Table IX. Azeotropic Data of the Systems at 200 mmHg

system	T, °C	x_1
o-toluidine (1)/tetraline (2)	151.10	0.632
m-toluidine (1)/tetraline (2)	152.50	0.551
m-cresol (1)/tetraline (2)	151.45	0.482

$\gamma_1^\infty = 1.52$ and $\gamma_2^\infty = 1.70$ for the *o*-toluidine/tetraline system.

Because of the steric hindrance of the $-CH_3$ group, which weakens hydrogen bonds between *o*-toluidine molecules, the *o*-toluidine/tetraline system shows lower deviations from ideality than the *m*-toluidine/tetraline system.

As tetraline is a molecule of low polarity, dipole–dipole interactions are weak and, therefore, do not play an important role in the deviations from ideality.

These systems show a minimum temperature boiling point azeotrope; azeotropic temperatures are given in Table IX.

Registry No. Tetraline, 119-64-2; *o*-toluidine, 95-53-4; *m*-toluidine, 108-44-1; *m*-cresol, 108-39-4.

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Vapor–Liquid Equilibria of Coal-Derived Liquids. 2. Binary Systems with *o*-Toluidine at 200 mmHg

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Vapor–liquid equilibrium (VLE) data for the binary systems of *o*-toluidine with 2,6-lutidine, α-picoline, and γ-picoline have been determined at 200-mmHg pressure. The systems show slight negative deviations from ideal behavior, the system 2,6-lutidine/*o*-toluidine being the closest to ideality. Data reduction based on the Margules, Van Laar, Wilson, NRTL, and UNIQUAC models provide a correlation for the liquid-phase activity coefficients.

Introduction

Nitrogen and sulfur are the major heteroatoms in the structure of coal. The nitrogen content ranges from 1–2 wt %, depending on the coal source. The processes of gasification and liquefaction to make synfuels and coking to make metallurgical coke generate a mixture of gases and liquids in which nitrogen compounds are present. A variety of nitrogen compounds have been found in coal-derived liquids; some of the most valuable products are those with heterocyclic nitrogen such as pyridines, quinolines, picolines, and lutidines. Separation of these compounds allows one to obtain products that are important in the chemical and pharmaceutical industries.

Information on vapor–liquid equilibrium (VLE) data is required for the design of separation processes involving coal-derived products. Work in this area has been carried out only recently (*1–5*). Despite the powerful methods developed for prediction of VLE data, such as UNIFAC (*6*) and ASOG (*7*), more experimental data are needed to enlarge the data base for these methods. This is particularly true for complex molecules such as heterocyclic compounds.

Table I. Physical Properties of Chemicals[a]

compound	property	exptl	lit.	ref
o-toluidine	d(25 °C)	0.9943	0.994 30	9
	n_D(25 °C)	1.5700	1.569 87	9
	bp (200 mmHg)	153.30		
α-picoline	d(25 °C)	0.9397		
	d(20 °C)	0.9443	0.9443	10
	n_D(25 °C)	1.4981		
	n_D(20 °C)	1.5009	1.501 02	11
	bp (200 mmHg)	87.50		
γ-picoline	d(25 °C)	0.9492		
	d(20 °C)	0.9545	0.954 78	11
	n_D(25 °C)	1.5029		
	n_D(20 °C)	1.5055	1.505 84	11
	bp (200 mmHg)	101.95		
2,6-lutidine	d(25 °C)	0.9181		
	d(20 °C)	0.9224	0.922 57	11
	n_D(25 °C)	1.4953		
	n_D(20 °C)	1.4978	1.497 79	11
	bp (200 mmHg)	100.85		

[a] Units: d, g/cm^3; bp, °C.

In part 1 of this work (*8*), VLE data were reported for binary systems with tetraline as the common solvent. Here, the results for binary systems of *o*-toluidine (2-aminotoluene) with three heterocyclic compounds, α-picoline (2-methylpyridine), γ-picoline (4-methylpyridine), and 2,6-lutidine (2,6-dimethylpyridine), at 200 mmHg are presented.

