

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

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Densities and refractive indices at 298.15 K and isobaric vapor–liquid equilibrium (VLE) data at 101.3 kPa have been measured for binary mixtures of water + *N*-ethylpiperazine. 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. VLE data are tested for thermodynamic consistency and are correlated by the Wilson equation with satisfactory results. This binary system has no azeotrope.

Introduction

N-Ethylpiperazine (NEP), one of the series products of piperazine, is a useful intermediate in pharmaceutical chemistry and in the fine chemical industry. NEP is a leuco transparent liquid with a strong odor similar to that of ammonia; it readily mixes with water. The open literature displays a shortage of physical and thermodynamic properties of this compound. Experimental measurements of the density, refractive index, and vapor–liquid equilibrium (VLE) data for binary mixtures of water + NEP have not been found in the literature. To further understand the nature of NEP, to augment its basic data, and to design a separation process, experimental information on phase equilibrium and related thermodynamic properties is required.

The purpose of the present work is to obtain experimental data of densities and refractive indices at 298.15 K and isobaric VLE data at a pressure of 101.3 kPa for binary mixtures of water + NEP. 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 Wilson equation.

Experimental Section

Materials. NEP 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. It is evaluated with purity better than 99.9 mass %. Deionized water was further twice distilled and degassed before its use. The binary mixtures were prepared directly by mass with a Mettler balance having a precision of ±0.0001 g. Precautions were taken in order to minimize evaporation losses during preparation and storage of the solutions.

Table 1. Boiling Point t_b , Density ρ , and Refractive Index n_D for Pure Liquids and Comparison with Literature Values at 298.15 K

liquid	$t_b/^\circ\text{C}$		$\rho/\text{g}\cdot\text{cm}^{-3}$		n_D	
	exptl	lit.	exptl	lit.	exptl	lit.
water	100.00	100.00	0.99708	0.99708 ^a	1.3325	1.3325 ^a
NEP	156.02	154 (100.39 kPa) ^a 157 ^b	0.89588	0.899 ^b	1.4620	

^a Lide (1993–1994). ^b Lane et al. (1998–1999).

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 with a circulating-water bath with a precision of ±0.01 K. Refractive indices were determined to ±0.0001 by using an Abbe refractometer connected to a Haake F3-C liquid thermostatic bath. The measured physical properties of the pure liquids are compared with literature values in Table 1.

VLE data for the water + NEP binary system and vapor pressures for NEP were measured by using an all-glass equilibrium still of modified Rose type with circulation of both the liquid and vapor phases. The authors (Gu and Zhang, 1998) have applied this apparatus to obtain VLE data for the *N*-methylpiperazine + piperazine and water + *N*-methylpiperazine binary systems. Details of the structure and operation of the circulation still have been previously described by Wang et al. (1989). During the measurements, the temperature was measured by using a platinum-resistance thermometer calibrated on the IPTS-68 scale. 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 relays, two reservoirs, and a vacuum pump. The compositions for the binary mixtures were analyzed by refractometry when the molar fraction of water was larger

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

x_1	$\rho/\text{g}\cdot\text{cm}^{-3}$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	n_D	δn_D
0.0000	0.895 88	0.0000	1.4620	0.0000
0.0499	0.898 66	-0.2759	1.4620	0.0065
0.1077	0.902 79	-0.6673	1.4619	0.0138
0.1535	0.906 12	-0.9409	1.4619	0.0198
0.1965	0.908 98	-1.1319	1.4617	0.0251
0.2597	0.913 95	-1.4388	1.4615	0.0331
0.2963	0.917 16	-1.6146	1.4610	0.0374
0.3413	0.921 32	-1.8113	1.4608	0.0430
0.4025	0.927 76	-2.0736	1.4603	0.0504
0.4468	0.932 93	-2.2452	1.4598	0.0557
0.5068	0.940 70	-2.4464	1.4587	0.0623
0.5419	0.945 72	-2.5455	1.4579	0.0661
0.5909	0.953 24	-2.6467	1.4563	0.0708
0.6134	0.957 35	-2.7041	1.4556	0.0730
0.6380	0.961 90	-2.7453	1.4542	0.0748
0.6550	0.964 85	-2.7481	1.4540	0.0768
0.6619	0.965 78	-2.7315	1.4539	0.0776
0.6738	0.968 13	-2.7389	1.4530	0.0783
0.7108	0.975 22	-2.7111	1.4510	0.0810
0.7515	0.983 33	-2.6270	1.4472	0.0825
0.8014	0.993 02	-2.4171	1.4375	0.0793
0.8532	1.001 76	-2.0497	1.4230	0.0715
0.9008	1.005 94	-1.5268	1.4022	0.0569
0.9538	1.001 62	-0.6998	1.3741	0.0356
1.0000	0.997 08	0.0000	1.3325	0.0000

