Volumetric and Viscous Properties at Several Temperatures for Binary Mixtures of *N*-Methylpiperazine with Methylcyclohexane or *n*-Heptane

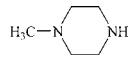
Xi Yang, Yan Xing, Dan Li, Yongsheng Guo, and Wenjun Fang*

Department of Chemistry, Zhejiang University, Hangzhou 310027, China

The data of density and viscosity for binary mixtures of *N*-methylpiperazine (NMP) with methylcyclohexane (MCH) or *n*-heptane have been measured from $T = 298.15$ K to $T = 313.15$ K at atmospheric pressure. Excess volume, V_m^E, for the binary mixtures are then calculated. Positive values of V_m^E are observed over the entire composition range, and the maximum value is 0.622 $cm^3 \cdot mol^{-1}$ at 313.15 K. The excess results are discussed in terms of the changes of molecular interactions in the mixtures, and the data of V_m^E are fitted against the composition with the Redlich−Kister type equation. The viscosities have also been correlated with several semiempirical equations. These physical property data and calculations provide valuable information on the development and application of piperazine derivatives.

Introduction

N-Methylpiperazine (NMP), $C_5H_{12}N_2$, one of the derivatives of piperazine, is an important intermediate in pharmacentical chemistry and useful material of some synthetic dyes, polymers, and surfactants.[1,2] The unique molecular structure determines



its biological activity, and NMP can serve as a biochemical model compound. It can also bond with metal surfaces through its ring nitrogen atoms to effectively inhibit metal corrosion. Accurate physical and thermodynamic properties of NMP and its mixtures with alkanes are very useful for development of alkyl piperazines and their applications in chemical industry.

In the present work, densities and viscosities at several temperatures for two binary systems, NMP + methylcyclohexane (MCH) and NMP + *n*-heptane, are measured as fundamental data for the chemical design and optimization process. The excess molar volume of the binary mixtures are calculated to provide important information on the molecular interactions.[3]

Experimental Section

Materials. NMP with a claimed mass fraction better than 0.998 and MCH with a mass fraction better than 0.980 were obtained from Sinopharm Chemical Reagent Co. Ltd. *n*-Heptane with a mass fraction better than 0.990 was provided by the Second Chemical Reagent Co., Yi Xing, China. The sample purities were analyzed by a Hewlett-Packard 6890/5973 gas chromatography/mass spectrometer (GC/MS). Each sample was degassed in an ultrasonic oscillator before its experimental use. The physical properties of these pure liquids are compared in Table 1, where ρ is the density in $g \cdot cm^{-3}$ and η is the viscosity in mPa·s. Reasonable agreements are exhibited between the measured and the reference values.[1,4–10] The binary mixtures of NMP + MCH and NMP + *n*-heptane were prepared by directly weighing the constituent components, using a Mettler Toledo AL204 balance with a precision of 0.0001 g. The uncertainty of mole fraction was estimated to be $\pm 1 \cdot 10^{-4}$.

Table 1. Physical Properties of Pure Liquids

	T	ρ/g·cm^{-3}		η/mPa·s	
compound	K	exptl	lit.	exptl	lit.
NMP	298.15	0.89928	0.89980[a]	1.856	1.841[b]
	303.15	0.89490	0.89454[a]	1.544	
	308.15	0.89050		1.370	
	313.15	0.88607		1.250	
MCH	298.15	0.76500	0.76496[c]	0.719	0.685[d]
	303.15	0.76067	0.76065[c]	0.655	0.637[c]
	308.15	0.75631	0.7563[d]	0.616	0.600[d]
	313.15	0.75194	0.75193[c]	0.573	0.568[e]
n-heptane	298.15	0.67972	0.6797[f]	0.404	0.396[h]
	303.15	0.67546	0.67547[f]	0.383	0.375[f]
	308.15	0.67117	0.67119[g]	0.363	0.356[f]
	313.15	0.66684	0.66686[g]	0.342	0.336[g]

[a] Ref 1. [b] Ref 4. [c] Ref 5. [d] Ref 6. [e] Ref 7. [f] Ref 8. [g] Ref 9. [h] Ref 10.

