Tie Line Correlation for Ternary Liquid Equilibria

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Since only a few tie lines have been experimentally determined in most systems described in the literature, several methods of interpolating and extrapolating such data over the entire range of composition have been devised. Except for the graphical methods[1,2], they are expected to give a straight line from the appropriate plot of conjugate values at equilibrium. Most of these are related to the systems which comprise two miscible pairs of liquids and one partially miscible pair (type 1), while only a few methods[3,4,5]

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[1] "International Critical Tables", McGraw-Hill Book Company, Inc., New York (1928), Vol. III, p. 398.
T.K. Sherwood, "Absorption and Extraction", McGraw-Hill Book Company, Inc., New York (1937), p. 242.
A. V. Brancker, T. G. Hunter and A. W. Nash, *Ind. Eng. Chem., Anal. Ed.*, **12**, 35 (1940).

[2] D. B. Hand, *J. Phys. Chem.*, **34**, 1961 (1930).

[3] K. A. Varteressian and M. R. Fenske, *Ind. Eng. Chem.*, **29**, 270 (1937).

[4] T. F. Brown, ibid., **40**, 103 (1948).

[5] J. B. Conway and J. B. Philip, ibid., **45**, 1083 (1953).

have been proposed to the systems which comprise two partially miscible pairs of liquids and one miscible pair (type 2).

It seems that no useful method applicable to both types has ever been proposed, thus, the method useful for type 1 does not always give satisfactory results when applied to type 2 and vice versa[6,7]. Since it is evident that both types may interchange with each other with changing temperatures, the useful method applicable for both types is desirable, if it is possible.

The upper critical solution temperature in the binary system containing toluene and liquid ammonia was found to be −7.4°C by the measurement of mutual solubilities of this system. Therefore, the equilibrium for the system *n*-heptane-toluene-liquid ammonia at the temperatures below −7.5°C involves two pairs of partially miscible liquids, and the binodal curve of the system at −7.5°C touches the side of the triangle which represents the binary mixture of toluene and liquid ammonia. It is considered that the methods resulting in a straight line for the tie-line data at the critical solution temperature of one pair of binary systems are generally applicable to systems for both types.

In the present study, the system *n*-heptane-toluene-liquid ammonia has been investigated at −7.5° and −15°C to determine whether the previous methods for obtaining the straight line correlation were applicable to both types independent of temperature.

Experimental Procedure and Results

The equilibrium data for the ternary system and mutual solubilities of toluene and liquid ammonia at the temperatures of −10°, −15° and −20°C were determined by the same way as described in the previous paper[8]. Alcohol cooled by dry ice in the Dewar vessel of large capacity was used as a constant temperature bath, and the desired temperature could be maintained within the range of ±0.1°C throughout the experiment. In order to minimize the change of temperature, thermal insulating tubes were used by means of which alcohol was made to circulate around the bottle containing the system. The heterogeneous liquid layers were separated and analysed after the saturation equilibrium was attained. The mutual solubilities of toluene and liquid ammonia at temperatures near the critical solution temperature were determined by noting the miscibility temperatures of mixtures of known composition. In these cases, the vapor pressure of a saturated solution at that temperature was determined experimentally, and the necessary correction for the composition of liquid components was estimated using the vapor pressure data and the volume of the vapor space.

The experimental data for the binary system toluene-liquid ammonia are given in Table I and the equilibrium data for the ternary system are given in Table II and shown in Fig. 1 and 2. In

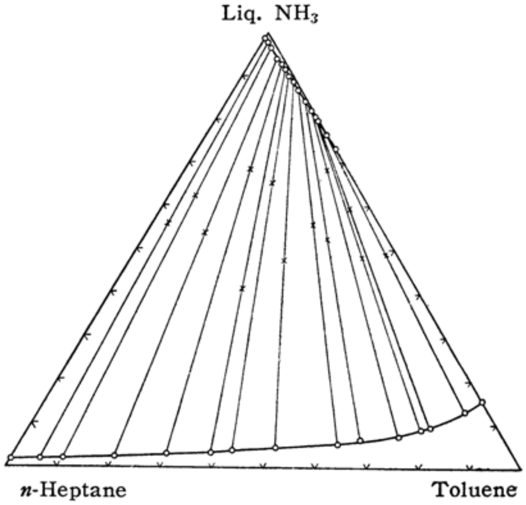

Fig. 1. System *n*-Heptane-Toluene-Liq. NH_3 at −15°C, wt. %.