than 0.75, and the Karl Fischer titration method was used in the remainder of the composition range.

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 binary mixtures of water + NEP.

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

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

with

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

where V_m is the molar volume of mixture and x_1 , V_1 , M_1 , x_2 , V_2 , and M_2 are the mole fraction, molar volume, and molecular weight of the components water and NEP, respectively. Figure 1 illustrates the excess molar volumes of this binary system at 298.15 K. It shows that the excess molar volumes are negative and the volume changes of mixing are relatively large for water + NEP mixtures over the entire composition range.

Figure 2 presents the refractive index at 298.15 K versus the composition. It indicates that the refractive index changes very slowly at mole fractions of water x_1 from 0 to 0.75 but decreases quickly with the composition of water at larger mole fractions. Therefore, the composition of the binary mixtures cannot be determined from measurements of the refractive index at mole fractions of water less than 0.75. The Karl Fischer titration method can be used in this composition range.

The refractive index deviation δn_D at 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

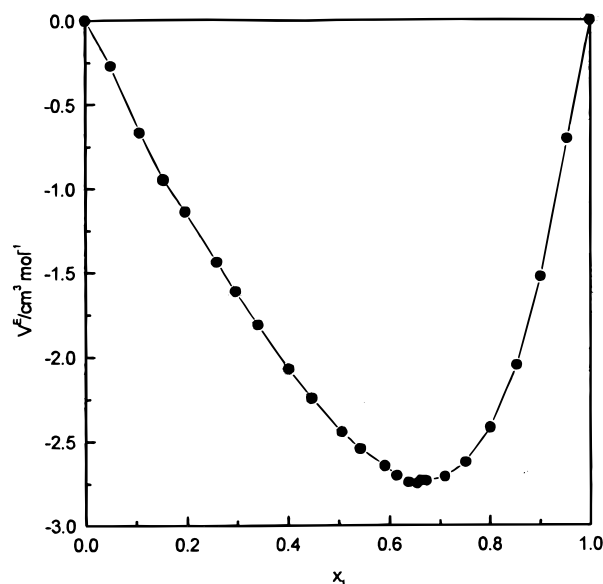


Figure 1. Excess molar volume V^E for binary mixtures of water (1) + *N*-ethylpiperazine (2) at 298.15 K.

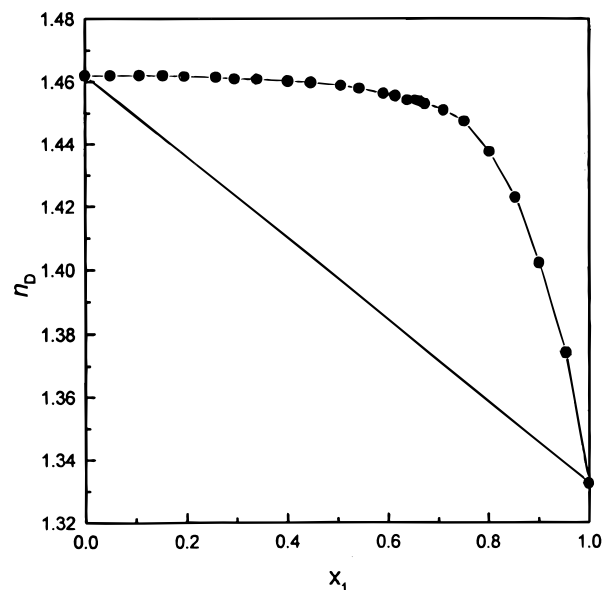


Figure 2. Refractive index n_D for binary mixtures of water (1) + *N*-ethylpiperazine (2) at 298.15 K.

