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Density and Refractive Index at 298.15 K and Vapor−Liquid Equilibria at 101.3 kPa for Four Binary Systems of Methanol, *n*-Propanol, *n*-Butanol, or Isobutanol with *N*-Methylpiperazine

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Density and refractive index data at 298.15 K, and isobaric vapor−liquid equilibrium (VLE) measurements at 101.3 kPa were reported for four binary systems of methanol, *n*-propanol, *n*-butanol, or isobutanol with *N*-methylpiperazine. Excess molar volumes and refractive index deviations were calculated. The measurement results exhibit no azeotropes for VLE, negative values for excess molar volume, and positive deviations from ideality for the refractive index over the whole mole fraction range. Liquid-phase activity coefficients and vapor-phase fugacity coefficients were estimated taking into account the nonideal nature of the vapor and liquid phases. The VLE data were shown to be thermodynamically consistent and were correlated by the UNIQUAC liquid-phase activity coefficient model with temperature-dependent parameters.

Introduction

The present work represents a continuation of a series of experimental studies on physical property and vapor−liquid equilibria for binary systems containing alkyl piperazine, such as *N*-methylpiperazine (NMP) and *N*-ethylpiperazine (NEP).[1−4] *N*-Methylpiperazine is an important intermediate for the broad-spectrum antibacterial medicines ofloxacin and clozapine. It is also a useful material for some synthetic dyes, insecticides, and synthetic polymeric compounds, polyurethane foaming plastic, sulfopolyester, and poly(tetrafluoro ethylene oxide). As a result of its special ring structure and biochemical activation, NMP can efficiently inhibit corrosion of some metals in water or alcohol through the linkage between its nitrogen atoms on the ring and the metal surface. It has been selected as a model compound in some chemical research and engineering processes. To describe the thermodynamic behavior and to study the mechanisms of these processes, physical and phase equilibrium properties of NMP with water or alcohol are necessary. Density, refractive index, and VLE measurements for ethanol + NMP binary systems have been presented in our previous work.[1] This work reports measurements of density and refractive index at 298.15 K, and isobaric vapor−liquid equilibria at 101.3 kPa for binary mixtures of methanol, *n*-propanol, *n*-butanol, or isobutanol with NMP. Excess molar volumes and refractive index deviations for these binary systems are calculated, and VLE data are correlated by the UNIQUAC method with temperature-dependent parameters.

Experimental Section

The chemicals methanol (99.8%), *n*-propanol (99.5%), *n*-butanol (99.8%), and isobutanol (99.5%) were obtained from Shanghai Chemical Corporation China. The purity of the materials was checked by gas chromatography (GC), and this analysis showed that the impurities did not exceed 0.2 mass %. These liquids were used without further purification. *N*-Methylpiperazine was a pharmaceutical quality product with a stated minimum purity of 99.8%. It was treated by the same procedure described previously[1] and dried with 0.4 nm freshly activated molecular sieves. The chemical purity of NMP was checked by GC analysis and was found to be higher than 99.9 mass %. The binary mixtures used for density and refractive index measurements were prepared by directly weighing the constituent components to give a precision within ±0.0001 g. Precautions were taken to minimize evaporation losses during storage and preparation of the mixtures. The comparison of measured physical properties (density, refractive index, and normal boiling point) with literature values[3,5,6] is shown in Table 1.

Densities of all the samples were measured by using 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 with an Abbe refractometer connected to a Haake F3-C liquid thermostatic bath. VLE data for the binary systems were measured by using an all-glass equilibrium still of the modified Rose type with circulation of both the liquid and vapor phases.[4] During the VLE measurements, the temperature was measured with an accuracy better than 0.01 K 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.

Results and Discussion

Refractive Index. Table 2 presents the measured refractive indices and the refractive index deviation values at 298.15 K for alkanol + NMP binary systems. The refractive index deviation from a mole fraction average δn_D

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

	t_b/°C		ρ/(g·cm^{-3})		n_D	
liquid	exptl	lit.[a]	exptl	lit.[a]	exptl	lit.[a]
methanol	64.54	64.546	0.786 48	0.796 37	1.3265	1.326 52
n-propanol	97.18	97.151	0.799 74	0.799 60	1.3836	1.383 70
n-butanol	117.67	117.725	0.806 14	0.805 75	1.3973	1.397 41
isobutanol	107.91	107.886	0.798 08	0.797 8	1.3939	1.393 89
NMP	136.81	135.9[c] 138[b]	0.903 78 (20 °C) 0.899 80 (25 °C) 0.894 54 (30 °C)	0.903 (20 °C)[b] 0.894 4 (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] Reference 5. [b] Reference 6. [c] Reference 3.

