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Extraction of Furfural from Aqueous Solutions with Chlorinated Hydrocarbons

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Liquid–liquid equilibrium data at 25 °C are reported for five ternary systems containing furfural, water, and the chlorinated hydrocarbons trichloroethylene, perchloroethylene, 1,2-dichloroethane, 1,1,1-trichloroethane, and 1,1,2-trichloroethane. Equilibrium data have been correlated by the method of Bachman as modified by Brown. Among the solvents studied, 1,2-dichloroethane and trichloroethylene show the highest selectivities.

The separation of furfural from aqueous solutions is of particular interest due to the significant demand for this product as a selective solvent in petroleum refining and as starting material for synthesis.[1] Furfural can be obtained by hydrolysis of pentosans-containing agricultural residues, the reaction being catalyzed by sulfuric acid; it is recovered from the reaction mixture by steam distillation. A complete recovery of furfural by distillation is not easy since when aqueous solutions of furfural are distilled at atmospheric pressure a minimum-boiling heteroazeotrope is formed, which contains 35% of furfural by weight.[2] Upon condensing, the organic phase contains 84.1% of furfural by weight and 18.4% is contained in the water phase.

Solvent extraction recovery of furfural from aqueous solutions with low content of solute can be a suitable industrial method and data on liquid–liquid extraction of furfural have been reported.[3-7] In an attempt to find suitable solvents for extraction of furfural, we used Ewell's rule as selection criteria,[8] and liquid–liquid equilibrium data with trichloroethylene, perchloroethylene, 1,2-dichloroethane, 1,1,1-trichloroethane, and 1,1,2-trichloroethane as solvents were studied at 25 °C.

Chemicals

Furfural and 1,2-dichloroethane were supplied by Probus Chemicals and trichloroethylene, perchloroethylene, 1,1,1-trichloroethane, and 1,1,2-trichloroethane by Fluka. All the solvents were of laboratory reagent grade and were further purified by distillation in a column filled with heli-packing with automatic regulation of the reflux ratio, the middle fraction being collected. Pure distilled water was used.

Furfural was distilled at reduced pressure (12 mmHg), the middle fraction was collected and stored in a closed automatic buret under nitrogen. Decomposition of furfural through autoxidation for a period of 5 days, average time for every set of experiments, was negligible; a slight color change was observed but it did not affect solubility data.

The physical properties of the products used along with the literature values are given in Table I.

Table I. Physical Properties of the Chemicals

	property	value exptl	value lit.	ref
furfural	d (25 °C)	1.1550	1.1550	9
	n_D (25 °C)	1.5237	1.5235	10
trichloroethylene	d (20 °C)	1.4642	1.4642	10
	n_D (20 °C)	1.4774	1.4773	10
perchloroethylene	d (20 °C)	1.6230	1.6227	10
	n_D (20 °C)	1.5058	1.5053	10
1,2-dichloroethane	d (20 °C)	1.2530	1.2531	10
	n_D (20 °C)	1.4449	1.4448	10
1,1,1-trichloroethane	d (20 °C)	1.3303	1.3390	10
	n_D (20 °C)	1.4366	1.4379	10
1,1,2-trichloroethane	d (20 °C)	1.4401	1.4397	10
	n_D (20 °C)	1.4711	1.4714	10

Table II. Mutual Solubility and Tie-Line Data for Furfural (F)–Water (W)–Trichloroethylene (S1) at 25 °C[a]

