

Vapor–Liquid Equilibria for *N*-Methyl-2-pyrrolidone + Benzene, +Toluene, +Heptane, and +Methylcyclohexane

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The total pressure and vapor and liquid compositions have been measured for *N*-methyl-2-pyrrolidone + benzene at 330.00 K and 350.00 K, for *N*-methyl-2-pyrrolidone + toluene at 343.15 K and 373.15 K, for *N*-methyl-2-pyrrolidone + heptane at 340.00 K and 365.00 K, and for *N*-methyl-2-pyrrolidone + methylcyclohexane at 340.00 K and 370.00 K. Measurements were made by either a recirculating still or a transpiration method, the method depending on the total pressure of the mixture. The results were correlated using the Redlich–Kister equation, the Wilson equation, and the NRTL equation, with allowance for vapor nonideality.

Introduction

This work constitutes a contribution to Project 805, Experimental Data on Mixtures, of the Design Institute for Physical Property Data (DIPPR) of the American Institute of Chemical Engineers. The aim of this project is to sponsor solubility, vapor–liquid equilibrium, and infinite dilution activity coefficient measurements on mixtures of industrial importance. Measurements on the system *N*-methyl-2-pyrrolidone + benzene have been reported by Zaretskii et al. (1971) and Gupta et al. (1989) at 101 kPa, by Aim (1978) at 287 K and 283 K, by Fabries et al. (1977) at 293 K and 363 K, by Gierycz et al. (1985) at 333 K, and 354 K and by Dojcansky et al. (1980) at 343 K. Measurements on *N*-methyl-2-pyrrolidone + toluene have been reported by Zaretskii et al. (1974) at 101 kPa, by Gupta and Rawat (1992) at 101 kPa, and by Gierycz et al. (1985) at 363 K and 383 K. Measurements on *N*-methyl-2-pyrrolidone + heptane have been reported by Gaube et al. (1987) at 298 K and Fabries et al. (1977) at 293 K and 371 K, while results for *N*-methyl-2-pyrrolidone + methylcyclohexane have been reported by Gierycz et al. (1985) at 354 K and 373 K. Additionally, Ferreira et al. (1987) reported limiting activity coefficients at (310, 318, and 328) K for the first three mixtures.

Experimental Section

Materials. *N*-Methyl-2-pyrrolidone, purum, better than 99 mass % (Fluka, Switzerland), was distilled under vacuum and stored over molecular sieves 4A and kept in a refrigerator. *N*-Methyl-2-pyrrolidone is very hygroscopic. Benzene, special purity for cryoscopy (better than 99.97 mass %), measured melting point (278.673 ± 0.005) K (Urx Chemical Works, Czechoslovakia), was not further purified. Toluene, puriss p.a., better than 99.5 mass %, containing less than 0.05 mass % of water (Fluka, Switzerland), was not further purified but was stored above molecular sieves 4A to reduce the water content. Heptane, puriss p.a., better than 99.5 mass %, containing less than 0.05 mass % of water (Fluka, Switzerland), was rectified on a 30-plate column packed with glass helices. The distillate was stored above molecular sieves 4A to reduce the water content. Methylcyclohexane, purum, better than 98.5 mass % (BDH, England), was purified as described for heptane.

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Table 1. Density ρ and Refractive Index n^D of the Pure Compounds

compound	property	this work	lit.	ref
benzene	$\rho(298.15\text{ K})/$ $\text{g}\cdot\text{cm}^{-3}$	0.87374	0.87370	Dreisbach (1955)
	$n^D(293.15\text{ K})$	1.501 10	1.501 12	Dreisbach (1955)
toluene	$\rho(298.15\text{ K})/$ $\text{g}\cdot\text{cm}^{-3}$	0.862 28	0.862 30	Dreisbach (1955)
	$n^D(293.15\text{ K})$	1.496 82	1.496 93	Dreisbach (1955)
heptane	$\rho(298.15\text{ K})/$ $\text{g}\cdot\text{cm}^{-3}$	0.679 53	0.679 51	Dreisbach (1959)
	$n^D(293.15\text{ K})$	1.387 6	1.387 64	Dreisbach (1959)
methylcyclohexane	$\rho(298.15\text{ K})/$ $\text{g}\cdot\text{cm}^{-3}$	0.765 09	0.765 06	Dreisbach (1955)
	$n^D(303.15\text{ K})$	1.418 0	1.418 03	Dreisbach (1955)
<i>N</i> -methyl-2-pyrrolidone	$\rho(298.15\text{ K})/$ $\text{g}\cdot\text{cm}^{-3}$	1.031 38	1.028 90	Aim (1978)
	$n^D(293.15\text{ K})$	1.470 51	1.470 65	Aim (1978)
	$n^D(303.15\text{ K})$	1.466 5		Aim (1978)

The density and refractive index, used as a criteria of purity, were measured for all compounds, and the values are summarized in Table 1, together with literature values. Density was measured both by classical pycnometry and by a DMA 60+602 vibrating tube densimeter (Paar, Austria). The differences between the two methods were in the fifth digit; therefore, the average values were used as the final ones. The thermostat was controlled to ±0.01 K. The accuracy of density determination is estimated to be better than ±2 × 10⁻⁵ g·cm⁻³. The refractive index was measured using two Abbe-type refractometers (Carl Zeiss, Jena) with either ±0.0001 (a fixed prism) or ±0.000 01 (interchangeable prisms) resolution.

