Table II. Measured Solubility of Oxygen at Various Concentration Levels of Three Sodium Salts[a]

sodium formate		sodium acetate		sodium adipate	
concn, mol/L	O_2, solubility, mg of O_2/L	concn, mol/L	O_2, solubility, mg of O_2/L	concn, mol/L	O_2, solubility, mg of O_2/L
0	9.2	0	9.2	0	9.2
0.5	7.5	0.25	8.4	0.083	8.2
1.0	6.5	0.50	7.7	0.21	7.2
2.0	4.7	1.0	6.4	0.31	6.6
3.0	3.2	2.0	4.3	0.42	5.8

[a] The data have been adjusted to 10^5 Pa; 20 °C and air.

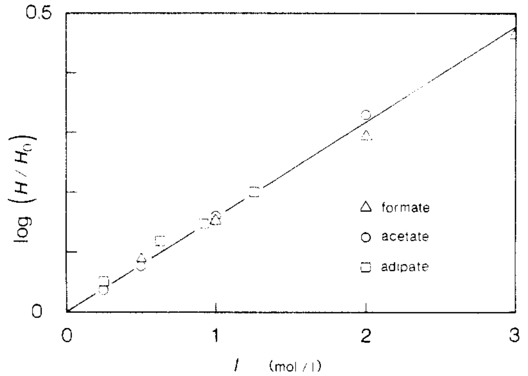

Figure 1. Plot of experimental data for organic sodium salts, using the parameters of eq 1; change in Henry's law constant for oxygen as a function of ion strength.

and dividing by 10^5. Calculated solubilities using eq 1-3 are also included in Table I; the salting-out parameters for oxygen, sodium ion, and chloride ion, respectively, are given by Onda et al. (*4*). When the experiments are compared with the predicted solubilities, it is seen that the mean deviation is less than 2%.

Experimental data using the organic sodium salts are given in Table II. Each point is a mean value of two to four measurements. The data as given in the table have been adjusted to 10^5 Pa as described above.

In all cases it was possible to reproduce the experimental data with an accuracy of greater than 0.1 mg of O_2/L. Figure 1 shows a plot of the experiments by using the parameters of eq 1. The straight line corresponds to a least-squares fit of all measurements; least-squares fits for each individual salt deviated by less than 2% from the mean value.

The salting-out parameter for the three anions can be obtained by subtracting the salting-out parameters for oxygen and sodium ion from the slope of the straight line in the figure. If one uses data given by Onda et al. ($h_+ = -0.0183$ and $h_g = -0.1771$), the value is: $h_- = 0.348$. On the other hand, if data given by Danckwerts are used ($h_+ = 0.091$ and $h_g = 0.028$), the following result is obtained: $h_- = 0.034$. The discrepancy stems from the fact that the two authors apply disimilar standard states; Danckwerts uses a system were the salting-out parameter for H^+ is zero. Both values give about the same result, provided the salting-out parameters for the anion and the gas are taken from the appropriate set of data.

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Vapor-Liquid Equilibria in Binary Systems Containing 1,3-Dioxolane at Isobaric Conditions. 3. Binary Mixtures of 1,3-Dioxolane with *o*-, *m*-, and *p*-Xylenes

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The vapor-liquid equilibrium data of the binary mixtures of 1,3-dioxolane with *o*-, *m*-, and *p*-xylenes were determined with a Stage-Müller apparatus at 300, 500, and 740 mmHg. The activity coefficients of the components were correlated by means of the Wilson equation, the parameters of which show marked differences in the three mixtures. The volatility of *m*- and *p*-xylenes, which have close boiling temperatures, are affected in the same way by 1,3-dioxolane.

In previous works (*1*-*3*), we studied the vapor-liquid equilibria of the binary systems of 1,3-dioxolane with water (*1*), 1,2-*trans*-dichloroethylene (*2*), trichloroethylene (*2*), tetrachloroethylene (*2*), and toluene (*3*). In this paper we extend our study to the binary mixtures of 1,3-dioxolane with *o*-, *m*-, and *p*-xylenes. Since *m*- and *p*-xylenes are a closely boiling pair at pressures near atmospheric and 1,3-dioxolane is more volatile than these aromatic compounds, this study makes a contribution to the problem of separating mixtures of similar compounds by treating 1,3-dioxolane as a possible separating