Mutual Solubility Data

F	W	S1	d_4^{26}	$n^{26}{}_D$
		Organic Phase		
0.00	0.03	99.97	1.4544	1.4744
11.72	0.11	88.17	1.4108	1.4815
20.32	0.22	79.46	1.3804	1.4868
26.11	0.27	73.62	1.3605	1.4898
35.75	0.43	63.82	1.3288	1.4949
40.53	0.61	58.85	1.3134	1.4972
45.04	0.70	54.26	1.2993	1.4998
47.73	0.75	51.52	1.2905	1.5004
54.55	1.08	44.37	1.2694	1.5038
59.52	1.22	39.25	1.2546	1.5059
64.29	1.56	34.15	1.2394	1.5073
73.06	2.04	24.90	1.2134	1.5104
80.34	2.97	16.69	1.1911	1.5122
86.44	3.54	10.02	1.1728	1.5131
94.97	5.03	0.00	1.1467	1.5143
		Aqueous Phase		
0.00	99.89	0.01	0.9972	1.3322
2.00	97.83	0.17	1.0006	1.3361
4.01	95.78	0.20	1.0039	1.3398
6.00	93.88	0.12	1.0076	1.3435
8.43	91.57	0.00	1.0115	1.3474

Tie-Line Data

aqueous phase			organic phase		
F	W	S1	F	W	S1
6.47	93.42	0.11	71.96	1.94	26.10
5.82	94.05	0.13	61.52	1.18	37.20
5.53	94.32	0.15	54.77	0.92	44.31
5.12	94.71	0.17	48.16	0.64	51.20
4.53	95.28	0.19	38.84	0.55	60.61
3.76	96.04	0.20	28.60	0.29	71.11
2.29	97.53	0.18	12.16	0.14	87.70

[a] Values expressed in weight percent.

Experimental Procedure

The mutual solubility line (binodal curve) and tie-line data were determined at a constant temperature of 25 ± 0.05 °C. The solubility line was determined following Othmer's method[11] by titrating mixtures of known composition of two components with the third one, until a permanent turbidity was observed. The mixture of known composition was kept in an Erlenmeyer flask with a silicon gum stopper to prevent evaporation and was titrated by adding the third component through a needle inserted in the stopper, while maintaining a constant agitation by means

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Table III. Mutual Solubility and Tie-Line Data for Furfural (F)-Water (W)-Perchloroethylene (S2) at 25 °C[a]

Mutual Solubility Data

F	W	S2	d_4^{26}	n^{26}_D
		Organic Phase		
0.00	0.01	99.99	1.6134	1.5027
19.93	0.17	79.90	1.4902	1.5061
29.16	0.41	70.43	1.4339	1.5081
35.56	0.48	63.97	1.4074	1.5099
43.22	0.74	56.04	1.3695	1.5111
53.89	1.11	45.00	1.3201	1.5130
56.25	1.18	42.57	1.3095	1.5135
64.84	1.67	33.49	1.2718	1.5144
67.80	1.80	30.40	1.2595	1.5149
75.06	2.41	22.53	1.2286	1.5154
89.04	4.06	6.90	1.1708	1.5151
94.97	5.03	0.00	1.1467	1.5143
		Aqueous Phase		
0.00	99.98	0.02	0.9964	1.3322
1.85	98.00	0.15	1.0001	1.3359
4.16	95.60	0.23	1.0043	1.3400
6.11	93.78	0.11	1.0078	1.3435
8.43	91.57	0.00	1.0115	1.3474

Tie-Line Data

aqueous phase			organic phase		
F	W	S2	F	W	S2
7.30	92.64	0.06	73.96	2.24	23.80
6.31	93.59	0.10	62.38	1.32	36.30
6.08	93.80	0.12	54.50	1.09	44.41
5.84	94.03	0.13	47.25	0.85	51.90
5.60	94.25	0.15	36.10	0.70	63.20
5.60	94.25	0.15	31.30	0.52	68.18
5.50	94.34	0.16	27.75	0.45	71.80
4.67	95.13	0.20	10.75	0.05	89.20

[a] Values expressed in weight percent.