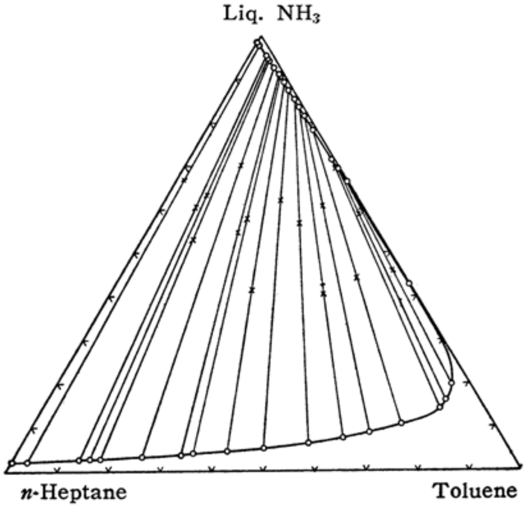

Fig. 2. System *n*-Heptane-Toluene-Liq. NH_3 at −7.5°C, wt. %.

TABLE I

SOLUBILITY DATA FOR THE SYSTEM TOLUENE AND LIQ. NH_3

Temperature °C	Wt. % NH_3 in NH_3 rich Layer	Wt. % NH_3 in Toluene rich Layer
−10	64.4	20.2
−15	73.2	15.3
−20	78.6	12.4
Cloud Point, °C	Wt. % NH_3 in Solution	
−8.0	29.3	
−7.6	35.9	
−7.4	39.6	
−7.4	41.1	
−7.5	46.0	
−7.8	54.4	
−7.8	56.1	
−8.3	59.7	

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[6] C. E. Dryden, ibid., 35, 492 (1943).

[7] D. DeB. Darwent and C. A. Winkler, *J. Phys. Chem.*, 47, 442 (1943).

[8] K. Ishida, *J. Chem. Soc. Japan* (Ind. Chem. Sect.,) 56, 469 (1953).

TABLE II

EQUILIBRIUM DATA FOR THE SYSTEM *n*-HEPTANE-TOLUENE-LIQUID AMMONIA

Total Mixture		Hydrocarbon Layer		Solvent Layer	
Toluene Wt. % (Solvent-free Basis)	NH_3 Wt. %	NH_3 Wt. %	Toluene Wt. % in the Raff. (Solvent-free Basis)	NH_3 Wt. %	Toluene Wt. % in the Ext. (Solvent-free Basis)
		At −15.0°C			
0.0	—	1.7	0.0	98.8	0.0
6.8	56.0	1.8	5.7	97.7	43.5[a]
13.3	62.4	2.0	10.3	96.4	59.5[a]
24.2	53.8	2.4	20.3	93.9	75.0
39.8	68.4	3.1	30.7	92.7	85.0
42.6	41.2	3.4	39.5	91.6	88.8
52.9	65.3	4.0	43.6	89.9	89.9
56.9	47.5	4.6	52.7	88.6	93.0
70.5	55.7	5.4	65.2	86.7	95.1
75.0	52.5	6.5	70.0	84.2	96.1
86.1	68.2	7.1	78.2	82.0	97.7
86.1	48.1	8.8	83.4	80.6	98.3
90.0	59.5	9.3	85.4	79.7	98.3
96.0	49.1	12.9	94.8	76.6	99.0
100.0	—	15.3	100.0	73.2	100.0
		At −7.5°C			
0.0	—	2.2	0.0	98.5	0.0
4.0	67.0	2.2	2.9	97.7	25.4[a]
17.7	60.6	2.7	13.3	95.3	72.1[a]
21.0	63.5	2.8	15.3	94.7	74.6[a]
21.5	53.0	2.8	17.5	94.3	77.0[a]
36.5	70.3	3.3	25.7	92.6	83.8[a]
39.7	54.9	3.7	33.4	90.9	87.7[a]
43.2	58.0	4.1	35.8	90.6	89.0
46.8	41.4	4.6	42.6	89.2	91.0
59.6	62.2	5.3	50.1	87.6	92.6
66.8	56.9	6.4	59.3	85.5	94.1
69.7	40.5	7.5	66.6	83.7	95.3
80.0	61.0	8.8	72.6	81.5	96.0
82.7	44.1	10.5	79.9	78.4	97.0
96.6	69.5	14.1	90.0	71.5	97.9
95.7	58.9	16.0	92.3	69.2	98.4
96.6	45.8	19.7	95.6	66.1	99.0
100.0	—	42.5[b]	100.0	42.5[b]	100.0
		At 0.0°C			
0.0	—	2.7	0.0	98.2	0.0
15.4	68.3	3.4	9.8	95.5	76.0
15.4	47.8	3.6	12.2	94.8	79.0
19.5	44.3	3.7	16.3	93.9	83.0
37.9	68.9	4.1	25.3	91.3	87.5
37.9	54.4	4.7	30.2	90.2	88.5
47.4	61.3	5.0	36.7	88.3	89.8
53.7	61.2	5.6	42.1	86.0	90.1
47.4	34.2	5.9	43.4	84.9	90.5
53.7	36.3	6.7	49.8	83.8	91.3
74.0	61.8	8.2	60.4	79.9	92.9
74.0	39.9	10.8	70.3	76.3	93.7
84.3	61.0	12.2	75.2	74.2	94.7
84.3	31.2	15.8	82.8	66.7	95.2

