

Densities and Viscosities of *N*-Formylmorpholine (NFM) + *p*-Xylene, + *o*-Xylene, + *m*-Xylene at Different Temperatures and Atmospheric Pressure

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Densities and viscosities for *N*-formylmorpholine (NFM) with *p*-xylene, *m*-xylene, and *o*-xylene were determined over several temperatures at atmospheric pressure. The measurements were carried out over the whole range of mole fractions, using a vibrating-tube densimeter and an Ubbelohde viscometer. Density and viscosity data were used to compute the excess molar volumes (V^E) and viscosity deviations ($\Delta\eta$). The excess molar volumes, V^E , and viscosity deviations, $\Delta\eta$, have been fitted to the Redlich–Kister equation.

Introduction

N-Formylmorpholine (NFM) is a highly polar and dense solvent with good stability as an extractive agent and has been successfully used in industry for the extraction and extractive distillation of pure monocyclic aromatic hydrocarbons from petroleum feedstocks.¹ To our knowledge, limited reports on physical properties of binary mixtures containing NFM are available in the literature.^{2–5}

This paper is part of our systematic program of research on the measurement of physical and transport properties of binary liquid mixtures containing NFM.⁶ Density and viscosity data for the binary systems NFM + *p*-xylene, + *o*-xylene, and + *m*-xylene from (298.15 to 353.15) K were determined. From the densities and viscosities, excess molar volumes and viscosity deviations were calculated. The Redlich–Kister equation was used to correlate the experimental excess molar volumes and viscosity deviations.

Experimental Section

Materials. *m*-Xylene and *o*-xylene were supplied by Tianjin Reagent Co. NFM was supplied by Shanghai Chemical Reagent Co. *p*-Xylene was supplied by Tianjin Petroleum Engineering Company. NFM was purified by distillation. Other liquids were subject to no further purification. All were dried over 0.4 nm molecular sieves and particularly degassed by ultrasound prior to their experimental use. The mass fraction purities tested by gas chromatography were as follows: NFM (> 0.995), *p*-xylene (> 0.998), *o*-xylene (> 0.995), *m*-xylene (> 0.995). The densities and viscosities determined in this study were compared with the literature data in Table 1.

Apparatus and Procedure. The densities of the pure components and their mixtures were measured with a high-precision vibrating-tube digital density meter (Density/Specific Gravity Meter DA 505, KEM, Japan) whose measurement cell temperature was controlled automatically within ± 0.01 K of the selected value. The uncertainty in density measurements was $\pm 5 \cdot 10^{-5}$ g·cm⁻³. Density measurements were reproducible to $\pm 3 \cdot 10^{-5}$ g·cm⁻³. The average uncertainty in molar excess volumes was less than ± 0.0002 cm³·mol⁻¹. A BS224S balance

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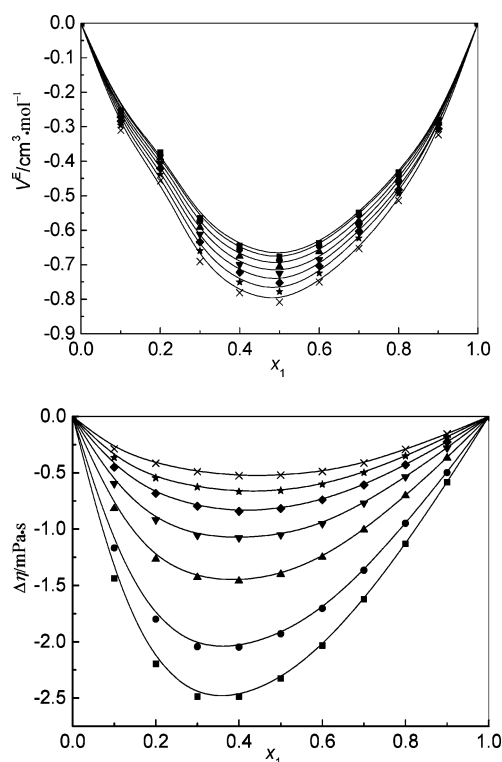