Table 2. Refractive Index n_D for Binary Mixtures of Alkanol (1) + *N*-Methylpiperazine (2) at 298.15 K with Refractive Index Deviation δn_D

x_1	n_D	δn_D	x_1	n_D	δn_D
Methanol (1) + NMP (2)			*n*-Propanol (1) + NMP (2)		
0.0545	1.4616	0.0057	0.0494	1.4614	0.0019
0.1137	1.4591	0.0113	0.1090	1.4590	0.0043
0.1494	1.4576	0.0146	0.1516	1.4568	0.0055
0.1974	1.4553	0.0189	0.2009	1.4546	0.0072
0.2576	1.4521	0.0240	0.2539	1.4519	0.0088
0.2965	1.4499	0.0271	0.2993	1.4495	0.0100
0.3461	1.4467	0.0306	0.3490	1.4466	0.0111
0.4040	1.4427	0.0346	0.3964	1.4438	0.0120
0.4513	1.4389	0.0372	0.4479	1.4404	0.0127
0.5193	1.4329	0.0406	0.4974	1.4370	0.0133
0.5603	1.4286	0.0419	0.5490	1.4332	0.0136
0.6233	1.4210	0.0429	0.6005	1.4295	0.0140
0.6592	1.4163	0.0431	0.6520	1.4250	0.0136
0.6996	1.4104	0.0427	0.7011	1.4207	0.0132
0.7669	1.3983	0.0399	0.7476	1.4162	0.0125
0.8036	1.3909	0.0375	0.8019	1.4099	0.0105
0.8507	1.3794	0.0325	0.8443	1.4052	0.0092
0.9023	1.3646	0.0247	0.9005	1.3984	0.0069
0.9357	1.3528	0.0175	0.9460	1.3920	0.0041
n-Butanol (1) + NMP (2)			Isobutanol (1) + NMP (2)		
0.0481	1.4611	0.0009	0.0491	1.4614	0.0011
0.1118	1.4583	0.0023	0.1034	1.4588	0.0023
0.1688	1.4555	0.0033	0.1494	1.4565	0.0032
0.2015	1.4540	0.0039	0.1986	1.4536	0.0038
0.2463	1.4518	0.0047	0.2481	1.4513	0.0049
0.3166	1.4481	0.0056	0.2980	1.4485	0.0056
0.3536	1.4460	0.0060	0.3377	1.4462	0.0061
0.4018	1.4433	0.0065	0.4016	1.4424	0.0067
0.4275	1.4419	0.0068	0.4929	1.4370	0.0077
0.4980	1.4376	0.0071	0.5467	1.4335	0.0080
0.5500	1.4343	0.0073	0.5931	1.4304	0.0081
0.6038	1.4310	0.0075	0.6451	1.4266	0.0079
0.6588	1.4274	0.0075	0.6987	1.4223	0.0074
0.6988	1.4243	0.0071	0.7470	1.4186	0.0070
0.7496	1.4204	0.0065	0.7991	1.4141	0.0062
0.7982	1.4164	0.0058	0.8355	1.4109	0.0055
0.8539	1.4117	0.0047	0.8934	1.4052	0.0039
0.8988	1.4075	0.0035	0.9490	1.3994	0.0019
0.9501	1.4025	0.0019			

is given by

$$\delta n_D = n_D - (x_1 n_{D1} + x_2 n_{D2}) \tag{1}$$

where n_D is the refractive index of the mixture and n_{D1} and n_{D2} are the refractive indices of components 1 and 2, respectively. The refractive index deviations at 298.15 K with variation of the mole fraction of alkanol for methanol + NMP, ethanol + NMP,[1] *n*-propanol + NMP, *n*-butanol + NMP, and isobutanol + NMP binary systems are simultaneouly illustrated in Figure 1. Positive deviations are exhibited for all these binary systems. It is found that the maximum deviations are at the mole fraction range from $x_1 = 0.6$ to 0.65 and that the positive deviation values increase with decreasing chain length of *n*-alkanols.

