way are presented in Table IV, along with their standard deviations. The values for d_0 may be compared with those of the National Bureau of Standards (*11*), ΔH°_{298} = 42.38 kJ/mol and ΔS°_{298} = 105.06 J/K mol. The latter were obtained from measurements covering a much wider temperature range, and on more highly purified material; they are doubtless more accurate.

Table IV shows, furthermore, that replacement of hydrogen by deuterium decreases the enthalpy of vaporization and therefore increases the vapor pressure at a given temperature. This is consistent with the behavior of other nonpolar compounds (*12*). Calculation of the ratio $[\Delta H^\circ_{298}(d_0) - \Delta H^\circ_{298}(d_6)]/[\Delta H^\circ_{298}(d_0) - \Delta H^\circ_{298}(d_{10})]$ gives the value 0.77 ± 0.31, and if replacement of a hydrogen by a deuterium atom always decreases the enthalpy of vaporization by the same amount, this ratio would be 0.60. There is reason to believe, however, that substitution of a deuterium for a hydrogen atom on the methyl group affects the properties more than substitution on the aromatic ring (*13*). (The normal boiling points quoted earlier can also be interpreted in this way.) If this were so, the ratio of the enthalpy differences would be greater than 0.60, as found. It must be admitted, however, that the uncertainties in the ΔH°_{298} values are such as to make the value 0.77 and the resulting inferences tenuous. Several other methods of treating the data, such as using smoothed rather than raw data or using vapor pressures for d_6 and d_{10} calculated from the d_0 values through the Bigeleisen expressions given above, were tried with virtually the same results.

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Vapor–Liquid Equilibria of Coal-Derived Liquids. 1. Binary Systems with Tetraline at 200 mmHg

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Vapor–liquid equilibrium (VLE) data for the binary systems of tetraline with *o*-toluidine, *m*-toluidine, and *m*-cresol were measured at 200-mmHg pressure. These systems show positive deviations from Raoult's law and form azeotropic mixtures for molar fractions of 0.632 (*o*-toluidine), 0.551 (*m*-toluidine), and 0.482 (*m*-cresol). Data reduction based on the Margules, Van Laar, Wilson, NRTL, and UNIQUAC models provides a correlation for γ_i.

Introduction

Manufacturing synthetic fuels from coal is considered uneconomical under the present competition of petroleum. In coal liquefaction processes, hydrogen is added to a coal suspension in a solvent such as tetraline. Some of the major problems encountered in hydrogenation plants are related to separation processes, i.e. removal of solid particles from the slurry and separation of hydrogenation fractions for recycling of the solvent.

The need for vapor–liquid equilibrium (VLE) data regarding mixtures of coal-derived liquids, which would allow prediction of data for the design of separation equipment, has been indicated elsewhere (*1*).

Table I. Physical Properties of the Chemicals[a]

compound	property	exptl	lit.	ref
o-toluidine	d(25 °C)	0.9943	0.994 30	2
	n_D(25 °C)	1.5700	1.569 87	2
	bp (200 mmHg)	153.30		
m-toluidine	d(25 °C)	0.9846		
	d(20 °C)	0.9890	0.9889	3
	n_D(25 °C)	1.5658	1.565 70	2
	bp(200 mmHg)	156.15		
tetraline	d(25 °C)	0.9660	0.9662	2
	n_D(25 °C)	1.5393	1.539 19	2
	bp(200 mmHg)	157.00		
m-cresol	d(25 °C)	1.0303	1.030 19	2
	n_D(25 °C)	1.5397	1.5396	2
	bp(200 mmHg)	157.10		

[a] Units: d, g/cm^3; bp, °C.