Density and Viscosity Measurement. The densities, ρ, of pure components and their binary mixtures were measured by a density meter (DMA 5000M) thermostatted by an autocontrolling temperature device with a precision of 0.001 K. The densimeter was calibrated with freshly twice-distilled water. The uncertainty of the density measurements was $\pm 5 \cdot 10^{-6}$ $g \cdot cm^{-3}$, corresponding to the uncertainty of $\pm 1 \cdot 10^{-3}$ $cm^3 \cdot mol^{-1}$ for the excess volume, V_m^E.

The dynamic viscosity η is calculated from the measured density ρ and the kinematic viscosity ν:

$$\eta = \rho\nu \quad (1)$$

The kinematic viscosities were determined using an Ubbelohde viscometer. The viscometer was filled with 20 cm^3 solution and was submerged into a thermostatic bath with a resolution of 0.01 K. The flow time was measured with a stopwatch to an accuracy of 0.01 s. The viscometer was calibrated with twice-distilled water. Each viscosity value of the fluid was reported by averaging over three consecutive runs. The flow time was reproducible to be ± 0.2 s, and the uncertainty of viscosity was within ± 0.008 mPa·s.

* Corresponding author. Tel.: +86 571 87952371. Fax: +86 571 87951895. E-mail: fwjun@zju.edu.cn.

10.1021/je900969u
Published on Web 02/12/2010

Table 2. Density ρ and Viscosity η of NMP + MCH and NMP + *n*-Heptane Binary Mixtures at Several Temperatures

x_{NMP}	ρ / g·cm^{-3}	η / mPa·s	x_{NMP}	ρ / g·cm^{-3}	η / mPa·s
NMP + MCH			NMP + *n*-heptane		
298.15 K			298.15 K		
0.0000	0.76500	0.719	0.0000	0.67972	0.404
0.0988	0.77501	0.716	0.1006	0.69586	0.429
0.1972	0.78584	0.751	0.2012	0.71324	0.466
0.2970	0.79752	0.801	0.3006	0.73162	0.511
0.3964	0.81157	0.867	0.4014	0.75150	0.571
0.4953	0.82293	0.945	0.5007	0.77243	0.648
0.5948	0.83659	1.057	0.5996	0.79438	0.756
0.6952	0.85068	1.190	0.7000	0.81802	0.905
0.7969	0.86590	1.362	0.7979	0.84273	1.094
0.8977	0.88136	1.585	0.9036	0.87101	1.474
1.0000	0.89928	1.856	1.0000	0.89928	1.856
303.15 K			303.15 K		
0.0000	0.76067	0.655	0.0000	0.67546	0.383
0.0988	0.77065	0.676	0.1006	0.69157	0.395
0.1972	0.78144	0.698	0.2012	0.70891	0.438
0.2970	0.79312	0.730	0.3006	0.72727	0.481
0.3964	0.80563	0.776	0.4014	0.74713	0.533
0.4953	0.81851	0.840	0.5007	0.76804	0.599
0.5948	0.83217	0.918	0.5996	0.78999	0.699
0.6952	0.84626	1.022	0.7000	0.81361	0.815
0.7969	0.86149	1.164	0.7979	0.83832	0.995
0.8977	0.87696	1.326	0.9036	0.86662	1.234
1.0000	0.89490	1.544	1.0000	0.89490	1.544
313.15 K			313.15 K		
0.0000	0.75194	0.573	0.0000	0.66684	0.342
0.0988	0.76189	0.582	0.1006	0.68290	0.360
0.1972	0.77264	0.604	0.2012	0.70020	0.389
0.2970	0.78426	0.634	0.3006	0.71849	0.424
0.3964	0.79674	0.674	0.4014	0.73830	0.467
0.4953	0.80959	0.725	0.5007	0.75918	0.527
0.5948	0.82326	0.791	0.5996	0.78110	0.603
0.6952	0.83734	0.868	0.7000	0.80471	0.691
0.7969	0.85258	0.970	0.7979	0.82943	0.826
0.8977	0.86808	1.087	0.9036	0.85775	1.024
1.0000	0.88607	1.250	1.0000	0.88607	1.250

Results and Discussion

Density and Viscosity Data. The experimental density and viscosity at several temperatures for the binary mixtures are given in Table 2. The excess volume, V_m^E, is calculated from eq 2.

$$V_m^E = \frac{M_1x_1 + M_2x_2}{\rho} - \left(\frac{M_1x_1}{\rho_1} + \frac{M_2x_2}{\rho_2}\right) \quad (2)$$

where M_i, x_i, and ρ_i are the molecular weight, the mole fraction, and the density of the pure component i, respectively. ρ is the density of the binary mixture.

