Mutual Solubility of Water and Aldehydes

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Mutual binary solubilities were measured for 29 aldehydes ranging from C_3 to C_{12}. Of this total, 7 were unsaturated aldehydes such as acrolein and crotonaldehyde, 5 were cyclic aldehydes such as benzaldehyde and 2-furaldehyde, and the remaining 17 were alkanecarbaldehydes. The solubility of aldehyde in water decreased very rapidly with increases in molecular weight; the solubility of water in aldehyde decreased less rapidly with molecular weight. No major differences were noted between the solubilities of unsaturated aldehydes such as acrolein and saturated aldehydes such as propionaldehyde. In some cases, the solubility increased with increases in temperature; in others, the solubility decreased with increases in temperature.

Introduction

The aldehydes are important intermediates for the synthesis of alcohols and carboxylic acids, rubber antioxidants, resins, dyestuffs, and plasticizers and polymers. Commercially, formaldehyde is by far the most important aldehyde because of its extensive use in the manufacture of resins and polymers. Formaldehyde is a gas at ordinary temperature and pressure. It is very soluble in water, but immediately polymerizes to form low molecular weight polymers. For this reason, formaldehyde is sold commercially as a 30–56 mass % solution containing 0.5–15 mass % methanol as a polymerization inhibitor.

Acetaldehyde, with a normal boiling point of 20 °C, is also miscible with water in all proportions. Most acetaldehyde produced commercially is for captive use as an intermediate for such compounds as acetic acid and butanol.

Previous Research

Limited measurements on the solubility of the aldehydes are summarized in the DECHEMA book by Sorensen and Arlt (*1*). Four previous papers (*2–5*) describe our research on the mutual solubility of organics and water, and give results for 265 binary and ternary systems. The present paper gives experimental values for an additional 29 water–organic pairs.

Fairly complete solubility measurements are available for acrolein and 2-furaldehyde, and very limited measurements have been made on straight-chain aldehydes from C_4 to C_9. Results for 2-furaldehyde given in Sorensen and Arlt show very close agreement with Table X. Thus, the solubility of 2-furaldehyde in water varies from 7.9 to 13.2 mass % (DECHEMA) in comparison with 7.94 to 12.56 mass % over the temperature range from 20 to 80 °C in Table X. The solubility of water in the aldehyde varies from 4.5 to 11.7 mass % (DECHEMA) in comparison with 4.81 to 11.27 mass % in Table X.

Results for acrolein given in Sorensen and Arlt are not as close. The solubility of aldehyde in water varies from 20.3 to about 23.1 mass % (DECHEMA) over the temperature range from 0 to 50 °C in comparison with 20.3 to about 24.5 mass % in Table II. The solubility of water in acrolein varies from 4.54 to 12.26 mass % (DECHEMA) in comparison with 6.73 to about 14.5 mass % in Table II.

Sorensen and Arlt also give results at one temperature only for butyraldehyde, valeraldehyde, hexanecarbaldehyde, heptanecarbaldehyde, octanecarbaldehyde, and nonanecarbaldehyde. In general, values given are close to those listed in Tables III, VII, XI, XVI, XX, and XXV.

Table I. Mutual Solubility *S* of Water (B) and Propionaldehyde[a] (A) (123-38-6)

	S/(mass %)			*S*/(mass %)	
t/°C	A in B	B in A	*t*/°C	A in B	B in A
12.3	47.7	23.2	40.0	23.5	8.92
15.6	36.8	13.2	50.0	19.7	9.02
20.0	31.0	9.61	std dev	0.3	0.1
30.0	26.9	8.98			

[a] Purity: 97 mass %. The boiling point of A is 46–50 °C. The lower critical solution temperature for this system is 12.3 °C. Below this temperature, A and B are miscible in all proportions.

