5		2.2_0		
Decalin	Upper		97.8_4		98.3_5		
	Lower		2.2_8		1.4_0		
1-Octene	Upper		93.6_9		96.8_3		
	Lower		7.8_8		4.0_9		
Cyclohexene	Upper	72.6_4	82.1_9	88.0_0	91.6_1		
	Lower	15.2_2	9.3_9	6.3_7	4.5_5		

TABLE III

SOLUBILITY OF AROMATICS IN LIQUID AMMONIA, Wt. % of NH_3

Material	Temperature, °C								
	30	25	20	15	10	5	0	−5	−15.5
Ethylbenzene		miscible			57.0_1	71.4_7	78.1_1	82.2_5	87.0_2
o-Xylene		miscible			61.8_3	72.6_3	78.8_2	82.9_6	
m-Xylene		miscible			69.5_0	76.7_2	81.0_2	84.2_0	
p-Xylene		miscible			64.9_2	74.4_7	79.9_4	83.7_5	
Propylbenzene	miscible		68.5_0	77.3_5	82.8_2	86.4_6	88.8_8		
iso-Propylbenzene	miscible		C.S.T.	70.8_2	78.9_2	83.3_1	86.7_2		
Mesitylene	67.6_7	76.2_0	81.0_9	84.8_5	87.5_7	89.9_2	91.4_4		
1-Methylnaphthalene		64.3_7	71.7_8	77.1_6	81.1_2	83.9_4	85.9_4		
Tetralin			86.3_9				93.7_2		

Temperature, °C (±0.1°) Material	−10	−15	−20	−25	−30
Toluene	64.4_4	73.1_8	78.5_9		
Styrene			68.7_6	76.3_4	79.8_8

hydrocarbons are given in Tables III and IV. *p*-Xylene is present as crystals at the experimental temperatures, but the mixture with liquid ammonia was liquid over the experimental temperature range above 5°C. *p*-Xylene-rich layer stayed in a supercooled liquid state at the temperatures of 0° and −5°C, and it was difficult to cause it to crystallize by mere agitation. Occasionally, *p*-xylene-rich layer was caused to crystallize by the stimulation such as the release of a portion of the solution from the bottle containing the system, which closed the reducing valve and made it impossible to continue the experiment. The data for *p*-xylene at the temperatures of 0° and −5°C given in Table IV are values in a supercooled condition. In Tables III and IV, the data for tetralin[12)] and toluene[9)] are also adopted for comparison from the previous paper.

In Table V are given the results of the determinations of compositions and cloud points for the binary systems of aromatics and liquid ammonia at temperatures near the critical solution temperature. The critical solution temperatures and their compositions estimated graphically from

TABLE IV

SOLUBILITY OF LIQUID AMMONIA IN AROMATIC HYDROCARBONS, Wt. % OF NH_3

Material	Temperature, °C 30	25	20	15	10	5	0	−5	−15.5
Ethylbenzene		miscible			30.7_6	18.9_0	14.1_3	11.3_1	8.0_0
o-Xylene		miscible			24.3_2	16.9_5	13.0_7	10.8_3	
m-Xylene		miscible			20.2_5	15.0_3	11.8_7	9.6_7	
p-Xylene		miscible			22.1_3	16.1_2	12.7_8	10.3_3	
Propylbenzene	miscible		22.5_4	16.5_5	13.1_7	10.8_9	9.1_5		
iso-Propylbenzene	miscible		C.S.T.	20.5_7	15.2_6	12.2_3	10.0_1		
Mesitylene	21.0_4	15.5_2	12.5_7	10.3_6	8.6_2	7.2_6	6.2_9		
1-Methylnaphthalene		22.2_4	17.3_6	14.3_0	12.1_9	10.4_3	9.1_2		
Tetralin			8.0_9				4.7_1		

