

Density and Refractive Index at 298.15 K and Vapor–Liquid Equilibria at 101.3 kPa for Binary Mixtures of Ethanol + *N*-Methylpiperazine

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Densities and refractive indices at 298.15 K, and isobaric vapor–liquid equilibrium (VLE) data at 101.3 kPa are reported for the binary mixtures of ethanol + *N*-methylpiperazine. Excess molar volumes and refractive index deviations are calculated from the measurement results. Negative values for excess molar volumes are observed over the whole composition range, whereas refractive indices exhibit positive deviations from linear additive values. The VLE data are correlated by the UNIQUAC liquid-phase activity coefficient model with satisfactory results. This binary system has no azeotrope.

Introduction

Piperazine and its derivatives are important intermediates in pharmaceutical chemistry. They are also useful materials of some synthetic dyes, synthetic polymeric compounds, and surfactants. Alkyl piperazines, such as *N*-methylpiperazine (NMP) and *N*-ethylpiperazine (NEP), are good bioactive substances, which can be selected as model compounds in some scientific research processes. Research and development on alkyl piperazines are of particular interest in the pharmaceutical industry and the fine chemical industry recently.^{1,2} The piperazines are easily mixed with water and alcohols. Accurate physical and thermodynamic properties about the piperazines and experimental information on the phase equilibrium of the piperazines with water or alcohols are necessary for the related separation process. VLE data of the binary systems piperazine + *N*-methylpiperazine and water + *N*-methylpiperazine have been reported previously by Gu and Zhang.¹ Experimental measurements of the density, refractive index, and vapor–liquid equilibrium (VLE) data for the binary mixtures of ethanol + NMP have not been found in the literature.

To further understand the nature of NMP, to augment its basic data, and to design a separation process, this work is to obtain experimental data of densities and refractive indices at 298.15 K, and isobaric VLE data at 101.3 kPa for the binary mixtures of ethanol + NMP. Then excess molar volumes and refractive index deviations are calculated from the measurements and are correlated using the Redlich–Kister polynomial equation. VLE data are correlated by the UNIQUAC method.

Experimental Section

Materials. Absolute ethanol with a purity better than 99.8% as claimed by the supplier, Shanghai Chemical Corporation China, was used without further purification.

NMP was purified and maintained under special conditions before its use. It was dried over freshly activated Al₂O₃ for at least 2 days and then distilled at atmospheric pressure with a glass column 0.025 m in diameter and 1.5 m high. The product was dehydrated by standing over 0.4 nm freshly activated molecular sieves. Chemical purity was checked by NMR and GC analysis; no peaks for impurities were observed. Its final purity is estimated to be better than 99.9 mass %. The binary mixtures were prepared by directly weighing the constituent components with a Mettler balance that has a precision of ± 0.0001 g. Precautions were taken in order to minimize evaporation losses during storage and preparation of the solutions. Comparisons of measured physical properties (densities, refractive indexes, and normal boiling point) with literature values^{1,3,4} are shown in Table 1.

Apparatus and Procedure. Densities of the pure liquids and binary mixtures were measured by means of a vibrating tube digital densimeter, model DMA 602 (Anton Paar), thermostated by a circulating-water bath with a precision of ± 0.01 K. The uncertainty in density measurements was about $\pm 1 \times 10^{-5}$ g·cm⁻³. Refractive indices were determined to ± 0.0001 by using an Abbe refractometer connected to a Haake F3-C liquid thermostatic bath.

VLE data for the ethanol + NMP binary system and the vapor pressures for NMP were measured by using an all-glass equilibrium still of the modified Rose type with circulation of both the liquid and vapor phases. The authors (Gu and Zhang,¹ Gu and Fang⁵) have applied this apparatus to obtain the VLE data for the piperazine + *N*-methylpiperazine, water + *N*-methylpiperazine, and water + *N*-ethylpiperazine binary systems. Details of the structure and operation of the circulation still have been previously described by Wang et al.⁶ During the measurements, the temperature was measured with a platinum-resistance thermometer calibrated on the IPTS-68. The accuracy of temperature measurements is within ± 0.01 K. The pressure in the equilibrium still was maintained at 101.3 ± 0.02 kPa with the help of a pressure control system, which consists of a mercury manometer, a water manometer, two solenoid valves, two electromagnetic type