Table II. Mutual Solubility *S* of Water (B) and Acrolein[a] (A) (107-02-8)

	S/(mass %)			*S*/(mass %)	
t/°C	A in B	B in A	*t*/°C	A in B	B in A
0	19.7	6.73	40.0	24.2	12.37
10.0	20.9	8.06	53.0	24.5	14.91
20.0	22.9	9.40	std dev	0.1	0.08
30.0	23.0	10.71			

[a] Purity: 97 mass %. The boiling point of A is 53 °C. Stabilized with hydroquinone.

Table III. Mutual Solubility *S* of Water (B) and Butyraldehyde[a] (A) (123-72-8)

	S/(mass %)			*S*/(mass %)	
t/°C	A in B	B in A	*t*/°C	A in B	B in A
0	11.82	4.17	50.0	4.25	3.34
10.0	9.12	3.37	60.0	4.17	3.54
20.0	7.44	2.90	70.0	3.89	3.92
30.0	5.48	2.95	std dev	0.1	0.1
40.0	4.71	3.01			

[a] Purity: 99+ mass %. The boiling point of A is 75 °C.

Experimental Section

As before, most samples were analyzed using the method of standard additions. Water and an organic were brought into equilibrium at a given temperature in a thermostat, and samples of each layer were removed with a syringe for analysis. To determine the amount of water in the organic layer sample, a weighed quantity of a solvent such as acetonitrile was added and the ratio of the water to the acetonitrile peak was

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Table IV. Mutual Solubility S of Water (B) and Isobutyraldehyde[a] (A) (78-84-2)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	7.66	2.18	40.0	3.99	2.74
10.0	6.50	2.21	50.0	3.63	3.22
20.0	5.62	2.33	60.0	3.25	3.26
30.0	4.57	2.51	std dev	0.08	0.03

[a] Purity: 99+ mass %. The boiling point of A is 63 °C.

Table V. Mutual Solubility S of Water (B) and Crotonaldehyde[a] (A) (123-73-9)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	19.0	8.2	60.0	14.5	12.7
10.0	17.8	8.2	70.0	14.6	14.4
20.0	17.6	9.0	80.0	14.2	16.6
30.0	15.3	9.4	90.0	16.0	18.9
40.0	14.4	10.3	std dev	0.1	0.1
50.0	14.6	11.9			

[a] Purity: 99+ mass %.

Table VI. Mutual Solubility S of Water (B) and Methacrolein[a] (A) (78-85-3)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	6.16	1.25	40.0	4.74	2.09
10.0	6.01	1.36	50.0	4.77	2.31
20.0	5.65	1.39	60.0	4.54	2.54
30.0	6.00	1.62	std dev	0.06	0.02

[a] Purity: 95.2 mass %. The boiling point of A is 66–70 °C. Stabilized with hydroquinone.

Table VII. Mutual Solubility S of Water (B) and Valeraldehyde[a] (A) (110-62-3)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	3.14	2.47	60.0	1.04	2.49
10.0	2.69	1.92	70.0	1.02	2.58
20.0	1.43	1.75	80.0	1.01	3.01
30.0	1.14	1.94	90.0	0.97	4.03
40.0	1.04	2.04	std dev	0.04	0.04
50.0		2.13			

[a] Purity: 98 mass %.

Table VIII. Mutual Solubility S of Water (B) and Isovaleraldehyde[a] (A) (590-86-3)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	3.56	2.22	60.0	1.28	2.38
10.0	2.36	2.15	70.0	1.19	2.68
20.0	2.02	1.58	80.0	1.24	2.88
30.0	1.78	1.65	90.0	0.97	3.15
40.0	1.60	1.82	std dev	0.03	0.02
50.0	1.41	2.11			

[a] Purity: 96.1 mass %.

measured with a Gow-Mac Series 550 thermal conductivity GC, a 6-ft by 2.2-mm-internal-diameter column, Chromosorb 101 packing, and a Hewlett-Packard 3390A recorder–integrator. The percentage of water in the sample could then be immediately calculated from the mass of acetonitrile added and the GC scale factors for water and acetonitrile, as determined from GC analyses of known water and acetonitrile solutions. This calibration was done for each system using at least three standards covering the composition range of the unknown solutions.