Total Mixture		Hydrocarbon Layer		Solvent Layer	
Toluene Wt. % (Solvent-free Basis)	NH_3 Wt. %	NH_3 Wt. %	Toluene Wt. % in the Raff. (Solvent-free Basis)	NH_3 Wt. %	Toluene Wt. % in the Ext. (Solvent-free Basis)
91.0	48.2	20.9	87.9	62.3	95.4
91.0	35.4	23.9	90.2	58.2	95.6
93.7	45.1	29.5	92.2	52.6	95.4
Plait Point[c]		45.4	94.8	45.4	94.8
At 20.0°C					
0.0	—	4.8	0.0	96.9	0.0
8.7	48.3	5.4	6.6	93.8	41.1
19.5	40.1	6.6	16.4	89.7	61.7
28.4	67.1	6.6	17.3	89.3	62.5
29.5	50.3	7.4	22.8	86.4	69.1
29.5	44.0	7.5	24.2	86.0	71.2
37.9	62.1	7.7	25.4	85.6	71.9
49.1	64.0	9.0	32.3	81.6	75.6
37.9	35.1	9.1	33.6	81.5	76.3
49.1	35.0	11.8	44.4	75.8	79.4
59.4	49.3	13.4	49.3	72.3	80.3
59.4	39.2	15.3	53.6	69.4	81.0
70.7	56.3	16.8	56.7	67.2	80.6
70.7	43.4	22.7	64.5	57.8	78.9
74.1	43.3	30.8	69.6	47.5	76.4
Plait Point[c]		43.4	75.0	43.4	75.0

a) This value was calculated from the concentrations of ammonia in both layers and the compositions of the total mixture and raffinate.

b) The upper critical solution temperature for the binary mixtures of toluene and liquid ammonia is −7.4°C. But, since in the equilibrium temperature the change of temperature within ±0.1°C was inevitable, the composition at the critical point were estimated to be the same as the solubility of toluene at −7.5°C.

c) The plait point was estimated according to Treybal et al.[9]

addition to the data at −15° and −7.5°C, the equilibrium data at the temperatures of 0° and 20°C for this ternary system are also given in Table II for convenience of discussion, as these data have not been presented in the previous paper[8]. It is found that in the neighborhood of the critical solution temperature for the binary mixtures of toluene and liquid ammonia, the selectivity[10] of liquid ammonia for toluene which is defined by the difference between the concentration of the solute in the extract, free from the solvent, and the corresponding concentration in the raffinate, is almost unaffected with the change of temperature at the higher concentrations of toluene, but at the lower concentrations of toluene its selectivity increases as the temperature rises to about 0°C. The effect of temperature on the selectivity will be discussed in the later paper.

Discussion

It has already been found that the Hand plot[2] and the Othmer-Tobias plot[11] give a straight line for the data at 20° and 0°C[8], but these plots were unsatisfactory for the data at −7.5° and −15°C, showing the curvature at the higher concentrations of toluene. This can be shown more conveniently by using a notation where E is the solute distributed between the substantially immiscible diluent R and solvent S, and the suffix r and s represent the concentration in the raffinate and the extract layer, respectively. It is clear that good results cannot be obtained for the systems of type 2 by these methods, because the values on the one hand give the definite values in all concentrations of the solute, while, the values on the other hand become infinite at $R=0$ on these coordinates, where a plot of conjugate values of Es/Ss against Er/Rr or $(1-Ss)/Ss$ against $(1-Rr)/Rr$ is made on double logarithmic coordinates.