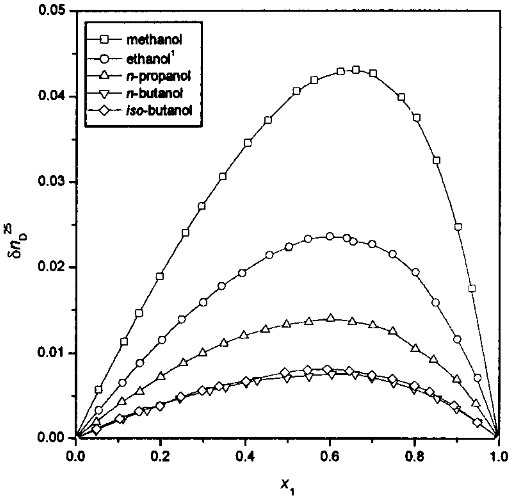

Figure 1. Refractive index deviation δn_D for binary mixtures of alkanol (1) + *N*-methylpiperazine (2) at 298.15 K.

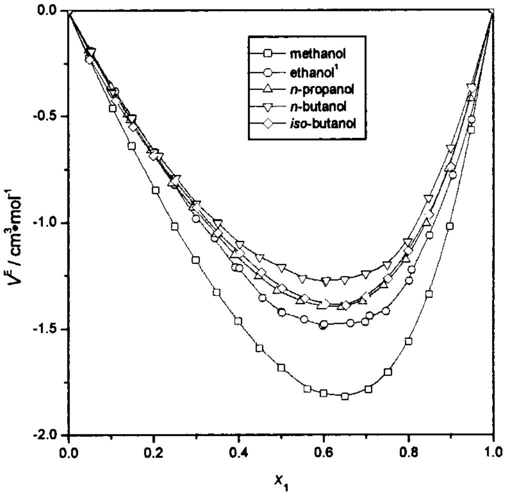

Figure 2. Excess molar volume V^E for binary mixtures of alkanol (1) + *N*-methylpiperazine (2) at 298.15 K.

Density and Volumetric Property. Table 3 lists the measured density ρ at 298.15 K with the corresponding excess molar volume V^E for the binary mixtures. The excess molar volume V^E is calculated from the density measurements by

$$V^E = V - (x_1 V_1 + x_2 V_2) \tag{2}$$

with

$$V = (x_1 M_1 + x_2 M_2)/\rho \tag{3}$$

where V is the molar volume of the mixture and x_i, V_i, and M_i (i = 1, 2) are the mole fraction, molar volume, and molecular weight of the components alkanol (1) and NMP

Table 3. Density ρ and Excess Molar Volume V^{E} for Binary Mixtures of Alkanol (1) + *N*-Methylpiperazine (2) at 298.15 K

x_1	ρ / $\mathrm{g \cdot cm^{-3}}$	V^{E} / $\mathrm{cm^3 \cdot mol^{-1}}$	x_1	ρ / $\mathrm{g \cdot cm^{-3}}$	V^{E} / $\mathrm{cm^3 \cdot mol^{-1}}$
Methanol (1) + NMP (2)			*n*-Propanol (1) + NMP (2)		
0.0498	0.899 54	−0.225	0.0483	0.898 02	−0.187
0.1050	0.899 14	−0.463	0.1012	0.895 74	−0.361
0.1491	0.898 68	−0.641	0.1395	0.894 07	−0.492
0.2052	0.897 88	−0.848	0.1465	0.893 78	−0.519
0.2503	0.897 23	−1.020	0.1950	0.891 38	−0.661
0.2996	0.896 17	−1.178	0.2439	0.888 98	−0.815
0.3488	0.894 96	−1.330	0.2936	0.886 06	−0.930
0.3989	0.893 39	−1.465	0.3473	0.882 79	−1.056
0.4492	0.891 59	−1.593	0.3914	0.879 95	−1.153
0.5006	0.889 11	−1.686	0.4476	0.875 98	−1.255
0.5618	0.885 69	−1.787	0.4913	0.872 65	−1.323
0.6001	0.882 75	−1.807	0.5452	0.868 03	−1.370
0.6497	0.878 42	−1.822	0.5934	0.863 55	−1.395
0.7052	0.872 25	−1.789	0.6424	0.858 59	−1.399
0.7521	0.865 54	−1.707	0.6922	0.853 04	−1.372
0.8001	0.856 87	−1.563	0.7420	0.846 78	−1.299
0.8490	0.845 58	−1.340	0.7941	0.839 47	−1.177
0.8978	0.831 09	−1.023	0.8425	0.831 79	−1.006
0.9490	0.811 44	−0.571	0.8954	0.822 30	−0.749
			0.9474	0.811 76	−0.419
n-Butanol (1) + NMP (2)			Isobutanol (1) + NMP (2)		
0.0537	0.897 16	−0.191	0.0503	0.897 38	−0.232
0.0558	0.897 01	−0.193	0.1122	0.893 59	−0.427
0.1033	0.894 85	−0.389	0.1519	0.891 10	−0.551
0.1505	0.892 04	−0.510	0.2000	0.887 91	−0.687
0.2026	0.889 10	−0.670	0.2514	0.884 21	−0.805
0.2135	0.888 34	−0.687	0.3016	0.880 60	−0.930
0.2544	0.885 79	−0.790	0.3512	0.876 93	−1.050
0.3008	0.882 89	−0.913	0.4030	0.872 78	−1.146
0.3504	0.879 34	−0.999	0.4534	0.868 61	−1.235
0.3517	0.879 27	−1.004	0.5021	0.864 42	−1.310
0.4034	0.875 56	−1.102	0.5555	0.859 43	−1.359
0.4501	0.871 93	−1.166	0.6048	0.854 57	−1.385
0.5022	0.867 57	−1.211	0.6520	0.849 67	−1.391
0.5504	0.863 56	−1.265	0.6998	0.844 20	−1.350
0.6051	0.858 51	−1.280	0.7515	0.837 84	−1.266
0.6066	0.858 32	−1.274	0.7995	0.831 36	−1.135
0.6497	0.854 12	−1.270	0.8492	0.824 25	−0.966
0.6996	0.848 97	−1.244	0.9001	0.816 39	−0.739
0.7501	0.843 52	−1.201	0.9520	0.807 06	−0.370
0.7982	0.837 64	−1.093			
0.8478	0.830 64	−0.889			
0.8999	0.822 99	−0.654			
0.9490	0.815 07	−0.365			

