

Densities and Viscosities of *N*-Formylmorpholine + Benzene, + Toluene at Different Temperatures and Atmospheric Pressures

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Densities and viscosities for *N*-formylmorpholine (NFM) with benzene and toluene 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 V^E and $\Delta\eta$ have been fitted to the Redlich–Kister equation.

Introduction

Studies on viscosity and density of binary mixtures along with other thermodynamic properties are being increasingly used as tools for the investigation of the properties of pure components and the nature of intermolecular interactions between the liquid mixture constituents. *N*-Formylmorpholine (NFM) is a highly polar and dense solvent, showing good suitability for the recovery of aromatic hydrocarbons from petroleum products such as gasoline and reformat. Recently the aqueous solutions of NFM have been used on an industrial scale for extraction processes.¹

This paper is part of our systematic program of research on the measurement of physical and transport properties of binary liquid mixtures containing NFM. Density and viscosity data for the binary systems NFM + benzene from (298.15 to 343.15) K and + toluene from (298.15 to 353.15) K were determined. From the densities and viscosities, excess molar volumes (V^E) and viscosity deviations ($\Delta\eta$) were calculated. The Redlich–Kister equation was used to correlate the experimental excess molar volumes and viscosity deviations.

A survey of the literature shows that Awwad et al.² determined densities of NFM with butanone at 298.15 K. Awwad et al.^{3,4} measured densities for NFM + water at (298.15 and 343.15) K, while Henni et al.⁵ measured volumetric properties and viscosities for aqueous NFM solutions from (298.15 to 343.15) K. The densities and viscosities of NFM + benzene and + toluene have not been reported.

Experimental Section

Materials. All chemicals used in this study were supplied by Tianjin Reagent Co. except NFM, which was supplied by Shanghai Chemical Reagent Co. 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), benzene (> 0.998), toluene (> 0.998). 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. Before each series of measurements, the instrument was calibrated at atmospheric pressure with double distilled water and dry air. Densities of both water and dry air at the various working temperatures were given by the manufacturer in the instruction manual. The uncertainty in density measurements was $\pm 5 \times 10^{-5}$ g·cm⁻³. Density measurements were reproducible to $\pm 3 \times 10^{-5}$ g·cm⁻³.

The liquid mixtures were prepared by mass using a BP210s balance accurate to within ± 0.01 mg. The average uncertainty in the mole fraction of the mixtures was estimated to be less than ± 0.0001 . The molar excess volumes were calculated from composition–density data with an uncertainty better than ± 0.002 cm³·mol⁻¹. 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 two Ubbelohde suspended-level viscometers. The viscometer was immersed in a well-stirred water bath (Lauda, Germany) with temperature control to within ± 0.01 K. An electronic digital stopwatch with a readability of ± 0.01 s was used for flow time measurement. Experiments are repeated a minimum of four times at each temperature for all compositions, and the results were averaged. The viscosity η of the liquid was then calculated from the following relationship:

$$\nu = \frac{\eta}{\rho} = k(t - \theta) \quad (1)$$

where t is the flow time; η is the kinematic viscosity; and k and θ are the viscometer constant and the Hagenbach correction factor, respectively.

The calibration of the viscometer was carried out with double distilled water and twice-distilled 1-octanol. During the heating, to minimize the evaporation losses, the viscometer's limbs are closed with Teflon caps. During the measurements of flow time, the caps of the limbs were removed. The overall uncertainty of the viscosity measurements is dependent on the temperature control of the viscometer, the time of the flow, and the