Figure 1. Excess molar volume variation and viscosity deviation variation with mole fraction to the system *p*-xylene (1) + NFM (2) for experimental values: ■, 298.15 K; ●, 303.15 K; ▲, 313.15 K; ▼, 323.15 K; ◆, 333.15 K; ★, 343.15 K; ×, 353.15 K.

with a precision of ± 0.1 mg was used. The average uncertainty in the mole fraction of the mixtures was less than ± 0.0001 . All molar quantities were based on the IUPAC relative atomic mass table. The viscosities of pure liquids and the mixtures were measured at atmospheric pressure and at different temperatures using an Ubbelohde suspended-level viscometer. The uncertainty of viscosity deviations was within ± 0.003 mPa·s. The density and viscosity of the pure compounds are given in Table 1 and compared with the literature values. It can be seen that the measured results agree well with literature values.

Table 1. Comparison of Experimental and Literature Values of Densities, ρ , and Viscosities, η , for Pure Components

liquid	T/K	$\rho/g\cdot cm^{-3}$		$\eta/mPa\cdot s$		liquid	T/K	$\rho/g\cdot cm^{-3}$		$\eta/mPa\cdot s$	
		exptl	lit.	exptl	lit.			exptl	lit.		
NFM	298.15	1.14598	1.14621 ³ 1.14628 ²	7.666	7.87 ⁴ 6.74 ³	<i>o</i> -xylene	298.15	0.87511	0.8750 ¹⁸ 0.87553 ⁹	0.761	0.758 ¹⁴ 0.761 ¹⁵
	303.15	1.14155	1.14226 ⁴	6.626	6.75 ⁴		303.15	0.87085	0.8715 ¹⁴ 0.87073 ¹⁶	0.709	0.711 ¹⁴ 0.708 ¹⁶
	313.15	1.13310	1.1333 ¹ 1.10677 ³	5.057	5.13 ⁴		323.15	0.85421	0.85379 ¹⁵	0.558	0.555 ¹⁵
<i>p</i> -xylene	298.15	0.85670	0.85673 ⁸ 0.85662 ⁹	0.612	0.611 ¹⁰ 0.613 ¹²	<i>m</i> -xylene	298.15	0.85990	0.85977 ⁹ 0.86000 ¹⁹	0.584	0.581 ¹⁶ 0.588 ¹⁴
	303.15	0.85235	0.85227 ¹⁰ 0.85239 ¹¹	0.575	0.576 ¹⁰ 0.570 ¹³		303.15	0.85555	0.85549 ¹⁶ 0.85587 ¹⁷	0.553	0.552 ¹⁶ 0.555 ¹⁴
	313.15	0.84364	0.84361 ¹² 0.8437 ¹³	0.513	0.509 ¹³		323.15	0.83855	0.83825 ¹⁵	0.448	0.444 ¹⁵

Results and Discussion

Excess molar volumes were calculated from our measurements according to the following equation

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \quad (1)$$

where x_1 and x_2 are mole fractions; M_1 and M_2 are the molar masses; and ρ_1 and ρ_2 are the densities of pure components 1 and 2, respectively. Quantities without subscripts refer to the mixture. The viscosity deviations were calculated from the following relation

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \quad (2)$$

where η is the viscosity of mixtures and η_1 and η_2 are the viscosities of pure components 1 and 2, respectively. The values

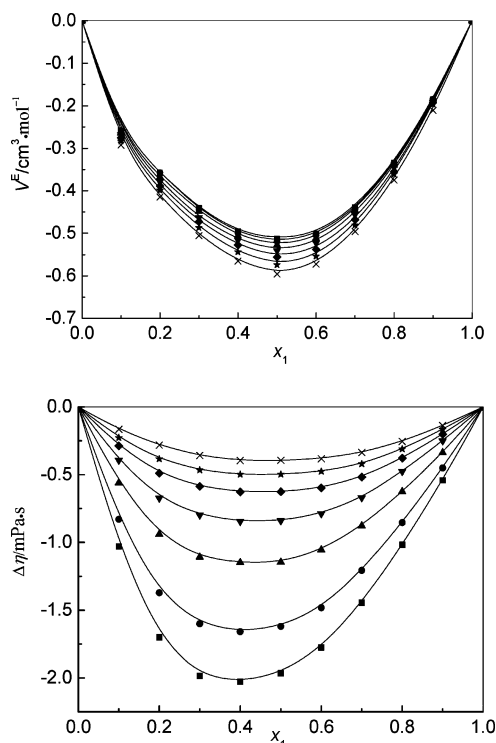


Figure 2. Excess molar volume variation and viscosity deviation variation with mole fraction to the system *o*-xylene (1) + NFM (2) for experimental values: ■, 298.15 K; ●, 303.15 K; ▲, 313.15 K; ▼, 323.15 K; ◆, 333.15 K; ★, 343.15 K; ×, 353.15 K.