Table 4. Correlated Parameters A_i with Standard Deviations σ of Excess Molar Volumes V^{E} at 298.15 K for Alkanol (1) + *N*-Methylpiperazine (2) Binary Systems by the Redlich−Kister Equation

parameter	methanol	*n*-propanol	*n*-butanol	isobutanol
A_1	−6.746 31	−5.310 96	−4.849 51	−5.213 84
A_2	−3.626 94	−2.489 74	−2.090 2	−2.765 08
A_3	−2.221 56	−1.187 45	−2.021 59	−1.224 93
A_4	−0.410 17	0.024 31	−0.013 58	0.989 52
A_5	0.368 76	0.063 36	1.291 75	−0.469 69
$\sigma/\mathrm{cm^3 \cdot mol^{-1}}$	0.005	0.005	0.011	0.010

(2), respectively. Figure 2 gives the excess molar volumes at 298.15 K for these binary systems of alkanols with NMP. It shows that the excess molar volumes are negative over the whole composition range with minimum values at the mole fraction range from $x_1 = 0.6$ to 0.65 for all the binary systems, and that the negative values increase with decreasing chain length of *n*-alkanols. These phenomena can be attributed to the strong cross-association between the alkanol and NMP molecules through the hydrogen bond of O—H···N, in which the value of the interaction energy is −39.3 kJ·mol^{-1}, higher than those for O—H···O, −25.1 kJ·mol^{-1}, and N—H···N, −13.2 kJ·mol^{-1}.[7]

The isothermal excess volumes are correlated by a Redlich−Kister type equation

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

where the parameters A_i determined by fitting the equations to the experimental values with a least-squares algorithm are given in Table 4, along with the standard deviations σ, defined as follows

$$\sigma = \sqrt{\frac{\sum (V^{E}_{\mathrm{cal}} - V^{E}_{\mathrm{exp}})_i^2}{N - m}} \tag{5}$$

where N is the number of experimental data points and m is the number of equation parameters.