Equipment. Vapor–liquid equilibria were measured by two methods, depending on the total pressure of the mixture. The circulation method was exploited at pressures higher than approximately 10 kPa where smooth boiling could be achieved; at lower pressures the transpiration (saturation) method was used.

Two recirculation stills were employed. The total volume of the liquid mixture was about 100 cm³ for systems

Table 2. Vapor Pressure of *N*-Methyl-2-pyrrolidone^a

<i>T</i> /K	<i>p</i> /kPa	{ <i>T</i> - <i>T</i> (calc)}/K	{ <i>p</i> - <i>p</i> (calc)}/kPa
330.00	0.373	0.03	-0.000
340.00	0.688	-0.36	0.011
343.09	0.753	0.42	-0.014
343.15	0.756	0.43	-0.015
343.15	0.807	-0.23	0.009
343.15	0.809	-0.26	0.010
350.00	1.138	-0.03	0.002
370.00	3.012	0.03	-0.004
373.15	3.454	0.10	-0.019
372.92	3.653	-0.11	0.023
mean		0.20	0.011

^a (calc) denotes the value calculated from the Antoine equation $\log_{10}(p/\text{kPa}) = 7.37470 - 2372.949/(T/K - 25.829)$.

containing toluene or heptane and about 170 cm³ for systems containing benzene or methylcyclohexane. In the larger still, the boiling point was measured using a quartz thermometer with the accuracy of ± 0.01 K. In the other one (with a smaller thermometer well), the temperature was measured with a mercury thermometer which was calibrated using the temperature calculated from the measured vapor pressure of the more volatile component determined from the Antoine equation with coefficients given in Table 6. With this calibration method, all corrections (thermometer calibration, emergent stem correction, etc.) were advantageously eliminated since, for one particular isotherm, the temperature was kept at the same value. Accuracy of the temperature determination was ± 0.05 K. The pressure was measured indirectly using the boiling point of water in an ebullimeter connected in parallel to the equilibrium still. The temperature in the ebullimeter was determined by a quartz thermometer with an accuracy better than ± 0.01 K on ITS-90. The details of the equilibrium still have been described previously by Dvorak and Boublik (1963).

At lower pressures, the saturation method was used to measure the partial pressure by passing a known amount of inert gas through a solution of known composition and subsequently determining the mass of vapor phase condensate collected in a cold trap. The method used was a modification of that described by Linek and Hala (1967).

The flow of carrier gas (nitrogen) was maintained constant by means of a needle valve and a simple manostat. The water vapor and other gaseous impurities are removed from the gas by absorbers containing molecular sieves 4A and glass-wool (to capture any mechanical particles). The volume buffer (approximately 100 cm³) with a glass capillary inlet was inserted into the line to smooth any flow disturbances. The all-glass saturator was designed so as to provide intimate contact between both phases. Bubbles formed in the jet (located at the bottom) flowed through a helical path of length exceeding 1 m. The volume of the liquid placed in the saturator was 4 cm³. On the top of the saturator there was a glass tubing which served for recharging the liquid. Immediately after the saturator was filled, the glass tubing was sealed with a burner. Each saturator in the battery of five or six had no opening or seals since they must be entirely immersed in the thermostat bath. The last saturator contains only glass packing (cut tubes); it served as a drop trap.

The portion of the line which was out of the bath, including the female ground joint at the end, was heated by a resistance element to prevent condensation of the less volatile component prior to its entering a cold trap placed in a mixture of dry ice and ethyl alcohol. The conical bulb at the bottom of the U-shaped trap made possible the collection of a small amount of sample. The pressure

Table 3. Refractive Index for Mixtures Containing *N*-Methyl-2-pyrrolidone^a

<i>x</i> _A	<i>n</i> ^D	10 ⁴ { <i>x</i> _A - <i>x</i> _A (calc)}	10 ⁴ { <i>n</i> ^D - <i>n</i> ^D (calc)}
Benzene (A) + <i>N</i> -Methyl-2-pyrrolidone (B) at <i>T</i> = 293.15 K			
0.0	1.4705		
0.2158	1.4788	-1	-0
0.2780	1.4811	-0	0
0.3789	1.4846	-1	0
0.4656	1.4874	5	-1
0.5212	1.4894	-2	1
0.6119	1.4922	0	-0
0.6958	1.4946	-1	0
0.7761	1.4967	-1	0
0.8415	1.4982	-0	0
0.9146	1.4996	2	-1
1.0	1.5011		
mean		1	0

$$A_1 = 0.016\ 863\ 8, A_2 = 0.009\ 350\ 29, A_3 = -0.006\ 725\ 36$$

Toluene (A) + *N*-Methyl-2-pyrrolidone (B) at *T* = 293.15 K

0.0	1.4705		
0.1110	1.4751	-2	1
0.1977	1.4783	-1	0
0.2955	1.4816	4	-1
0.3855	1.4846	-1	0
0.4759	1.4873	-0	0
0.5670	1.4896	0	-0
0.6686	1.4920	-1	0
0.7689	1.4939	-0	0
0.8858	1.4956	1	-1
1.0	1.4968		
mean		1	0

$$A_1 = 0.018\ 170\ 7, A_2 = 0.015\ 438\ 7, A_3 = 0.000\ 819\ 705$$

Methylcyclohexane (A) + *N*-Methyl-2-pyrrolidone (B) at *T* = 303.15 K

0.0	1.4665		
0.1357	1.4610	12	3
0.2406	1.4556	-4	-1
0.3189	1.4515	-10	-2
0.3825	1.4483	-5	-1
0.4838	1.4431	2	0
0.5683	1.4390	19	3
0.7028	1.4313	-9	-2
0.7859	1.4275	5	1
0.8444	1.4242	-15	-3
0.9237	1.4214	12	3
1.0	1.4180		
mean		9	2

$$A_1 = 0.010\ 563\ 2, A_2 = 0.009\ 051\ 114, A_3 = 0.002\ 138\ 53$$

^a (calc) denotes the value calculated from eq 1 with parameters given in this table.

difference between the outlet and atmospheric pressure was measured by a tempered mercury U-manometer.

