DMF+NMF+Water 삼성분계의 혼합시 몰부피 및 점도 변화

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Changes in Molar Volumes and Viscosities of Mixing for the Ternary Mixtures of DMF+NMF+Water

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INTRODUCTION

Studies on phase equilibria and excess molar properties (V^E, H^E, $\Delta\eta$) of liquid mixtures are of considerable importance for the design of separation processes and theoretical understanding the nature of molecular behavior[1]. Many investigations have already been carried out for binary mixtures, while that of ternary mixtures are rare in the literature. Especially, the excess properties for ternary mixtures, required to get insight into the nature and degree of interactions, are quite rare. It is therefore interesting to estimate excess functions of ternary mixtures from binary data[2,3].

The separation of N-methylformamide(NMF) and N,N-dimethylformamide(DMF) is usually carried out by extraction process or extractive distillation. The thermodynamic analysis, predictions and computer simulations of phase equilibria and thermophysical properties, help to understand the separation process. However, when dealing with complex mixtures, experimental data are still needed for a reliable design.

In this work, excess molar volumes(V^E) at 298.15K for the constituent binary and ternary systems of DMF(1)+NMF(2)+water(3) were determined from measured densities by using a digital tube densimeter. And the viscosties at the same temperature for the same mixtures were measured by using Ubbelhode viscometer, then viscosity deviations($\Delta\eta$) were determined from the experimental data. The experimental excess molar volumes and viscosity deviations were correlated using Redlich-Kister polynomial and Cibulka's equation for the binary and ternary systems respectively, and especially for the ternary system, excess molar volumes and viscosity deviations were compared with estimated values from the calculation using binary Redlich-Kister parameters.

EXPERIMENTAL

All the chemicals used in this investigation were of analytical commercial grade of purity and doubly distilled water was used. The purity of chemicals was checked by gas chromatography and by measuring densities and comparing with those reported in the literature.

Excess molar volumes, V^E, were calculated from directly measured densities of the pure and mixture samples. Densities were measured using a digital vibrating glass tube densimeter (Anton Paar, model DMA 48, Graz, Austria). The uncertainty of this densimeter is less than 1×10^{-4} gcm^{-3}. Before each set of measurements, the apparatus was calibrated with doubly distilled water and dried air. Mixture samples were prepared in ca. 5ml vial by mass using a microbalance with a precision of 1×10^{-5}g, charging the heavier component first to minimize vaporization effects. The detail operating procedures have been described elsewhere [4,5].

Absolute viscosities, η, of the pure components and mixtures are determined from the kinematic viscosities measured by using Ubbelhode viscometer with automatic measuring unit (LAUDA, model PVS1, Deutschland). The accuracy of the flowing time measurement is ±0.01s. Mixrure samples were prepared with the same procedure of the density measurements.

RESULTS AND DISCUSSIONS

The excess molar volumes(V^E) for the multi-component mixtures are calculated from the measured densities of pure substances and mixtures from eq. (1). The experimental excess molar volumes for the binary systems are correlated with five-parameter Redlich-Kister polynomial equation.

$$V^E = \frac{\sum_i x_i M_i}{\rho_m} - \sum_i \left(\frac{x_i M_i}{\rho_i} \right) \tag{1}$$

$$V^E_{12} = x_1 x_2 \sum_{i=1}^{5} A_i (x_1 - x_2)^{i-1} \tag{2}$$

Where A_i are adjustable parameters. The standard deviations of the fits, σ_{st} are defined as

$$\sigma_{st} = \left[\frac{\sum_i (V^E_{cal} - V^E_{\exp})^2_i}{N-n} \right]^{1/2} \tag{3}$$

Where N is the number of experimental data points and n is the number of fitted parameters, A_i.

For the binary systems, three constituent binaries show negative deviations from the ideal solution, and it represented in Figure 1. DMF+NMF system shows very small deviations from the ideality, because the molecular structures of two components and properties are silmilar each other. And DMF+water system shows relatively large deviations caused interactions between two components from the structural difference and polarities. These binary data were correlated very well with Redlich-Kister polynomial equation, and the correlation parameters and the standard deviations are listed in Table 1.