From the experimental density ρ and excess molar volume V^{E} values and eq 4, some important volumetric properties, apparent molar volume $\Phi_{V,i}$, excess partial molar volume $\bar{V}_i^{E}$, and partial molar volume $\bar{V}_i$ of component i can be calculated from the following thermodynamic relations

$$\Phi_{V,1} = \frac{M_1}{\rho} + \frac{x_2}{x_1}M_2\left(\frac{1}{\rho} - \frac{1}{\rho_2}\right) \tag{6}$$

$$\Phi_{V,2} = \frac{M_2}{\rho} + \frac{x_1}{x_2}M_1\left(\frac{1}{\rho} - \frac{1}{\rho_1}\right) \tag{7}$$

where $\Phi_{V,1}$ is the apparent molar volume of alkanol (1) in NMP (2) and $\Phi_{V,2}$ is the apparent molar volume of NMP (2) in alkanol (1).

$$\bar{V}_1^{E} = V^{E} + (1 - x_1)\left(\frac{\partial V^{E}}{\partial x_1}\right)_{T,p} \tag{8}$$

$$\bar{V}_2^{E} = V^{E} + (1 - x_2)\left(\frac{\partial V^{E}}{\partial x_2}\right)_{T,p} \tag{9}$$

$$\bar{V}_1 = \frac{M_1}{\rho_1} + V^{E} + (1 - x_1)\left(\frac{\partial V^{E}}{\partial x_1}\right)_{T,p} \tag{10}$$

$$\bar{V}_2 = \frac{M_2}{\rho_2} + V^{E} + (1 - x_2)\left(\frac{\partial V^{E}}{\partial x_2}\right)_{T,p} \tag{11}$$

Infinite dilution values, $\Phi^{\infty}_{V,i}$, $\bar{V}_i^{E,\infty}$, and $\bar{V}_i^{\infty}$, are estimated from the extrapolation of these volumetric properties against the compositions, which are listed in Table 5.

VLE Data. Vapor−liquid equilibrium data (T, x_1, y_1) together with calculated liquid-phase activity coefficients and vapor-phase fugacity coefficients at 101.3 kPa for alkanol + NMP binary systems are presented in Table 6. The y_1−x_1 and T−x_1−y_1 phase diagrams are illustrated in Figures 3 and 4, respectively. The experimental results show that these binary systems have no minimum or maximum boiling azeotropes.

The activity coefficients γ_i are calculated, taking into account the nonideality of the vapor phase, from the

Table 5. Infinite Dilution Volumetric Properties at 298.15 K for the Components of Alkanol (1) + *N*-Methylpiperazine (2) Binary Systems

	infinite dilution volumetric property/$\mathrm{cm^3 \cdot mol^{-1}}$			
alkanol (1)	$\bar{V}_1^{E,\infty}$	$\bar{V}_2^{E,\infty}$	$\bar{V}_1^{\infty}$, $\Phi^{\infty}_{V,1}$	$\bar{V}_1^{\infty}$, $\Phi^{\infty}_{V,2}$
methanol	−4.562	−12.636	36.179	98.678
ethanol	−3.948	−12.083	54.734	99.231
n-propanol	−3.970	−8.900	71.174	102.414
n-butanol	−3.476	−7.683	88.472	103.631
isobutanol	−5.133	−8.684	87.744	102.630

Table 6. Vapor−Liquid Equilibrium Data for Binary Systems of Alkanol (1) + *N*-Methylpiperazine (2) at 101.3 kPa

