## **Mutual Solubility of Water and Aliphatic Amines**

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Mutual binary solubilities in water have been experimentally measured for aliphatic amines up to  $C_{12}$ . Data are given for 51 water-organic pairs at temperatures of 0-90 °C. It was found that 19 binary systems are miscible in all proportions, 19 are only partially miscible over the entire temperature range, and 13 are partially miscible at higher temperatures but have lower critical solution temperatures and are completely miscible at lower temperatures. The characteristic feature of the solubility is the strong dependence on molecular weight. All amines up to  $C_4$  are miscible with water in all proportions up to the boiling point of the amine. Higher amines such as  $C_8$  to  $C_{12}$  show very low solubility in water, although the solubility of water in the amine often remains high. For a given molecular weight, there is no major difference in the solubility of primary, secondary, and tertiary amines.

### Introduction

The aliphatic amines are important industrial chemicals, with approximately two dozen produced commercially in the United States. Their chief use is as intermediates for the manufacture of insecticides and herbicides, ion exchange resins, surfactants, rubber accelerators, and a host of other products.

Very little experimental work on the solubility of the amines has been reported in the literature, and much of that is subject to considerable error. Early work on the amines was hindered because the materials are difficult to handle and there were substantial problems associated with the availability and purity of the materials. Summaries of the little work available are given in books by Sorensen and Arlt (1) and the Solubility Data Series of the International Union of Pure and Applied Chemistry (2). Four previous papers (3-6) describe our research on the mutual solubility of organics and water, and give experimental data for 265 binary and ternary systems. The present paper gives experimental data for an additional 51 water-organic pairs, including 19 which are miscible in all proportions.

Sorensen and Arlt give data for the solubility of three amines, N-ethylbutylamine, dipropylamine, and triethylamine. Their data for N-ethylbutylamine cover the temperature range from 10 to 40 °C, and show good agreement with Table XI. Data for dipropylamine cover a temperature range from 0 to 50 °C, and show fairly good agreement with Table VIII except that the lower critical solution temperature is missed. Old data for triethylamine cover the temperature range from about 20 to 70 °C, and show moderately good agreement with Table X.

#### **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 pyridine was added and the ratio of the water to pyridine peak measured with a Gow-Mac Series 550 thermal conductivity gas chromatograph (GC), a 1.9-m by 2.2-mm-i.d. column, Chromosorb 103 packing, and a Hewlett-Packard 3390A recorder-integrator. The percentage of water in the sample could then be immediately calculated from the mass of pyridine added and the GC scale factors for water and pyridine, as determined from GC analyses of known water and pyridine solutions.

Table I. Amines Miscible with Water in All Propor	tie	0	1	٥	1	l	1	1	1	1	1	Ņ	)	0	0	C	(	ļ	Ì	İ	j	i	1	1		ļ	Ġ	ĺ	1	1		1	l	,	)	ſ	(	1	)	J	l	1	,	)	(	1	ſ	1	1	)		]			l	1	l	]	1	١	1	ŀ			Ì	Ċ	I	Ĺ	1		ľ	J	Ê	1	1	1	8	7	V	1	I	1	L		1		t	t	İ	i	q	ľ	2	٦	1	)	E	(		)	)	l	ĺ	1	;	C	(	5	1	1	ĺ	i	Ŀ		l	ľ	Ì	ŀ	1				,	1	1	1	)	)	e	e	1	(	U	b	1	1	1	ľ	ľ	I	1	1	1	1	i	b
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amine	consolute range/°C
methylamine (74-89-5)	gas, consolute under pressure
ethylamine (75–04–7)	gas, consolute under pressure
dimethylamine (124–40–3)	gas, consolute under pressure
propylamine (107-10-8)	0-48
isopropylamine	0-33
trimethylamine (75-50-3)	gas, consolute under pressure
N-ethylmethylamine (624–78–2)	0-36
allylamine (107-11-9)	0-53
hutvlamine $(109-73-9)$	0-78
sec-butylamine (33966-50-6)	0-63
tert-hutylamine (75-64-9)	0-46
isobutylamine (78–81–9)	0-64
diethylamine (109-89-7)	0-55
N N-dimethylethylemine	0-36
(598-56-1)	0.00
pentylamine $(110-58-7)$	0-95
(1.1-dimethylpropyl)amine	0-77
(594-39-8)	• • • •
N.N-dimethylisopropylamine	0-66
(996-35-0)	
isopentylamine (107-85-7)	0-95
(1.2-dimethylpropyl)amine	0-85
(598-74-3)	

