Vapor-Liquid Equilibria for Binary Systems Made of *N,N*-Dimethylformamide with Acrylonitrile or Trichloroethylene

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Vapor-liquid equilibrium relations were measured for binary systems made of *N,N*-dimethylformamide with acrylonitrile or trichloroethylene at 98.66 kPa by the dew-bubble point temperature method. Combining the dew point temperature curve and the bubble point one, vapor-liquid equilibrium relationships were obtained for the binary systems. Literature data are not available for the systems of the present study. The present experimental method does not require any analytical instrument for the vapor-liquid equilibrium measurements. For the correlation of the experimental data, the Wilson equation was applied.

1. INTRODUCTION

Vapor-liquid equilibrium relations are required for the practical use, such as in the design and operation of distillation equipment. In the conventional experimental methods of vapor-liquid equilibria, analytical instruments are required. For measurements of isobaric dew points, a vapor-mixing type apparatus was proposed by Kojima *et al.*[1] For measurement of isobaric bubble points, many researchers[2,3] have proposed some ebulliometers.

However, in the general batch-type ebulliometer, it is necessary to correct the difference between the liquid composition at steady state and the feed composition. The authors previously proposed two types of apparatus for measuring isobaric dew and bubble points. The one is vapor mixing-type[4] and the another is flow-type[5].

The flow-type apparatus was modified by the author[6] to reduce the time required for the experiment and to keep the constant flow rate. Using the modified apparatus[6], vapor-liquid equilibrium relations were measured for the binary systems of *N,N*-dimethylformamide(DMF) with acrylonitrile or trichloroethylene at 98.66kPa. Literature data are not available for the systems of the present study. The present vapor-liquid equilibrium data seem useful for chemical engineers especially in polymer industries.

2. EXPERIMENTAL

The experimental apparatus and procedures are completely the same with those in the previous study[6].

Special grade reagents of DMF and acrylonitrile supplied by the Tokyo Kasei Co., Ltd. were further purified with distillation. Special grade reagents of trichloroethylene were used without further purification. The physical properties of materials used are listed in Table 1. The densities were measured with pycnometer.

3. RESULTS

The dew and bubble points were measured with an accuracy of 0.01K for the binary systems of DMF with acrylonitrile or trichloroethylene at the atmospheric pressure. The experimental dew and bubble points obtained are listed in Table 2, and shown in Figs.1 and 2.

The experimental temperatures were corrected to the values at 98.66kPa, using the same procedure described in the previous work[3]. The smoothed vapor-liquid equilibrium data obtained are listed in Table 3. The consistencies of the present isobaric equilibrium data obtained could not be precisely checked for lack of excess enthalpies and virial coefficients.

The vapor-liquid equilibrium data were correlated with

Table 1 Normal Boiling Point and Density of Materials Used

Material	Normal Boiling Point, K		Density at 298.15K, kg m ⁻³	
	Experimental	Literature	Experimental	Literature
DMF	425.99	426.15[10]	944.0	943.97[10]
Acrylonitrile	350.35	350.45[11]	800.5	800.4[11]
Trichloroethylene	360.07	360.05[11]	1455.4	1464.2*[11]

* At 293.15K.

Table 2 Experimental Dew and Bubble Point Temperatures at 98.66kPa

Mole Fraction of Component(1)	Acrylonitrile(1)-DMF(2)		Trichloroethylene(1)-DMF(2)	
	Dew Point,K	Bubble Point,K	Dew Point,K	Bubble Point,K
0.000	-----	425.00	-----	425.00
0.050	424.93	418.16	424.69	415.50
0.100	423.30	411.10	423.04	407.25
0.200	420.03	398.30	418.83	394.90
0.300	416.23	388.16	414.28	386.29
0.400	412.09	380.61	409.79	379.45
0.500	407.46	373.26	404.51	374.61
0.600	401.98	366.75	399.53	370.80
0.700	395.26	361.40	391.09	367.30
0.800	387.49	356.40	382.16	364.10
0.900	375.33	352.17	372.26	361.44
0.950	366.35	350.77	366.71	360.47
1.000	-----	349.50	-----	359.18

