DMF, NMF 포함계의 기액 및 액액 평형에 관한 연구

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Vapor-liquid equilibria and liquid-liquid equilibria for the systems containing N,N-Dimethylformamide(DMF) and N-Methylformamide (NMF)

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INTRODUCTION

Many investigations have already been carried out for amides compounds, while N,N-dimethylformamide(DMF) and N-methylformamide(NMF) are rare in the literature, especially NMF. DMF and NMF is a solvent used in the manufacturing of artificial leather, using a chemical treatment method. The separation of NMF and DMF is usually carried out by extraction process or extractive distillation. The thermodynamic analysis, prediction and computer simulation of phase equilibria, help to understand and the design of separation process. However, when dealing with real design process, experimental data are still needed for a reliable design.

This work has been carried out to study on the separation of NMF and DMF by extraction process or extractive distillation. To design the separation process, the phase equilibrium data is required essentially. A way to improve process simulation might be to obtain a reliable interaction parameter from experimental data. Exact experimental VLE data for some binary mixtures, consisting of NMF and DMF, and experimental LLE data gives such parameters.

Hence, VLE data for the some binary mixtures and LLE data for some ternary mixtures were experimentally determined. Data correlation was carried out using the Margules, van Laar, Wilson, NRTL, UNIQUAC equation.

EXPERIMENT

Chemicals : All the chemicals used in this work were of analytical commercial grade of purity and double distilled water. The amides used for experiment were supplied from Aldrich, with quoted purities-NMF(99%) and DMF(99.9%). Other chemicals were supplied from Junsei Chemical Co. All chemicals were used without further purification.

Equipment and procedure for VLE determination : Isothermal VLE experiments have been carried out using headspace gas chromatography (HSGC) for all the binary systems. The HSGC consists of gas chromatography (HP 5890 series II) and a headspace sampler (HP 19395A), which has an electro-pneumatic sampling system and a precision thermostat, having an accuracy of ±0.1K. HP-FFAP capillary column and a thermal conductivity dector were used for the analysis. The procedure is described in detail elsewhere[1,2].

Apparatus and experimental procedure for LLE : End point determination of the tie lines were performed in ca. 50 ml equilibrium cell by using stirring method. In general, shaking and stirring method[3,4] are most commonly used to measure liquid-liquid equilibria. In this work, self-designed simple stirring apparatus was used. The sample mixtures were prepared by adding DMF or NMF to mother solution of water and solvent, with mass ratio of 1:1. Equilibrated sample in an equilibrium cell were collected from the upper and lower layers by using sampling syringe and analyzed directly. Analysis has been carried out using gas chromatography.

RESULT AND DISCUSSION

To calculate the true liquid mole compositions, the thermo-physical data for SRK equation were adopted from pure properties in the DDB and Reid et al. [5]. This method has been described elsewhere [2,3]. The measured isothermal VLE data and the equilibrium pressure and composition data (P-x-y) for for solvent(1)+NMF(2), +DMF(2) systems at 353.15K are plotted in Fig. 1-3. All the experimental binary systems were correlated with the most common g^E models (Margules, van Laar, Wilson, NRTL, UNIQUAC). The calculated and experimental data were agreed very well and their deviations were less than 0.1 mol%. These comparisons are listed in Table 2 with fitted g^E model parameters.

The experimental tie line data for the ternary systems, water(1)+DMF(2)+ benzene(3), toluene(3) are given in Table 2. The presented liquid-liquid equilibtium data of the systems indicate that NMF and DMF is more soluble in water layer than solvent layer. Future work will focus on the development of more effective solvent.