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Table 1. Normal Boiling Point, t_b , Density, ρ , and Refractive Index, n_D , for Pure Liquids and Comparison with Literature Values

liquid	$t_b/^\circ\text{C}$		$\rho/(\text{g}\cdot\text{cm}^{-3})$		n_D	
	exptl	lit.	exptl	lit.	exptl	lit.
ethanol	78.32	78.293 ^a	0.785 06 (25 °C)	0.78509 (25 °C) ^a	1.3595 (25 °C)	1.35941 (25 °C) ^a
NMP	136.81	138 ^b 135.9 ^c	0.903 78 (20 °C) 0.899 80 (25 °C) 0.894 54 (30 °C)	0.903 (20 °C) ^b 0.8944 (30 °C) ^c	1.4655 (20 °C) 1.4634 (25 °C) 1.4614 (30 °C)	1.4655 (20 °C) ^b 1.4615 (30 °C) ^c

^a TRC Databases.³ ^b Dean.⁴ ^c Gu and Zhang.¹

Table 2. Density, ρ , and Refractive Index, n_D , for Ethanol (1) + *N*-Methylpiperazine (2) at 298.15 K with Excess Molar Volume, V^E , and Refractive Index Deviation, δn_D

x_1	$\rho/(\text{g}\cdot\text{cm}^{-3})$	$V^E/(\text{cm}^3\cdot\text{mol}^{-1})$	x_1	n_D	δn_D
0.0546	0.898 00	-0.192	0.0546	1.4610	0.0033
0.1110	0.895 98	-0.385	0.1110	1.4584	0.0065
0.1517	0.894 33	-0.510	0.1517	1.4564	0.0088
0.2037	0.892 10	-0.669	0.2037	1.4537	0.0115
0.2504	0.890 09	-0.824	0.2504	1.4513	0.0139
0.3001	0.887 79	-0.984	0.3001	1.4481	0.0159
0.3434	0.885 21	-1.075	0.3434	1.4455	0.0178
0.3920	0.882 49	-1.212	0.3920	1.4420	0.0193
0.4023	0.881 63	-1.214	0.4563	1.4374	0.0214
0.4563	0.878 26	-1.357	0.5008	1.4337	0.0223
0.5008	0.874 75	-1.422	0.5034	1.4335	0.0224
0.5034	0.874 54	-1.426	0.5475	1.4298	0.0233
0.5540	0.869 82	-1.457	0.5990	1.4248	0.0236
0.5990	0.865 39	-1.488	0.6388	1.4204	0.0234
0.6015	0.865 03	-1.481	0.6547	1.4184	0.0230
0.6635	0.857 90	-1.477	0.6988	1.4135	0.0227
0.6988	0.853 49	-1.468	0.7473	1.4073	0.0215
0.7087	0.851 92	-1.441	0.8019	1.3995	0.0194
0.7473	0.846 59	-1.419	0.8503	1.3910	0.0159
0.8019	0.837 14	-1.277	0.9013	1.3814	0.0116
0.8071	0.835 73	-1.225	0.9501	1.3718	0.0071
0.8503	0.827 01	-1.065			
0.9052	0.814 09	-0.783			
0.9501	0.802 26	-0.520			

relays, two reservoirs, and a vacuum pump. The compositions for the binary mixtures were analyzed by refractometry.

Results and Discussion

Density and Refractive Index. Table 2 lists the measured density ρ and refractive index n_D data at 298.15 K with the corresponding excess molar volume V^E and refractive index deviation δn_D for the binary mixtures of ethanol + NMP.