Table IX. Mutual Solubility S of Water (B) and 2-Methylbutyraldehyde[a] (A) (96-17-3)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	2.60	1.62	60.0	1.00	2.19
10.0	1.86	1.64	70.0	0.93	2.17
20.0	1.34	1.16	80.0	0.93	2.46
30.0	1.41	1.76	90.0	0.69	2.99
40.0	1.23	1.57	std dev	0.01	0.02
50.0	1.09	2.18			

[a] Purity: 98.4 mass %.

Table X. Mutual Solubility S of Water (B) and 2-Furaldehyde[a] (A) (98-01-1)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	8.22	3.34	60.0	10.28	8.42
10.0	7.86	4.03	70.0	10.97	9.75
20.0	7.94	4.81	80.0	12.56	11.27
30.0	8.40	5.51	90.0	14.74	13.34
40.0	8.94	6.45	std dev	0.01	0.1
50.0	9.50	7.21			

[a] Purity: 99+ mass %.

Table XI. Mutual Solubility S of Water (B) and Hexanecarbaldehyde[a] (A) (66-25-1)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	1.00	1.95	60.0	0.28	1.78
10.0	0.65	1.72	70.0	0.31	1.97
20.0	0.53	1.15	80.0	0.34	2.03
30.0	0.44	1.24	90.0	0.40	2.57
40.0	0.42	1.35	std dev	0.01	0.02
50.0	0.35	1.48			

[a] Purity: 97.1 mass %.

Table XII. Mutual Solubility S of Water (B) and 2-Ethylbutyraldehyde[a] (A) (97-96-1)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.66	0.96	60.0	0.32	1.33
10.0	0.47	0.98	70.0	0.36	1.61
20.0	0.46	0.81	80.0	0.28	1.79
30.0	0.40	0.88	90.0	0.27	1.92
40.0	0.36	1.24	std dev	0.02	0.02
50.0	0.33	1.13			

[a] Purity: 98.4 mass %.

Table XIII. Mutual Solubility S of Water (B) and 2-Methylvaleraldehyde[a] (A) (123-15-9)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.55	0.97	60.0	0.36	1.50
10.0	0.57	1.01	70.0	0.39	1.65
20.0	0.47	0.78	80.0	0.36	2.01
30.0	0.49	0.98	90.0	0.36	2.01
40.0	0.38	1.04	std dev	0.02	0.03
50.0	0.42	1.24			

[a] Purity: 99.5 mass %.

The amount of organic in the water layer was determined in a similar way by using a standard which appeared at a different place on the GC plot. For example, butyraldehyde was determined using ethanol as standard. As in the case of the organic layer, the calibration was done for each system using at least three standard solutions.

Table XIV. Mutual Solubility S of Water (B) and 2-Ethylcrotonaldehyde[a] (A) (19780-25-7)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	1.12	1.55	60.0	0.68	2.37
10.0	0.96		70.0	0.78	2.61
20.0	0.84	1.37	80.0	0.81	3.01
30.0	0.77	1.54	90.0	0.88	3.28
40.0	0.73	1.73	std dev	0.01	0.04
50.0	0.72	2.02			

[a] Purity: 98.2 mass %.

Table XV. Mutual Solubility S of Water (B) and *trans*-2-Hexenecarbaldehyde[a] (A) (6728-26-3)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.92	1.28	60.0	0.71	2.70
10.0	0.85	1.40	70.0	0.92	3.03
20.0	0.80	1.71	80.0	0.87	3.11
30.0	0.73	1.98	90.0	0.96	3.51
40.0	0.71	2.16	std dev	0.01	0.03
50.0	0.75	2.39			

[a] Purity: 99.5 mass %.

Table XVI. Mutual Solubility S of Water (B) and Heptanecarbaldehyde[a] (A) (111-71-7)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.32	2.60	60.0	0.13	1.27
10.0	0.18	1.46	70.0	0.13	1.41
20.0	0.16	0.87	80.0	0.14	1.43
30.0	0.14	0.96	90.0	0.16	1.69
40.0	0.12	1.07	std dev	0.01	0.05
50.0	0.13	1.14			

[a] Purity: 95.6 mass %.