In this work, VLE data for binary mixtures of a hydroaromatic compound, tetraline, a typical hydrogen donor molecule in liquefaction processes, with two aromatic nitrogen isomers, *o*-toluidine and *m*-toluidine, and a phenolic compound, *m*-cresol, are reported at 200 mmHg. VLE data for the tetraline/*m*-cresol system have been previously reported at isothermic

Table II. Densities at 25 °C of *m*-Cresol (*m*-c)/Tetraline (T) and Refractive Indices at 25 °C of *o*-Toluidine (*o*-t)/Tetraline (T) and *m*-Toluidine (*m*-t)/Tetraline (T)

$x_{m\text{-c}}$	d, g/cm^3	$x_{o\text{-t}}$	n_D	$x_{m\text{-t}}$	n_D
0.0000	0.9660	0.0000	1.5393	0.0000	1.5393
0.0848	0.9692	0.0795	1.5408	0.1172	1.5411
0.1338	0.9715	0.1459	1.5421	0.2310	1.5432
0.2481	0.9775	0.2439	1.5442	0.3436	1.5456
0.3564	0.9837	0.3498	1.5469	0.4439	1.5480
0.4673	0.9905	0.4618	1.5501	0.5619	1.5512
0.5508	0.9958	0.5526	1.5527	0.6081	1.5524
0.6419	1.0021	0.6564	1.5560	0.6484	1.5535
0.7317	1.0086	0.7381	1.5591	0.7429	1.5566
0.8227	1.0157	0.8333	1.5627	0.8350	1.5597
0.9100	1.0228	0.9237	1.5666	0.9178	1.5627
1.0000	1.0303	1.0000	1.5700	1.0000	1.5658

Table III. VLE Data for the *m*-Cresol (1)/Tetraline (2) System at 200 mmHg

x_1	y_1	T, °C	γ_1	γ_2	ϕ_1	ϕ_2
0.000	0.000	157.00		1.0000	0.9969	0.9827
0.109	0.176	154.00	1.8047	1.0077	0.9923	0.9826
0.163	0.245	153.20	1.7271	1.0072	0.9907	0.9829
0.249	0.320	152.30	1.5237	1.0394	0.9891	0.9833
0.361	0.402	151.85	1.3412	1.0893	0.9875	0.9841
0.433	0.443	151.50	1.2475	1.1559	0.9868	0.9846
0.441	0.448	151.50	1.2387	1.1620	0.9867	0.9846
0.481	0.483	151.50	1.2244	1.1722	0.9862	0.9851
0.549	0.527	151.50	1.1705	1.2341	0.9856	0.9857
0.551	0.524	151.50	1.1596	1.2475	0.9856	0.9857
0.580	0.543	151.50	1.1415	1.2804	0.9853	0.9860
0.583	0.552	151.50	1.1545	1.2642	0.9852	0.9861
0.601	0.568	151.55	1.1503	1.2720	0.9850	0.9864
0.608	0.561	151.55	1.1231	1.3157	0.9851	0.9863
0.619	0.577	151.65	1.1306	1.3004	0.9849	0.9865
0.643	0.590	151.80	1.1071	1.3389	0.9848	0.9868
0.738	0.655	152.40	1.0486	1.5070	0.9842	0.9880
0.806	0.726	153.40	1.0279	1.5674	0.9838	0.9895
0.836	0.758	153.60	1.0275	1.6276	0.9836	0.9902
0.893	0.823	154.50	1.0125	1.7751	0.9834	0.9917
1.000	1.000	157.10	1.0000		0.9834	0.9962