n_{D2} are the refractive indices of the components water and NEP, respectively. The plot of δn_D versus the mole fraction of water x_1 is given in Figure 3.

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

$$V^E = x_1(1 - x_1) \sum_{i=1}^9 A_i (2x_1 - 1)^{i-1} \quad (4)$$

$$\delta n = x_1(1 - x_1) \sum_{i=1}^9 B_i (2x_1 - 1)^{i-1} \quad (5)$$

where the parameters A_i and B_i are determined by the least-squares fit method and the standard deviations σ are given in Table 3.

VLE Data. Vapor–liquid equilibrium data (T , x_1 , y_1) for the water + NEP 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

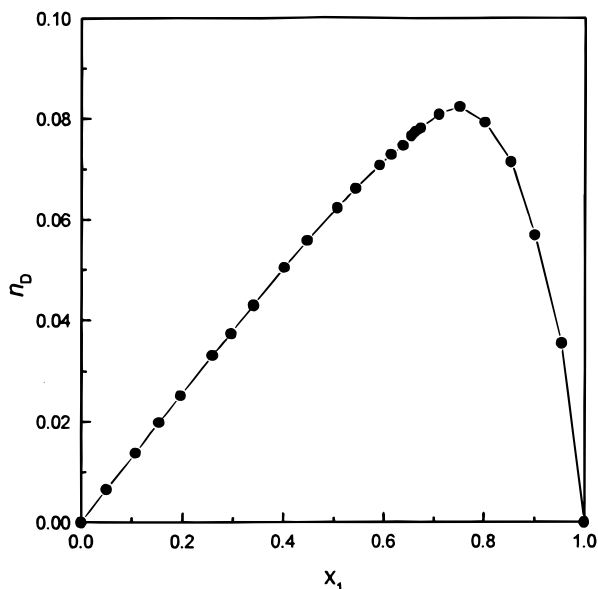


Figure 3. Refractive index deviation δn_D from the linear additive values for binary mixtures of water (1) + *N*-ethylpiperazine (2) at 298.15 K.

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	-9.688 869	B_1	0.247 098 8
A_2	-6.437 966	B_2	0.200 867 9
A_3	-5.103 517	B_3	0.142 651 8
A_4	-0.312 777 5	B_4	0.467 826 5
A_5	9.340 351	B_5	0.707 947 6
A_6	-1.989 042	B_6	-0.949 725 8
A_7	-29.032 62	B_7	-1.760 823
A_8	4.301 343	B_8	0.763 366 9
A_9	28.269 4	B_9	1.329 135
$\sigma/\text{cm}^3\cdot\text{mol}^{-1}$	0.007 0	σ	0.000 3