Experimental Section

All the products, *o*-toluidine (>99.5% GC), α-picoline (>98% GC), γ-picoline (>98% GC), and 2,6-lutidine (>98% GC) were

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Table II. Refractive Indices at 25 °C of the Systems α-Picoline (α-p)/*o*-Toluidine (*o*-t), γ-Picoline (γ-p)/*o*-Toluidine (*o*-t), and 2,6-Lutidine (l)/*o*-Toluidine (*o*-t)

$x_{\alpha\text{-p}}$	n_D	$x_{\gamma\text{-p}}$	n_D	x_l	n_D
0.0000	1.5700	0.0000	1.5700	0.0000	1.5700
0.1104	1.5645	0.0960	1.5653	0.0872	1.5645
0.2175	1.5584	0.1648	1.5617	0.1989	1.5572
0.3158	1.5528	0.2137	1.5591	0.2850	1.5515
0.4050	1.5472	0.3114	1.5538	0.3801	1.5451
0.4972	1.5412	0.4320	1.5467	0.4897	1.5374
0.6184	1.5326	0.5239	1.5410	0.5890	1.5302
0.7136	1.5251	0.6156	1.5348	0.6948	1.5220
0.7886	1.5187	0.7297	1.5263	0.7902	1.5141
0.8851	1.5098	0.8089	1.5199	0.8451	1.5095
0.9460	1.5038	0.9101	1.5111	0.9351	1.5013
1.0000	1.4981	1.0000	1.5029	1.0000	1.4953

Table III. Vapor–Liquid Equilibrium Data for α-Picoline (1)/*o*-Toluidine (2) at 200 mmHg

x_1	y_1	T, °C	γ_1	γ_2	ϕ_1	ϕ_2
0.000	0.000	153.30		1.0000	0.9993	0.9847
0.040	0.185	147.10	0.7591	1.0382	0.9966	0.9839
0.060	0.295	144.50	0.8624	1.0025	0.9952	0.9838
0.090	0.399	140.95	0.8527	0.9991	0.9939	0.9838
0.127	0.498	137.10	0.8352	0.9979	0.9926	0.9839
0.177	0.602	132.40	0.8231	0.9970	0.9914	0.9842
0.210	0.662	129.10	0.8362	0.9986	0.9907	0.9843
0.260	0.737	124.55	0.8559	0.9886	0.9897	0.9847
0.318	0.807	119.95	0.8766	0.9451	0.9888	0.9851
0.355	0.838	117.40	0.8800	0.9305	0.9884	0.9853
0.430	0.891	112.25	0.9042	0.8785	0.9875	0.9856
0.485	0.910	109.05	0.9053	0.9212	0.9870	0.9855
0.507	0.930	107.60	0.9269	0.7974	0.9867	0.9858
0.579	0.956	103.60	0.9497	0.7013	0.9861	0.9858
0.609	0.953	101.95	0.9504	0.8694	0.9858	0.9855
0.688	0.972	98.45	0.9649	0.7631	0.9852	0.9855
0.775	0.980	94.90	0.9755	0.8944	0.9845	0.9851
0.853	0.990	92.00	0.9910	0.7880	0.9839	0.9850
0.868	0.978	91.45	0.9810	1.9836	0.9838	0.9844
0.914	0.993	90.00	0.9961	1.0409	0.9835	0.9847
0.949	0.995	88.90	1.0001	1.3246	0.9833	0.9846
0.980	0.997	88.00	1.0026	2.1207	0.9831	0.9845
1.000	1.000	87.50	1.0000		0.9830	0.9845

supplied by Fluka. They were distilled under vacuum in nitrogen and stored in the dark. The collected distillated fractions were analyzed by gas chromatography. The physical properties of the materials used are listed in Table I.

Vapor–liquid equilibria and some vapor-pressures of the components were measured with a commercial recirculating still of the Gillespie type (*12*). The apparatus is as described in the preceding paper of this issue (*8*).

Compositions of the vapor and liquid phases were determined by gas–liquid chromatography (GLC, Perkin Elmer, Model 990, with a flame ionization detector) and refractive indices at 25 °C. The chromatographic column (3 m × 0.3 cm) was packed with 15 wt % Carbowax 1500 on Chromosorb WHP 60/80 mesh. Chromatographic analyses were carried out at 145 °C. No significant differences were found in the composition determined by both techniques.