Table IV. VLE Data for the *o*-Toluidine (1)/Tetraline (2) System at 200 mmHg

x_1	y_1	T, °C	γ_1	γ_2	ϕ_1	ϕ_2
0.000	0.000	157.00		1.0000	0.9943	0.9827
0.033	0.055	156.40	1.4997	0.9900	0.9933	0.9826
0.076	0.107	155.75	1.2936	0.9985	0.9924	0.9826
0.100	0.149	155.10	1.3981	0.9963	0.9917	0.9826
0.136	0.205	154.30	1.4515	0.9934	0.9907	0.9826
0.168	0.245	154.00	1.4180	0.9887	0.9901	0.9827
0.201	0.284	153.50	1.3965	0.9915	0.9895	0.9828
0.250	0.314	153.05	1.2598	1.0260	0.9891	0.9829
0.281	0.358	152.70	1.2926	1.0125	0.9885	0.9832
0.325	0.395	152.35	1.2473	1.0273	0.9880	0.9834
0.379	0.436	151.80	1.2022	1.0588	0.9875	0.9836
0.423	0.477	151.45	1.1921	1.0682	0.9870	0.9839
0.471	0.516	151.35	1.1620	1.0816	0.9866	0.9843
0.510	0.541	151.20	1.1307	1.1126	0.9864	0.9845
0.547	0.569	151.15	1.1107	1.1318	0.9861	0.9848
0.580	0.593	151.10	1.0935	1.1545	0.9859	0.9851
0.615	0.621	151.10	1.0799	1.1728	0.9857	0.9854
0.657	0.652	151.10	1.0613	1.2088	0.9855	0.9858
0.692	0.678	151.20	1.0444	1.2417	0.9853	0.9861
0.743	0.724	151.25	1.0370	1.2735	0.9851	0.9868
0.796	0.770	151.30	1.0277	1.3349	0.9848	0.9874
0.859	0.850	151.50	1.0444	1.2518	0.9846	0.9887
0.912	0.900	151.85	1.0296	1.3227	0.9845	0.9896
0.955	0.952	152.50	1.0180	1.2170	0.9845	0.9906
1.000	1.000	153.30	1.0000		0.9847	0.9915

Table V. VLE Data for the *m*-Toluidine (1)/Tetraline (2) System at 200 mmHg

x_1	y_1	T, °C	γ_1	γ_2	ϕ_1	ϕ_2
0.000	0.000	157.00		1.0000	0.9935	0.9827
0.032	0.043	156.50	1.3432	0.9985	0.9927	0.9826
0.084	0.123	155.80	1.4974	0.9876	0.9912	0.9826
0.121	0.178	155.10	1.5391	0.9854	0.9903	0.9827
0.165	0.236	154.55	1.5236	0.9804	0.9894	0.9828
0.211	0.269	154.30	1.3692	1.0003	0.9889	0.9829
0.250	0.305	153.80	1.3320	1.0159	0.9884	0.9830
0.284	0.339	153.40	1.3206	1.0245	0.9879	0.9832
0.330	0.374	153.05	1.2684	1.0481	0.9874	0.9834
0.368	0.410	152.90	1.2532	1.0521	0.9869	0.9836
0.411	0.443	152.55	1.2265	1.0773	0.9865	0.9838
0.456	0.476	152.35	1.1957	1.1040	0.9862	0.9841
0.523	0.521	152.20	1.1468	1.1563	0.9857	0.9845
0.568	0.558	152.20	1.1310	1.1782	0.9854	0.9849
0.630	0.615	152.30	1.1201	1.1945	0.9849	0.9855
0.681	0.652	152.60	1.0876	1.2408	0.9847	0.9860
0.726	0.688	152.90	1.0659	1.2832	0.9845	0.9865
0.769	0.730	153.30	1.0537	1.3011	0.9844	0.9872
0.814	0.777	153.65	1.0474	1.3204	0.9842	0.9879
0.852	0.813	154.00	1.0350	1.3767	0.9841	0.9885
0.892	0.856	154.40	1.0273	1.4352	0.9840	0.9892
0.926	0.890	154.85	1.0138	1.5782	0.9840	0.9898
0.960	0.951	155.35	1.0280	1.2810	0.9840	0.9909
0.986	0.983	155.75	1.0212	1.2545	0.9841	0.9915
1.000	1.000	156.15	1.0000		0.9841	0.9918

conditions (T = 150, 175, and 190 °C) (*1*).

Experimental Section

All the chemicals, tetraline (>97% GC), *m*-cresol (>98% GC), and analytical grade *o*-toluidine (>99.5% GC) and *m*-toluidine (>99% GC), were supplied by Fluka. They were further purified in a distillation column under vacuum and stored away from light. Analysis of the distilled products was carried out by gas chromatography, and some physical properties were also measured. These physical properties of the chemicals are given in Table I.

Vapor-liquid equilibrium and some vapor-pressures of the pure components were measured by using a recirculation still of the Gillespie type (*4*) as modified by Röck and Sieg (*5*). The still is a commercial unit manufactured by Fritz GmbH (Normag) (Hofheim, Federal Republic of Germany). The temperature was measured with a mercury-in-glass thermometer (0.1 °C divisions) calibrated against a standard thermometer. Pressures were measured with a mercury manometer (±0.5 mmHg).