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

experimental data			Wilson equation			
T/K	x_1	y_1	T_{cal}/K	$\Delta T/\text{K}$	$y_{1,\text{cal}}$	Δy_1
373.15	1.0000	1.0000	373.15	0.00	1.0000	0.0000
373.31	0.9900	0.9954	373.35	0.04	0.9954	0.0000
374.22	0.9250	0.9788	374.24	0.02	0.9752	-0.0036
374.62	0.8980	0.9699	374.65	0.03	0.9690	-0.0009
375.00	0.8730	0.9648	375.01	0.01	0.9637	-0.0011
376.31	0.7990	0.9497	376.28	-0.03	0.9483	-0.0014
377.34	0.7500	0.9389	377.28	-0.06	0.9376	-0.0013
379.89	0.6460	0.9109	379.90	0.01	0.9111	0.0002
380.60	0.6220	0.9038	380.62	0.02	0.9050	0.0012
381.85	0.5800	0.8911	381.96	0.11	0.8899	-0.0012
386.30	0.4540	0.8437	387.01	0.71	0.8355	-0.0082
393.47	0.3286	0.7571	393.72	0.25	0.7568	-0.0003
403.10	0.2010	0.6093	403.59	0.49	0.6007	-0.0086
412.31	0.1150	0.4310	412.40	0.09	0.4290	-0.0020
416.96	0.0786	0.3171	416.99	0.03	0.3183	0.0012
425.04	0.0230	0.1115	424.92	-0.12	0.1145	0.0030
425.87	0.0177	0.0874	425.76	-0.11	0.0897	0.0023
429.17	0.0000	0.0000	429.56	0.39	0.0000	0.0000
AAD				0.14		0.0020

illustrated in Figures 4 and 5, respectively. The experimental results show that this binary system has no minimum or maximum boiling azeotrope.

The thermodynamic consistency of the experimental data was checked by the point-to-point test of Van Ness-Byer-

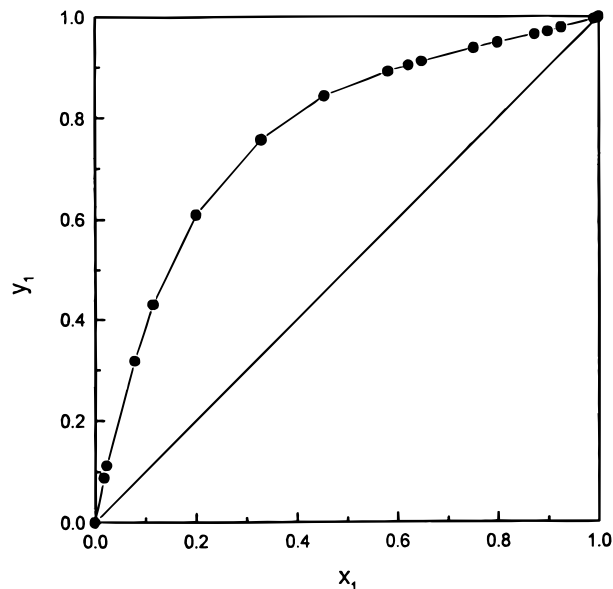


Figure 4. y_1 - x_1 phase diagram for the binary system water (1) + *N*-ethylpiperazine (2) at 101.3 kPa.

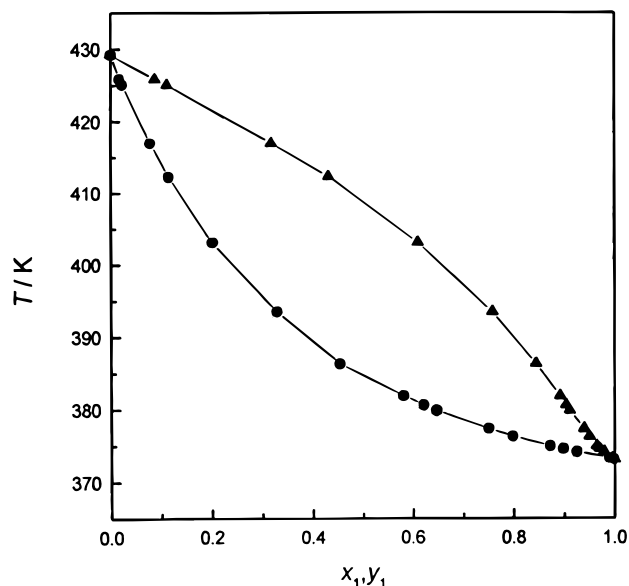


Figure 5. T - y_1 - x_1 phase diagram for the binary system water (1) + *N*-ethylpiperazine (2) at 101.3 kPa.