of V^E and $\Delta\eta$ for each mixture were fitted to the Redlich–Kister polynomial equation⁷

$$Y = x_1(1 - x_1) \sum_{i=0}^n A_i(2x_1 - 1)^i \quad (3)$$

where $Y = V^E$ or $\Delta\eta$; A_i are adjustable parameters; and x_1 is the mole fraction of component 1. In each case, the optimum parameters of coefficients A_i were determined from an examination of the variation of the average absolute deviations and standard deviations

$$AAD = \frac{\sum |(V_{\text{calcd}}^E - V_{\text{exptl}}^E)/V_{\text{exptl}}^E|}{n} \quad (4)$$

$$SD = [\sum (Y_{\text{calcd}} - Y_{\text{exptl}})^2 / (n - 1)]^{(1/2)} \quad (5)$$

where n is the total number of experimental values.

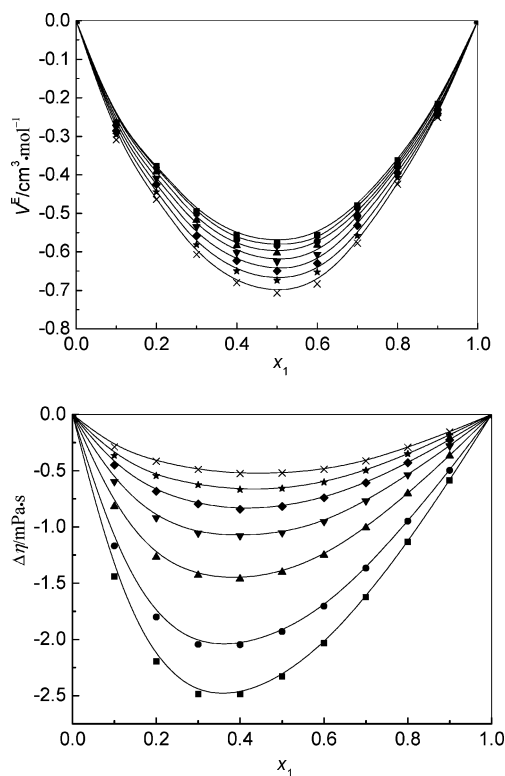


Figure 3. Excess molar volume variation and viscosity deviation variation with mole fraction to the system *m*-xylene (1) + NFM (2) for experimental values: ■, 298.15 K; ●, 303.15 K; ▲, 313.15 K; ▼, 323.15 K; ◆, 333.15 K; ★, 343.15 K; ×, 353.15 K.

The experimental results at different temperatures and at atmospheric pressure are listed in Table 2 and shown graphically in Figures 1, 2, and 3. The values of the parameters A_i together with the average absolute deviations and standard deviations are listed in Table 3. It can be seen from the figures that V^E values for these two binary mixtures over the whole composition range are negative and that the absolute value of V^E increases with rising temperature. The figures also show the viscosity deviations for these two binary mixtures, plotted against mole fraction of xylenes at several temperatures. The viscosity deviations for these systems at selected temperatures are negative over the entire composition range.

Conclusion

Densities and viscosities of the binary systems of NFM + *p*-xylene, + *o*-xylene, and + *m*-xylene have been measured at several temperatures and for the whole composition range. The excess molar volumes and viscosity deviations were computed and fitted to the Redlich–Kister equation. Excess molar volumes and viscosity deviations show a systematic change with increasing temperature. V^E values are negative for all the mixtures over the entire composition range and become more negative with increasing temperature. The deviations of viscosity, $\Delta\eta$, are also negative and become less negative with increasing temperature.

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