The excess molar volume V^E is calculated from the density measurements by

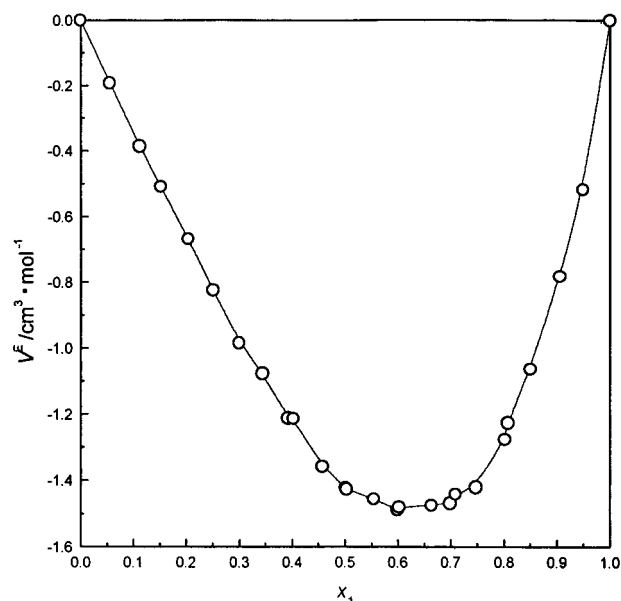
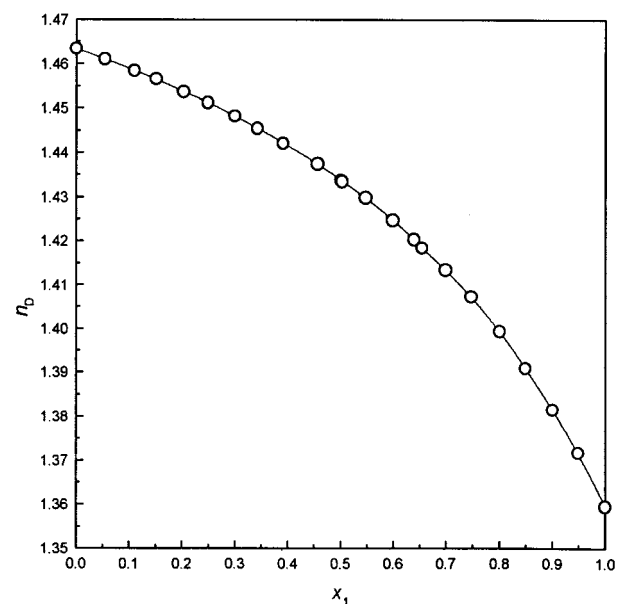
$$V^E = V - (x_1 V_1 + x_2 V_2) \quad (1)$$

with

$$V = (x_1 M_1 + x_2 M_2) / \rho \quad (2)$$

where V is the molar volume of the mixture and x_i , V_i , and M_i ($i = 1, 2$) are mole fraction, molar volume, and molecular weight of the components ethanol (1) and NMP (2), respectively. The uncertainty in the calculation of V^E from density measurements was estimated to be $\pm 0.001 \text{ cm}^3\cdot\text{mol}^{-1}$. Figure 1 illustrates the excess molar volumes of this binary system at 298.15 K. It shows that the excess molar volumes are negative with a minimum at $x_1 \approx 0.6$.

Figure 2 presents the refractive index at 298.15 K versus the composition. The refractive index deviation δn_D at

**Figure 1.** Excess molar volume V^E for binary mixtures of ethanol (1) + *N*-methylpiperazine (2) at 298.15 K.**Figure 2.** Refractive index n_D for binary mixtures of ethanol (1) + *N*-methylpiperazine (2) at 298.15 K.

298.15 K from the linear additive value of the mole fraction is obtained by

$$\delta n_D = n_D - (x_1 n_{D1} + x_2 n_{D2}) \quad (3)$$

where n_D is the refractive index of the mixture and n_{D1} and n_{D2} are the refractive indices of the components ethanol and NMP, respectively. The plot of δn_D versus the mole

Table 3. Correlated Values of Parameters, A_i and B_i , with the Standard Deviations, σ , for Excess Molar Volumes, V^E , and Refractive Index Deviations, δn_D

V^E		δn_D	
A_1	-5.679 18	B_1	$8.984\ 018 \times 10^{-2}$
A_2	2.591 156	B_2	$-3.712\ 675 \times 10^{-2}$
A_3	$-2.077\ 777 \times 10^{-2}$	B_3	$9.196\ 683 \times 10^{-2}$
A_4	1.477 372	B_4	$-1.028\ 468 \times 10^{-2}$
A_5	-2.303 204	B_5	$1.203\ 628 \times 10^{-2}$
$\sigma/\text{cm}^3\cdot\text{mol}^{-1}$	0.018	σ	0.0034

fraction of ethanol x_1 is given in Figure 3. δn_D is positive with a maximum at $x_1 \approx 0.6$.

