equivalent solution of iodine in toluene. No more than half the expected amount of iodine reacted; the silver precipitate was heavier than computed, and contained silver chloride. Decomposition with iodine evolution occurred during distillation; no tolyl iodide was obtained; a small, charred iodine colored residue remained.

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Heat Capacity of the Furfuryl Alcohol–Aniline System(1)

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The isobaric heat capacities of furfuryl alcohol–aniline mixtures in the liquid phase at compositions from 0.0 to 1.0 weight fraction furfuryl alcohol were determined at bubble-point pressure in a stainless steel bomb calorimeter. Six sets of heat capacity measurements were made for compositions of approximately 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0 weight fraction furfuryl alcohol in the temperature ranges 50 to 175, 30 to 115, 25 to 100, 30 to 95, 30 to 95, and 30 to 65°, respectively. The density of these mixtures was determined for atmospheric pressure at 5, 40, and 70°. The refractive index of these mixtures was determined at 25°.

Table I

Smoothed Values of Isobaric Heat Capacity of Furfuryl Alcohol-Aniline System at Bubble Point

Composition, weight fraction furfuryl alcohol	Isobaric heat capacity, cal./g., °C.							
	40°	60°	80°	100°	120°	140°	160°	180°
0.00	0.503	0.511	0.520	0.528	0.536	0.544	0.552	0.561
.10	.502	.511	.520	.529	.537	...	...	...
.20	.501	.511	.521	.530	.539	...	...	...
.30	.501	.512	.522	.531	.541[a]	...	...	...
.40	.501	.512	.523	.533	.544[a]	...	...	...
.50	.501	.512	.524	.536	.547[a]	...	...	...
.60	.501	.513	.526	.538	.551[a]	...	...	...
.70	.501	.514	.528	.542	.555[a]	...	...	...
.80	.501	.516	.531	.547	.561[a]	...	...	...
.90	.501	.517	.535[a]	.552[a]	.568[a]	...	...	...
1.00	.501	.519	.538[a]	.557[a]	.576[a]	...	...	...

[a] These values are extrapolated.

Table II

Smoothed Values of Density of Furfuryl Alcohol–Aniline System at Bubble Point

Composition, weight fraction furfuryl alcohol	Density, g./ml.								
	10°C.	20°C.	30°C.	40°C.	50°C.	60°C.	70°C.	80°C.	90°C.
0.00	1.033[a]	1.023[a]	1.014[a]	1.006	0.9966	0.9874	0.9785	0.9692	0.9602
.10	1.043	1.034	1.025	1.016	1.007	0.9976	0.9885	0.9794	0.9704
.20	1.054	1.045	1.036	1.027	1.017	1.007	0.9989	0.9898	0.9808
.30	1.065	1.056	1.046	1.038	1.028	1.019	1.009	1.000	0.9909
.40	1.076	1.066	1.057	1.048	1.038	1.029	1.020	1.010	1.001
.50	1.086	1.077	1.068	1.059	1.049	1.039	1.030	1.020	1.011
.60	1.097	1.088	1.078	1.069	1.060	1.050	1.040	1.031	1.021
.70	1.108	1.099	1.090	1.080	1.071	1.061	1.051	1.042	1.038
.80	1.120	1.110	1.101	1.091	1.082	1.072	1.062	1.053	1.044
.90	1.131	1.122	1.112	1.102	1.093	1.084	1.074	1.064	1.055
1.00	1.143[a]	1.133[a]	1.124	1.114	1.105	1.095	1.086[a]	1.076[a]	1.067[a]

[a] These values are extrapolated.

Experimental.—A description of the equipment and techniques employed is available.[3,4,5] A stainless steel bomb calorimeter with a volume of approximately 1 liter was suspended by small wires within a vacuum jacket. An electrical heater was used to raise the temperature of the calorimeter and contents. The temperature was established within 0.002° by means of a platinum resistance thermometer. The liquid sample within the calorimeter was agitated by a small centrifugal impeller. (The energy measurements were made in watt-seconds and were converted to gram calories by the relation: 1 thermochemical calorie = 4.1840 abs. joules.)

The apparatus was calibrated[6] by measurements with water for which accurate thermodynamic data are available. The volume of the gas phase was less than 2.5% of the total volume of the calorimeter, and therefore simplifying assumptions in the calculations of the heat capacity from the thermal data are justified at temperatures below 100°.[3]

The furfuryl alcohol and aniline were purified by fractional distillation at reduced pressure in an Oldershaw column. The mixtures were prepared by weighing the constituents and mixing them before introduction into the calorimeter.