Brown plot[4] of conjugate values of Rr/Ss against Rr made on arithmetic coordinates, which has been found to be applicable for the systems of type 2, gave lines of considerable curvature for the present data. Both methods of Conway and Philip[5] plotting the conjugate values of $\log Ss$ against Rr and Varteressian and Fenske[3] in which the equa-

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[9] R. E. Treybal, L. D. Weber and J. F. Daley, *Ind. Eng. Chem.*, 38, 817 (1946).

[10] K. Ishida, *Sience Repts. Research Inst. Tohoku Univ.*, Ser. A, 5, 377 (1953); *C. A.*, 48, 9045h (1954).

[11] D. F. Othmer and P. E. Tobias, ibid., 34, 693 (1942).

tion of distribution ratio may be represented by hyperbola and a straight line results from a plot of *Es/Er* against *Es* in the systems of type 2, did not give good results showing large curvature at higher concentrations of toluene.

No satisfactory method giving a straight line by the simple plot for the present data was found in many other previous methods in which a plot of conjugate values of *Ss/Rr* against *Ss* proposing by Bachman[12], Smith plot[13] of conjugate values of log (*Es/Er*) against log *Es*, Campbell plot[14] of log *Es* against log *Er* at equilibrium, and a plot of log $(1-Es)/Es$ against log $(1-Er)/Er$ by Major and Swenson[15] were included.

Of these methods just described, coordinates by Othmer and Tobias and Conway and Philip indicated a relatively good straight line except for the higher concentration of toluene.

The method by Dryden[6] which correlates the concentrations of the solute at equilibrium phases on the solvent free basis, namely a plot of conjugate values of $\{Er/(Er+Rr)\}/\{Es/(Es+Rs)\}$ against $Er/(Er+Rr)$, showed goood results for the data at the temperatures of −15°, −7.5° and 0°C, but was unsatisfactroy for the data at 20°C, since the relative distribution ratio was not always constant, as he pointed out.

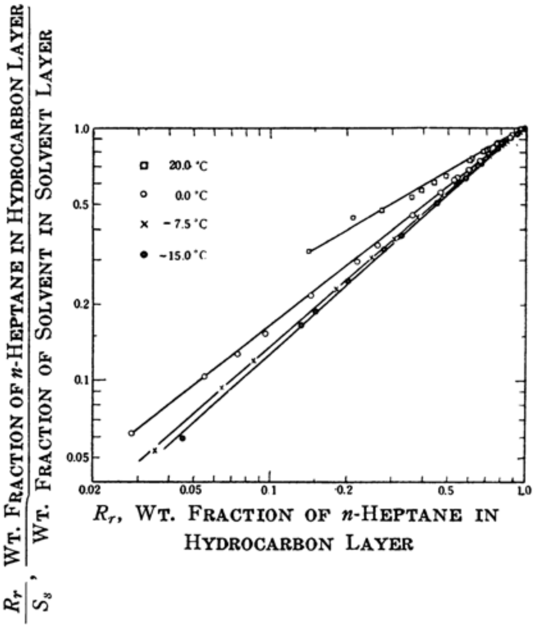

Fig. 3. Plot on logarithmic coordinates of R_r/S_s against R_r for the system *n*-Heptane-Toluene-Liq. NH_3.

Tests of these methods for the system *n*-hexane-methylcyclopentane-aniline[7], which is another system investigated at several temperatures neighbouring the critical solution temperature for the binary mixtures of the solute and the solvent, indicated the same results as the present data.

The author has found that a straight line results from a plot of log (*Rr/Ss*) against log *Rr* at equilibrium, where *Ss* is the fraction of the solvent in the solvent phase and *Rr* is the fraction of the diluent in the diluent phase. Plots by this method for the present data at the various temperatures are shown in Fig. 3, and for the system of *n*-hexane-methylcyclopentane-aniline[7] in Fig. 4. In Fig. 4, plots for the systems using liquid ammonia as a solvent are also included. It is clear that satisfactory results are obtained not only for the systems of type 2, but also type 1. In Fig. 5, several systems investigated by various