The absolute amount of inert gas was measured by means of a eudiometer described and designed by Erdos and Bares (1964). The volume of the graduated flask was maintained at constant temperature using a water thermostat; the volume was calibrated from the known mass of water required to fill the flask. The flasks, with nominal volumes of (0.1, 0.4, and 1.0) L, were used alternatively as required.

Procedure. The procedure for determining the vapor-liquid equilibrium using the recirculation still is described by Polednova and Wichterle (1984). Generally, the recirculation method can only be used if both liquid and vapor phase samples are homogeneous at the temperature of the cooled condensate receiver. Some problems appear for the mixtures containing heptane and methylcyclohexane, which are only partially miscible with *N*-methyl-2-pyrrolidone. Preferably, the cooling water for the still must not be cooled with running water but should be cooled with a fluid in a closed thermostated circuit at the "maximum possible" temperature. In this way complete mutual solubility of the

Table 4. Vapor-Liquid Equilibrium for Mixtures Containing *N*-Methyl-2-pyrrolidone^a

x_A	y_A	P/kPa	δx_A	δy_A	$\delta P/\text{kPa}$	$\delta T/\text{K}$	x_A	y_A	P/kPa	δx_A	δy_A	$\delta P/\text{kPa}$	$\delta T/\text{K}$
Benzene (A) + <i>N</i> -Methyl-2-pyrrolidone (B)													
$T = 330.00\text{ K}$													
0.0	0.0	0.37					0.6265	0.9900	31.48	-0.0024	-0.0054	0.00	-0.01
0.0378	0.8043	2.20	-0.0013	-0.0333	0.00	-0.03	0.6830	0.9890	33.70	0.0015	-0.0072	-0.00	0.00
0.0455	0.8420	2.55	-0.0009	-0.0188	0.00	-0.02	0.7190	0.9870	35.06	0.0041	-0.0097	-0.01	0.01
0.0615	0.8709	3.21	0.0014	-0.0201	0.00	-0.01	0.7260	0.9915	35.48	0.0012	-0.0053	-0.00	0.00
0.0654	0.8804	3.43	0.0007	-0.0182	0.00	-0.01	0.9135	0.9970	43.08	-0.0037	-0.0020	0.01	-0.01
0.1792	0.9605	9.02	0.0025	-0.0056	-0.00	0.00	0.9520	0.9940	44.63	-0.0027	-0.0054	-0.01	-0.01
0.2925	0.9778	14.80	0.0043	-0.0043	-0.00	0.00	0.9850	0.9990	45.86	0.0013	-0.0008	-0.00	0.01
0.5407	0.9870	27.64	-0.0034	-0.0068	0.00	-0.01	1.0	1.0	46.63 ^b				
0.5807	0.9890	29.44	-0.0025	-0.0056	0.00	-0.01							
$T = 350.00\text{ K}$													
0.0	0.0	1.14					0.6020	0.9880	59.65	-0.0059	-0.0042	0.01	-0.01
0.0378	0.7335	4.56	0.0001	-0.0241	0.00	-0.03	0.6370	0.9885	62.99	-0.0071	-0.0048	0.02	-0.02
0.0455	0.7680	5.31	-0.0005	-0.0259	0.00	-0.03	0.6870	0.9890	66.98	-0.0024	-0.0054	0.01	-0.01
0.0615	0.8248	6.94	-0.0023	-0.0204	0.00	-0.02	0.7945	0.9940	75.33	0.0039	-0.0024	-0.02	0.01
0.0623	0.8248	6.72	-0.0019	-0.0057	0.00	-0.01	0.8655	0.9960	80.66	0.0049	-0.0016	-0.03	0.02
0.0623	0.8405	6.98	0.0009	-0.0149	0.00	-0.01	0.9085	0.9975	84.53	-0.0030	-0.0009	0.02	-0.01
0.0654	0.8303	7.09	0.0000	-0.0183	0.00	-0.02	0.9540	0.9999	87.59	0.0010	0.0008	-0.01	0.00
0.1792	0.9381	16.39	-0.0146	-0.0033	-0.00	0.01	0.9825	0.9999	90.19	-0.0017	0.0002	0.01	-0.01
0.2925	0.9647	28.25	0.0059	-0.0062	-0.00	0.00	1.0	1.0	91.57 ^b				
0.4284	0.9830	42.26	0.0004	-0.0013	-0.00	0.00							
Toluene (A) + <i>N</i> -Methyl-2-pyrrolidone (B)													
$T = 343.15\text{ K}$													
0.0	0.0	0.81					0.1565	0.8453	6.34	-0.0027	-0.0486	0.01	0.00
0.0204	0.3903	1.40	0.0055	-0.0319	0.05	-0.01	0.3088	0.9191	10.85	0.0002	-0.0287	0.00	-0.00
0.0303	0.4235	1.69	0.0090	-0.0883	0.09	-0.03	0.3714	0.9398	12.54	0.0017	-0.0185	-0.00	0.00
0.0365	0.5236	2.01	0.0053	-0.0832	0.06	-0.02	0.4317	0.9521	14.17	0.0009	-0.0140	-0.00	0.00
0.0459	0.5782	2.50	0.0010	-0.1125	0.05	-0.02	0.5051	0.9574	16.06	-0.0006	-0.0159	0.00	-0.00
0.0459	0.5774	2.45	0.0026	-0.1054	0.05	-0.02	0.5778	0.9685	17.84	-0.0015	-0.0104	0.00	-0.00
0.0644	0.6554	3.08	0.0026	-0.1005	0.03	-0.01	0.7341	0.9810	21.32	-0.0007	-0.0066	0.00	-0.00