For the ternary system of DMF(1)+NMF(2)+water(3), excess molar volumes were estimated by Radojkovic's equation(eq.4)[6], and compared with the experimental data. Then the experimental V^E values were correlated with Cibulka's equation(eq.5)[7] as a modification of Radojkovic's equation.

$$V^E_{123} = V^E_{12*} + V^E_{23*} + V^E_{13*} \tag{4}$$

$$V^E_{123} = V^E_{12*} + V^E_{23*} + V^E_{13*} + x_1 x_2 x_3 (A_1 + A_2 x_1 + A_3 x_2) \tag{5}$$

Where V^E_{12*}, V^E_{23*} and V^E_{13*} represent the excess molar volumes and x_1, x_2 and x_3 are mole fractions of each components of ternary system.

The correlated values agreed well with the experimental data with standard deviations of 0.0134. These results are represented in Figure 2, and the correlation parameters of Cibulka's equation are listed in Table 1.

The absolute viscosity is determined from the experimental density(ρ) and kinematic viscosity(ν) as eq. (6) The viscosity deviations($\Delta\eta$) for the multi-component system are calculated from the absolute viscosity of pure substances and mixtures from eq. (7). The experimental $\Delta\eta$ for the binary systems are correlated with four-parameter Redlich-Kister polynomial equation.

$$\eta = \rho\nu \tag{6}$$

$$\Delta\eta = \eta_m - \sum_{i=1}^{n} x_i\eta_i \tag{7}$$

For the binary mixtures, DMF+NMF system shows small negative deviations from the ideal solution, but DMF+water and NMF+water systems show relatively large positive deviations from the ideality as represented in Figure 3. The experimental $\Delta\eta$ were correlated well with Redlich-Kister polynomial, and the correlation results are listed in Table 1 together with the values of excess molar volumes.

For the ternary system, the viscosity deviations were determined by the same procedure with binary systems. And the experimental values were compared with the estimated values by Radojkovic's equation(eq.4) and with correlated values by Cibulka's equation(eq.5). These results are listed and plotted in Figure 4 and Table 1.

CONCLUSION

The new V^E and $\Delta\eta$ at 298.15K were experimentally determined for the three constituent binary systems and the ternary system of DMF(1)+NMF(2)+water(3). The measured binary V^E show negative deviations from the ideality and they were correlated well with the Redlich-Kister polynomial, while the Cibulka's equation was applied well for the ternary systems with the standard deviation of 0.0134. The measured binary $\Delta\eta$ show negative deviations from the ideality for DMF+NMF system and positive deviations for DMF+water, NMF+water systems. They were correlated well with the Redlich-Kister polynomial, while the Cibulka's equation was applied well for the ternary systems with the standard deviation of 0.0621.

ACKNOWLEDGEMENTS

This work was supported by grant No. 2000-1-30700-011-2 from the Basic Research Program of the Korea Science & Engineering Foundation.

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Table 1. Fitted Redlich-Kister parameters and Cibulka parameters with the standard deviations for DMF(1)+NMF(2)+water(3) at 298.15K

system		A_1	A_2	A_3	A_4	A_5	σ_{st}
V^E	1+2	-0.0795	-0.0283	-0.0052	-0.0546	0.0093	0.0015
	2+3	-2.1162	1.2348	-0.1851	-0.4598	0.5398	0.0051
	1+3	-4.2600	1.9922	0.1142	-1.7065	1.0397	0.0089
	1+2+3	5.1849	-3.7233	-1.3734	-	-	0.0134
$\Delta\eta$	1+2	-0.6404	0.1568	0.1232	0.1670	-	0.0102
	2+3	3.0215	-2.7664	0.3345	0.8924	-	0.0049
	1+3	4.3620	-7.8642	1.8511	4.0871	-	0.0514
	1+2+3	-4.5644	3.0561	-1.3487	-	-	0.0621

