Ternary Liquid Equilibria in System n-Heptane-Thiophene-Liquid Ammonia. New Tie Line Correlation

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(Received October 19, 1959)

The removal of organic sulfur compounds from petroleum products has been one of the most important problems in the petroleum refinery field for many years, although the success of the hydro-refining process has reduced the difficulties of the desulfurization. It has been reported that there is a possibility of the use of liquid ammonia and its mixed solvents as desulfurizing agents on the extraction process[1], but no fundamental data in connection with this matter have been given. This paper presents the equilibrium data at temperatures of 20 and 0°C for the system *n*-heptane-thiophene-liquid ammonia, and a new method correlating tie line data for ternary liquid equilibria has been described.

The method used to obtain data for the construction of phase equilibria was the same analytical method as described in the previous paper[2]. The heterogeneous liquid layers were separated and analyzed after the saturation equilibrium was attained in a constant temperature bath regulated within the range of ±0.05°C throughout the experiment. An aliquot of each layer, which was determined from the difference of weight of the bottle containing the system, was released to the receiver and the ammonia was absorbed by the definite quantity of the 2 N sulfuric acid solution after it was removed from the receiver by volatilization, and then backtitrated with 0.5 N standard hydroxide solution. The compositions of ammonia-free organic liquid were determined by measuring their densities and refractive indices to the nearest 0.0001 unit. The results were adjusted for the slight loss of organic liquid by volatilization by means of the lever rule[3] from the composition of the total mixture and the concentrations of ammonia in both layers. It was observed that when the vaporization loss of binary mixtures of heptane and thiophene was less than about 15%, the compositions of organic binary mixtures were practically unaffected with the vaporization of organic liquid accompanied by the determination of ammonia, though the vapor pressure of thiophene has about twice that of *n*-heptane in the neighborhood of 0°C.

n-Heptane used in this investigation was the reference fuel for octane number determination, having the following physical constants, b.p., 98.3°C; d_4^{20}, 0.6838; n_D^{20}, 1.3878. Commercially available thiophene was dissolved in liquid ammonia, allowed to stand overnight, and then redistilled after the yellowish precipitates were removed; the middle fractions having the constants b. p. 84.1°C, d_4^{20} 1.0638, n_D^{20} 1.5288 were used.

Results and Discussion

The data of densities and refractive indices for the binary system of *n*-heptane and thiophene from which the compositions of the raffinate and the extract were determined are given in Table I, and the equilibrium data for the ternary system are given in Table II and shown in Figs. 1 and 2. As will be clear from the figures, tie lines are almost parallel to the base of the triangle and in the case of equilibrium at 0°C the distribution ratio changes from more than unity to less than unity as shown in Fig. 2. The maximum selectivity[5] for this system regarding liquid ammonia as a solvent for the separation of thiophene from paraffin are given to be 72.9 and 62.0 wt. % at 0 and 20°C., respectively. The respective maximum concentrations of thiophene in the extract are 89.3 and 78.8 wt.% at 0 and 20°C., then the maximum

TABLE I. DENSITIES AND REFRACTIVE INDICES FOR *n*-HEPTANE-THIOPHENE BINARY SYSTEM

Thiophene wt. %	d_4^{20}	n_D^{20}
0.0	0.6838	1.3878
12.73	0.7154	1.3977
25.89	0.7514	1.4103
31.73	0.7688	1.4164
53.36	0.8414	1.4432
58.37	0.8607	1.4508
62.36	0.8766	1.4565
74.19	0.9285	1.4764
79.82	0.9554	1.4865
85.98	0.9866	1.4988
92.71	1.0229	1.5128
100.0	1.0638	1.5288

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TABLE II. EQUILIBRIUM DATA FOR THE SYSTEM *n*-HEPTANE-THIOPHENE-LIQUID AMMONIA AT 20.0 AND 0.0°C., wt. %