Compositions of the vapor and liquid phases were determined by gas-liquid chromatography (GLC, Perkin Elmer, Model 990, flame ionization detector) and density or refractive index at 25 °C. No significant differences in composition were found. The chromatographic column (3 m × 0.3 cm) was packed with 15% Carbowax 1500 on Chromosorb WHP 60/80 mesh. Chromatographic analyses were carried out at the following column temperatures: *m*-cresol (170 °C), *o*-toluidine (165 °C), and *m*-toluidine (150 °C).

Experiments were begun by evacuating the equilibrium still and filling it with dried nitrogen and then the still was filled with the system under investigation. Once the system reached steady state, samples of both phases were withdrawn for analysis.

Results and Discussion

Densities, d, at 25 °C for the system *m*-cresol/tetraline and refractive indices, n_D, at 25 °C for the systems *o*-toluidine/tetraline and *m*-toluidine/tetraline are presented in Table II.

Experimental VLE data for the binary systems of *m*-cresol, *o*-toluidine, and *m*-toluidine with tetraline are listed in Tables III–V as well as the vapor-phase fugacity coefficients and liquid-phase activity coefficients. The x-y diagram for the aforementioned systems is shown in Figure 1.

The liquid-phase activity coefficient of a component i in a nonideal mixture is given by the equation

$$\phi_i y_i P = x_i \gamma_i \phi_i^s P_i^s \exp[v_i(P - P_i^s)/RT]$$

Table VI. Vapor Pressure Data for *m*-Toluidine, Tetraline, and *m*-Cresol[a]

m-toluidine		tetraline		*m*-cresol	
T_{exp}	P_{exp}	T_{exp}	P_{exp}	T_{exp}	P_{exp}
146.35	144.20	147.30	148.00	148.30	146.70
147.55	149.15	150.20	162.20	151.90	167.50
150.40	163.95	153.10	177.00	154.20	181.80
151.40	170.00	155.20	189.20	156.30	195.80
153.65	183.70	157.00	200.00	157.05	200.00
156.15	200.00	161.05	226.30	157.10	200.00
159.10	219.90	164.40	248.80	160.35	223.50
160.40	230.10	166.60	265.50	163.40	247.70
162.80	248.90			165.75	267.30
165.90	274.40				

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

Table VII. Antoine Equation Parameters

compound	*A*	*B*	*C*
m-toluidine	15.071 9	11297.2	728.386
tetraline	7.530 15	2078.61	240.491
m-cresol	6.109 50	975.505	99.130
o-toluidine[a]	7.032 10	1575.64	179.900

[a] Reference 6.

where ϕ_i is the fugacity coefficient; y_i, the vapor-phase mole fraction; P, the total pressure, γ_i, the activity coefficient at system T and P; x_i, the liquid-phase mole fraction; T, temperature; ϕ_i^s, the pure-component fugacity coefficient at saturation; P_i^s, the pure-component saturation pressure; v_i, the liquid molar volume; and R, the universal gas constant.

The exponential term (Poynting correction) was taken as unity for the experimental conditions of this work. Vapor pressures were measured for tetraline (147–167 °C), *m*-cresol (148–166 °C), and *m*-toluidine (146–166 °C); experimental data are shown in Table VI.

Table VII shows the Antoine equation parameters obtained from experimental data for the aforementioned compounds and the parameters available in the literature for *o*-toluidine (*6*).

Fugacity coefficients ϕ_i and ϕ_i^s were calculated by means of the virial equation of state, and the second virial coefficients were calculated by the Tsonopoulos correlation (*7*). All the fugacity coefficients for this study were between 1.00 (ideal) and 0.98. Therefore, vapor-phase nonideality was assumed to be unimportant to data reduction and correlation of liquid-phase nonideality.

The activity coefficients were correlated with the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations (*8*).