Table XVII. Mutual Solubility S of Water (B) and 2-Butylacrolein[a] (A) (1070-66-2)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.09	0.35	60.0	0.10	1.05
10.0	0.07	0.43	70.0	0.17	1.03
20.0	0.07	0.51	80.0	0.15	1.21
30.0	0.14	0.61	90.0	0.13	1.35
40.0	0.11	0.79	std dev	0.01	0.03
50.0	0.10	0.81			

[a] Purity: 95 mass %.

Table XVIII. Mutual Solubility S of Water (B) and Benzaldehyde[a] (A) (100-52-7)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.84	0.89	60.0	0.93	2.14
10.0		1.08	70.0	1.02	2.59
20.0	0.72	1.23	80.0	1.24	2.95
30.0	0.74	1.56	90.0	1.40	3.38
40.0	0.79	1.92	std dev	0.03	0.02
50.0	0.82	1.77			

[a] Purity: 99+ mass %.

All experimental measurements were done at atmospheric pressure. Most organics came from laboratory supply houses such as Aldrich or TCI America. The purities and boiling points are those supplied by the manufacturer.

For each system studied, three to five measurements of standard solutions were made to determine GC scale factors. From these, standard deviations are calculated on the basis of an average composition, and are listed in Tables I-XXIX. The temperature of the thermostat was controlled by a Braun Thermomix 1480 or a Lauda Brinkmann RM 20 water bath for the lower temperatures. The absolute temperature was measured by a calibrated thermometer accurate to 0.1 °C.

Several of the systems showed a high solubility which covered a large composition range. These were simply

Table XIX. Mutual Solubility S of Water (B) and Salicyaldehyde[a] (A) (90-02-8)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.29	0.52	60.0	0.48	1.52
10.0	0.30	0.63	70.0	0.57	1.71
20.0	0.30	0.75	80.0	0.82	2.15
30.0	0.33	0.91	90.0	0.91	2.42
40.0	0.45	1.03	std dev	0.01	0.01
50.0	0.48	1.27			

[a] Purity: 99.2 mass %.

Table XX. Mutual Solubility S of Water (B) and Octanecarbaldehyde[a] (A) (124-13-0)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
10.0	0.1		60.0	trace	1.10
20.0	0.1	0.82	70.0	trace	1.05
30.0	0.1	0.95	80.0	trace	1.28
40.0	trace	1.00	90.0	trace	1.81
50.0	trace	1.00	std dev		0.03

[a] Purity: 99.6 mass %.

Table XXI. Mutual Solubility S of Water (B) and 2-Ethylhexanecarbaldehyde[a] (A) (123-05-7)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.032	0.65	60.0	0.060	0.94
10.0	0.052	0.68	70.0	0.047	1.00
20.0	0.029	0.62	80.0	0.052	1.43
30.0	0.049	0.57	90.0	0.052	1.59
40.0	0.036	0.72	std dev	0.01	0.03
50.0	0.043	0.88			

[a] Purity: 99.3 mass %.

Table XXII. Mutual Solubility S of Water (B) and *o*-Tolualdehyde[a] (A) (529-20-4)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.21	0.70	60.0	0.27	1.66
10.0	0.16	0.81	70.0	0.31	1.99
20.0	0.14	1.07	80.0	0.30	2.06
30.0	0.15	1.18	90.0	0.32	2.44
40.0	0.16	1.45	std dev	0.01	0.03
50.0	0.23	1.61			

[a] Purity: 95.9 mass %.

Table XXIII. Mutual Solubility S of Water (B) and *p*-Tolualdehyde[a] (A) (104-87-0)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.15	1.05	50.0	0.24	2.33
10.0	0.17	0.98	70.0	0.23	2.64
20.0	0.18	1.49	80.0	0.25	2.35
30.0	0.19	1.86	90.0	0.30	3.16
40.0	0.19	1.91	std dev	0.01	0.03

[a] Purity: 99.9 mass %. Below 60 °C, organic layer on bottom; above 60 °C, organic layer on top.