x_1	y_1	T/K	γ_1	γ_2	φ_1	φ_2	x_1	y_1	T/K	γ_1	γ_2	φ_1	φ_2
Methanol (1) + NMP (2)													
0.000	0.000	409.96		0.998	1.010	0.960	0.649	0.951	355.70	0.763	0.808	0.983	0.960
0.060	0.265	400.74	0.626	0.979	1.001	0.958	0.706	0.967	352.62	0.793	0.752	0.982	0.960
0.080	0.367	396.97	0.714	0.953	0.998	0.957	0.729	0.975	350.61	0.830	0.683	0.982	0.960
0.112	0.467	392.62	0.725	0.938	0.995	0.957	0.768	0.982	348.59	0.852	0.628	0.981	0.959
0.154	0.559	388.30	0.705	0.925	0.993	0.957	0.794	0.986	347.11	0.874	0.582	0.981	0.959
0.210	0.640	383.95	0.667	0.924	0.991	0.958	0.832	0.991	345.28	0.895	0.521	0.981	0.959
0.269	0.716	379.34	0.663	0.913	0.989	0.959	0.872	0.995	342.62	0.946	0.403	0.980	0.958
0.334	0.780	374.56	0.668	0.912	0.988	0.959	0.896	0.996	341.66	0.955	0.390	0.980	0.957
0.407	0.835	370.15	0.671	0.899	0.986	0.960	0.936	0.999	339.58	0.991	0.275	0.979	0.956
0.487	0.887	364.87	0.702	0.873	0.985	0.960	0.944	0.999	339.43	0.988	0.251	0.979	0.956
0.569	0.923	360.44	0.720	0.849	0.984	0.960	1.000	1.000	337.69	0.998		0.979	0.956
Ethanol (1) + NMP (2)													
0.000	0.000	409.96		0.998	0.995	0.967	0.550	0.876	371.88	0.766	0.834	0.980	0.961
0.062	0.195	404.19	0.591	0.985	0.991	0.966	0.591	0.894	370.13	0.771	0.839	0.980	0.961
0.097	0.303	400.49	0.641	0.975	0.990	0.965	0.617	0.909	368.55	0.791	0.818	0.979	0.960
0.136	0.392	397.30	0.647	0.967	0.988	0.964	0.641	0.922	366.98	0.815	0.793	0.979	0.960
0.175	0.468	394.38	0.647	0.961	0.987	0.964	0.681	0.935	365.11	0.830	0.796	0.978	0.959
0.208	0.533	391.57	0.674	0.950	0.986	0.964	0.709	0.946	363.76	0.847	0.756	0.978	0.959
0.245	0.590	388.92	0.683	0.946	0.985	0.963	0.741	0.963	361.95	0.879	0.640	0.977	0.959
0.275	0.630	386.96	0.688	0.943	0.984	0.963	0.773	0.972	360.35	0.900	0.580	0.977	0.958
0.311	0.685	384.33	0.715	0.916	0.984	0.963	0.818	0.982	358.23	0.928	0.505	0.976	0.957
0.356	0.732	381.98	0.717	0.898	0.983	0.963	0.851	0.989	356.38	0.962	0.409	0.976	0.957
0.391	0.763	379.97	0.724	0.897	0.982	0.962	0.886	0.993	354.88	0.981	0.351	0.976	0.956
0.429	0.790	378.12	0.723	0.900	0.982	0.962	0.920	0.996	353.52	0.998	0.291	0.975	0.955
0.462	0.821	376.40	0.737	0.864	0.981	0.962	0.948	0.999	352.47	1.010	0.141	0.975	0.955
0.492	0.845	374.78	0.752	0.835	0.981	0.962	1.000	1.000	351.47	0.997		0.974	0.954
0.524	0.869	373.07	0.767	0.801	0.980	0.961							
n-Propanol (1) + NMP (2)													
0.000	0.000	409.96		0.998	0.994	0.960	0.564	0.803	388.65	0.757	0.799	0.978	0.956
0.024	0.059	408.79	0.717	0.990	0.995	0.957	0.632	0.859	385.83	0.792	0.738	0.976	0.957
0.081	0.165	406.79	0.641	0.978	0.992	0.956	0.713	0.916	382.34	0.840	0.632	0.975	0.958
0.143	0.275	404.58	0.639	0.962	0.990	0.955	0.774	0.951	379.28	0.890	0.512	0.974	0.959
0.211	0.381	402.28	0.641	0.945	0.987	0.954	0.843	0.978	376.11	0.938	0.373	0.973	0.960
0.277	0.478	399.91	0.655	0.926	0.985	0.954	0.886	0.989	374.31	0.962	0.264	0.973	0.960
0.342	0.569	397.40	0.678	0.899	0.983	0.954	0.945	0.998	372.07	0.985	0.128	0.972	0.960
0.417	0.654	394.67	0.694	0.878	0.981	0.954	1.000	1.000	370.33	0.994		0.971	0.959
0.492	0.733	391.82	0.719	0.843	0.979	0.955							
n-Butanol (1) + NMP (2)													
0.000	0.000	409.96		0.998	0.985	0.960	0.735	0.873	399.33	0.896	0.630	0.971	0.965
0.075	0.087	409.67	0.638	0.993	0.983	0.960	0.770	0.890	398.73	0.890	0.636	0.971	0.965
0.138	0.154	409.49	0.624	0.990	0.981	0.960	0.780	0.906	397.78	0.922	0.582	0.970	0.965
0.159	0.184	409.27	0.651	0.984	0.981	0.960	0.810	0.920	397.30	0.915	0.586	0.970	0.966
0.277	0.326	408.51	0.672	0.964	0.978	0.961	0.834	0.944	395.92	0.955	0.483	0.970	0.966
0.343	0.415	407.79	0.705	0.938	0.977	0.961	0.843	0.940	396.10	0.935	0.545	0.970	0.966
0.433	0.518	406.67	0.720	0.921	0.975	0.962	0.874	0.966	394.34	0.982	0.408	0.969	0.966
0.508	0.626	405.19	0.776	0.855	0.974	0.963	0.902	0.973	394.07	0.967	0.423	0.969	0.966
0.572	0.703	403.84	0.805	0.810	0.973	0.964	0.911	0.980	393.10	0.996	0.348	0.969	0.966
0.632	0.770	402.44	0.834	0.755	0.972	0.964	0.940	0.990	392.08	1.009	0.275	0.968	0.965
0.684	0.824	400.90	0.866	0.699	0.972	0.965	1.000	1.000	390.82	1.001		0.968	0.965
0.728	0.855	400.07	0.867	0.684	0.971	0.965							
Isobutanol (1) + NMP (2)													
0.000	0.000	409.96		0.998	0.987	0.960	0.632	0.803	395.95	0.776	0.766	0.973	0.963
0.059	0.082	409.30	0.575	0.989	0.985	0.960	0.635	0.818	395.39	0.800	0.726	0.972	0.963
0.130	0.171	408.35	0.556	0.989	0.983	0.960	0.687	0.858	393.74	0.818	0.693	0.972	0.963
0.192	0.259	407.36	0.590	0.974	0.981	0.960	0.695	0.873	392.90	0.845	0.648	0.971	0.963
0.265	0.356	406.16	0.607	0.958	0.980	0.960	0.745	0.905	391.02	0.869	0.615	0.971	0.963
0.334	0.446	404.70	0.627	0.945	0.978	0.960	0.787	0.936	388.88	0.913	0.525	0.970	0.963
0.391	0.534	403.18	0.670	0.904	0.977	0.961	0.818	0.950	387.75	0.925	0.498	0.970	0.963
0.449	0.606	401.68	0.692	0.878	0.976	0.961	0.836	0.962	386.80	0.946	0.431	0.969	0.963
0.510	0.677	400.07	0.715	0.844	0.975	0.962	0.889	0.980	384.98	0.964	0.358	0.969	0.963
0.554	0.734	398.36	0.751	0.800	0.974	0.962	0.948	0.993	382.64	0.993	0.278	0.968	0.962
0.584	0.768	397.30	0.769	0.772	0.973	0.962	1.000	1.000	381.06	1.001		0.967	0.962