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Table I. *P-t-x-y* Data

$P = 300$ mmHg			$P = 500$ mmHg			$P = 740$ mmHg		
t/°C	x_1	y_1	t/°C	x_1	y_1	t/°C	x_1	y_1
1,3-Dioxolane-*o*-Xylene								
48.9	1.000	1.000	62.4	1.000	1.000	73.8	1.000	1.000
52.3	0.813	0.980	67.9	0.776	0.969	80.4	0.750	0.970
56.4	0.676	0.965	71.9	0.602	0.952	83.4	0.649	0.949
60.8	0.534	0.946	75.3	0.495	0.930	88.1	0.524	0.925
70.2	0.312	0.869	90.8	0.231	0.795	93.0	0.395	0.885
76.5	0.235	0.804	96.3	0.159	0.738	107.9	0.205	0.746
81.2	0.180	0.745	100.2	0.135	0.685	114.5	0.136	0.649
86.0	0.135	0.685	110.2	0.075	0.535	120.1	0.095	0.604
90.8	0.100	0.605	117.3	0.050	0.382	123.4	0.075	0.490
95.5	0.070	0.516	120.0	0.035	0.290	132.4	0.035	0.301
99.2	0.049	0.417	122.2	0.025	0.225	135.0	0.025	0.295
106.5	0.016	0.217	124.6	0.010	0.150	136.6	0.020	0.175
108.2	0.013	0.165	127.4	0.005	0.060	138.3	0.015	0.126
113.3	0.000	0.000	129.2	0.000	0.000	140.0	0.010	0.080
						142.7	0.000	0.000
1,3-Dioxolane-*m*-Xylene								
48.8	1.000	1.000	62.4	1.000	1.000	73.8	1.000	1.000
50.9	0.914	0.987	64.4	0.921	0.988	77.5	0.825	0.974
52.5	0.829	0.977	67.2	0.783	0.970	81.2	0.688	0.949
54.5	0.730	0.965	69.3	0.697	0.957	83.9	0.589	0.937
57.7	0.577	0.946	72.2	0.584	0.943	87.5	0.503	0.911
63.7	0.394	0.890	82.7	0.348	0.852	99.2	0.289	0.793
68.2	0.310	0.852	87.7	0.251	0.801	105.5	0.214	0.724
71.8	0.238	0.824	91.3	0.205	0.753	110.6	0.150	0.662
85.2	0.110	0.608	95.8	0.160	0.698	115.4	0.110	0.585
91.3	0.067	0.470	99.6	0.125	0.635	120.0	0.070	0.490
101.4	0.014	0.201	104.2	0.090	0.540	125.5	0.037	0.352
114.8	0.005	0.098	108.7	0.067	0.462	133.9	0.010	0.125
106.0	0.003	0.055	119.4	0.012	0.179	136.4	0.005	0.050
107.6	0.000	0.000	122.1	0.009	0.075	137.8	0.000	0.000
			124.1	0.000	0.000			
1,3-Dioxolane-*p*-Xylene								
48.9	1.000	1.000	62.4	1.000	1.000	73.8	1.000	1.000
54.0	0.796	0.971	70.7	0.688	0.951	82.2	0.716	0.948
56.9	0.676	0.953	74.8	0.547	0.924	87.2	0.548	0.917
60.7	0.542	0.915	78.8	0.426	0.904	92.2	0.425	0.877
67.0	0.375	0.855	85.9	0.300	0.825	100.0	0.280	0.790
76.9	0.200	0.737	90.7	0.234	0.759	107.5	0.177	0.691
83.5	0.130	0.642	97.2	0.160	0.651	115.0	0.132	0.571
86.0	0.115	0.595	102.2	0.122	0.570	119.2	0.100	0.490
91.9	0.080	0.474	105.0	0.100	0.520	125.0	0.065	0.315
99.9	0.032	0.263	107.2	0.085	0.480	127.3	0.048	0.306
101.4	0.025	0.205	110.6	0.066	0.408	131.3	0.026	0.186
106.9	0.000	0.000	117.6	0.034	0.226	137.2	0.000	0.000
			123.2	0.000	0.000			

Table II. Values of Constants *A* and *B* in the Vapor Pressure Expression $\log P = A + B/T$ for 1,3-Dioxolane and the Xylenes

	dioxolane	*o*-xylene	*m*-xylene	*p*-xylene
A	7.9456	7.8660	7.7891	7.6188
B	−1761.0	−2078.6	−2021.4	−1950.3

agent in an azeotropic distillation process.