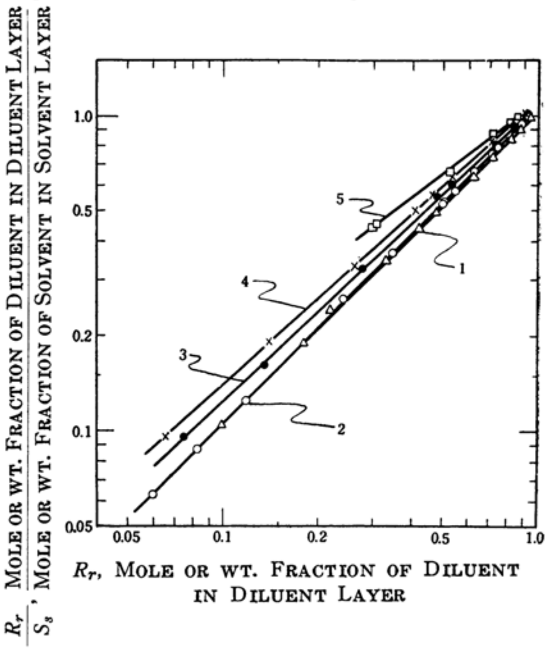

Fig. 4. Plot on logarithmic coordinates R_r/S_s against R_r for the systems *n*-Hexane-Methylcyclopentane-Aniline (3, 4, 5), *n*-Hexane-Cyclohexane-Liq. NH_3 (2) and *n*-Heptane-Octene-1-Liq. NH_3 (1).

Number	System	Temperature, °C	Reference
	R E S		
1	*n*-Heptane-Octene-1-Liq. NH_3, wt. fraction.	20.0	(16)
2	*n*-Hexane-Cyclohexane-Liq. NH_3, wt. fraction.	20.0	(16)
3	*n*-Hexane-Methylcyclopentane-Aniline, mole fraction.	25.0	(7)
4	*n*-Hexane-Methylcyclopentane-Aniline, mole fraction.	34.5	(7)
5	*n*-Hexane-Methylcyclopentane-Aniline, mole fraction.	45.0	(7)

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[12] I. Bachman, ibid., Anal. Ed. **12**, 38 (1940).

[13] A. S. Smith. ibid., **42**. 1206 (1950).

[14] J. A. Campbell, ibid., **36**, 1158 (1944).

[15] C. J. Major and O. J. Swenson, ibid., **38**, 834 (1946).

[16] K. Ishida, *J. Chem. Soc. Japan*, (Ind. Chem. Sect.,) **57**, 479 (1954).

workers are plotted and plots for systems having the distribution ratio greater than unity are shown in Fig. 6. These systems were selected at random. Among the systems represented by two straight lines changing their slopes, the system water-isopropanol-benzene and the system *n*-heptane-pyridine-liquid ammonia are the instances, in which curves or two straight lines having different slopes have also been obtained by the other methods.

Although plots for all systems do not always give a straight line, the plotted data fall on straight lines almost within their probable experimental accuracy, and especially for the systems containing two pairs of partially miscible liquids fair straight lines are obtained.

The straight lines can be represented by equations of the form

$$\log (Rr/Ss) = n \log Rr + m \qquad (1)$$

If the value of n is near unity, letting $m = \log m'$, it follows approximately,

$$Rr/Ss = m'Rr \qquad (2)$$

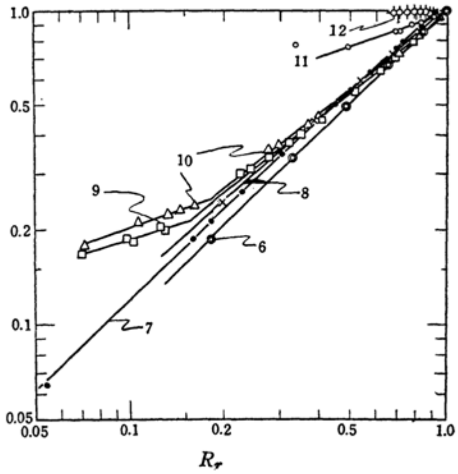

Fig. 5. Plot on logarithmic coordinates of R_r/S_s against R_r for systems of various investigators.

Number	System R	E	S	Temperature, °C	Reference
6	Toluene-	Aniline-	Water	25	(17)
7	*n*-Heptane-	Methylcyclohexane-	Aniline	25.0	(3)
8	1,1,2-Trichloroethane-	Methyl ethyl Ketone-	Water	25	(18)
9	Water-	Acetic acid-	Toluene	25	(19)
10	Water-	Acetic acid-	Benzene	25	(2)
11	Water-	Acetaldehyde-	Toluene	17	(20)
12	Water-	Acetic acid-	Furfural	26.7	(21)