Gibbs (1973), as described by Fredenslund et al. (1977). For the Van Ness method, a five-parameter Legendre polynomial was used for the excess Gibbs energy. According to this test, the experimental data are consistent, since the average value for Δy is 0.0034.

The fundamental equation of vapor-liquid equilibrium can be expressed by the equation

$$P\varphi_i y_i = P_i^S \varphi_i^S x_i \gamma_i^S \exp\left[\frac{V_i^L}{RT}(P - P_i^S)\right] \quad (6)$$

where P is the total pressure, x_i and y_i are the liquid- and vapor-phase mole fractions of component i , respectively, φ_i is 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 . V_i^L is the liquid molar volume of pure component i . At low pressure, the term $\exp[(V_i^L/RT)(P - P_i^S)]$ is approximately equal to

Table 5. Critical Properties and Acentric Factors of Water and *N*-Ethylpiperazine

liquid	P_c /MPa	T_c /K	V_c /cm ³ ·mol ⁻¹	ω
water	22.048	647.30	56.0	0.344
NEP	3.849	641.78	402.45	0.341

1. Then eq 6 may be simply rewritten for the vapor–liquid equilibrium as

$$P\varphi_i y_i = P_i^S \varphi_i^S x_i \gamma_i \quad (7)$$

In the present work, the vapor-phase fugacity coefficients φ_i and φ_i^S are evaluated using the virial equation of state truncated after the second term. The second virial coefficients are calculated with the correlation of Tsonopoulos (1974) and Prausnitz et al. (1986). The critical properties P_c , T_c , and V_c and the acentric factor ω of NEP have been estimated by a group contribution method, and P_c , T_c , V_c , and ω of water are given elsewhere (Reid et al., 1987). The values of P_c , T_c , V_c , and ω are listed in Table 5. The vapor pressure data of NEP have been measured over the temperature range 365.4 to 429.2 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 NEP is

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

with $A = 13.5143$, $B = 3103.97$, and $C = -79.944$.

The liquid-phase activity coefficients are calculated with the Wilson equation (Gmehling et al., 1977)

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2[\Lambda_{12}/(x_1 + x_2\Lambda_{12}) - \Lambda_{21}/(\Lambda_{21}x_1 + x_2)] \quad (9)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) + x_1[\Lambda_{21}/(x_2 + x_1\Lambda_{21}) - \Lambda_{12}/(\Lambda_{12}x_2 + x_1)] \quad (10)$$

where Λ_{12} and Λ_{21} are two Wilson parameters with the following expressions:

$$\Lambda_{12} = (V_2/V_1) \exp[-(g_{12} - g_{11})/RT] \quad (11)$$

$$\Lambda_{21} = (V_1/V_2) \exp[-(g_{21} - g_{22})/RT] \quad (12)$$

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

T /K	P_i^S /kPa	T /K	P_i^S /kPa	T /K	P_i^S /kPa
365.40	14.00	397.75	42.35	420.66	81.97
369.50	16.38	405.35	53.24	422.84	86.66
380.05	21.80	408.35	56.86	426.20	95.30
385.71	28.91	413.73	68.11	427.06	97.06
389.45	30.66	415.25	69.99	429.17	101.33

The energy binary parameters in the Wilson equation are obtained by minimizing the objective function

$$F = \frac{1}{N} \sum_{i=1}^N \left[\left(\frac{y_{\text{cal}} - y_{\text{exp}}}{y_{\text{exp}}} \right)^2 + \left(\frac{T_{\text{cal}} - T_{\text{exp}}}{T_{\text{exp}}} \right)^2 \right] \quad (13)$$

with the values of $g_{12} - g_{11} = 4333.88 \text{ J}\cdot\text{mol}^{-1}$ and $g_{21} - g_{22} = -501.142 \text{ J}\cdot\text{mol}^{-1}$. N is the number of experimental data. The VLE correlation results from the Wilson equation are also listed in Table 4. The average value of ΔT is 0.14 K, and that of Δy is 0.0020 absolute mole fraction.

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