Experimental Section

1,3-Dioxolane was a Fluka product analytical grade, 99%; for purification see ref *1*; *o*-, *m*-, and *p*-xylenes were Carlo Erba RPE products. Major impurities in the xylenes are benzene (0.15%), toluene (0.15%), and ethylbenzene (0.15%).

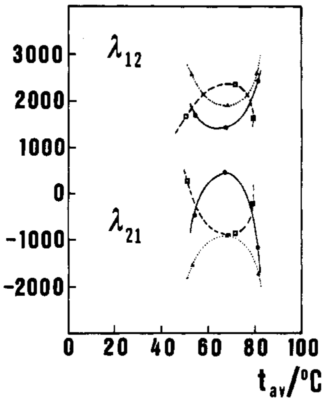

Figure 1. Values of the parameters λ_{12} and λ_{21} in the Wilson equation as a function of the average temperature in the isobaric set of vapor–liquid data for the binary mixtures of 1,3-dioxolane with *o*-xylene (—), *m*-xylene (– – –), and *p*-xylene (···).

The vapor–liquid data were obtained with a Stage-Müller apparatus, described elsewere (*4*), at pressures $p = 300$, 500, and 740 mmHg. *P-t-x-y* data are shown in Table I, with estimated uncertainties of 2 mmHg, 0.1 °C, and 0.2%, 0.2%, respectively; t is the temperature (°C); x_1 and y_1 are the mole fractions of 1,3-dioxolane in the liquid and vapor phases, respectively, and were obtained with an Abbe refractometer. The refractive index–composition data for the mixtures of 1,3-dioxolane with *o*-, *m*-, and *p*-xylenes are reported in Table A. (See paragraph at end of text regarding supplementary material.) The literature refractive indexes ($n^{25}{}_{D}$) of *o*-, *m*-, and *p*-xylene are 1.502 95, 1.494 64, and 1.493 25, respectively. The vapor pressures of 1,3-dioxolane and of the xylenes are given by the usual expression $\log P = A + B/T$ (P in mmHg; T is the absolute temperature), with constants A and B obtained from a best fit of our vapor–liquid data (see Table II). The activity coefficients γ_1 and γ_2, calculated from the Wilson equation

$$\ln \gamma_k = -\ln (x_k + \Lambda_{kj}x_j) + x_j\{\Lambda_{kj}/(x_k + \Lambda_{kj}x_j) - \Lambda_{jk}/(x_j + \Lambda_{jk}x_k)\} \quad (1)$$

where

$$\Lambda_{kj} = v_j/v_k \exp(-\lambda_{kj}/RT) \qquad k = 1, 2;\ k \neq j \quad (2)$$

and λ_{kj} = adjustable parameters, obtained with a least-squares procedure, are shown in Table B (supplementary material), together with σ, the root-mean-square deviation in the least-squares method, evaluated at the minimum value of the objective function used in ref *1* and *2*, whereas the parameters λ_{kj} appear in Table III. Figure 1 reports the dependence of the parameters λ_{kj} on the temperature (t_{av} is the average temperature in each isobaric set of experimental data).

The strong similarity of the xylene isomers agrees with the small differences in the value of γ_1 and γ_2 for the three isomers, with small positive deviations of the liquid phase from ideality. Hence, 1,3-dioxolane seems not to act as a separating agent in an azeotropic distillation of *m*- and *p*-xylenes, since the activity coefficients γ_2 (and volatilities) of these isomers are

Table III. Values of the Parameters λ_{12} and λ_{21}[a] in the Wilson Equation in the Isobaric Vapor–Liquid Data for the Binary Mixtures of 1,3-Dioxolane with *o*-, *m*-, and *p*-Xylenes

	o-xylene		*m*-xylene		*p*-xylene	
P/mmHg	λ_{12}	λ_{21}	λ_{12}	λ_{21}	λ_{12}	λ_{21}
300	1701.0 ± 42	−442.9 ± 51	1699.3 ± 28	272.5 ± 40	2567.2 ± 48	−1532.8 ± 41
500	1425.5 ± 17	479.8 ± 26	2331.4 ± 29	−852.8 ± 30	1933.0 ± 31	−918.5 ± 34
740	2409.0 ± 21	−1152.9 ± 21	1611.3 ± 23	−180.7 ± 31	2633.5 ± 25	−1753.9 ± 21

[a] Both in units of J/mol.

affected in the same direction by the introduction of 1,3-dioxolane. The parameters λ_{12} and λ_{21} are about the same magnitude for the three systems but vary differently with temperature.