Results and Discussion

Refractive indices, n_D, at 25 °C for the three systems reported in this work are presented in Table II. The experimental VLE data for the binary systems of α-picoline, γ-picoline, and 2,6-lutidine with *o*-toluidine are given in Tables III–V, respectively. Figure 1 shows the x–y diagrams for the aforementioned systems.

Table IV. Vapor–Liquid Equilibrium Data for γ-Picoline (1)/*o*-Toluidine (2) at 200 mmHg

x_1	y_1	T, °C	γ_1	γ_2	ϕ_1	ϕ_2
0.000	0.0000	153.30		1.0000	0.9974	0.9847
0.010	0.077	151.30	1.7312	0.9905	0.9962	0.9844
0.040	0.157	149.30	0.9299	0.9971	0.9950	0.9842
0.103	0.315	144.90	0.8148	1.0068	0.9927	0.9840
0.152	0.424	141.75	0.8097	0.9990	0.9913	0.9842
0.203	0.512	139.15	0.7868	0.9873	0.9902	0.9845
0.240	0.594	136.30	0.8365	0.9543	0.9892	0.9849
0.313	0.683	132.05	0.8332	0.9638	0.9880	0.9853
0.344	0.723	129.90	0.8546	0.9561	0.9875	0.9855
0.397	0.785	127.30	0.8684	0.8914	0.9868	0.9861
0.435	0.815	125.10	0.8791	0.8914	0.9863	0.9863
0.475	0.848	122.90	0.8958	0.8594	0.9859	0.9867
0.532	0.884	119.60	0.9235	0.8396	0.9852	0.9869
0.612	0.919	116.05	0.9337	0.8177	0.9845	0.9872
0.673	0.946	113.30	0.9551	0.7256	0.9839	0.9875
0.737	0.963	110.70	0.9668	0.6906	0.9834	0.9876
0.795	0.977	108.30	0.9850	0.6111	0.9829	0.9877
0.846	0.985	106.40	0.9949	0.5767	0.9825	0.9877
0.936	0.998	103.55	1.0046	0.2102	0.9818	0.9877
0.975	0.999	102.60	0.9977	0.2809	0.9816	0.9878
1.000	1.000	101.95	1.0000		0.9815	0.9878

Table V. Vapor–Liquid Equilibrium Data for 2,6-Lutidine (1)/*o*-Toluidine (2) at 200 mmHg

x_1	y_1	T, °C	γ_1	γ_2	ϕ_1	ϕ_2
0.000	0.000	153.30		1.0000	0.9977	0.9847
0.052	0.226	146.35	1.0743	1.0243	0.9943	0.9839
0.083	0.318	143.75	1.0164	1.0202	0.9930	0.9838
0.130	0.429	140.10	0.9684	1.0231	0.9916	0.9839
0.165	0.497	137.40	0.9537	1.0342	0.9907	0.9840
0.217	0.588	133.80	0.9512	1.0300	0.9896	0.9843
0.267	0.663	130.30	0.9657	1.0254	0.9886	0.9846
0.318	0.721	127.35	0.9629	1.0208	0.9879	0.9850
0.364	0.767	124.80	0.9669	1.0091	0.9873	0.9853
0.404	0.794	122.60	0.9650	1.0382	0.9869	0.9854
0.462	0.830	119.90	0.9597	1.0574	0.9863	0.9856
0.514	0.866	117.20	0.9805	1.0299	0.9858	0.9859
0.573	0.894	114.75	0.9827	1.0264	0.9853	0.9862
0.635	0.920	112.10	0.9953	1.0133	0.9848	0.9864
0.696	0.939	110.10	0.9905	1.0107	0.9844	0.9866
0.750	0.953	108.15	0.9962	1.0307	0.9841	0.9866
0.791	0.958	106.55	1.0026	1.1820	0.9838	0.9867
0.836	0.978	105.25	1.0127	0.8359	0.9835	0.9869
0.878	0.986	103.95	1.0169	0.7580	0.9832	0.9870
0.935	0.994	102.25	1.0217	0.6585	0.9829	0.9870
0.970	0.997	101.30	1.0214	0.7451	0.9827	0.9870
1.000	1.000	100.85	1.0000		0.9826	0.9870