0.0651	0.6665	3.10	0.0027	-0.0912	0.03	-0.01	0.8378	0.9892	23.45	0.0020	-0.0030	-0.00	0.00
0.0929	0.7609	3.96	0.0052	-0.0557	0.00	-0.00	1.0	1.0	27.16 ^b				
$T = 373.15\text{ K}$													
0.0	0.0	3.45					0.2330	0.8791	24.40	-0.0090	-0.0099	0.01	-0.01
0.0204	0.3118	5.45	-0.0008	-0.0457	0.04	-0.14	0.3272	0.9085	31.84	-0.0065	-0.0159	0.02	-0.01
0.0303	0.3675	5.87	0.0042	-0.0405	0.04	-0.11	0.5313	0.9489	46.10	0.0012	-0.0123	0.01	-0.00
0.0365	0.3494	5.73	0.0120	-0.0423	0.04	-0.12	0.5990	0.9510	50.49	0.0008	-0.0177	0.02	-0.01
0.0459	0.4664	6.87	0.0082	-0.0350	0.03	-0.08	0.6774	0.9685	55.28	-0.0006	-0.0073	0.01	-0.00
0.0651	0.5524	8.14	0.0128	-0.0338	0.03	-0.07	0.7559	0.9816	59.49	0.0035	0.0001	-0.01	0.00
0.1024	0.7028	12.30	0.0025	-0.0370	0.03	-0.05	0.8474	0.9866	64.93	-0.0019	-0.0017	0.01	-0.00
0.1320	0.7917	15.30	-0.0029	-0.0076	0.00	-0.01	1.0	1.0	74.17 ^b				
0.1773	0.8453	19.61	-0.0078	-0.0069	0.01	-0.01							
Heptane (A) + <i>N</i> -Methyl-2-pyrrolidone (B)													
$T = 340.00\text{ K}$													
0.0	0.0	0.66 ^b					0.1751	0.9804	29.52	-0.0142	0.0010	0.02	-0.03
0.0145	0.9104	5.43	0.0010	0.0314	-0.00	0.02	0.1751	0.9793	29.53	-0.0143	-0.0001	0.02	-0.03
0.0145	0.8928	5.49	0.0009	0.0127	-0.00	0.01	0.2299	0.9847	31.33	-0.0134	0.0038	0.03	-0.06
0.0535	0.9669	15.50	0.0012	0.0084	-0.00	0.00	0.3047	0.9815	32.27	0.0018	-0.0002	-0.01	0.02
0.0757	0.9714	19.48	0.0011	0.0040	-0.00	0.00	0.3848	0.9821	32.66	0.0069	-0.0002	-0.10	0.15
0.0916	0.9734	21.61	0.0021	0.0026	-0.00	0.00	0.5108	0.9828	33.09	0.0000	0.0003	-0.03	0.06
0.0916	0.9736	22.07	-0.0014	0.0021	0.00	0.00	0.8388	0.9869	34.71	-0.0368	0.0022	0.26	-0.43
0.1215	0.9764	25.74	0.0068	0.0005	-0.00	-0.01	0.9855	0.9966	35.88	-0.0030	-0.0005	0.01	-0.02
0.1215	0.9774	26.04	-0.0104	0.0012	0.01	-0.01	0.9866	0.9958	35.88	-0.0021	-0.0013	0.01	-0.01
0.1496	0.9786	28.04	-0.0158	0.0028	0.01	-0.02	1.0	1.0	36.15 ^b				
0.1496	0.9812	28.33	-0.0110	0.0004	0.01	-0.02							
$T = 365.00\text{ K}$													
0.0	0.0	2.44 ^b					0.3994	0.9739	72.02	0.0010	0.0026	-0.01	-0.01
0.0229	0.8928	15.56	0.0011	0.0457	-0.01	0.06	0.7356	0.9733	76.90	0.0020	-0.0019	-0.08	0.05
0.0426	0.9297	25.33	0.0007	0.0228	-0.01	0.02	0.8696	0.9831	79.53	-0.0118	0.0044	0.20	-0.13
0.0721	0.9448	37.26	-0.0020	0.0071	-0.00	-0.00	0.9862	0.9962	82.65	-0.0019	0.0009	0.01	-0.01
0.0736	0.9410	38.36	-0.0040	0.0014	0.00	-0.00	1.0	1.0	83.19 ^b				
0.1694	0.9667	58.24	-0.0086	0.0048	0.01	-0.01							
Methylcyclohexane (A) + <i>N</i> -Methyl-2-pyrrolidone (B)													
$T = 340.00\text{ K}$													
0.0	0.0	0.69					0.5055	0.9793	29.87	0.0040	-0.0028	-0.02	0.04
0.0796	0.9642	15.14	0.0019	0.0058	-0.00	0.00	0.6165	0.9818	30.78	0.0015	-0.0014	-0.01	0.02
0.1247	0.9717	19.83	-0.0025	0.0026	0.00	-0.00	0.7388	0.9818	31.58	-0.0018	-0.0026	0.02	-0.04
0.1891	0.9742	22.77	0.0133	0.0005	-0.01	0.01	0.8400	0.9895	32.25	-0.0033	0.0035	0.02	-0.04
0.2405	0.9742	26.18	-0.0242	-0.0035	0.04	-0.07	0.9207	0.9895	33.20	-0.0060	-0.0001	0.03	-0.05
0.3717	0.9793	28.19	0.0055	-0.0009	-0.02	0.03	1.0	1.0	34.63 ^b				
$T = 370.00\text{ K}$													
0.0	0.0	3.01					0.2706	0.9617	64.80	-0.0088	0.0014	0.02	-0.02
0.0076	0.6817	6.77	-0.0010	0.1231	-0.02	0.25	0.4737	0.9742	75.51	0.0101	0.0054	-0.10	0.06
0.0200	0.8187	11.42	0.0002	0.0807	-0.02	0.10	0.6355	0.9818	79.94	-0.0003	0.0095	0.00	-0.00
0.0371	0.8998	18.22	-0.0006	0.0625	-0.01	0.05	0.7731	0.9818	81.74	0.0015	0.0070	-0.04	0.02
0.0773	0.9421	28.32	0.0086	0.0447	-0.01	0.02	0.8357	0.9844	84.10	-0.0105	0.0070	0.17	-0.09
0.1180	0.9494	41.76	-0.0033	0.0167	-0.00	0.00	0.9207	0.9870	86.64	-0.0077	0.0028	0.08	-0.04
0.1637	0.9567	50.97	-0.0058	0.0102	0.00	-0.00	1.0	1.0	90.17 ^b				
0.1995	0.9592	57.68	-0.0152	0.0053	0.02	-0.02							