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Table 1. Experimental LLE data for the ternary systems at 298.15K

Water(1)+N,N-dimethylformamide(2)+benzene(3)					
benzene rich phase			water rich phase		
x_1	x_2	x_3	x_1	x_2	x_3
0.00000	1.70562	98.29438	90.96621	8.53063	0.50316
0.00000	3.79400	96.20600	82.57031	16.59036	0.83933
0.13455	7.53694	92.32851	66.83556	31.68420	1.48024
0.59478	15.47159	83.93363	45.84733	51.30429	2.84838
Water(1)+N,N-dimethylformamide(2)+toluene(3)					
toluene rich phase			water rich phase		
x_1	x_2	x_3	x_1	x_2	x_3
0.00000	0.60079	99.39921	96.30773	3.69227	0.00000
0.00000	2.05485	97.94515	90.49468	9.50532	0.00000
0.00000	4.73012	95.26988	82.37055	17.62945	0.00000
0.00000	8.24948	91.75052	74.97515	25.02485	0.00000
0.06807	15.98073	83.95120	61.26487	38.73513	0.00000

Table 2. g^E model parameters and mean deviation between the calculated and experimental vapor-phase mole fraction(Δy_1) for the binary systems at 353.15K

Model equation	A_{12}	A_{21}	α	Δy_1
Water(1)+N,N-dimethylformamide(2)				
Margules	0.19260	-0.48557		0.00685
Wilson	624.09763	-624.15272		0.01463
NRTL	-1085.34385	2063.75318	0.30000	0.00744
UNIQUAC	664.20668	-664.		0.01326
Water(1)+N-methylformamide(2)				
Margules	-0.77929	-1.59718		0.01050
Wilson	-36.92177	-495.42468		0.01080
NRTL	-953.38568	-1258.23287	0.30000	0.01107
UNIQUAC	-56.52359	-603.86706		0.01079
Cyclohexane(1)+N,N-dimethylformamide(2)				
Margules	1.91838	2.32791		0.00785
van Laar	1.92436	2.36049		0.00754
Wilson	679.97569	1710.38079		0.00500
NRTL	1354.57828	952.82661	0.45696	0.00423
UNIQUAC	766.97877	-121.29045		0.00678
Cyclohexane(1)+N-methylformamide(2)				
Margules	2.67753	2.94597		0.00326
van Laar	2.66357	2.97398		0.00329
Wilson	1763.73861	3927.33860		0.00072
NRTL	2150.57430	1856.52067	0.41038	0.00069
UNIQUAC	1098.41002	-46.03725		0.00285
Benzene(1)+N,N-dimethylformamide(2)				
Margules	0.40795	0.66846		0.00325
van Laar	0.43150	0.69795		0.00325
Wilson	-199.39052	701.35701		0.00326
NRTL	768.32157	-254.39739	0.30000	0.00324
UNIQUAC	418.53256	-236.38367		0.00333
Toluene(1)+N,N-dimethylformamide(2)				
Margules	0.49085	0.61285		0.00458
van Laar	0.49794	0.61673		0.00462
Wilson	-167.55171	605.73626		0.00464
NRTL	466.95684	-33.58033	0.30000	0.00462
UNIQUAC	349.22533	-194.97956		0.00466

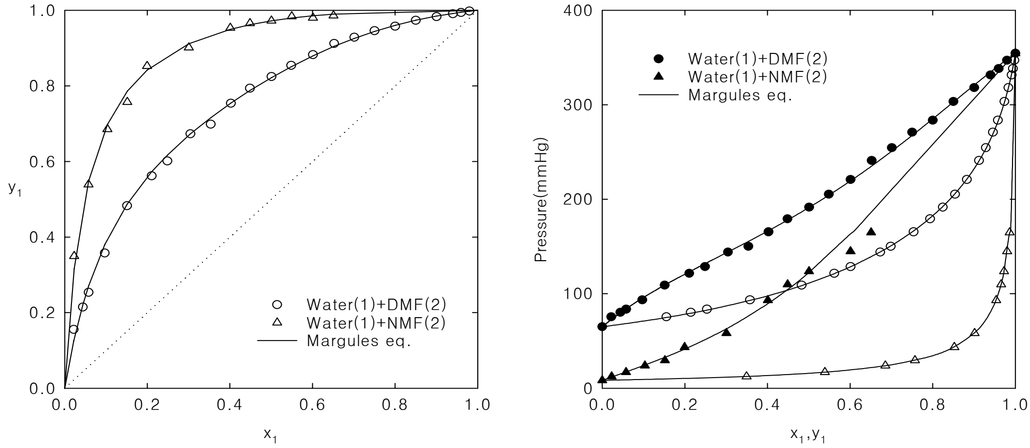

Fig. 1. Isothermal VLE data and P-x-y diagrams for water(1)+NMF(2), DMF(2) binary systems at 353.15K (hollow symbols are liquid phase in P-x-y diagram).