Results.—Smoothed values of the isobaric heat capacity of the furfuryl alcohol–aniline system are shown in Table I for compositions from 0.0 to 1.0 weight fraction in the temperature range from 40 to 180°. In Fig. 1 the data are presented graphically and, for comparison, literature

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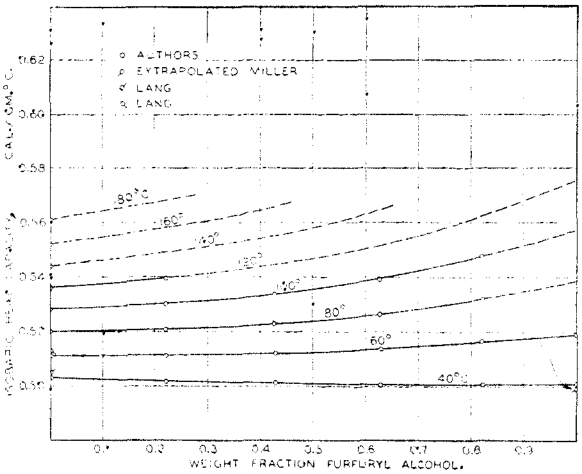

Fig. 1.—Isobaric heat capacity of the furfuryl alcohol–aniline system.

values for pure furfuryl alcohol[7] and aniline[8] are included. The maximum error of these data is estimated to be 1.0%. Density measurements were made with a pycnometer for a number of mixtures at compositions between 0.0 and 1.0 weight fraction furfuryl alcohol at temperatures between 5 and 90°, and the smoothed data are presented in Table II. In Table III is presented the refractive index for several mixtures at compositions between 0.0 and 1.0 weight fraction furfuryl alcohol at 25°. For comparison, data reported in the literature for pure furfuryl alcohol[9] and pure aniline[10] are included.

TABLE III

REFRACTIVE INDEX OF FURFURYL ALCOHOL–ANILINE SYSTEM AT 25°

Composition, weight fraction furfuryl alcohol	Refractive index, λ = 5893 Å. Measured	Literature[9,10]
0.0000	1.5832	1.5863(20°)
.2184	1.5631	....
.4247	1.5433	....
.6248	1.5219	....
.8213	1.5023	....
1.0000	1.4835	1.4843–5

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The Chemistry of Scandium. III[1,2]

BY MORTON J. KLEIN AND PETER M. BERNAYS

The exact nature of the precipitate obtained when a scandium-containing solution is treated with oxalic acid has been the subject of much disagreement in the literature.

Based upon the complete analysis of the salt, Nilson[3] assigned to it the formula $Sc_2(C_2O_4)_3 \cdot 6H_2O$. However, Crookes,[4] who did not determine the scandium oxide, refers varyingly to a mono-, di-, tri- and pentahydrate. Meyer and Winter[5] prepared an oxalate salt whose analysis corresponds closely to that of a tetrahydrate. By precipitating scandium out of acid solution, using oxalic acid or ammonium oxalate, Meyer and Wassjuchnow[6] prepared the pentahydrate. These authors reported no analyses. By far the most careful work was done by Sterba-Böhm. He precipitated the salt from a slightly acid solution at 60° and allowed the crystals to dry in air, excluding all ammonia vapors.[7] The analyses he reports strongly indicate the hexahydrate. The method described below produces pure scandium oxalate hexahydrate.

Experimental

A dilute solution of $ScCl_3$ was heated to 60° and treated with an excess of dilute oxalic acid solution. After 20 minutes, shiny white crystals appeared. Two days drying in air, protected from ammonia vapors, did not yield a homogeneous material. A second batch of crystals were prepared as described above, and dried in a desiccator over anhydrous calcium chloride. After 2 days the material fell apart into a fine powder.

In order to determine the composition of the product, weighed samples were heated in a closed system through which dried nitrogen was passed. The moisture evolved was collected in a phosphorus pentoxide drying tower. Oxalate was determined by the permanganate method, and scandium by the basic tartrate procedure.[8] Typical results are

Preparation no.	Sc, %	$C_2O_4^=$, %	H_2O, %
1	19.39	57.10	23.25
2	19.93	57.02	23.77
3	19.60	57.23	23.46
Calcd. for $Sc_2(C_2O_4)_3 \cdot 6H_2O$	19.51	57.11	23.38

All analyses are the average of two or more determinations.

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(1) Paper II, submitted to *Analytical Chemistry*.

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The Carbonation of Grignard Reagent Solutions

BY ALLEN S. HUSSEY

A convenient technique for the carbonation of Grignard reagents to give high yields of carboxylic acids involves the addition of the Grignard solution to a well-stirred slurry of powdered Dry Ice and dry ether. This procedure[1] permits rapid carbonation at a low temperature, conditions which minimize the secondary reactions which form ketones and tertiary alcohols,[2–5] but has the advantage over the use of powdered Dry Ice[6] in that the reaction mixture can be easily stirred, thus immediately exposing all of the organometallic compound to the action of carbon dioxide.

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