Table VI. Vapor Pressure Data for α-Picoline, γ-Picoline, and 2,6-Lutidine[a]

α-picoline		γ-picoline		2,6-lutidine	
T_{exp}	P_{exp}	T_{exp}	P_{exp}	T_{exp}	P_{exp}
81.40	159.10	95.05	155.60	91.80	142.18
81.45	159.30	101.95	200.00	100.90	200.50
87.50	200.00	110.50	268.65	109.10	267.30
91.80	232.15	118.75	351.10	117.15	348.40
95.25	264.40	126.60	445.45	125.10	445.70
97.80	288.15	131.80	521.60	131.50	541.20
101.40	325.95	137.35	613.20	135.25	601.65
105.00	368.15	145.00	760.00	143.50	760.00

[a] Units: T_{exp}, °C; P_{exp}, mmHg.

Table VII. Antoine Equation Parameters

compound	A	B	C
α-picoline	8.316 88	2277.00	290.945
γ-picoline	7.102 26	1506.26	211.750
2,6-lutidine	6.601 91	1470.17	208.015
o-toluidine[a]	7.032 10	1575.64	179.900

[a] Reference 13.

Activity coefficients were calculated by neglecting the vapor-phase nonideality, since the correction factors are practically unity for the experimental conditions of this work. Vapor-pressure data for α-picoline, γ-picoline, and 2,6-lutidine were not found in the available literature. Hence, they were determined from measurements made with the still. The ex-

Table VIII. Binary Correlation Parameters for Activity Coefficients[a]

	A_{12}	A_{21}	α_{12}	γ_1^∞	γ_2^∞	(MAD *T*)	(MAD *Y*)
		2,6-Lutidine (1)/*o*-Toluidine (2)					
Margules	0.1310	−0.3711		1.14	0.69	0.77	0.0067
Van Laar	−0.0788	−0.5546		0.92	0.57	0.86	0.0039
Wilson	1680.2702	−768.5309		1.47	0.81	0.56	0.0057
NRTL	−4753.8482	5846.4465	0.0330	1.16	0.72	0.53	0.0056
UNIQUAC	−579.1617	882.6447		1.24	0.76	0.52	0.0056
		α-Picoline (1)/*o*-Toluidine (2)					
Margules	−0.2221	−0.3539		0.80	0.70	0.20	0.0059
Van Laar	−0.2521	−0.3426		0.78	0.71	0.26	0.0059
Wilson	−192.6884	−14.7150		0.78	0.70	0.25	0.0058
NRTL	267.2495	−444.4479	0.3067	0.79	0.69	0.22	0.0058
UNIQUAC	828.3074	−587.9931		0.84	0.68	0.17	0.0059
		γ-Picoline (1)/*o*-Toluidine (2)					
Margules	−0.0300	−0.5864		0.97	0.56	0.57	0.0151
Van Laar	−0.2212	−0.5147		0.80	0.60	0.41	0.0105
Wilson	−802.3393	1319.1133		0.79	0.70	0.35	0.0087
NRTL	763.4923	−676.3582	0.5349	0.79	0.64	0.38	0.0089
UNIQUAC	891.7725	−625.0191		0.80	0.68	0.34	0.0083

[a] (MAD *T*) = $(1/n)\sum_n|T_{\text{exp}} - T_{\text{calc}}|$, (MAD *Y*) = $(1/n)\sum_n|Y_{\text{exp}} - Y_{\text{calc}}|$, and *n* = data point.