Table IV. Mutual Solubility and Tie-Line Data for Furfural (F)-Water (W)-1,2-Dichloroethane (S3) at 25 °C[a]

Mutual Solubility Data

F	W	S3	d_4^{26}	n^{26}_D
		Organic Phase		
0.00	0.18	99.82	1.2435	1.4419
15.36	0.32	84.32	1.2270	1.4549
23.59	0.51	75.90	1.2185	1.4612
31.45	0.64	67.91	1.2109	1.4680
39.86	0.85	59.29	1.2024	1.4750
47.50	1.12	51.37	1.1949	1.4810
55.42	1.39	43.19	1.1870	1.4871
63.74	1.81	34.45	1.1789	1.4935
72.12	2.19	25.69	1.1702	1.4998
75.82	2.62	21.56	1.1668	1.5020
87.69	3.85	8.46	1.1545	1.5100
94.97	5.03	0.00	1.1467	1.5143
		Aqueous Phase		
0.00	98.94	1.06	0.9989	1.3330
1.91	97.24	0.85	1.0017	1.3361
4.04	95.37	0.59	1.0049	1.3400
6.29	93.44	0.27	1.0084	1.3440
8.43	91.57	0.00	1.0115	1.3474

Tie-Line Data

aqueous phase			organic phase		
F	W	S3	F	W	S3
6.48	93.26	0.26	81.34	3.06	15.60
5.63	94.00	0.37	71.23	1.97	26.80
5.05	94.51	0.44	60.12	1.58	38.30
3.93	95.48	0.59	49.80	1.20	49.00
3.20	96.12	0.68	41.87	0.93	57.20
2.23	96.96	0.81	29.08	0.52	70.40
1.70	97.42	0.88	20.94	0.36	78.70
0.75	98.25	1.00	11.03	0.27	88.70

[a] Values expressed in weight percent.

Table V. Mutual Solubility and Tie-Line Data for Furfural (F)-Water (W)-1,1,1-Trichloroethane (S4) at 25 °C[a]

Mutual Solubility Data

F	W	S4	d_4^{26}	n^{26}_D
		Organic Phase		
0.00	0.02	99.98	1.3182	1.4329
14.86	0.15	84.96	1.2913	1.4489
22.50	0.27	77.23	1.2778	1.4570
30.22	0.41	69.38	1.2646	1.4651
39.96	0.64	59.40	1.2476	1.4749
46.31	0.81	52.88	1.2366	1.4810
54.40	1.13	44.47	1.2221	1.4885
62.70	1.57	35.73	1.2075	1.4945
70.72	2.10	27.18	1.1932	1.5005
78.78	2.71	18.51	1.1782	1.5060
87.00	3.75	9.25	1.1625	1.5108
94.97	5.03	0.00	1.1467	1.5143
		Aqueous Phase		
0.00	99.99	0.01	0.9967	1.3322
2.09	97.86	0.05	1.0004	1.3361
3.92	96.02	0.05	1.0033	1.3394
6.13	93.86	0.01	1.0076	1.3435
8.43	91.57	0.00	1.0115	1.3474

Tie-Line Data

aqueous phase			organic phase		
F	W	S5	F	W	S5
7.69	92.30	0.01	84.29	3.26	12.45
6.89	93.10	0.01	74.55	2.44	23.01
6.15	93.84	0.01	62.05	1.55	36.40
5.86	94.12	0.02	54.60	0.98	44.42
5.41	94.57	0.02	47.05	0.85	52.10
5.06	94.91	0.03	38.70	0.62	60.70
4.49	95.47	0.04	28.87	0.52	70.61
3.18	96.77	0.05	11.20	0.19	88.61

[a] Values expressed in weight percent.

Table VI. Mutual Solubility and Tie-Line Data for Furfural (F)-Water (W)-1,1,2-Trichloroethane (S5) at 25 °C[a]

Mutual Solubility Data

F	W	S5	d_4^{26}	n^{26}_D
		Organic Phase		
0.00	0.08	99.92	1.4298	1.4681
13.91	0.25	85.84	1.3830	1.4774
21.19	0.37	78.44	1.3590	1.4818
28.68	0.50	70.82	1.3353	1.4862
36.35	0.59	63.06	1.3121	1.4908
44.28	0.87	54.85	1.2881	1.4948
52.42	1.31	46.27	1.2645	1.4989
60.76	1.55	37.69	1.2411	1.5030
69.10	2.12	28.78	1.2177	1.5064
77.60	2.80	19.60	1.1945	1.5097
86.55	3.59	9.87	1.1705	1.5125
94.97	5.03	0.00	1.1467	1.5143
		Aqueous Phase		
0.00	99.49	0.51	0.9982	1.3328
1.96	97.64	0.40	1.0015	1.3361
4.23	95.51	0.29	1.0050	1.3401
6.15	93.70	0.16	1.0080	1.3433
8.43	91.57	0.00	1.0115	1.3474