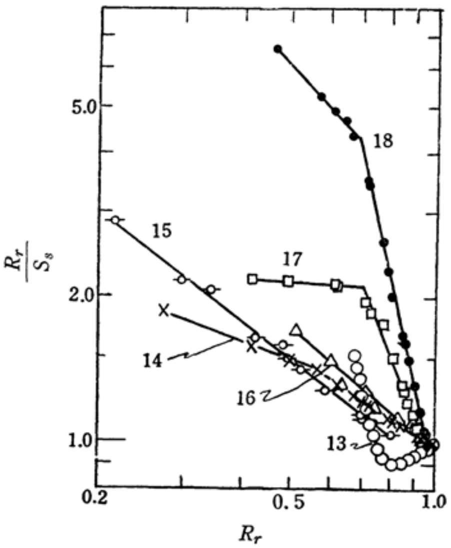

Fig. 6. Plot on logarithmic coordinate of R_r/S_s against R_r for systems having distribution ratio more than unity. (except for No. 16)

Number	System R	E	S	Temperature, °C	Reference
13	Water-	Isopropanol-	Benzene	25.0	(22)
14	Water-	Acetone-	1,1,2-Trichloroethane	25.0	(10)
15	Water-	Dioxane-	Benzene	25.0	(23)
16	Water-	Methanol-	Butanol	0.0	(24)
17	*n*-Heptane-	Pyridine-	Liq. NH_3	20.0	(25)
18	*n*-Heptane-	Pyridine-	Liq. NH_3	0.0	(25)

The method represented by equation 2 is that of Brown[4], of course. Therefore, it is possible to say that the author's method is Brown's generalized. In this plot, it is clear from equation 1 that a straight line will be obtained by using mole fraction on values of *Rr* and *Ss*, as well as weight fraction.

In equation 1, m is estimated from the mutual solubilities of R and S. When the same components are used for the diluent and the solvent, there is another possibility that the distribution ratio of the various solutes distributed between the diluent and the solvent can be compared by the values of slope n at the same temperature, since the value of m becomes constant, and distribution curves of the various solutes are given by lines which have various slopes and converge to a point representing the value of m.

If the value of n does not equal unity in equation 1 in all cases, equation 3 can be followed.

$$\log (Ss/Rr) = \{n/(n-1)\} \log Ss + m/(n-1) \qquad (3)$$

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17) J. C. Smith and R. E. Drexel, *Ind. Eng. Chem.*, **37**, 601 (1945).

18) M. Newman, C. B. Hayworth and R. E. Treybal, ibid., **41**, 2039 (1949).

19) R. M. Woodman, *J. Phys. Chem.*, **30**, 1283 (1926).

20) D. F. Othmer and P. E. Tobias, *Ind. Eng. Chem.*, **34**, 690 (1942).

21) A. E. Skrzec and N. F. Murphy, ibid., **46**, 2245 (1954).

22) A. L. Olsen and E. R. Washburn, *J. Am. Chem. Soc.*, **57**, 303 (1935).

23) R. J. Berndt and C. C. Lynch, ibid., **66**, 282 (1944).

24) A. J. Mueller, L. I. Pugsley and J. B. Ferguson, *J. Phys. Chem.*, **35**, 1314 (1931).

25) K. Ishida, *Bull. Chem. Res. Inst. Non-Aqueous Sol.*, Tohoku Univ., **3**, 109 (1953).

Therefore, it is possible to consider that the author's method is the modification of the Bachman plot, and a plot using equation 3 is also possible. However, the application of equation 3 for the systems containing the formation of two pairs of partially miscible liquids gives lines of curvature which approach the definite values at the infinite, since the value of n in these systems almost equals unity.

It is interesting that the method of Othmer and Tobias and the method presented in this paper are introduced by modifying the method of Bachman.

Summary

The various methods for obtaining straight lines were examined for the tie-line data investigated at several temperatures near the critical solution temperature for binary mixtures of the solute and the solvent, and the following results were obtained.

1. The Hand plot and the Othmer and Tobias plot which are useful for the systems containing one partially miscible pair are unsatisfactory for the systems containing two partially miscible pairs.
2. The method proposed by Brown and the method by Conway and Philip which have been said to be applicable for the systems containing the formation of two pairs of partially miscible liquids do not give good results for the systems at temperatures near the critical solution temperature for binary mixtures of the solute and the solvent.
3. If a plot is made of the logarithm of the ratio of the concentration of the diluent in the diluent phase to the concentration of the solvent in the solvent phase against the logarithm of the concentration of the diluent in the diluent phase, a straight line will be obtained not only for systems containing two partially miscible pairs, but also for systems containing one partially miscible pair.

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