The experimental molar excess volumes and refractive index deviations are correlated by the Redlich–Kister polynomials

$$V^E = x_1(1 - x_1) \sum_{i=1}^5 A_i(2x_1 - 1)^{i-1} \quad (4)$$

$$\delta n = x_1(1 - x_1) \sum_{i=1}^5 B_i(2x_1 - 1)^{i-1} \quad (5)$$

where the parameters A_i and B_i determined by a least-squares fit method are given in Table 3, along with the standard deviations σ , defined as follows

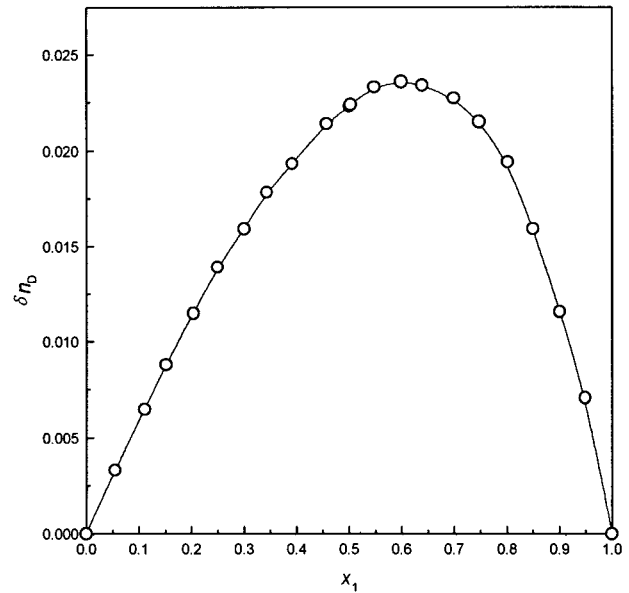
$$\sigma = \sqrt{\frac{\sum (Z_{\text{cal}} - Z_{\text{exp}})_i^2}{N - m}} \quad (6)$$

where N is the number of experimental data, m is the number of equation parameters, and Z is the considered property (V^E or δn_D).

VLE Data. Vapor–liquid equilibrium data (T , x_1 , y_1) for the ethanol (1) + NMP (2) binary system at 101.3 kPa are presented in Table 4. The y_1 – x_1 and T – x_1 – y_1 phase diagrams are illustrated in Figures 4 and 5, respectively.

Table 4. Vapor–Liquid Equilibrium Data for the Ethanol (1) + *N*-Methylpiperazine (2) System at 101.3 kPa

experimental data			UNIQUAC method					
T/K	x_1	y_1	$y_{1,\text{cal}}$	Δy_1	T_{cal}/K	$\Delta T/\text{K}$	$\Delta P/\text{kPa}$	$\Delta P/P \times 100\%$
409.96	0.000	0.000						
404.19	0.062	0.195	0.209	0.014	403.46	-0.73	2.09	2.06
400.49	0.097	0.303	0.304	0.001	400.27	-0.22	0.66	0.65
397.30	0.135	0.392	0.393	0.001	397.11	-0.19	0.57	0.56
394.38	0.175	0.468	0.472	0.004	394.09	-0.29	0.92	0.91
391.57	0.207	0.533	0.529	-0.004	391.77	0.20	-0.63	-0.62
388.92	0.245	0.590	0.587	-0.003	389.24	0.32	-1.03	-1.02
386.96	0.275	0.630	0.630	0.000	387.28	0.32	-1.06	-1.04
384.33	0.311	0.685	0.676	-0.009	384.99	0.66	-2.22	-2.19
381.98	0.356	0.732	0.727	-0.005	382.31	0.33	-1.13	-1.11
379.97	0.391	0.762	0.762	-0.000	380.27	0.30	-1.02	-1.01
378.12	0.429	0.790	0.797	0.007	378.07	-0.05	0.16	0.16
376.40	0.462	0.821	0.824	0.003	376.26	-0.14	0.49	0.49
374.78	0.492	0.845	0.845	0.000	374.65	-0.13	0.46	0.46
373.07	0.524	0.869	0.867	-0.002	372.95	-0.12	0.45	0.45
371.88	0.550	0.876	0.883	0.007	371.57	-0.31	1.14	1.12
370.13	0.591	0.894	0.906	0.012	369.46	-0.67	2.52	2.49
368.55	0.617	0.908	0.918	0.010	368.12	-0.43	1.62	1.60
366.98	0.641	0.922	0.929	0.007	366.91	-0.07	0.28	0.28
365.11	0.681	0.935	0.945	0.010	364.92	-0.19	0.71	0.71
363.76	0.708	0.946	0.955	0.009	363.59	-0.17	0.63	0.62
361.95	0.741	0.963	0.965	0.002	362.04	0.09	-0.34	-0.34
360.35	0.773	0.972	0.973	0.001	360.52	0.17	-0.65	-0.65
358.23	0.818	0.982	0.982	0.000	358.46	0.23	-0.90	-0.89
356.38	0.851	0.989	0.988	-0.001	357.01	0.63	-2.46	-2.43
354.88	0.886	0.993	0.992	-0.001	355.55	0.67	-2.64	-2.60
353.52	0.920	0.996	0.996	-0.000	354.26	0.74	-2.90	-2.87
352.47	0.948	0.999	0.998	-0.001	353.24	0.77	-3.05	-3.01
351.47	1.000	1.000						
AAD				0.004		0.34	1.21	1.20