Table II. Mutual Solubility S of Water (B) and N-Methylbutylamine<sup>4</sup> (A) (110-68-9)

	S/(ma	<b>188</b> %)		S/(m	<b>158</b> %)
t/°C	A in B	B in A	t/°C	A in B	B in A
43.0	11.87	69.1	70.0	4.65	42.1
44.0	11.00	63.6	80.0	4.51	36.4
50.0	6.05	50.5	<del>9</del> 0.0	3.69	32.7
60.0	4.82	47.1	std dev	0.05	0.8

<sup>a</sup> Purity: 96 mass %. The lower critical solution temperature for this system is 43 °C. Below this temperature, A and B are miscible in all proportions.

Table III. Mutual Solubility S of Water (B) and N-Ethylpropylamine<sup>4</sup> (A) (20193-20-8)

	$S/(m_{e})$	<b>158</b> %)		S/(mt)	ass %)
t/°C	A in B	B in A	t/°C	A in B	B in A
49.0	21.33	52.4	70.0	5.67	29.7
50.0	17.07	50.0	79.0	4.92	25.3
52.0	12.26	46.2	std dev	0.30	0.4
60.0	7.60	35.7			

<sup>a</sup> Purity: 99.9 mass %. The lower critical solution temperature for this system is 49 °C. Below this temperature, A and B are miscible in all proportions. The boiling point of A is 79 °C.

This calibration was done for each system using at least three standards covering the approximate composition range of the unknown solutions.

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Table IV. Mutual Solubility S of Water (B) and N,N-Diethylmethylamine<sup>4</sup> (A) (616-39-7)

	S/(m)	ass %)		S/(m)	ass %)
t/°C	A in B	B in A	t/°C	A in B	B in A
51.0	19.3	54.6	60.0	9.2	23.6
52.0	14.8	41.4	62.0	7.9	27.6
54.0	12.9	38.3	64.0	7.8	25.4
56.0	11.2	30.3	std dev	0.6	1.0
58.0	10.4	27.4			

<sup>a</sup> Purity: 98 mass %. The lower critical solution temperature for this system is 51 °C. Below this temperature, A and B are miscible in all proportions. The boiling point of A is 63-65 °C.

Table V. Mutual Solubility S of Water (B) and (1-Methylbutyl)amine<sup>4</sup> (A) (625-30-9)

	S/(ma	ass %)		S/(m	<b>168</b> %)
t/°C	A in B	B in A	t/°C	A in B	B in A
87.0	19.0	81.0	90.0	10.1	69.4
88.0	11.8	71.5	std dev	0.8	2.0
89.0	11.7	69.9			

<sup>a</sup> Purity: 97 mass %. The lower critical solution temperature for this system is 87 °C. This is very close to the listed boiling point of 90.5–91.5 °C for A. Undoubtedly the two-phase region could be extended by going, under pressure, to higher temperatures.

Table VI. Mutual Solubility S of Water (B) and (1-Ethylpropyl)amine<sup>4</sup> (A) (616-24-0)

	S/(m/	ass %)		$S/(m_{e})$	ass %)
t/°C	A in B	B in A	t/°C	A in B	B in A
64.0	15.0	66.2	80.0	6.7	50.8
66.0	11.6	56.8	90.0	6.1	43.4
68.0	10.5	55.4	std dev	0.2	1.0
70.0	8.8	55.2			

<sup>a</sup> Purity: 98 mass %. The lower critical solution temperature for this system is 64 °C. Below this temperature, A and B are miscible in all proportions. The boiling point of A is 89–91 °C.