The excess volume as a function of composition is fitted to the Redlich−Kister type equation[11]

$$V_m^E = x_1x_2\sum_{i=1}^{k} A_i(x_1 - x_2)^{i-1} \quad (3)$$

where A_i are the polynomial coefficients. The standard deviation, σ, of the correlation is defined as

$$\sigma = [\sum (Y - Y_{cal})^2/(n - k)]^{1/2} \quad (4)$$

where n is the number of data points, k is the number of parameters, Y is the experimental value, and Y_{cal} is the calculated value. The regression results of excess volume are given in Table 3, in which the σ values are less than 0.013 cm^3·mol^{-1}.

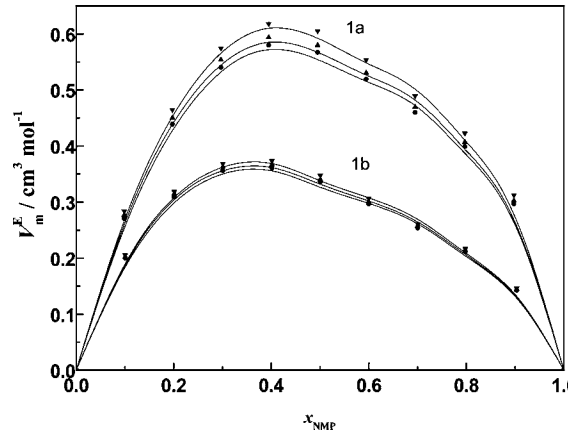


Figure 1. Plots of excess molar volume, V_m^E, against mole fraction x_{NMP} for NMP + MCH (a) and NMP + *n*-heptane (b) binary mixtures at several temperatures: ●, 298.15 K; ▲, 303.15 K; ▼, 313.15 K.

Table 3. Parameters of the Redlich−Kister Type Equation and Standard Deviations σ of V_m^E (cm^3·mol^{-1}) Correlations for NMP + MCH and NMP + *n*-Heptane Binary Mixtures

T/K	A_1	A_2	A_3	A_4	A_5	σ
NMP + MCH						
298.15	2.26259	−0.72310	0.51850	1.34989	1.34783	0.012
303.15	2.31251	−0.75296	0.54686	1.38315	1.33888	0.012
313.15	2.41383	−0.76696	0.51308	1.43264	1.38374	0.013
NMP + *n*-Heptane						
298.15	1.34445	−0.68791	0.59081	0.50052	0.47158	0.008
303.15	1.36258	−0.71290	0.64400	0.53013	0.40154	0.008
313.15	1.39183	−0.72414	0.59318	0.53976	0.48412	0.009

The excess volume, V_m^E, against the mole fraction for the investigated binary mixtures at different temperatures is shown in Figure 1. It is observed that the V_m^E values are positive for both binary systems over the entire composition range. NMP molecules are self-associated through hydrogen bonds resulting from the ring nitrogen atoms. When each of the two nonpolar components is mixed with NMP, the induction forces between two different molecules are formed, and the hydrogen bonds among NMP molecules are weakened. Because the induction force between the permanent dipole and the induced dipole is a type of van der Waals force, also known as a Debye force, the energy of the molecular hydrogen bond should be much greater than that of the induction force, and positive V_m^E of the binary mixtures can be observed. Both NMP and MCH are cyclic molecules, while *n*-heptane is a chain alkane. Thus, the *n*-heptane molecule might enter the space of a NMP molecule. This means that the distance between *n*-heptane and NMP molecules at the equilibrium state becomes shorter, while the cyclic MCH molecule hinders the molecular packing between the two components.[12] As a result, the V_m^E values of NMP + MCH are larger than those of NMP + *n*-heptane at the same composition and temperature.

Viscosity Correlation. Viscosity data and viscosity models for pure liquids and their mixtures are useful for practical and theoretical purposes.[4,13–15] Four typical semiempirical equations are employed to correlate the experimental viscosities in this work. The Kendall−Monroe equation[4] without adjustable parameters is expressed as

$$\eta = (x_1\eta_1^{1/3} + x_2\eta_2^{1/3})^3 \quad (5)$$

The single-parameter equations of Hind,[16] Grunberg−Nissan,[17] and the double-parameter McAllister[18] are expressed as eqs 7, 8, and 9, respectively.