following equations:

$$\gamma_i = \frac{y_i P}{x_i P_i^{\mathrm{S}}} \exp\left[\frac{(B_{ii} - V_i^{\mathrm{L}})(P - P_i^{\mathrm{S}}) + (1 - y_i)^2 P \delta_{ij}}{RT}\right] \qquad (12)$$

$$\ln \varphi_i = \frac{P}{RT}[B_{ii} + (1 - y_i)^2 \delta_{ij}] \qquad (13)$$

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \qquad (14)$$

where P is the total pressure, P_i^{S} are the vapor pressures of the pure components, 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,[8] B_{ii} are the second virial coefficients of the pure gases, B_{ij} are the cross second virial coefficients, and φ_i is the vapor-phase fugacity coefficient of component i in the mixture, which was calculated from the explicit virial equation of state truncated after the second term. The molar virial coefficients B_{ii} and B_{ij} are estimated from the generalized correlation of Hayden and O'Connell. [9] The critical properties, P_{C}, T_{C}, V_{C}, and Z_{C}, acentric factor ω, and vapor pressures P_i^{S} of NMP and alkanols are taken from the literature.[3,10] The

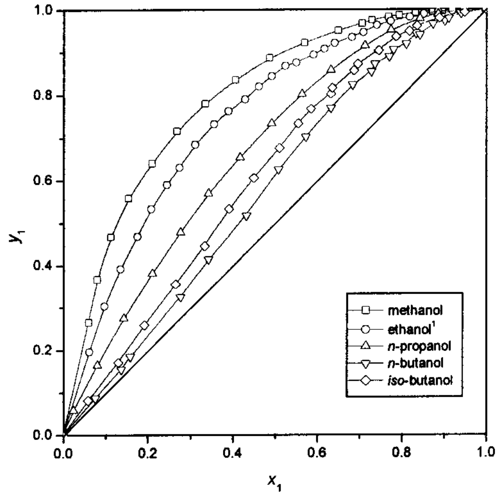

Figure 3. y_1−x_1 phase diagram for binary mixtures of alkanol (1) + *N*-methylpiperazine (2) at 101.3 kPa.