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Supplementary Material Available: Table A, listing refractive index–composition data of 1,3-dioxolane with *o*-, *m*- and *p*-xylenes; and Table B, listing values of γ_k, calculated from the Wilson equation, for the systems 1,3-dioxolane/*o*-, *m*-, or *p*-xylenes at 300, 500, and 740 mmHg (10 pages). Ordering information is given on any current masthead page.

Vapor–Liquid Equilibrium in Binary Mixtures of Nitrogen and Quinoline

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Compositions of saturated vapor and liquid mixtures of nitrogen and quinoline at equilibrium were experimentally determined at 462, 542, 624, and 704 K at pressures of 20–254 bar. A flow apparatus was employed to minimize residence time and thermal decomposition of quinoline in the high temperature zone.

Introduction

This work is part of a continuing study of phase equilibrium in asymmetric mixtures of light solutes and heavy solvents. The objective is to enlarge the state of knowledge in the direction of high temperature for high-pressure systems and to extend it to new solutes and solvents. In this work we report the phase behavior of mixtures of nitrogen + quinoline. There are no previous investigations of this binary system.

Experimental Method and Materials

A flow apparatus was used in this work to achieve short residence time and thereby to minimize thermal decomposition of quinoline at high temperature. The experimental apparatus and procedure were described by Simnick and co-workers (*1*, *2*). A minor change has been made in the apparatus with the addition of a Heise gauge (Model CMM) which reads pressures below 34 bar to an increased accuracy of ±0.03 bar.

The temperature of the equilibrium cell was kept constant within 0.2 K during the course of measurement of a complete isotherm. Nitrogen gas was supplied by Airco with a reported purity of 99.995+%. Quinoline purchased from Fisher Scientific Co. was certified reagent grade of 99+% purity. Samples from the condensates of both the overhead and the bottom cell effluents were collected at all conditions studied and analyzed for thermal decomposition by gas chromatography. The analysis showed a small amount of impurities in the condensates from experiments at the higher temperatures. The sum of the peak areas of the impurities amounted to about 1.5% of the total peak areas at the highest temperature of this work. The samples from the cell bottom effluent showed a dark brown color.

Table I. Nitrogen + Quinoline Vapor–Liquid Equilibrium Data

p, bar	x_N	y_N	K_N	K_Q
		462.1 K		
20.82	0.00868	0.98375	113.34	0.0164
30.34	0.01294	0.98795	76.38	0.0122
50.9	0.01985	0.99204	49.98	0.0081
101.3	0.03873	0.99470	25.69	0.0055
150.8	0.05589	0.99513	17.81	0.0052
202.0	0.07331	0.99522	13.58	0.0052
252.7	0.08884	0.99497	11.20	0.0055
		541.9 K		
20.38	0.0103	0.8975	87.13	0.1036
30.36	0.0158	0.9272	58.85	0.0739
50.20	0.0264	0.9523	36.11	0.0490
101.7	0.0533	0.9701	18.21	0.0316
152.3	0.0774	0.9758	12.61	0.0263
203.0	0.1019	0.9775	9.594	0.0251
253.7	0.1243	0.9782	7.868	0.0249
		623.9 K		
20.37	0.0107	0.6037	56.47	0.4006
30.17	0.0178	0.7145	40.20	0.2907
51.0	0.0335	0.8156	24.35	0.1907
101.5	0.0704	0.8886	12.63	0.1198
151.6	0.1055	0.9037	8.566	0.1077
201.8	0.1397	0.9212	6.596	0.0916
253.7	0.1738	0.9260	5.330	0.0895
		703.7 K		
30.80	0.0124	0.2661	21.40	0.7431
51.2	0.0357	0.4889	13.70	0.5300
102.1	0.0926	0.6784	7.330	0.3544
153.4	0.1465	0.7421	5.065	0.3022
203.0	0.2014	0.7682	3.814	0.2902
252.9	0.2516	0.7831	3.112	0.2898

Results

Measurements were made at four temperatures: 462.1, 541.9, 623.9, and 703.7 K. Seven pressures were observed from 20 to 254 bar at each of the three lower temperatures. Observation started at a higher pressure of 30 bar at the highest temperature owing to the elevated vapor pressure of quinoline.

Table I presents the mole fractions x of the saturated liquid and y of the saturated vapor at various temperatures T and

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