Table 4. Correlation Deviations and Adjustable Parameters of Semi-empirical Viscosity Equations for NMP + MCH and NMP + *n*-Heptane Binary Mixtures at (298.15, 303.15, and 313.15) K

		NMP + MCH			NMP + *n*-heptane		
equation		298.15	303.15	313.15	298.15	303.15	313.15
Kendall−Monroe	Dev/%	15.6	13.3	11.4	27.2	22.5	19.5
	σ/mPa·s	0.178	0.139	0.100	0.237	0.175	0.132
Grunberg−Nissan	A_{12}	−0.7602	−0.6692	−0.6051	−1.1971	−0.9901	−0.8926
	Dev/%	0.99	0.28	0.28	1.42	0.75	0.67
	σ/mPa·s	0.012	0.024	0.003	0.016	0.006	0.005
Hind et al.	A_{12}	0.5822	0.5807	0.5380	0.1250	0.2258	0.2358
	Dev/%	2.00	2.23	3.97	9.06	6.06	11.12
	σ/mPa·s	0.025	0.024	0.029	0.078	0.051	0.058
McAllister	A_{12}	0.6545	1.0390	0.4450	0.3354	0.3991	0.2985
	A_{21}	0.2837	0.0443	0.2244	0.2576	0.2406	0.2048
	Dev/%	6.24	8.96	6.81	1.96	5.19	2.76
	σ/mPa·s	0.085	0.098	0.064	0.021	0.067	0.025

$$\eta = x_1^2\eta_1 + x_2^2\eta_2 + 2x_1x_2A_{12} \quad (6)$$

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1x_2A_{12} \quad (7)$$

$$\ln \eta = x_1^3 \ln \eta_1 + x_2^3 \ln \eta_2 + 3x_1^2x_2 \ln A_{12} + 3x_1x_2^2 \ln A_{21} - \ln[x_1 + x_2M_2/M_1] + 3x_1^2x_2 \ln[2 + (M_2/M_1)/3] + 3x_1x_2^2 \ln[1 + (2M_2/M_1)/3] + x_2^3 \ln[M_2/M_1] \quad (8)$$

where A_{12} and A_{21} are interaction parameters.

The correlation parameters along with the average percentage deviation (Dev)

$$\text{Dev} = \frac{1}{n}\sum_{i=1}^{n}\frac{|\eta_{\text{calcd},i} - \eta_{\text{exptl},i}|}{\eta_{\text{exptl},i}} \cdot 100\ \% \quad (9)$$

and the standard deviation (σ) for the binary mixtures of NMP + MCH and NMP + *n*-heptane are listed in Table 4. The Hind and McAllister equations give comparatively similar deviations. The Kendall−Monroe equation gives large prediction deviations, which is not appropriate for these investigated binary mixtures. The Grunberg−Nissan equation gives relatively satisfactory results.

Conclusions

Densities and viscosities of the binary systems of NMP + MCH and NMP + *n*-heptane have been measured at several temperatures over the entire composition range. Excess volumes, V_m^E, for the binary mixtures have been calculated, and positive values of V_m^E are observed. These deviation results can be explained in terms of the changes of molecular shapes and interactions. The deviation functions fitted with the Redlich−Kister type equation and the viscosities correlated with semiempirical equations are performed with valuable information.

Literature Cited

(1) Chen, S. D.; Fang, W. J.; Yao, J.; Zong, H. X. Density and Refractive Index at 298.15 K and Vapor-Liquid Equilibria at 101.3 kPa for Binary Mixtures of Ethanol + *N*-Methylpiperazine. *J. Chem. Eng. Data* **2001**, *46*, 596–600.

(2) Gu, F. Y. Density and Refractive Index at 298.15 K and Vapor-liquid Equilibria at 101.3 kPa for Binary Mixtures of Water + *N*-Ethylpiperazine. *J. Chem. Eng. Data* **2000**, *45*, 288–291.

(3) Yang, F. J.; Guo, Y. S.; Xing, Y.; Li, D.; Fang, W. J.; Lin, R. S. Densities and Viscosities of Binary Mixtures of JP-10 with *n*-Octane or *n*-Decane at Several Temperatures. *J. Chem. Eng. Data* **2008**, *53*, 2237–2240.