 Fig.1 Experimental Dew-Bubble Points for Acrylonitrile-DMF System at 98.66kPa
 ●:Experimental, — :Wilson Equation

 Fig.2 Experimental Dew-Bubble Points for Trichloroethylene-DMF System at 98.66kPa
 ●:Experimental, — :Wilson Equation

the Wilson equation[7].

$$\ln \gamma_1 = -\ln (x_1 + \Lambda_{12} x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right] \quad (1)$$

$$\ln \gamma_2 = -\ln (\Lambda_{21} x_1 + x_2) - x_1 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right] \quad (2)$$

where, x , Λ , and γ , respectively, denote the liquid phase mole fraction, Wilson parameter, and activity coefficient.

For vapor pressures of pure components, the Antoine constants of the data books[8,9] were used as shown in Table 4.

Assuming that the vapor phase is an ideal gas, the Wilson parameters, Λ_{12} and Λ_{21} , as shown in Table 5, were determined to minimize the sum of squares of deviations between the calculated and experimental bubble points, in a same manner as the previous work[3]. The average difference values on equilibrium temperature and vapor

Table 3 Smoothed Data of Vapor-Liquid Equilibria at 98.66kPa

Acrylonitrile(1)-DMF(2)			Trichloroethylene(1)-DMF(2)		
T	x_1	y_1	T	x_1	y_1
425.00	0.000	0.000	425.00	0.000	0.000
423.15	0.013	0.103	423.15	0.010	0.095
418.15	0.050	0.250	418.15	0.035	0.215
413.15	0.085	0.373	413.15	0.065	0.322
403.15	0.163	0.577	408.15	0.096	0.425
393.15	0.249	0.731	403.15	0.132	0.522
383.15	0.363	0.842	393.15	0.220	0.672
373.15	0.498	0.915	383.15	0.342	0.788
363.15	0.662	0.966	373.15	0.532	0.895
358.15	0.759	0.985	368.15	0.670	0.940
353.15	0.881	0.994	363.15	0.853	0.978
349.50	1.000	1.000	359.18	1.000	1.000

T :Temperature,K x_1 :Liquid Phase Mole Fraction of Component(1) y_1 :Vapor Phase Mole Fraction of Component(1)

Table 4 Antoine Constants for Vapor Pressure Calculations

$$\log P [\text{kPa}] = A - B / (T [\text{K}] + C)$$

Component	A	B	C
DMF[8]	6.23340	1537.78	-62.76
Acrylonitrile[9]	6.04117	1208.30	-51.15
Trichloroethylene[9]	6.15296	1315.10	-43.15

Table 5 Wilson Parameters Obtained

System	Λ_{12}	Λ_{21}	$ \Delta T _{\text{av}}$	$ \Delta y _{\text{av}}$
Acrylonitrile(1)-DMF(2)	1.2343	1.0339	0.27	0.012
Trichloroethylene(1)-DMF(2)	1.3861	0.3647	0.22	0.014

$|\Delta T|_{\text{av}}$:Average Absolute Difference of Bubble Point Temperature,K

$|\Delta y|_{\text{av}}$:Average Absolute Difference of Vapor Phase Mole Fraction

mole fraction are satisfactory as shown in Table 5. The solid lines in Figs.1 and 2 present the equilibrium curves calculated by the Wilson equation using the parameters given in Table 5, showing the good agreements with the experimental data.

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NOMENCLATURE

A, B, C : Antoine constants

P : vapor pressure

T : temperature

x : mole fraction in liquid phase

y : mole fraction in vapor phase

γ : activity coefficient

Λ : Wilson parameter

<Subscripts>

1,2 : components

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アクリロニトリルあるいはトリクロロエチレンと*N,N*-ジメチルホルムアミドからなる2成分系の気液平衡

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アクリロニトリル-*N,N*-ジメチルホルムアミド系およびトリクロロエチレン-*N,N*-ジメチルホルムアミド系の98.66kPaにおける気液平衡を露点沸点温度法で測定した。得られた露点温度曲線と沸点温度曲線を組み合わせて気液平衡関係を得た。本実験法は気液平衡測定において組成分析機器を必要としない。得られた実験値をWilson式で相関した。

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