**Figure 3.** Refractive index deviation δn_D from the linear additive values for binary mixtures of ethanol (1) + *N*-methylpiperazine (2) at 298.15 K.

The experimental results show that this binary system has no minimum or maximum boiling azeotrope.

The vapor–liquid equilibrium is expressed by the equation

$$P\varphi_i y_i = P_i^S \varphi_i^S x_i \gamma_i \exp\left[\frac{V_i^L}{RT}(P - P_i^S)\right] \quad (7)$$

where P is the total pressure, x_i and y_i are the liquid- and vapor-phase mole fractions of component i , respectively, V_i^L is the liquid molar volume of pure component i , which was calculated from the modified Rackett equation,⁷ φ_i is

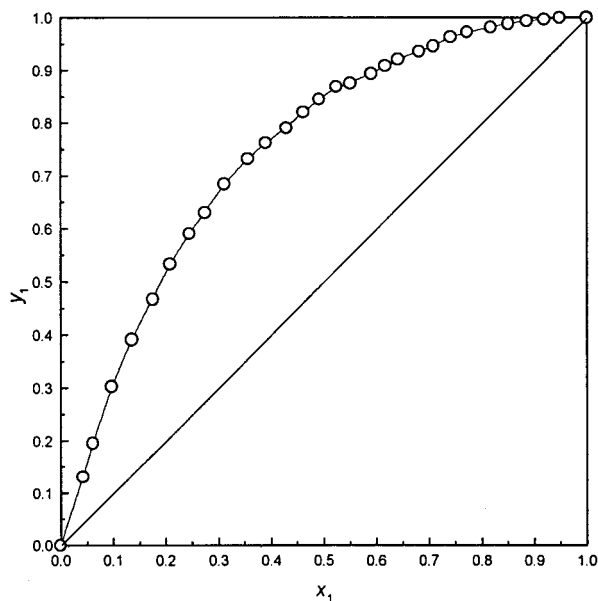


Figure 4. y_1-x_1 phase diagram for the binary system ethanol (1) + *N*-methylpiperazine (2) at 101.3kPa.

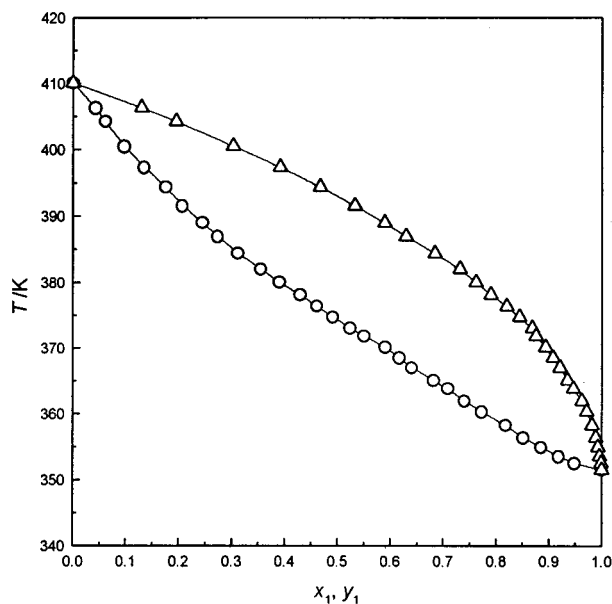


Figure 5. $T-y_1-x_1$ phase diagram for the binary system ethanol (1) + *N*-methylpiperazine (2) at 101.3kPa: Δ , vapor; \circ , liquid.