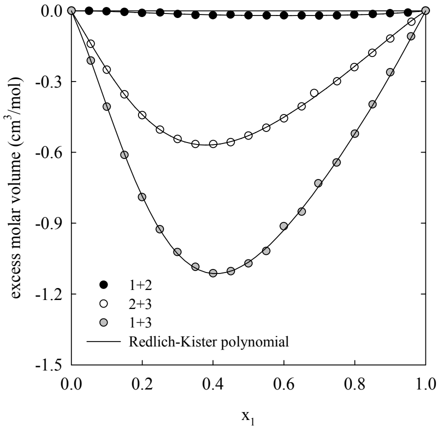

Figure 1. V^E for the three binary systems of DMF(1), NMF(2) and water(3) at 298.15K.

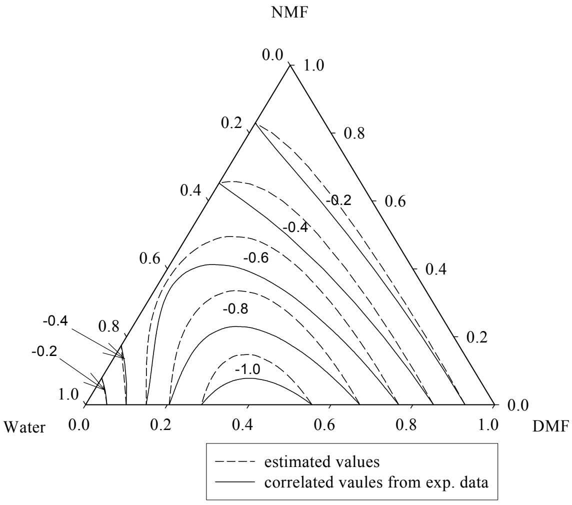

Figure 2. Lines of constant V^E for the ternary system of DMF(1)+NMF(2)+water(3) at 298.15K.

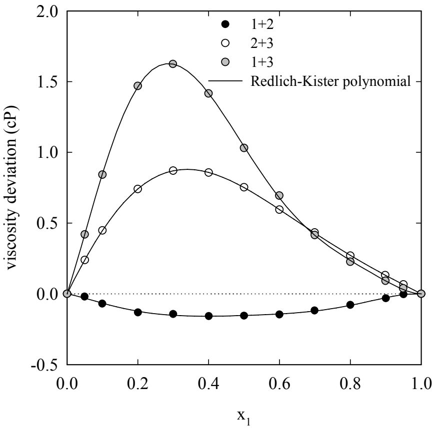

Figure 3. $\Delta\eta$ for the three binary systems of DMF(1), NMF(2) and water(3) at 298.15K.

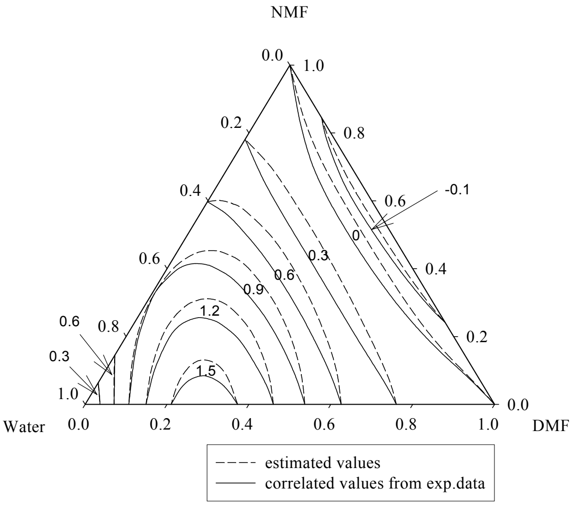

Figure 4. Lines of constant $\Delta\eta$ for the ternary system of DMF(1)+NMF(2)+water(3) at 298.15K.