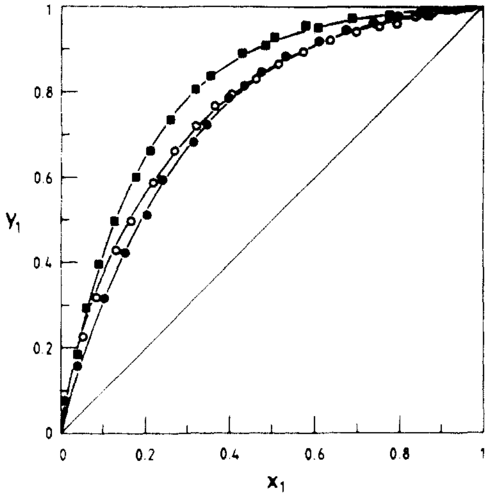

Figure 1. Vapor-liquid equilibrium data of binary systems with *o*-toluidine at 200 mmHg: ○, 2,6-lutidine (1)/*o*-toluidine (2); ■, α-picoline (1)/*o*-toluidine (2); ●, γ-picoline (1)/*o*-toluidine (2).

perimental data are shown in Table VI and were fitted to the Antoine equation. The parameters *A*, *B*, and *C* of the Antoine equation are shown in Table VII, along with the values reported in the literature for *o*-toluidine.

The experimental activity coefficients were checked for consistency with use of the point-to-point test, as described by Christiansen and Fredenslund (*14*). Data were found consistent for both 2,6-lutidine/*o*-toluidine and α-picoline/*o*-toluidine systems and inconsistent for the system γ-picoline/*o*-toluidine. No special experimental difficulties were encountered, so that the slight inconsistency in the data shown in Table VIII cannot be attributed to the experimental procedure. The mean absolute deviations in *T* and *y* (obtained by data reduction) are not very large. Thus, it is thought that the (H^E/RT) d*T* term of the Gibbs–Duhem equation (heat of mixing for this system is not available) is not negligible, as assumed by the thermodynamic consistency test. Further, this is supported by the fact that the γ-picoline/*o*-toluidine system shows the largest negative deviations from ideality among the piridine-derivatives/*o*-toluidine systems studied here, giving rise to relatively large negative values of G^E/RT. On the other hand, the excess entropy will most probably be negative because of the formation of NH–N hydrogen bonds between γ-picoline and *o*-toluidine molecules. Since $G^E/RT = H^E/RT - S^E/T$, a negative S^E and G^E could give rise to significant H^E values.

Activity coefficients were correlated with the Margules, Van Laar, Wilson, NRTL, and UNIQUAC models (*14*).

The parameters A_{12} and A_{21} for the following correlation equations are listed in Table VIII: Wilson, $A_{ij} = \lambda_{ij} - \lambda_{ii}$ (cal/mol); NRTL, $A_{ij} = g_{ij} - g_{jj}$ (cal/mol); UNIQUAC, $A_{ij} = u_{ij} - u_{jj}$ (cal/mol). Mean absolute deviations in *Y* (MAD *Y*) and *T* (MAD *T*) and infinite dilution activity coefficients γ_1^∞ and γ_2^∞ are also listed. The MAD *T* values are larger for the *o*-toluidine series than for the tetraline series. This is due to the data-reduction method. The activity coefficients are functions of the temperature, but for the tetraline series, this temperature dependence is very weak. Thus, the values obtained for the temperature, when calculated from activity coefficient equations, are closer to the experimental values used for data reduction than for the tetraline series, where the temperature dependence of the activity coefficients is more important.

The systems measured in this study show small deviations from ideality. In the absence of specific interactions, aromatic/aromatic systems show, in general, positive deviations from Raoult's law (*2*, *15*). However, if one substituent is highly polar, negative deviations can result because of induction effects. Thus, the dipolar moment of γ-picoline (μ = 2.60) is the largest in the series of aromatic compounds, and hence the γ-picoline/*o*-toluidine system shows the largest deviations from ideality. Also, steric hindrance resulting from the presence of CH_3 groups tends to eliminate molecular interactions. In fact 2,6-lutidine has the largest steric hindrance followed by α-picoline and γ-picoline, and deviations from ideality increase in the same order.

Registry No. *o*-Toluidine, 95-53-4; 2,6-lutidine, 108-48-5; α-picoline, 109-06-8; γ-picoline, 108-89-4.