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

liquid	T/K	$\rho/\text{g}\cdot\text{cm}^{-3}$		$\eta/\text{mPa}\cdot\text{s}$		liquid	T/K	$\rho/\text{g}\cdot\text{cm}^{-3}$		$\eta/\text{mPa}\cdot\text{s}$	
		exptl	lit	exptl	lit			exptl	lit		
NFM	298.15	1.14606	1.14621 ⁴ 1.14628 ³	7.625	7.87 ⁵ 6.74 ⁴	toluene	298.15	0.86165	0.8622 ¹⁵ 0.86201 ⁷ 0.8609 ¹⁸	0.553	0.554 ⁷ 0.556 ²¹ 0.5542 ¹⁸
	303.15	1.14170	1.14226 ⁵	6.631	6.75 ⁵		303.15	0.85701	0.8576 ¹⁵ 0.8565 ¹⁷ 0.8578 ²⁰	0.522	0.5226 ¹⁹ 0.5171 ¹⁷ 0.5227 ²⁰
	313.15	1.13296	1.1333 ²	5.097	5.13 ⁵		313.15	0.84763	0.8482 ¹⁵ 0.8479 ¹⁷	0.467	0.470 ¹⁵ 0.4669 ¹⁷ 0.4659 ¹⁹
	323.15	1.12433	1.12482 ⁵	4.051	4.03 ⁵						
	333.15	1.11563	1.11611 ⁵	3.316	3.25 ⁵						
	343.15	1.10796	1.10739 ⁵ 1.10677 ⁴	2.782	2.68 ⁵						
benzene	298.15	0.87357	0.87357 ⁶ 0.8735 ⁹ 0.87360 ¹⁰	0.601	0.601 ¹¹ 0.5984 ¹² 0.602 ¹⁰ 0.5612 ¹²	323.15	0.83823	0.8385 ¹⁷ 0.8387 ¹⁸ 0.8389 ¹⁶	0.421	0.4219 ¹⁷ 0.4216 ¹⁸	
	303.15	0.86824	0.86821 ⁶ 0.8682 ⁸	0.562	0.5627 ¹⁴	333.15	0.82871	0.8292 ¹⁷	0.381	0.3824 ¹⁷	
	313.15	0.85734	0.8574 ⁸ 0.8575 ¹³	0.493	0.4948 ⁶ 0.4921 ¹³	343.15	0.81986	0.82030 ⁷ 0.8197 ¹⁷	0.349	0.3491 ¹⁷	
	323.15	0.84659	0.84665 ⁶ 0.8466 ¹¹	0.436	0.4362 ⁶ 0.4358 ¹¹	353.15	0.80968	0.8197 ¹⁷ 0.81054 ⁷	0.321	0.350 ⁷ 0.3176 ¹⁷	
	333.15	0.83575	0.8354 ¹³	0.389	0.3894 ¹³						

concentration, which are of the order of 1×10^{-2} , 1×10^{-2} , and 3×10^{-4} , respectively. The uncertainty of viscosity was within ± 0.003 mPa·s.

In the experiments, the density and viscosity for one composition sample were measured at different temperatures. Densities and viscosities of pure components are reported in Table 1 together with the corresponding literature values. For the densities, good agreement was found between the measured and literature values for all these pure substances. There is an appreciable difference for the viscosity data among the literatures for NFM.

Results and Discussion

The experimental values of density and viscosity for binary mixture at different temperatures and at atmospheric pressure are listed in Table 2. Excess molar volumes were calculated from our measurements according to the following equation:⁶

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \quad (2)$$

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 derivations were calculated from the following relation:⁶

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \quad (3)$$

where η is the viscosity of mixtures, and η_1 and η_2 are the viscosity of components 1 and 2, respectively. The values of V^E and η for each mixture were fitted to the Redlich–Kister polynomial equation:⁷

$$Y = x_1(1 - x_1) \sum_{i=0}^n A_i(2x_1 - 1)^i \quad (4)$$

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 number of coefficients A_i was determined from an examination of the variation of the average absolute derivations (AAD) and standard derivations (SD):

$$\text{AAD} = \frac{\sum |(V_{\text{cal}}^E - V_{\text{exp}}^E)/V_{\text{exp}}^E|}{n} \quad (5)$$

$$\text{SD} = \left[\frac{\sum (Y_{\text{cal}} - Y_{\text{exp}})^2}{(n-1)} \right]^{1/2} \quad (6)$$

where n is the total number of experimental values.