Temperature, °C (±0.1°) Material	−10	−15	−20	−25	−30
Toluene	20.2_2	15.3_4	12.4_1		
Styrene			20.7_5	14.6_6	11.9_5

TABLE V

CLOUD POINTS AND THEIR COMPOSITION FOR AROMATICS WITH LIQUID AMMONIA

Cloud Pt., °C	NH_3 Wt. %	Cloud Pt., °C	NH_3 Wt. %	Cloud Pt., °C	NH_3 Wt. %
Styrene		*o*-Xylene		*p*-Xylene	
−16.8	27.6_5	11.5	34.3_8	12.3	29.9_3
−16.3	30.2_5	11.9	41.9_7	12.8	42.9_0
−15.85	32.1_1	11.9	45.3_4	12.6	48.0_9
−15.7	34.7_1	11.8	47.9_3	12.6	48.2_2
−15.5	40.3_8	11.5	54.5_5	12.5	52.0_0
−15.5	42.4_4	11.3	56.6_8	11.7	58.0_3
−15.5	43.9_1	11.2	57.0_6	11.6	58.9_9
−15.8	50.2_2	11.1	57.6_2	10.2	64.0_9
−17.8	62.5_3	10.6	60.2_6	12.8*	40.5**
−15.5*	43.9**	11.9*	43.3**		
Ethylbenzene		*m*-Xylene		Propylbenzene	
9.0	26.2_1	14.1	31.6_8	21.3	24.9_3
10.2	32.1_1	14.6	42.1_0	23.6	36.0_4
10.5	36.0_7	14.4	46.5_1	23.9	40.2_3
10.6	37.2_2	13.9	54.0_9	23.9	41.8_7
10.7	44.2_4	13.8	54.9_4	23.0_5	56.7_4
10.4	51.7_7	13.5	56.7_5	22.6	58.8_5
10.1	55.4_4	11.6	65.0_7	22.4_5	59.5_9
0.0	62.2_0	14.6*	41.5**	23.9*	44.7**
10.7*	43.4**				
iso-Propylbenzene		Mesitylene		1-Methylnaphthalene	
18.0	25.2_7	32.6	26.8_2	26.0	23.7_3
19.0_5	28.5_0	33.8	36.5_1	27.4	27.4_1
19.8	34.2_3	33.9	39.6_2	27.4_5	27.4_9
20.0	42.5_7	33.9	41.8_3	28.6	36.1_7
19.9	48.5_8	33.9	45.0_2	28.8	42.3_4
19.7	52.7_4	33.9	45.4_7	28.8	44.4_7
19.6	54.3_4	33.8_5	48.7_2	28.7_5	47.6_7
19.3	56.7_9	33.7	52.7_8	28.7	48.8_3
18.0	63.7_5	33.6	53.0_7	28.5	50.9_8
20.0*	71.7**	33.5_5	53.6_1	28.2	53.5_2
		32.9	59.5_6	27.0	59.2_6
		32.4_5	61.1_8	28.8*	42.6**
		33.9*	42.9**		

* Critical solution Temperature.
** Critical Composition.

the data given in Tables III, IV and V are also given in Table V.

The critical solution temperatures for toluene⁹⁾ and *iso*-propylbenzene with liquid ammonia in the present investigation, −7.4° and 20.0°C, are lower than those given in the literature⁶⁾, −5° and 25°C, respectively. But, the value for *m*-xylene, 14.6°C, agrees with that obtained by Kraus, et al.⁴⁾, 14.7°C, which is believed to be accurate. The critical composition for this system is 81.5 mole per cent. of ammonia and compared with the Kraus' value of 81.4 mole per cent. ammonia. The critical solution temperature for 1-methylnaphthalene with liquid ammonia is 28.8°C by the present determination, compared with the Francis' value of 28°C⁶⁾.