(4) Chen, S. D.; Lei, Q. F.; Fang, W. J. Viscosities and Densities for Binary Mixtures of *N*-methylpiperazine with Methanol, Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol and *iso*-Butanol at 293.15, 298.15 and 303.15 K. *Fluid Phase Equilib.* **2005**, *234*, 22–33.

(5) Pereiro, A. B.; Rodríguez, A.; Canosa, J.; Tojo, J. Density, Viscosity, and Speed of Sound of Dialkyl Carbonates with Cyclopentane and Methyl Cyclohexane at Several Temperatures. *J. Chem. Eng. Data* **2004**, *49*, 1392–1399.

(6) Ye, J. D.; Tu, C. H. Densities, Viscosities, and Refractive Indices for Binary and Ternary Mixtures of Diisopropyl Ether, Ethanol, and Methylcyclohexane. *J. Chem. Eng. Data* **2005**, *50*, 1060–1067.

(7) Zeberg-Mikkelsen, C. K.; Barrouhou, M.; Baylaucq, A.; Boned, C. Viscosity and Density Measurements of Binary Mixtures Composed of Methylcyclohexane + *cis*-Decalin Versus Temperature and Pressure. *Int. J. Thermophys.* **2003**, *24*, 361–374.

(8) Fang, S.; Zhao, C. X.; He, C. H. Densities and Viscosities of Binary Mixtures of Tri-*n*-butyl Phosphate + Cyclohexane, + *n*-Heptane at T = (288.15, 293.15, 298.15, 303.15, and 308.15) K. *J. Chem. Eng. Data* **2008**, *53*, 2244–2246.

(9) Landaverde-Cortes, D. C.; Estrada-Baltazar, A.; Iglesias-Silva, G. A. Densities and Viscosities of MTBE + Heptane or Octane at P = 0.1 MPa from (273.15 to 363.15) K. *J. Chem. Eng. Data* **2007**, *52*, 1226–1232.

(10) Xie, W. J.; Fang, W. J.; Li, D.; Guo, Y. S.; Lin, R. S. Coking of Model Hydrocarbon Fuels under Supercritical Condition. *Energy Fuels* **2009**, *23*, 2997–3001.

(11) Redlich, O. R.; Kister, A. T. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345–348.

(12) Yang, C. S.; Lai, H. X.; Liu, Z. G.; Ma, P. S. Densities and Viscosities of Diethyl Carbonate + Toluene, + Methanol, + 2-Propanol from (293.15 to 363.15) K. *J. Chem. Eng. Data* **2006**, *51*, 584–589.

(13) Lei, Q.; Hou, Y. Correlation of Viscosity of Binary Liquid Mixtures. *Fluid Phase Equilib.* **1999**, *154*, 153–163.

(14) Lei, Q.; Hou, Y.; Lin, R. Correlation of Viscosities of Pure Liquids in a Wide Temperature Range. *Fluid Phase Equilib.* **1997**, *140*, 221–231.

(15) Adel, S. A. J.; Al-Kandary Jasem, A.; Abdul-Latif, A. M. Densities and Viscosities for Binary Mixtures of Phenetole with 1-Pentanol, 1-Hexanol, 1-Heptanol, 1-Octanol, 1-Nonanol, and 1-Decanol at Different Temperatures. *Fluid Phase Equilib.* **2004**, *218*, 247–260.

(16) Matos, J. S.; Trenzado, J. L.; Gonzalez, E. Volumetric Properties and Viscosities of the Methylbutanoate + *n*-Heptane + *n*-Octane Ternary Systems its Binary Constituents in the Temperature Range from 283.15 to 313.15 K. *Fluid Phase Equilib.* **2001**, *186*, 207–234.

(17) Grunberg, L.; Nissan, A. H. Rheological Measurements and Adhesion. *Nature* **1949**, *164*, 799–800.

(18) Frenkel Y. I. *Kinematic Theory of Liquids*; Oxford University Press: London, 1949.

Received for review November 12, 2009. Accepted January 28, 2010. The authors are grateful for the financial support from the National Natural Science Foundation of China (No. 20973154) and Scientific Research Foundation for Returned Scholars, Ministry of Education of China (No. J20080412).

JE900969U