Total mixture		Hydrocarbon layer		Solvent layer	
Thiophene wt. % (Solvent-free basis)	NH_3 wt. %	NH_3 wt. %	Thiophene wt. % (Solvent-free basis)	NH_3 wt. %	Thiophene wt. % (Solvent-free basis
		At 20.0°C			
0.0	—	4.8	0.0	96.9	0.0
12.7	53.2	5.7	5.6	89.4	61.2
25.9	54.1	6.7	11.5	82.9	73.4
44.7	51.7	8.8	22.0	71.3	78.8
42.3	40.1	10.1	26.8	65.6	77.9
53.4	38.9	13.6	36.0	55.0	75.0
50.8	30.6	15.6	40.6	49.4	72.7
58.4	32.6	22.0	49.2	41.2	67.3
60.7	34.8	23.8	51.1	38.8	65.5
Plait point[a]		30.7	58.1	30.7	58.1
		At 0.0°C			
0.0	—	2.7	0.0	98.2	0.0
8.9	45.5	2.9	4.8	93.2	74.2[b]
19.3	52.0	3.4	9.4	88.6	82.4[b]
33.5	50.7	4.1	17.1	81.2	88.0
36.0	33.7	5.3	25.2	73.3	89.3
50.1	34.5	7.4	35.7	63.4	88.8
56.5	32.8	8.8	41.9	56.9	87.5
62.4	30.0	11.4	49.8	49.0	85.0
63.9	30.6	11.9	50.9	48.1	84.6
78.2	42.3	12.9	52.8	46.5	84.1
73.6	32.8	18.2	61.9	38.4	79.8
Plait point[a]		28.3	72.5	28.3	72.5

a) The plait point was estimated according to Treybal et al.[4]

b) This value was calculated from the concentration of ammonia in both layers and the composition of the total mixture and the raffinate.

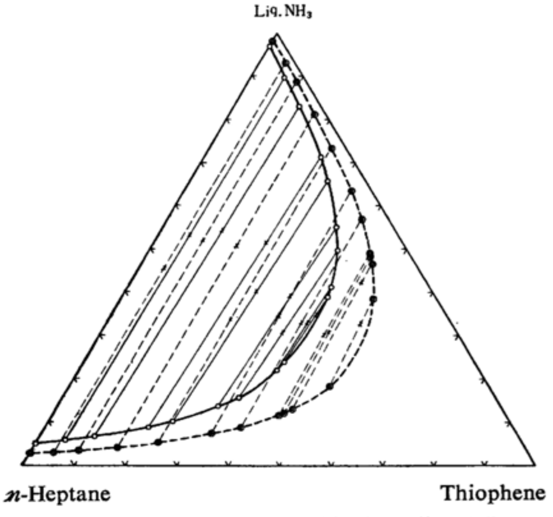

Fig. 1. System *n*-heptane-thiophene-liq. NH_3 at 20 and 0°C, wt. %.

—○— 20.0°C --◎-- 0.0°C

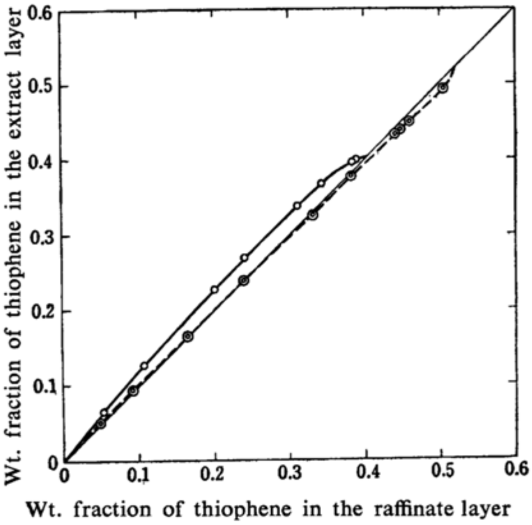

Fig. 2. Equilibrium distribution diagrams for the system *n*-heptane-thiophene-liq. NH_3.

—○— 20.0°C --◎-- 0.0°C

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[4] R. E. Treybal, L. D. Weber and J. F. Daley, ibid., 38, 817 (1946).

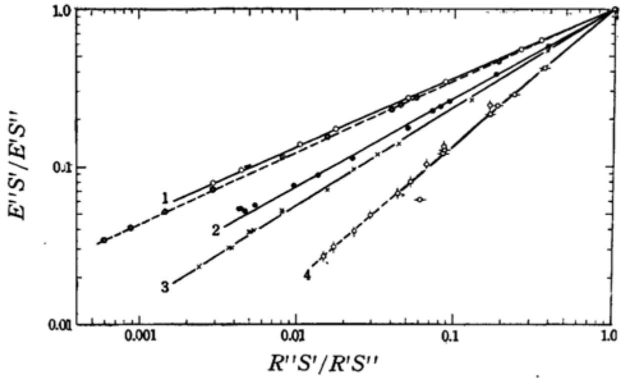

Fig. 3. Plot on logarithmic coordinates $E''S'/E'S''$ against $R''S'/R'S''$ for liquid ammonia systems.