^a δ = experimental - calculated (NRTL). ^b Calculated from the Antoine equation.

Table 5. Virial Coefficients B and Molar Volumes V of Pure Compounds and Mixtures

system	$X/\text{cm}^3\cdot\text{mol}^{-1}$	T/K						
		330.00	340.00	343.15	350.00	365.00	370.00	373.15
benzene	B	-1135.9			-975.0			
	V	93.2			95.4			
toluene	B			-1600.4				-1269.0
	V			112.3				116.2
heptane	B		-1957.0			-1593.0		
	V		155.4			160.5		
methylcyclohexane	B		-1709.4				-1357.8	
	V		134.8				139.7	
N-methyl-2-pyrrolidone	B	-4748.9	-4249.8	-4108.2	-3822.6	-3289.0	-3134.8	-3042.9
	V	98.5	99.4	99.6	100.2	101.6	102.0	102.3
benzene + N-methyl-2-pyrrolidone	B_{AB}	-1643.0			-1388.7			
toluene + N-methyl-2-pyrrolidone	B_{AB}			-1570.9				-1250.2
heptane + N-methyl-2-pyrrolidone	B_{AB}		-2138.3			-1731.2		
methylcyclohexane + N-methyl-2-pyrrolidone	B_{AB}		-1979.3				-1551.4	

sample was ensured. The equilibrium samples were taken for analysis only when the boiling temperature in the still and the ebulliometer did not change for at least 20 min, indicating a steady state condition.

The procedure for making measurements with the saturation method consisted of the following: (1) The liquid mixture was prepared by mass from the pure components. The mixture was then added carefully into the individual saturators and sealed with a burner. (2) The flow rate of the carrier gas was adjusted and the battery of saturators was slowly immersed in a (hot) thermostated bath. This step was necessary to avoid shock pressure changes inside the battery due to thermal expansion of the gas phase. The outlet tubing was preheated. (3) After sufficient time of thermostating, the trap was attached and immediately immersed into the freezing bath. The entire line to the eudiometer was opened, and the flow rate through the battery was maintained at about $2.0 \text{ L}\cdot\text{h}^{-1}$. (4) When the whole graduated vessel of the eudiometer was full of carrier gas, the line was closed and the trap was disconnected and closed with ground stoppers. The mass of condensed sample was measured as an increment to the empty trap. (5) The composition of the vapor phase was determined on the assumption of ideal behavior of the gas mixture leaving the last saturator. The accuracy of the determination was dependent on the system and was believed to be between $\pm 0.1\%$ and $\pm 1\%$.

Results

N-Methyl-2-pyrrolidone. The vapor pressure of N-methyl-2-pyrrolidone was measured since no reliable values were found within the temperature range studied. The results were obtained by the transpiration method described above. Experimental results are presented in Table 2 together with deviations from values correlated using the Antoine equation with coefficients given in Table 6. The maximum likelihood method was used for data reduction assuming standard deviations $s(T) = 0.01 \text{ K}$ and $s(p) = 0.001 \text{ kPa}$.