Table 5. Critical Properties and Acentric Factors of Ethanol and *N*-Methylpiperazine

liquid	P_c /MPa	T_c /K	V_c /(cm ³ ·mol ⁻¹)	Z_c	ω
ethanol	6.14	513.9	167.1	0.240	0.644
NMP	4.562	629.72	338.99	0.3389	0.3330

the vapor-phase fugacity coefficient of component i in the mixture, and φ_i^S is the vapor-phase fugacity coefficient of pure component i at the system temperature and the corresponding saturated vapor pressure P_i^S , which was calculated from the explicit virial equation of state truncated after the second term. The second virial coefficients are estimated from the generalized correlation of Hayden and O'Connell.⁸ The critical properties, P_c , T_c , V_c , and Z_c and acentric factors ω of NMP and ethanol were selected from the literature.^{1,9} The values of P_c , T_c , V_c , Z_c , and ω are listed in Table 5. The vapor pressures of NMP have been measured over the temperature range 355.8 to 409.9

Table 6. Experimental Vapor Pressure of *N*-Methylpiperazine

T /K	P_i^S /kPa	T /K	P_i^S /kPa	T /K	P_i^S /kPa
355.88	17.20	387.81	55.13	405.76	91.54
369.91	29.86	395.24	68.92	408.62	98.41
379.68	42.72	400.85	80.46	409.96	101.33

Table 7. Temperature Dependence of the Parameters of the UNIQUAC Equation for the Ethanol (1) + *N*-Methylpiperazine (2) Binary System

	α_{12}		α_{21}
$a_{12}^{(0)}$	-42.553 83	$a_{21}^{(0)}$	-337.304 4
$a_{12}^{(1)}$	34.574 97	$a_{12}^{(1)}$	23.773 57
$a_{12}^{(2)}$	21.186 10	$a_{21}^{(2)}$	33.640 24

K. The results are given in Table 6. The Antoine constants are calculated by a nonlinear optimization method to minimize the mean relative deviation. The Antoine equation for NMP is

$$\ln P_i^S = A - \frac{B}{T + C} \quad (8)$$

with $A = 9.833 79$, $B = 1108.546$, and $C = -197.3339$. The vapor pressures for ethanol were obtained from Reid et al.⁹

Fredenslund's test for thermodynamic consistency¹⁰ was applied to the experimental data. The average value for $\Delta y = y_{\text{cal}} - y_{\text{exp}}$ absolute (mole fraction) is 0.009, which shows that the experimental data are consistent.

The liquid-phase activity coefficients γ_i are calculated from the UNIQUAC equation. The parameters of the UNIQUAC equation as a function of temperature are given by the following equation¹¹

$$\alpha_{ij} = a_{ij}^{(0)} + a_{ij}^{(1)} T/T_0 + a_{ij}^{(2)} (T/T_0)^2 \quad (9)$$

where T_0 is an arbitrarily chosen reference temperature, in this case $T_0 = 315$ K. The temperature dependence parameters are obtained by minimizing the objective function

$$F = \frac{1}{N} \sum_{i=1}^N \left[(y_{\text{cal}} - y_{\text{exp}})^2 + (T_{\text{cal}} - T_{\text{exp}})^2 + \left(\frac{P_{\text{cal}} - P_{\text{exp}}}{P_{\text{exp}}} \right)^2 \right] \quad (10)$$

where N is the number of experimental data. The values of the temperature dependence parameters are presented in Table 7. VLE correlation results from the UNIQUAC equation are compared with experimental data in Table 4. The average value of Δy is 0.004 absolute mole fraction, that of ΔT is 0.34 K, and that of $\Delta P/P$ is 1.2%.

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