Number	Symbol	System			Temperature, °C	Reference
		R	E	S		
1	—○—	*n*-Heptane—	Thiophene—	Liq. NH_3	20.0	
	--◎--	*n*-Heptane—	Thiophene—	Liq. NH_3	0.0	
2	—●—	*n*-Hexane—	Benzene—	Liq. NH_3	20.0	5)
3	—×—	*n*-Heptane—	Toluene—	Liq. NH_3	20.0	6)
4	—○—	Ethylbenzene—	Styrene—	Liq. NH_3	0.0	5)
	--ϕ--	Ethylbenzene—	Styrene—	Liq. NH_3	−15.5	5)

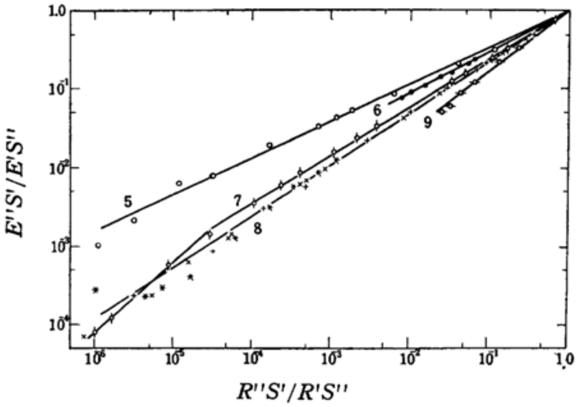

Fig. 4. Plot on logarithmic coordinates of $E''S'/E'S''$ against $R''S'/R'S''$ for systems of various investigators.

Number	Symbol	System			Temperature, °C	Reference
		R	E	S		
5	○	Benzene—	Dioxane—	Water	25	7)
6	●	Water—	Acetic Acid—	Furfural	26.7	8)
7	ϕ	Water—	Acetic Acid—	Toluene	25	9)
8	+	Water—	Ethanol—	Benzene	25	10)
	×	〃	〃	〃	25	11)
	✳	〃	〃	〃	25	12)
9	-○-	Water—	Methanol—	Butano	15	13)

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12) E. R. Washburn, V. Hnizda and R. Vold, *J. Am. Chem. Soc.*, **53**, 3237 (1931).

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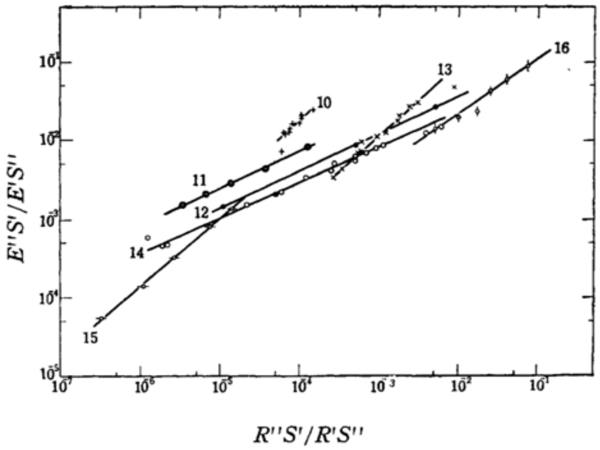

Fig. 5. Plot on logarithmic coordinates of $E''S'/E'S''$ against $R''S'/R'S''$ for systems containing two partially miscible pairs.

Number	Symbol	System R	System E	System S	Temperature, °C	Reference
10	+	*n*-Heptane	Methylcyclohexane	Aniline	25	14)
11	◎	Water	Aetone	Chlorobenzene	25∼26	15)
12	●	*n*-Hexane	Methyl ethyl ketone	Water	37.8	16)
13	×	*n*-Heptane	Toluene	Liq. NH_3	−15	6)
14	○	Benzene	Butanol	Water	25	17)
15	-○-	Toluene	Aniline	Water	25	18)
16	ϕ	Ethyl acetate	*sec*-Butanol	Water	20	19)

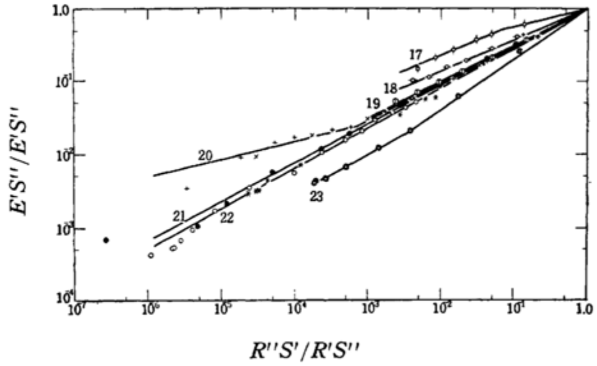

Fig. 6. Plot on logarithmic coordinates of $E''S'/E'S''$ against $R''S'/R'S''$ for solutropic systems.