Benzene + N-Methyl-2-pyrrolidone. Both components are miscible over the whole mole fraction range at ambient temperature. Refractometric analysis was used since only a small amount of sample was required. The refractometer with a resolution of ± 0.00001 was employed. The dependence of refractive index on composition at 293.15 K is given in Table 3. The results were smoothed using the maximum likelihood method applied to the three-parameter equation

$$n^D = x_A n_A^D + x_B n_B^D + x_A x_B (x_A A_1 + x_B A_2 - x_A x_B A_3) \quad (1)$$

assuming standard deviations equal to $\sigma(x) = 0.0001$ and

Table 6. Antoine Vapor Pressure Constants for $\log_{10}(P/\text{kPa}) = A - B/(TK + C)$

compound	A	B	C	ref
benzene	6.017 62	1203.531	-53.262	Boublik et al. (1973)
toluene	6.082 95	1346.773	-53.457	Boublik et al. (1973)
heptane	6.027 43	1267.828	-56.327	Boublik et al. (1973)
methylcyclohexane	5.951 79	1272.865	-51.52	Boublik et al. (1973)
N-methyl-2-pyrrolidone	7.374 70	2372.949	-25.829	this work

$\sigma(n) = 0.00001$. Equation 1 was used to calculate compositions from the measured refractive index of the samples. The composition of the liquid phase (used for the saturation measurements) was determined from the measured mass of the various components. The P , x , y values were measured at 330.00 K and 350.00 K and are summarized in Table 4.

Toluene + N-Methyl-2-pyrrolidone. The technique was the same as for benzene + N-methyl-2-pyrrolidone. The dependence of the refractive index on composition at 293.15 K and results of data reduction are given in Table 3. The P , x , y values were measured at two temperatures, 343.15 K , and 373.15 K . and the results are summarized in Table 4.

Heptane + N-Methyl-2-pyrrolidone. Both components are completely miscible at temperatures higher than 327 K (Hradetzky et al., 1989). Limited miscibility occurs at ambient temperature; therefore the samples in the middle of the composition range are heterogeneous. Because neither the densimetric nor refractometric method was suitable for analysis due to the small differences between these properties for the pure components, the gas chromatographic method was selected for analysis. An excess amount of inert solvent (1-butanol) was added in order to homogenize the two-phase liquid samples. The chromatographic analyses were repeated until an average of 1% deviation was attained. The P , x , y values were measured at 340.00 K and 365.00 K ; the results are summarized in Table 4.

Methylcyclohexane + N-Methyl-2-pyrrolidone. The published upper critical solution temperature was 290.75 K (Hradetzky et al., 1989) so the refractometric analyses were made at 303.15 K . The dependence of refractive index on composition and the results of the correlation are presented in Table 3. This system was the only one measured completely using the recirculation still. The vapor-liquid equilibria were determined at 340.00 K and 370.00 K . The results are given in Table 4.

Data Reduction

The results were reduced using the maximum likelihood procedure as described by Hala et al. (1982). A

Table 7. Parameters of the Fourth-Order Redlich–Kister Equation and Mean Deviations for Systems Containing *N*-Methyl-2-pyrrolidone

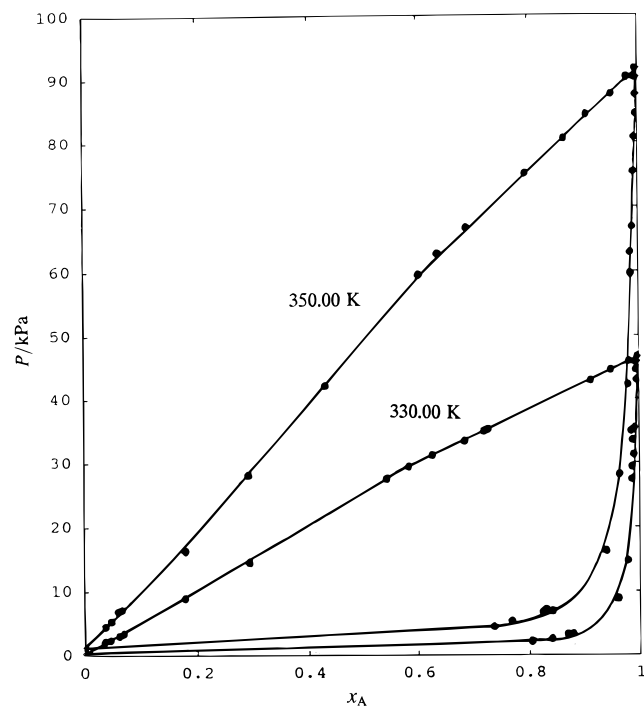
component	<i>T</i> /K	a_1	a_2	a_3	δx	δy	δP /kPa	δT /K
benzene	330.00	0.1534	0.2063	0.0925	0.0020	0.0099	0.00	0.01
	350.00	0.0919	0.2158	0.2060	0.0026	0.0082	0.01	0.01
toluene	343.15	0.4416	0.1153	0.0916	0.0035	0.0476	0.04	0.04
	373.15	0.4103	0.2154	-0.0281	0.0046	0.0212	0.02	0.04
heptane	340.00	2.2501	0.1106	0.2443	0.0074	0.0040	0.03	0.05
	365.00	2.0524	0.2134	0.3234	0.0050	0.0102	0.05	0.03
methylcyclohexane	340.00	1.9745	0.1624	0.3157	0.0077	0.0024	0.03	0.05
	370.00	1.7766	0.2779	0.1692	0.0071	0.0284	0.05	0.08

Table 8. Parameters of the Wilson Equation and Mean Deviations for Mixtures Containing *N*-Methyl-2-pyrrolidone