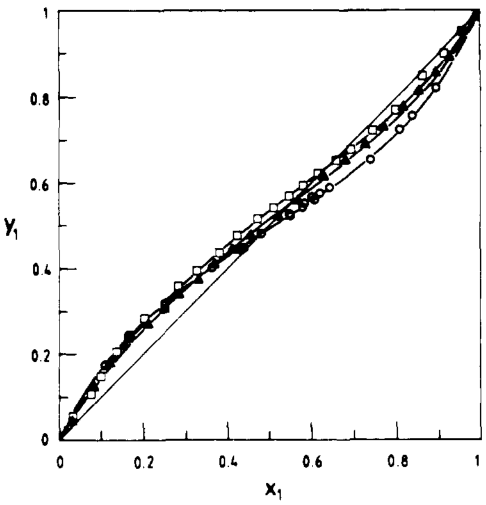

Figure 1. Vapor–liquid equilibrium data of binary systems with tetraline at 200 mmHg: □, *o*-toluidine (1)/tetraline (2); ▲, *m*-toluidine (1)/tetraline (2); ○, *m*-cresol (1)/tetraline (2).

The parameters A_{12} and A_{21} for the correlation equations, mean absolute deviations, and activity coefficients at infinite dilution are listed in Table VIII. Mean absolute deviations between experimental and calculated temperatures (MAD *T*) and vapor compositions (MAD *Y*) are of the order of the estimated experimental uncertainty.

The experimental data are thermodynamically consistent according to the criteria of Van Ness et al. (*9*) and Christiansen and Fredenslund (*10*).

All of the systems show positive deviations from Raoult's law. In the absence of specific interactions, the aromatic/aromatic systems show small positive deviations from ideality (*11*). Nevertheless, if one substituent is self-associating, large positive deviations can result. For example, *m*-cresol is strongly self-associating by hydrogen bonds, leading to more significant deviations from Raoult's for the *m*-cresol/tetraline system. The extrapolated infinite-dilution activity coefficients for this system are γ_1^∞ = 2.08 and γ_2^∞ = 2.04.

Toluidines are also self-associated by hydrogen bonds; however, N–HN bonds are weaker than O–HO bonds, and therefore, positive deviations from Raoult's law are lower for the *o*-toluidine/tetraline and *m*-toluidine/tetraline systems than for *m*-cresol/tetraline system.

The extrapolated infinite dilution activity coefficients are γ_1^∞ = 1.55 and γ_2^∞ = 1.80 for the *m*-toluidine/tetraline system and

Table VIII. Correlation Parameters for Activity Coefficents[a]

	A_{12}	A_{21}	α_{12}	γ_1^∞	γ_2^∞	(MAD *T*)	(MAD *Y*)
			o-Toluidine (1)/Tetraline (2)				
Margules	0.4159	0.5280		1.52	1.70	0.11	0.0059
Van Laar	0.4253	0.5323		1.53	1.70	0.11	0.0060
Wilson	230.2929	221.6680		1.53	1.70	0.11	0.0060
NRTL	536.5414	-85.6500	0.3001	1.52	1.70	0.11	0.0060
UNIQUAC	102.2339	9.3596		1.52	1.70	0.11	0.0060
			m-Toluidine (1)/Tetraline (2)				
Margules	0.4280	0.5767		1.53	1.78	0.15	0.0062
Van Laar	0.4357	0.5896		1.55	1.80	0.16	0.0061
Wilson	183.9003	318.3238		1.55	1.80	0.15	0.0060
NRTL	661.7960	-156.2685	0.2982	1.54	1.79	0.15	0.0061
UNIQUAC	171.3714	-46.1516		1.54	1.79	0.15	0.0060
			m-Cresol (1)/Tetraline (2)				
Margules	0.7390	0.7162		2.09	2.05	0.07	0.0037
Van Laar	0.7391	0.7164		2.09	2.05	0.07	0.0037
Wilson	598.5158	86.8137		2.10	2.05	0.07	0.0037
NRTL	284.0059	370.5433	0.2991	2.08	2.04	0.07	0.0036
UNIQUAC	-98.9869	300.6127		2.08	2.04	0.07	0.0037

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

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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