Number	Symbol	System R	System E	System S	Temperature, °C	Reference
17	ϕ	Water	*t*-Butanol	Ethyl acetate	20	19)
18	-○-	Water	Isopropanol	Ethyl acetate	20	19)
19	⦶	Water	Acetic acid	Ether	25	20)
20	+	Water	Pyridine	Benzene	25	21)
	×	〃	〃	〃	25	22)
	✳	〃	〃	〃	25	23)
21	●	Water	*t*-Butanol	Benzene	25	24)
22	○	Water	Isopropanol	Benzene	25	25)
23	◎	Water	Ethanol	3-Heptanol	25	26)

separation factors[5] become the respective values of 0.650 and 0.488, these values being considerably greater when compared with those in cases of the separation of hydrocarbon mixtures.

Tie Line Correlation

This system as in the other solutropic systems fails to give a straight line having a definite slope from the appropriate plot of conjugate values at equilibrium according to any method which has been proposed by any one of the many investigators as tie line correlations. The author has found that a straight line results from a plot of logarithm of $E''S'/E'S''$ against logarithm of $R''S'/R'S''$ where S, E and R are the respective fractions of the solvent, the solute and the diluent at equilibrium and one prime and two primes denote the diluent-rich layer and the solvent-rich layer, respectively. Plots by this method for the present data are shown in Fig. 3. In Fig. 3, plots for the several systems using liquid ammonia as a solvent are also included. It is observed that these data are correlated by this method satisfactorily.

Several ordinary systems investigated by various workers are plotted in Fig. 4, and plots for systems containing two pairs of partially miscible liquids are given in Fig. 5. Plots by this method for several solutropic systems are shown in Fig. 6. Except for some systems where it seems to be plausible that the data are correlated by two straight lines changing their slopes, the plotted data for most systems fall on straight lines having definite slopes almost within their probable experimental accuracy. When the solvent and the diluent are practically insoluble as in the case of benzene-water binary, values of $S'R''/S''R'$ and $S'E''/S''E'$ become more inaccurate at the lower concentrations of the solute, because the concentrations of the solute are very small and their accurate determinations by ordinary methods are difficult. For this reason, it may be said roughly that plots by this method would give a straight line for most ternary systems.

Since the values of $S'R''/S''R'$ for the binary systems of the diluent and the solvent are located as the abscissa on the left ends of straight lines in these figures, the initial distribution ratio at zero concentration of the solute can be estimated from the ordinate on these points. The ordinate on the right ends of straight lines in Fig. 5 represent the values of $S'E''/S''E'$ for the binary systems of the solute and the solvent, and the abscissa the product of the distribution coefficient at zero concentration of the diluent and the ratio of the concentration of the solvent in the solute rich phase to that in the solvent rich phase.

The straight lines can be represented by equations of the form

$$\log\frac{E''S'}{E'S''}=n\log\frac{R''S'}{R'S''}+k \qquad (1)$$

For the ordinary systems which comprise two miscible pairs of liquids and one partially miscible pair, the value of k should be extremely near zero, since the values of $S'E''/S''E'$ and $S'R''/S''R'$ at the plait point are equal to unity. If the relative distribution ratio is designated by β,

$$\beta=\frac{E''}{E'}\cdot\frac{R'}{R''} \qquad (2)$$

Then,

$$\log\beta=(n-1)\log\frac{R''S'}{R'S''}+k \qquad (3)$$

Therefore, if a plot is made of the relative distribution ratio against the quotient of the ratio of the concentration of the solvent in the diluent rich phase to that in the solvent rich phase and that of the solute or the diluent on the double logarithmic coordinates, a straight line will be given as well not only for ordinary systems, but also for solutropic systems and those containing two partially miscible pairs.

Summary

Phase equilibria for the system *n*-heptane-thiophene-liquid ammonia has been determined at temperatures of 0 and 20°C. A new method has been proposed which correlates tie line data in such a manner that a straight line is obtained for most systems including solutropic systems.

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