Table VII. Mutual Solubility S of Water (B) and Hexylamine<sup>4</sup> (A) (111-26-2)

	S/(m	ass %)		$S/(m \epsilon)$	ass %)
t/°C	A in B	B in A	t/°C	A in B	B in A
30.0	0.97	61.8	70.0	0.90	47.3
40.0	0.78	61.2	80.0	0.95	41.4
50.0	0.92	54.0	90.0	0.85	36.8
60.0	0.94	51.5	std dev	0.04	0.5

<sup>a</sup> Purity: 99 mass %. Gelatinous hydrates are formed below 30 °C.

Table VIII. Mutual Solubility S of Water (B) and Dimensional (A) (142-84-7)

Dipropy	ISTUING- (%	1) (142-04-	()		
	S/(m)	ass %)		S/(m	ass %)
t/°C	A in B	B in A	t/°C	A in B	B in A
0	12.96	51.85	60.0	1.64	9.87
10.0	7.73	36.37	70.0	1.48	7.93
20.0	5.30	21.38	80.0	1.15	7.59
30.0	3.37	14.24	90.0	1.04	6.34
40.0	2.66	11.73	std dev	0.10	0.50
50.0	1.98	11.25			

<sup>a</sup> Purity: 99 mass %.

Table IX. Mutual Solubility S of Water (B) and Diisopropylamine<sup>4</sup> (A) (108-18-9)

	S/(ma)	<b>158</b> %)		S/(ma	<b>155</b> %)
t/°C	A in B	B in A	t/°C	A in B	B in A
28.0	12.39	42.6	70.0	2.15	7.1
30.0	10.32	27.2	80.0	1.76	5.4
40.0	6.35	18.6	84.0	1.61	5.1
50.0	4.57	12.8	std dev	0.1	0.5
60.0	2.90	8.1			

<sup>o</sup> Purity: 99 mass %. The lower critical solution temperature for this system is 28 °C. Below this temperature, A and B are miscible in all proportions. The boiling point of A is 84 °C.

Table X. Mutual Solubility S of Water (B) and Triethylamine<sup>2</sup> (A) (121-44-8)

	S/(ma)	ass %)		S/(ma)	ass %)
t/°C	A in B	B in A	t/°C	A in B	B in A
18.0	14.38	36.68	30.0	3.93	4.28
19.0	12.38	29.14	40.0	3.60	3. <b>96</b>
20.0	11.24		50.0	2.59	2.83
21.0	10.23	20.23	60.0	1.96	2.63
22.0	10.29	16.70	70.0	1.60	2.27
24.0	8.91	11.42	80.0	1.38	1.35
26.0	8.00	9.83	std dev	0.12	0.14
28.0	6.51	7.68			

<sup>a</sup> Purity: 99 mass %. The lower critical solution temperature for this system is 18 °C. Below this temperature, A and B are miscible in all proportions. The boiling point of A is 88.8 °C.

Table XI. Mutual Solubility S of Water (B) and N-Ethylbutylamine<sup>4</sup> (A) (13360-63-9)

	S/(ma	uss %)		$S/(m \epsilon)$	ass %)
t/°C	A in B	B in A	t/°C	A in B	B in A
15.0		42.8	60.0	1.40	18.3
17.4	5.96	36.0	70.0	1.29	14.8
20.0	5.06	30.7	80.0	1.12	12.9
30.0	4.19	24.3	90.0	1.04	12.3
40.0	2.55	21.9	std dev	0.1	1.5
50.0	1.80	22.2			

 $^{\rm a}$  Purity: 99 mass %. The lower critical solution temperature for this system is 15 °C. Below this temperature, A and B are miscible in all proportions.