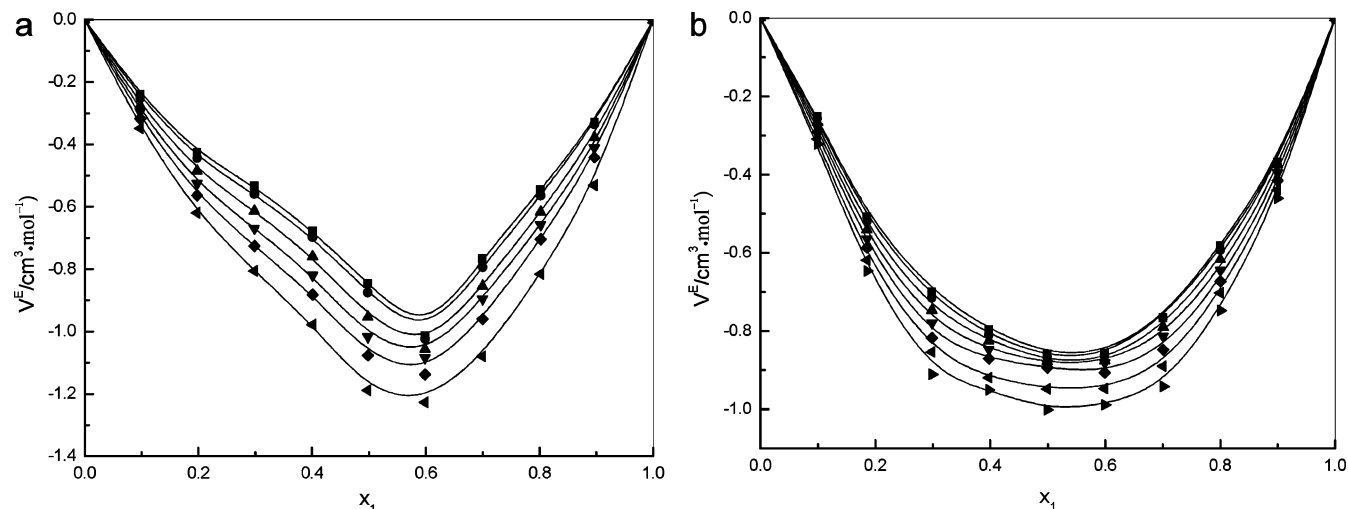


Figure 1. Excess molar volume variation with mole fraction to systems (a) benzene (1) + NFM (2); (b) toluene (1) + NFM (2): ■, 298.15 K; ●, 303.15 K; ▲, 313.15 K; ▼, 323.15 K; ◆, 333.15 K; left-facing solid triangle, 343.15 K; right-facing solid triangle, 353.15 K; solid curves, calculated with Redlich–Kister equation; symbols, experimental values.

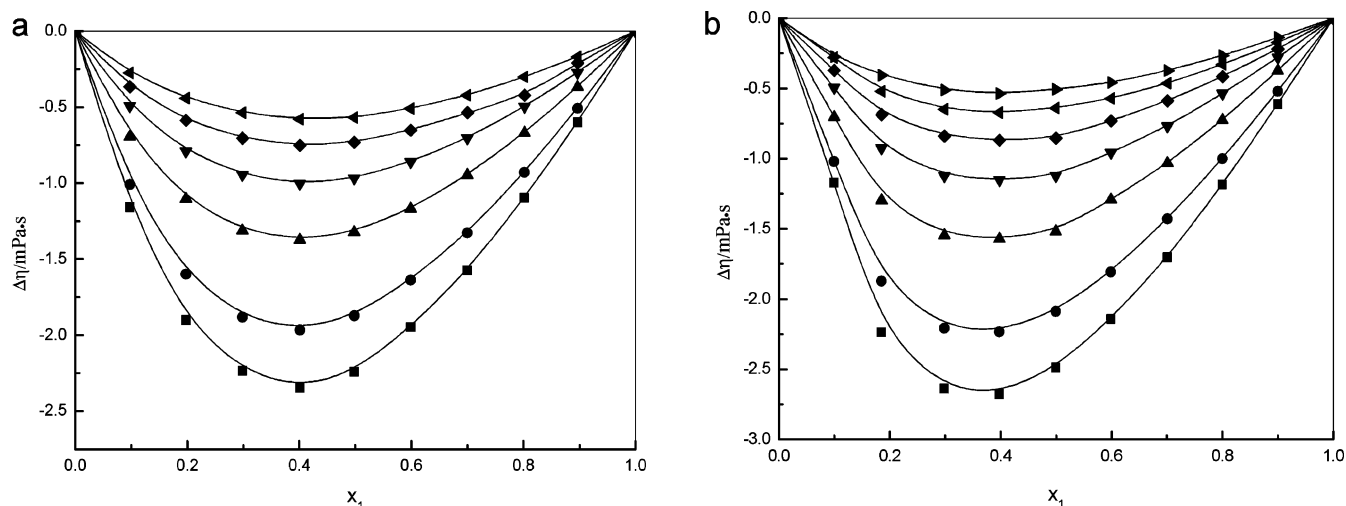


Figure 2. Viscosity deviation variation with mole fraction to systems (a) benzene (1) + NFM (2); (b) toluene (1) + NFM (2); ■, 298.15 K; ●, 303.15 K; ▲, 313.15 K; ▼, 323.15 K; ◆, 333.15 K; left-facing solid triangle, 343.15 K; right-facing solid triangle, 353.15 K; solid curves, calculated with Redlich–Kister equations; symbols, experimental values.

Table 3. Coefficients of the Redlich–Kister Equation and Standard Deviation for Excess Molar Volumes and Viscosity Deviations of Mixtures