Table XXIV. Mutual Solubility S of Water (B) and 2-Ethyl-2-hexenal[a] (A) (645-62-5)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.175	1.16	60.0	0.118	1.34
10.0	0.120	1.11	70.0	0.149	1.29
20.0	0.073	0.75	80.0	0.135	1.17
30.0	0.107	0.89	90.0	0.130	1.24
40.0	0.127	0.89	std dev	0.005	0.04
50.0	0.138	1.06			

[a] Purity: 93.6 mass %.

Table XXV. Mutual Solubility S of Water (B) and Nonanecarbaldehyde[a] (A) (124-19-6)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
10.0		1.05	60.0	0.03	0.80
20.0	0.03	0.64	70.0	0.06	0.92
30.0	0.06	0.76	80.0	0.05	0.96
40.0	0.04	0.74	90.0	0.05	1.13
50.0	0.07	0.79	std dev	0.01	0.1

[a] Purity: 95 mass %.

Table XXVI. Mutual Solubility S of Water (B) and 3,5,5-Trimethylhexanecarbaldehyde[a] (A) (5435-64-3)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.16	0.53	60.0	0.04	1.18
10.0	0.06	0.53	70.0	0.06	1.13
20.0	0.04	0.47	80.0	0.06	1.39
30.0	0.06	0.56	90.0	0.09	1.32
40.0	0.08	0.75	std dev	0.01	0.03
50.0	0.05	1.04			

[a] Purity: 95.7 mass %.

analyzed directly with the GC, using scale factors determined from an analysis of standard solutions.

Summary of Data

All aldehydes studied showed only partial miscibility over the temperature range from 0 to 90 °C. As expected, the solubility shows a consistent decrease as the molecular weight increases from C_3 (Table I) to C_{12} (Table XXIX). Even where the aldehyde shows low solubility in water, there still may be fairly high solubility of water in the aldehyde. Cyclic aldehydes (Tables X, XVIII, XIX, XXII, and XXIII) shown slightly higher solubilities than straight-chain aldehydes; for example, benzaldehyde (Table XVIII) has a higher solubility than heptanecarbaldehyde (Table XVI), and 2-furaldehyde (Table X) has a higher solubility than valeraldehyde (Table VII). There is no major difference between the solubilities

Table XXVII. Mutual Solubility S of Water (B) and Decanecarbaldehyde[a] (A) (112-31-2)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.09	0.88	50.0	0.02	0.67
10.0	0.03	0.71	60.0	0.02	0.97
20.0	0.03	0.87	70.0	0.03	0.92
30.0	0.02	1.03	80.0	0.03	
40.0	0.02	0.94	90.0	0.04	1.26

[a] Purity: 97.5 mass %.

Table XXVIII. Mutual Solubility S of Water (B) and Undecanecarbaldehyde[a] (A) (112-44-7)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
20.0	0.12	0.36	70.0	0.15	0.49
30.0	0.07	0.66	80.0	0.21	1.13
40.0	0.07	0.27	90.0	0.20	1.43
50.0	0.10	0.36	std dev	0.01	0.03
60.0	0.16	0.76			

[a] Purity: 97 mass %. Some decomposition noted in organic layer.

Table XXIX. Mutual Solubility S of Water (B) and Dodecanecarbaldehyde[a] (A) (112-54-9)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.18	0.80	60.0	trace	0.75
10.0		0.83	70.0	trace	0.81
20.0	0.03		80.0	trace	0.72
30.0	0.04	0.86	90.0	trace	0.93
40.0	0.03	0.88	std dev	0.01	0.02
50.0	trace				

[a] Purity: 97+ mass %.

of saturated aldehydes such as propionaldehyde (Table I) or butyraldehyde (Table III) and those of the corresponding unsaturated aldehydes such as acrolein (Table II) or crotonaldehyde (Table V).

The registry numbers in this paper were supplied by the author.

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