Tie-Line Data

aqueous phase			organic phase		
F	W	S5	F	W	S5
6.23	93.63	0.14	73.16	2.43	24.41
5.32	94.48	0.20	62.21	1.29	36.20
4.61	95.14	0.25	55.30	1.40	43.30
4.09	95.63	0.28	48.53	1.18	50.29
3.19	96.48	0.33	37.47	0.92	61.61
2.41	97.21	0.38	29.64	0.65	69.71
1.12	98.43	0.45	14.06	0.24	85.70

[a] Values expressed in weight percent.

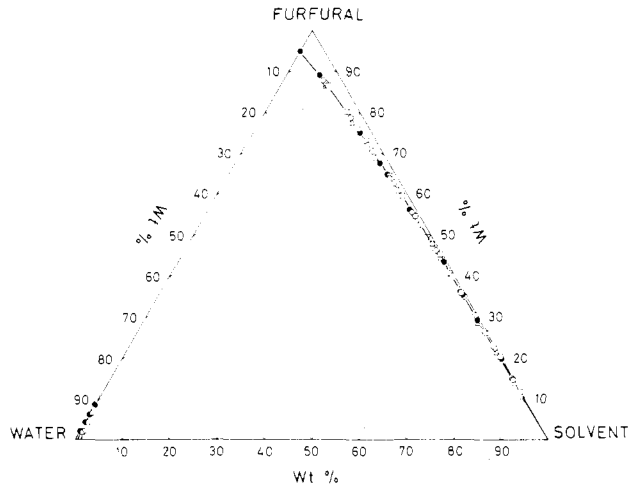

Figure 1. Saturation isotherms for furfural (F)-water (W)-chlorinated hydrocarbons (S) at 25 °C. Solvent: □, trichloroethylene; ●, perchloroethylene; ○, 1,2-dichloroethane; ◇, 1,1,1-trichloroethane; △, 1,1,2-trichloroethane.

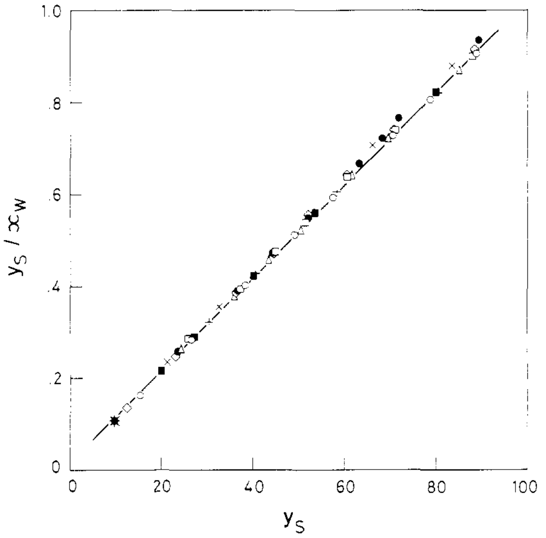

Figure 2. Bachman-Brown plot of tie-line data. Solvent: □, trichloroethylene; ●, perchloroethylene; ○, 1,2-dichloroethane; ◇, 1,1,1-trichloroethane; △, 1,1,2-trichloroethane; ■, methylene chloride; +, chloroform; ×, carbon tetrachloride.

of a magnetic stirrer. The Erlenmeyer flask was immersed in a constant-temperature glass bath, through which water from a Haake FS2 thermostat was circulated. Density and refractive index of each saturated mixture were determined at 26 ± 0.05 °C to avoid the occurrence of turbidity.