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Experimental Measurement of Vapor–Liquid Equilibrium in Alcohol/Water/Salt Systems

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Vapor–liquid equilibrium measurements have been performed on a set of alcohol/water/salt solutions at atmospheric pressure with a modified Othmer still and a modified Boublík–Benson still. The systems studied are methanol and water with NaCl, NaBr, KCl, and KBr; 1-propanol and water with NaCl, KBr, and NaBr; and 2-propanol with water and NaBr. The measurements are for salt concentrations ranging from infinite dilution to saturation for each water/alcohol solvent mixture. These experimental results constitute part of a database being developed to test theoretical models of mixed-solvent–electrolyte systems.

1. Introduction

A mixed-solvent electrolyte system consists of an electrolyte (such as a salt) dissolved in a solvent that is a mixture of two or more nonelectrolyte species (such as alcohol and water). Such systems have been the subject of intense research for a century, and the experimental and theoretical literature related to these systems is voluminous, as is evidenced by the thorough reviews of Furter (*1*, *2*) and the diversity of papers published in two American Chemical Society symposium volumes (*3*, *4*) devoted to the subject.

Mixed-solvent electrolytes are important because they arise in many naturally occurring systems (such as brine-containing oil reservoirs and biological fluids) and as intermediates or products in many industrial processes. A significant portion of the industrial interest in mixed-solvent electrolytes arises from their potential application in extractive distillation. When a nonvolatile salt is added to a nonelectrolyte mixture, the relative volatility of the nonelectrolyte species is altered. For example, suppose a strong electrolyte (3) such as potassium acetate or sodium chloride (which dissociate to form $K^+/C_2H_3O_2^-$ and Na^+/Cl^- ions, respectively) is added to an ethanol (2)/water (1) solution. The conventional qualitative picture is that the ions preferentially complex with the water molecules, creating a high molecular weight species that, compared to the salt-free case, has lower vapor pressure relative to the ethanol. Thus, the relative volatility of ethanol, defined by

$$\alpha_2 = \frac{y_2/x_2}{y_1/x_1} \qquad (1)$$

where x_i and y_i are respectively the liquid- and vapor-phase compositions of species i at equilibrium, is increased by the addition of salt. Even at very small concentrations of these salts, this increase in volatility is sufficient to eliminate the azeotrope at 95 mol % ethanol, suggesting that salt may be a useful mass separating agent for extractive distillation. This alteration of phase equilibria in nonelectrolyte mixtures due to the presence of salt is known as the "salt effect", and the component with increased volatility is said to be "salted out" while the other component is said to be "salted in".

The salting out of alcohol from aqueous solutions has been recognized and exploited commercially at least since the twelfth century when Italian vintners discovered that the addition of salt to water/ethanol mixtures yielded higher concentration alcohol solutions upon distillation (*5*, *6*). However, there are many other important azeotropic systems that can be separated via extractive distillation using salts as the separating agent (*1*, *2*). Compared to an extractive distillation using a liquid mass separating agent, the use of salt requires that the salt enter the distillation column by dissolution into the reflux stream since the nonvolatile salt remains entirely in the descending liquid phase. If the salt is not introduced through the reflux stream, at several plates vapor would be in contact with salt-free liquid. Thus, the applicability of extractive distillation is restricted somewhat by the solubility of the salt in the reflux stream.

If the salt is fed at a constant rate to the reflux stream of a continuous distillation column operating at steady state (assuming constant molar overflow), then the molar salt concentration in the liquid phase will remain constant throughout the rectifying and stripping sections of the column despite progressive changes in solvent composition as the column is descended. Therefore, vapor–liquid equilibrium data required for column design should consist of T-x-y (where T is temperature) measurements at constant salt concentration. Recovery of the salt from the bottoms product for recycle operations is a simple evaporation operation.

Several authors (*7*, *8*) have evaluated the advantages and disadvantages of using salts as separating agents for aqueous nonelectrolyte systems. Discussion of these pros and cons is beyond the scope of the present paper; it is sufficient to note that where solubility relationships permit, extractive distillation by salt effect at least offers a viable alternative to presently used methods for difficult separations.

There are several separations that have proved economically favorable to perform using salt as the mass separating agent:

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