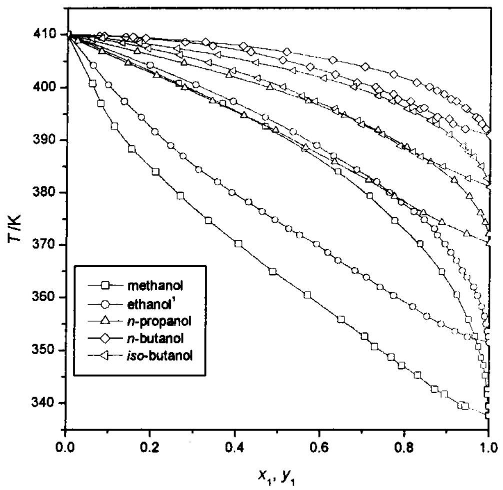

Figure 4. T−y_1−x_1 phase diagram for binary mixtures of alkanol (1) + *N*-methylpiperazine (2) at 101.3 kPa.

Antoine equation for NMP is $\ln P_i^S = A - B/(T + C)$ with $A = 9.833\,79$, $B = 1108.546$, and $C = -197.3339$.

The thermodynamic consistency of the experimental results was checked using the Herington area test[11] and the Fredenslund point-to-point test.[12] For the Fredenslund's method, a five-parameter Legendre polynomial was used for the excess Gibbs free energy. The average values for $\Delta y = y_{\mathrm{cal}} - y_{\mathrm{exp}}$ absolute (mole fraction) for the systems studied were Δy(methanol + NMP) = 0.0064, Δy(*n*-propanol + NMP) = 0.0035, Δy(*n*-butanol + NMP) = 0.0048, and Δy(isobutanol + NMP) = 0.0059. For Herington's method, the values of the deviation $D - J$ described in ref 11 were − 24.7, 4.8, −1.3, and −8.0, respectively, for these binary systems, which were less than 10. According to both empirical methods, the experimental data are thermodynamically consistent.

The VLE data are correlated with the UNIQUAC liquid-phase activity coefficient model with temperature-dependent parameters. The parameters of the UNIQUAC equation as a function of temperature are given by the following equation[13]

$$\alpha_{ij} = a_{ij}^{(0)} + a_{ij}^{(1)}T/T_0 + a_{ij}^{(0)}(T/T_0)^2 \qquad (15)$$

where T_0 is an arbitrarily chosen reference temperature, in this case T_0 = 315 K. The binary parameters are obtained by a nonlinear optimization method to minimize

Table 7. Temperature-Dependent Parameters of the UNIQUAC Equation for Binary Systems of Alkanol (1) + *N*-Methylpiperazine (2) at 101.3 kPa and Deviations for Vapor Composition, Temperature, and Pressure

		methanol	*n*-propanol	*n*-butanol	isobutanol
α_{12}	$a_{12}^{(0)}$	48.024	69.632	233.529	155.697
	$a_{12}^{(1)}$	75.236	103.481	127.938	79.462
	$a_{12}^{(2)}$	34.726	20.908	41.929	23.743
α_{21}	$a_{21}^{(0)}$	−502.543	−455.040	−460.000	−436.761
	$a_{21}^{(1)}$	30.724	3.245	−14.232	−14.117
	$a_{21}^{(2)}$	59.148	32.180	25.509	23.809
Δy_1		0.0069	0.0041	0.0067	0.0080
ΔT/K		0.38	0.39	0.52	0.44
$\Delta P/P \times 100\%$		1.30	1.14	1.54	1.34

the following objective function

$$F = \frac{1}{N}\sum_{i=1}^{N}\left[(y_{\mathrm{cal}} - y_{\mathrm{exp}})^2 + (T_{\mathrm{cal}} - T_{\mathrm{exp}})^2 + \left(\frac{P_{\mathrm{cal}} - P_{\mathrm{exp}}}{P_{\mathrm{exp}}}\right)^2\right]_i \qquad (16)$$

where N is the number of experimental data points. The values of the temperature-dependent parameters and comparison of calculated VLE results from the UNIQUAC equation with experimental data are presented in Table 7. It shows that the average values of ΔT are smaller than 0.52 K and those of $\Delta P/P$ are smaller than 1.54%. The predicted vapor-phase composition deviations from the experimental values Δy are less than 0.008 absolute mole fraction. These, to a certain degree, further verify the thermodynamic consistency of the experimental results, and it follows that the UNIQUAC equation correlates the VLE data with reasonably satisfactory results.

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