For the determination of tie-line data, ternary mixtures having compositions within the two-phase region were prepared. They were shaken throughly in thermostated settling cells and kept at 25 ± 0.05 °C for nearly 4 h to allow separation in two phases. This length of time was enough to obtain clear layers with no apparent change in color of the furfural. Taking samples from both layers and measuring the density and refractive index at 26 ± 0.05 °C, we could determine the composition of furfural in both phases. The complete compositions of the conjugated layers were obtained from the binodal curve.

For the furfural-water-trichloroethylene system, in addition to density and refractive index data, gas chromatography was used as the analytical method. The column used was a stainless steel column (180 × 0.3 cm) filled with UCC W-982 (10%) on Chromosorb W-AW as stationary phase. The internal standard method of analysis with acetone as standard was used. Nitrogen was used as carrier gas at a flow of 5 cm^3/min and a column temperature of 140 °C.

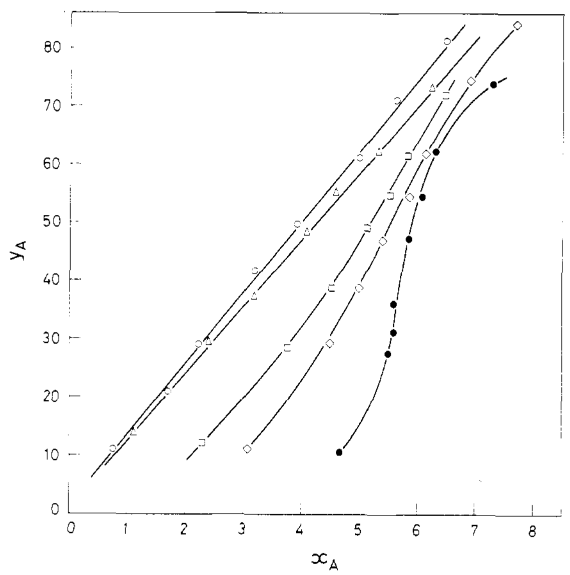

Figure 3. Equilibrium distribution diagram. Solvent: □, trichloroethylene; ●, perchloroethylene; ○, 1,2-dichloroethane; ◇, 1,1,1-trichloroethane; △, 1,1,2-trichloroethane.

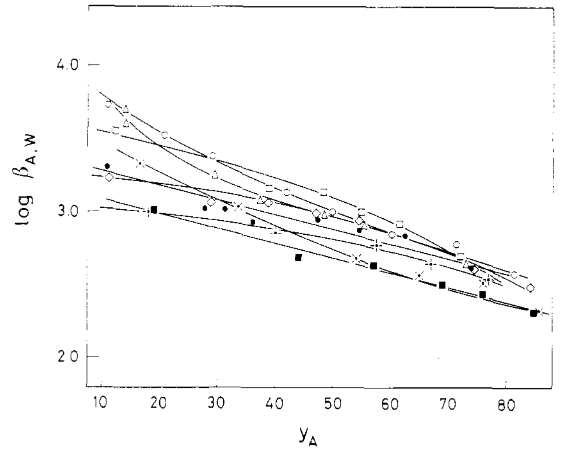

Figure 4. Selectivity plot. Solvent: □, trichloroethylene; ●, perchloroethylene; ○, 1,2-dichloroethane; ◇, 1,1,1-trichloroethane; △, 1,1,2-trichloroethane; ■, methylene chloride; +, chloroform; ×, carbon tetrachloride.

Results and Discussion

The experimental data for the mutual solubility and equilibrium distribution of aqueous solutions of furfural with the solvents trichloroethylene (S1), perchloroethylene (S2), 1,2-dichloroethane (S3), 1,1,1-trichloroethane (S4), and 1,1,2-trichloroethane (S5) are given in Tables II–VI, respectively. Binodal curve data for the five systems are shown in Figure 1. Tie-line data for the system furfural-water-trichloroethylene determined by the three aforementioned methods are in fairly good agreement.

As shown in Figure 1, the mutual solubility lines coincide for the solvent trichloroethylene and perchloroethylene, and in the solvent-rich region the line is practically the same for all the solvent used. The area of the two-phase region increases in the following order of solvents 1,2-dichloroethane > 1,1,2-trichloroethane > trichloroethylene > 1,1,1-trichloroethane; with perchloroethylene as solvent the area is almost the same as with trichloroethylene. Equilibrium data were examined by several correlations reported in the literature.[3,12-15] The Bachman correlation with Brown's modification[16] seemed to fit the data best.