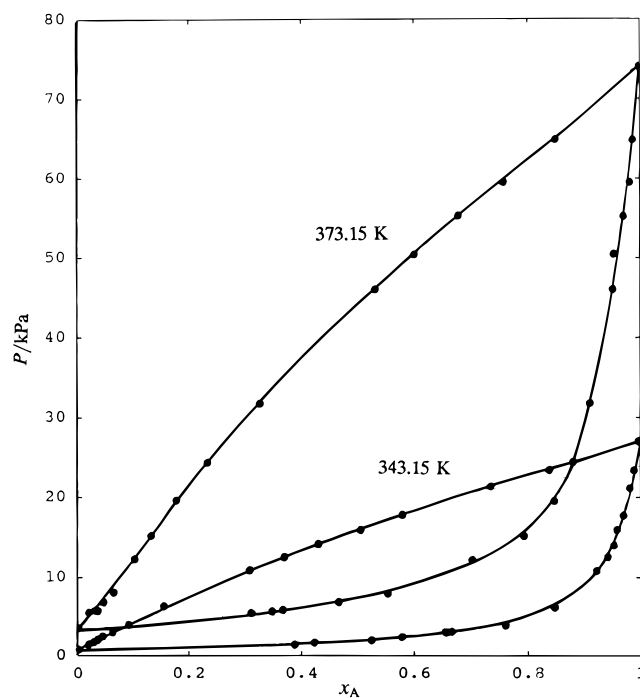
component	<i>T</i> /K	$A_{AB}/\text{J}\cdot\text{mol}^{-1}$	$A_{BA}/\text{J}\cdot\text{mol}^{-1}$	δx	δy	δP /kPa	δT /K
benzene	330.00	-2034.6	4910.8	0.0033	0.0099	0.00	0.01
	350.00	-2295.3	5589.6	0.0038	0.0083	0.01	0.01
toluene	343.15	-1237.8	3203.7	0.0019	0.0503	0.02	0.08
	373.15	-2046.6	4743.1	0.0069	0.0213	0.01	0.08
heptane	340.00	3176.2	8566.7	0.0107	0.0042	0.03	0.05
	365.00	2511.1	7737.5	0.0031	0.0103	0.03	0.02
methylcyclohexane	340.00	2554.8	6238.7	0.0064	0.0024	0.02	0.03
	370.00	1612.4	6707.9	0.0051	0.0290	0.03	0.05

Table 9. Parameters of the NRTL Equation and Mean Deviations for Mixtures Containing *N*-Methyl-2-pyrrolidone

component	<i>T</i> /K	$A_{AB}/\text{J}\cdot\text{mol}^{-1}$	$A_{BA}/\text{J}\cdot\text{mol}^{-1}$	α	δx	δy	δP /kPa	δT /K
benzene	330.00	9370.7	-6209.9	0.1185	0.0023	0.0099	0.00	0.01
	350.00	2711.6	-748.1	1.2924	0.0033	0.0083	0.01	0.01
toluene	343.15	1564.8	466.1	1.8020	0.0028	0.0509	0.02	0.01
	373.15	8462.3	-5258.8	0.1272	0.0050	0.0209	0.02	0.04
heptane	340.00	2204.3	2551.2	-0.8310	0.0076	0.0040	0.03	0.05
	365.00	5942.8	4169.4	0.4729	0.0037	0.0102	0.04	0.03
methylcyclohexane	340.00	1820.0	2201.3	-1.1401	0.0064	0.0024	0.02	0.03
	370.00	1594.2	2599.7	-0.8730	0.0057	0.0289	0.04	0.05

**Figure 1.** Vapor and liquid compositions for benzene (A) + *N*-methyl-2-pyrrolidone (B) at 330.00 K and 350.00 K. Solid lines are calculated from the NRTL equation.

symmetrical objective function was evaluated using standard deviations estimated as $s(x) = s(y) = 0.004$, $s(P) = 0.001P$, and $s(T) = 0.04$ K for phase compositions, pressure, and temperature, respectively. The whole correlation procedure was presented in detail by Wolfova et al. (1990). The real gas phase behavior was taken into account and was described using the virial equation of state. The second virial coefficients B were evaluated by

**Figure 2.** Vapor and liquid compositions for toluene (A) + *N*-methyl-2-pyrrolidone (B) at 343.15 K and 373.15 K. Solid lines are calculated from the NRTL equation.

means of the Hayden and O'Connell (1975) method, and the molar volumes V were calculated using a generalized Watson relation (Hougen and Watson, 1947). The values used for the pure components and mixtures are summarized in Table 5. The necessary vapor pressures were calculated from the Antoine equation parameters which are given in Table 6. The activity coefficients γ_x were fitted both to classical and to nonclassical equations