T/K	property	A_0	A_1	A_2	A_3	A_4	A_5	AAD	SD
(x)Benzene + (1 - x)NFM									
298.15	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-3.5122	-3.5345	2.5976	13.6203	-3.3258	-14.1540	0.026	0.025
	$\Delta\eta/\text{mPa}\cdot\text{s}$	-8.9095	4.0323	-1.1608	0.2394	-0.4365		0.004	0.009
303.15	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-3.5934	-3.4422	2.3610	12.9792	-2.9748	-13.2460	0.023	0.021
	$\Delta\eta/\text{mPa}\cdot\text{s}$	-7.4689	3.2710	-0.9983	0.6412	-0.8504		0.003	0.004
313.15	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-3.8386	-3.1864	2.3156	11.4598	-3.1868	-11.7762	0.015	0.014
	$\Delta\eta/\text{mPa}\cdot\text{s}$	-5.2736	2.1073	-0.6144	0.4818	-0.5923		0.001	0.002
323.15	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-4.0488	-2.8774	2.2559	10.1379	-3.3241	-10.6332	0.012	0.012
	$\Delta\eta/\text{mPa}\cdot\text{s}$	-3.8685	1.4200	-0.3296	0.3247	-0.4763		0.003	0.002
333.15	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-4.2896	-2.8139	2.0279	9.5717	-3.0496	-10.0088	0.009	0.010
	$\Delta\eta/\text{mPa}\cdot\text{s}$	-2.8984	0.9171	-0.6908	0.2155	0.2367		0.019	0.010
343.15	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-4.6977	-2.7877	1.7460	8.2071	-3.2398	-8.8453	0.007	0.009
	$\Delta\eta/\text{mPa}\cdot\text{s}$	-2.2687	0.6735	-0.0489	0.1894	-0.4153		0.003	0.001
(x)Toluene + (1 - x)NFM									
298.15	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-3.4334	-0.2782	-0.4625	-0.4736	0.6616		0.023	0.014
	$\Delta\eta/\text{mPa}\cdot\text{s}$	-9.8297	6.2384	-5.4751	-2.5797	7.7468		0.024	0.049
303.15	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-3.4681	-0.1814	-0.5591	-0.6768	0.7089		0.021	0.013
	$\Delta\eta/\text{mPa}\cdot\text{s}$	-8.2597	5.0375	-4.1749	-1.6271	5.2960		0.022	0.037
313.15	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-3.5043	-0.1630	-1.2550	-0.6362	1.7660		0.018	0.012
	$\Delta\eta/\text{mPa}\cdot\text{s}$	-5.9318	3.3130	-2.3645	-1.0356	3.1988		0.021	0.028
323.15	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-3.5322	-0.0382	-1.9789	-0.9654	2.5878		0.016	0.010
	$\Delta\eta/\text{mPa}\cdot\text{s}$	-4.3848	2.3204	-1.4506	-0.8836	2.1984		0.020	0.020
333.15	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-3.5994	-0.0179	-2.6367	-1.0799	3.3881		0.017	0.012
	$\Delta\eta/\text{mPa}\cdot\text{s}$	-3.3385	1.6459	-0.8817	-0.6312	1.3021		0.019	0.014
343.15	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-3.8001	0.0037	-2.4951	-1.1551	3.0786		0.016	0.012
	$\Delta\eta/\text{mPa}\cdot\text{s}$	-2.5527	1.2039	-1.0082	-0.5163	1.5562		0.016	0.008
353.15	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-3.9734	-0.0052	-2.9812	-1.2504	3.8141		0.016	0.014
	$\Delta\eta/\text{mPa}\cdot\text{s}$	-2.0505	0.7737	-0.3127	0.2167	-0.0802		0.007	0.003

The excess molar volume data and the viscosity derivations are presented in Table 2 and graphically in Figures 1 and 2. Comparison is made with literature data in Table 1. In Table 3, the values of the parameters A_i together with the AAD and SD are listed. It can be seen from Figure 1 that V^E values for these two binary mixtures over the whole composition range are negative. The absolute values of V^E increases with temperature rising. It can be summarized that^{1,11} V^E values may be affected by two factors. The first factor is the physical intermolecular forces including electrostatic forces between charged particles and between permanent dipoles etc., induction forces between a permanent dipole and an induced dipole, and forces of attraction (dispersion forces) and repulsion between nonpolar molecules. Physical intermolecular forces are weak usually, and the sign of V^E values may be positive or negative. The second factor is the structural characteristics of the components, arising from geometrical fitting of one component

into the other's structure due to the differences in shape and size of components and free volume. Because of the interaction between the polarity of NFM and π electron in aromatic ring, the values of excess molar volumes are negative for the NFM mixture. The apparent intermolecular interactions in binary mixtures of NFM with benzene or toluene may be classified as weak dipolar induced-type forces resulting from the polarization of benzene or toluene molecules by the dipoles of the surrounding NFM molecules. This effect can be super-imposed upon dipole–dipole interactions and leads to a slight increase in the attraction, giving negative V^E values.

Figure 2 shows viscosity deviations for these two binary mixtures, plotted against the mole fraction together with the fitted curve, obtained from the Redlich–Kister equation. The viscosity deviations for these systems at selected temperatures are negative over the entire composition.

Conclusion

Densities and viscosities of the binary systems of NFM + benzene and + toluene 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 deviation 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. The effect of interactions of components on excess molar volumes and viscosity deviation is discussed.

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