Liquid-liquid equilibrium data reported by Krupatkin and Glagoleva[6] for systems of furfural-water-chloromethanes follow the same correlation and together with data given in this work are shown in Figure 2. Fitting the data by the least squares method leads to the equation

$$y_S/x_W = 0.0102y_S + 0.0145$$

with a correlation coefficient of 0.9995

To evaluate the extractive effectiveness of a solvent, it is useful to study the distribution coefficient and selectivity. These properties can be obtained from Figures 3 and 4, respectively; as seen from the selectivity[17] and distribution diagrams, the order of solvents is 1,2-dichloroethane, 1,1,2-trichloroethane, trichloroethylene, 1,1,1-trichloroethane, and perchloroethylene.

Glossary

A	solute
S	solvent
W	water
d	density
n_D	refractive index
x_A	weight fraction of solute in aqueous phase
x_W	weight fraction of water in aqueous phase
y_A	weight fraction of solute in organic phase
y_S	weight fraction of solvent in organic phase
y_W	weight fraction of water in organic phase

Greek Letters

$\beta_{A,W}$	solvent selectivity ($\beta_{A,W} = y_Ax_W/x_Ay_W$)

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NEW COMPOUNDS

Synthesis and Spectral Properties of β-Anilino-α-(*p*-chlorobenzoyl)styrene Derivatives

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(*p*-Chlorobenzoyl)phenylacetylene reacted with aniline derivatives to give the corresponding β-anilino-α-(*p*-chlorobenzoyl)styrene derivative. NMR, UV, IR, and mass spectra of these compounds are presented. The Hammett correlation is applied to substituent effects on absorption bands. Chemical shift data for the methine proton in these compounds are reported.

The reactions of acetylenic ketones with amine (*1*) and hydrazine derivatives (*2*, *3*) have been reported.

The present investigation was intended to study the reaction of (*p*-chlorobenzoyl)phenylacetylene with aniline derivatives and to account for the manipulated methods and reasoning in establishing the mechanism of this reaction as well as the structure and configuration of the products.

When (*p*-chlorobenzoyl)phenylacetylene (I) was refluxed with aniline derivatives in methanol, it gave the corresponding β-anilino-α-(*p*-chlorobenzoyl)styrene derivative (III) (cf. Figure 1).

The structure and configuration of the reaction products were established spectroscopically and chemically. Thus, their IR spectra show no absorption in the region around 1700 cm^{-1}, the free carbonyl group, and hence structure V was ruled out. The presence of strong bands at 1597–1591 and 1572–1567 cm^{-1} as well as the absence of any absorption in the region 4000–3100 cm^{-1} (Table I) indicated that these compounds are present in chelated form III in which the ν(NH) or ν(OH) absorption may be lowered by intrahydrogen bonding and lie masked under –CH absorption (*4*). The UV spectra of these compounds in ethanol and cyclohexane (Table II) are very similar and show two absorption bands in the regions 385–380 and 262.5–256 nm indicating their structural analogy. The wavelengths and the intensities of these bands are not changed by the polarity of the solvents showing the presence of a strong intrahydrogen bonding system. The ultraviolet or visible absorption in 1% ethanolic ferric chloride do not show any significant change in the wavelength or intensities of absorption bands. This fact gave further evidence for the structure and the stability of these compounds (III) compared with those previously reported by Weinstein and Wyman (*5*). Confirmation of the above conclusion is forthcoming from the NMR spectra of these compounds (Table I). They show a signal in the region 13.01–12.93 ppm (NH), exchangeable with D_2O. The appearance of NH signal and the absence of any signal which can be attributed to the (–CH_2–) group give a further support to the exclusion of structure V. The data in Table III show that the methine proton in this series absorbs in the region 366.2–361.6 Hz and that these shifts depend markedly on the substituent.

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