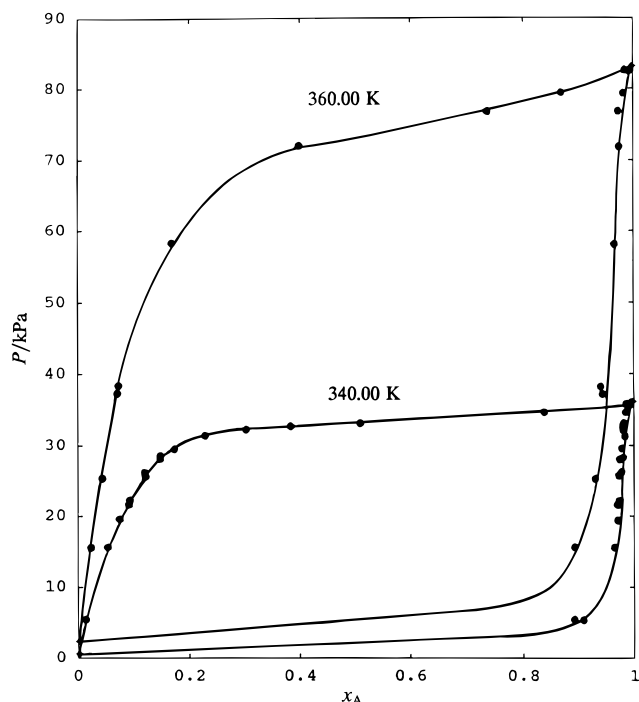


Figure 3. Vapor and liquid compositions for heptane (A) + *N*-methyl-2-pyrrolidone (B) at 340.00 K and 360.00 K. Solid lines are calculated from the NRTL equation.

expressed as follows:

(i) the Redlich–Kister equation in the form

$$\ln \gamma_{x,A} = x_B^2 [a_1 + a_2(4x_A - 1) + a_3(x_A - x_B)(6x_A - 1)] \quad (2)$$

where a_1 , a_2 , and a_3 are adjustable parameters;

(ii) the Wilson equation

$$\ln \gamma_{x,A} = \ln(x_A + x_B \Lambda_{AB}) + x_B \Lambda_{AB} / (x_A + x_B \Lambda_{AB}) - x_B \Lambda_{BA} / (x_B + x_A \Lambda_{BA}) \quad (3)$$

where $\Lambda_{AB} = (V_B/V_A) \exp[-A_{AB}/RT]$ and $\Lambda_{BA} = (V_A/V_B) \exp[-A_{BA}/RT]$, where V_A and V_B are the molar volumes and A_{AB} and A_{BA} are adjustable parameters;

(iii) the NRTL equation

$$\ln \gamma_{x,A} = x_B^2 [\{\tau_{BA} G_{BA} / (x_A + x_B G_{BA})\}^2 + \{\tau_{AB} G_{AB} / (x_B + x_A G_{AB})\}^2] \quad (4)$$

where $\tau_{AB} = A_{AB}/RT$, $\tau_{BA} = A_{BA}/RT$, $G_{AB} = \exp(-\alpha\tau_{AB})$, and $G_{BA} = \exp(-\alpha\tau_{BA})$ and A_{AB} , A_{BA} , and α are adjustable parameters. The expressions for the activity coefficient $\gamma_{x,B}$ can be obtained by interchanging subscripts A and B in eqs 2–4.

The results of the correlation are summarized in Table 7. As an example, the deviations in compositions, pressure, and temperature corresponding to the correlation using the NRTL equation are presented in Table 4 along with the direct experimental results. The experimental x , y , p values are compared with the curve derived from the NRTL equation in Figures 1–4. The correlation of the results and the resulting distribution of deviations from the smoothed results confirm that there are no large errors in the measurements. For benzene (A) + *N*-methyl-2-pyrrolidone (B) direct comparisons with the results of Gierycz et al.

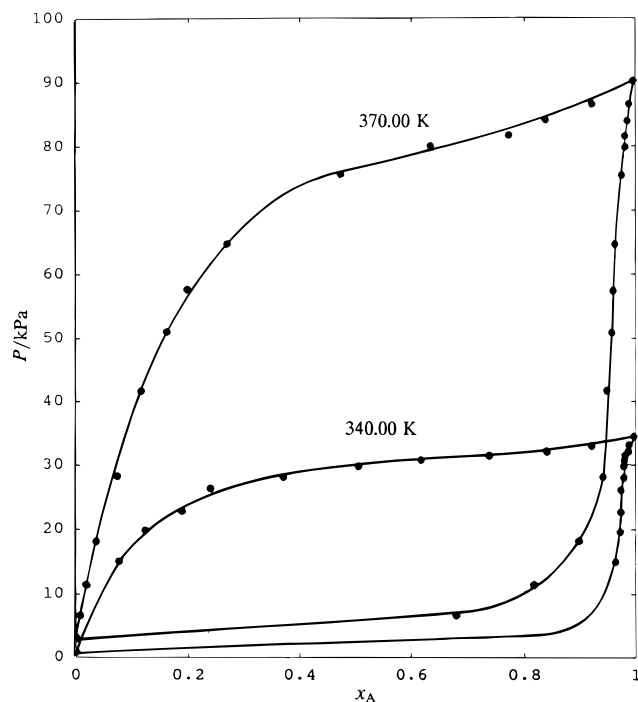


Figure 4. Vapor and liquid compositions for methylcyclohexane (A) + *N*-methyl-2-pyrrolidone (B) at 340.00 K and 370.00 K. Solid lines are calculated from the NRTL equation.

(1985) and Dojcansky et al. (1980) are possible, as both papers reported P , x values. From the P , x plot, our values agree, within the estimated uncertainties, with those of Dojcansky et al. while the results of Gierycz et al. cannot be extrapolated from their lowest value of $x_A = 0.27$ to the vapor pressure of *N*-methyl-2-pyrrolidone without an improbable inflection on the P , x curve. This same effect occurs on the lower isotherms for the toluene + *N*-methyl-2-pyrrolidone and methylcyclohexane + *N*-methyl-2-pyrrolidone mixtures measured by Gierycz et al. (1985).

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