In the case of all these systems, it will be clear from Tables II, III and IV that solubilities in both phases are smaller at lower temperatures exhibiting positive deviations from Raoult's law, and roughly symmetrical on the basis of weight fraction. However, as the molecular weight of ammonia is considerably small compared with that of any other component, the solubility curves lean to the ammonia side on the basis of mole fraction expressing unsymmetrical form, as shown in Fig. 1. The mole fractions of ammonia in hydrocarbon-rich phase are greater than those of oils in liquid ammonia rich phase. Solubilities of these hydrocarbons in liquid ammonia are less than 10 mole per cent., except for the cases in the neighborhood of the critical solution temperature, and the solubility change in ammonia-rich phase due to temperature variation is small compared with that in the hydrocarbon-rich phase.

In Fig. 1, in addition to the mutual solubilities of aromatic hydrocarbons and liquid ammonia, the concentrations of ammonia in hydrocarbon-rich phase for other representative hydrocarbons are shown on the basis of mole fraction. The values of Kraus, et al. for *m*-xylene are also given for comparison. Solubility curves for paraffins, naphthenes and olefins in liquid ammonia-rich phase are omitted in the figure except for *n*-heptane, because they are so nearly of the same order that the curves for them can not be expressed clearly without overlapping.

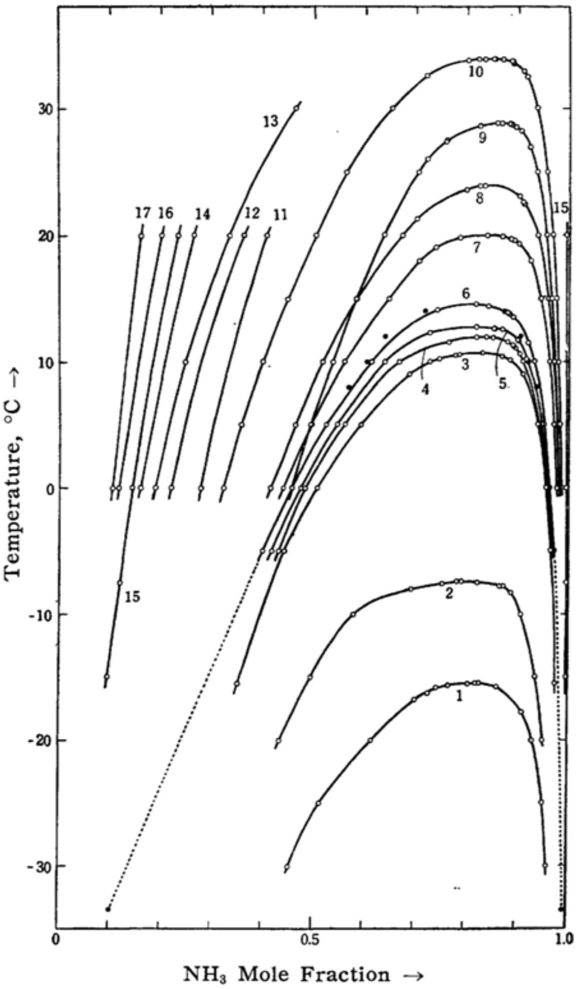

Fig. 1. Solubility curves for some hydrocarbons and liquid ammonia.

1. Styrene
2. Toluene
3. Ethylbenzene
4. *o*-Xylene
5. *p*-Xylene
6. *m*-Xylene (• Kraus value)
7. *iso*-Propylbenzene
8. Propylbenzene
9. 1-Methylnaphthalene
10. Mesitylene
11. Tetralin
12. 1-Octene
13. Cyclohexene
14. 2, 2, 4-Trimethylpentane
15. *n*-Heptane
16. Methylcyclohexane
17. Decalin

Summary

In order to obtain the quantitative knowledge on the solubility relations for liquid ammonia systems, mutual solubilities of aromatic hydrocarbons and liquid ammonia were determined at the several temperatures near the critical

solution temperature, and data for other hydrocarbons were mainly obtained at 20° and 0°C. These results were presented in tables and a figure.

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