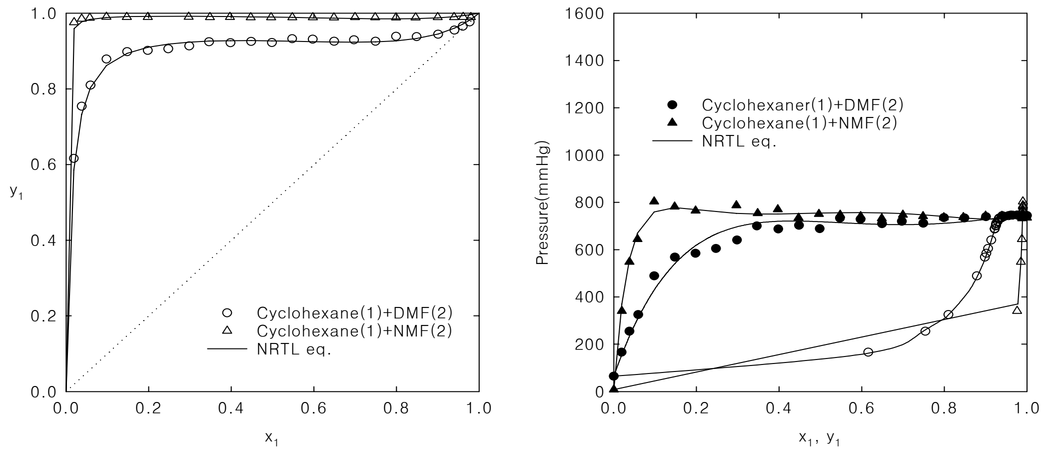

Fig. 2. Isothermal VLE data and P-x-y diagrams for cyclohexane(1)+NMF(2), DMF(2) binary systems at 353.15K (hollow symbols are liquid phase in P-x-y diagram).

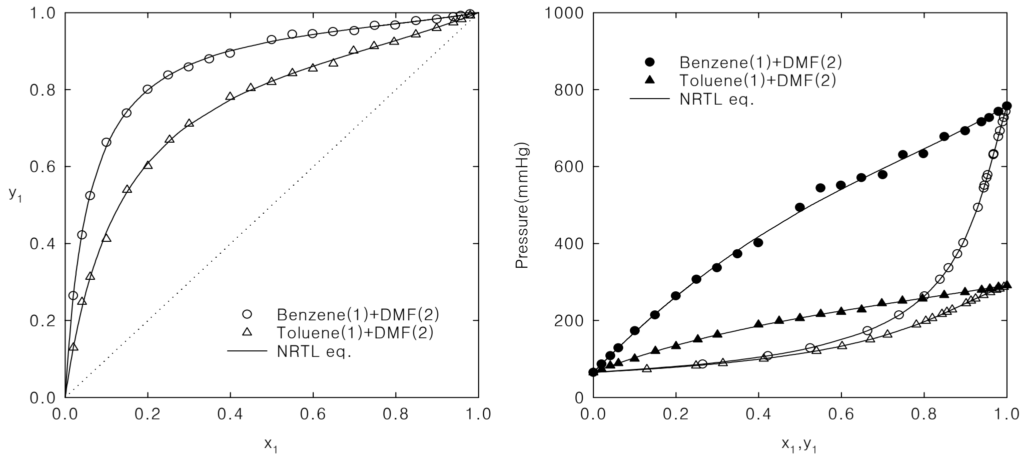

Fig. 3. Isothermal VLE data and P-x-y diagrams for benzene(1), toluene(1)+DMF(2) binary systems at 353.15K (hollow symbols are liquid phase in P-x-y diagram).