Table XII. Mutual Solubility S of Water (B) and N,N-Dimethylbutylamine<sup>4</sup> (A) (927-62-8)

	$S/({ m mass}~\%)$			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
3.8	8.64	65.8	50.0	1.12	6.9
6.0	5.10	52.9	60.0	0.84	5.5
10.0	4.92	40.9	70.0	0.78	5.0
20.0	3.52	30.8	80.0	0.56	4.6
30.0	2.47	19.9	90.0	0.55	3.0
40.0	1.50	10.5	std dev	0.1	0.1

 $^a$  Purity: 99 mass %. The lower critical solution temperature for this system is 3.8 °C. Below this temperature, A and B are miscible in all proportions.

Table XIII. Mutual Solubility S of Water (B) and Diallylamine<sup>4</sup> (A) (124-02-7)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
6.0	23.53	74.6	50.0	4.95	15.5
8.0	20.66	65.1	60.0	4.51	12.8
10.0	16.04	43.3	70.0	3.93	10.8
20.0	11.64	26.7	80.0	3.74	9.7
30.0	9.86	23.9	<del>9</del> 0.0	3.51	9.4
40.0	6.31	18.5	std dev	0.1	0.2

<sup>a</sup> Purity: 99 mass %. The lower critical solution temperature for this system is 6 °C. Below this temperature, A and B are miscible in all proportions.

Table XIV. Mutual Solubility S of Water (B) and N-Ethyl(2-methylallyl)amine<sup>4</sup> (A) (18328-90-0)

S/(mass %)				S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
18.6	12.31	47.5	60.0	2.74	8.2
20.0	11.41	43.3	70.0	1.96	6.9
30.0	6.82	19.2	80.0	1.94	6.3
40.0	5.66	15.8	90.0	1.62	5.6
50.0	3.75	11.2	std dev	0.2	0.5

<sup>a</sup> Purity: 98 mass %. The lower critical solution temperature for this system is 18.6 °C. Below this temperature, A and B are miscible in all proportions.

Table XV. Mutual Solubility S of Water (B) and Heptylamine<sup>4</sup> (A) (111-68-2)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.62	98.3	30.0	0.30	80.4
3.0	0.38	97.0	40.0	0.30	46.7
6.0	0.38	97.1	50.0	0.30	37.9
10.0	0.33	97.1	60.0	0.33	34.2
15.0	0.35	95.7	70.0	0.27	30.4
16.0	0.35	93.3	80.0	0.29	28.9
18.0	0.33	92.1	90.0	0.33	23.8
20.0	0.29	91.3	std dev	0.01	1.3

<sup>a</sup> Purity: 98.9 mass %. The lower critical solution temperature for this system is slightly below 0 °C.

Table XVI. Mutual Solubility S of Water (B) and (1-Methylhexyl)amine<sup>4</sup> (A) (123-82-0)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
3.0	0.97	77.6	50.0	0.40	30.1
4.0	0.99	58.0	60.0	0.41	26.6
6.0	0.89	55.7	70.0	0.38	22.9
10.0	0.77	49.8	80.0	0.37	20.0
20.0	0.50	44.5	90.0	0.36	17.7
30.0	0.44	40.1	std dev	0.01	0.5
40.0	0.40	34.5			

<sup>a</sup> Purity: 99 mass %. The lower critical solution temperature for this system is 3 °C. Below this temperature, A and B are miscible in all proportions.

Table XVII. Mutual Solubility S of Water (B) and Octylamine<sup>4</sup> (A) (111-86-4)

t/°C	$S/({ m mass}~\%)$		S/(mass %)		S/(mass %)	
	A in B	B in A	t/°C	A in B	B in A	
40.0	0.15	57.9	80.0	0.26	24.7	
50.0	0.25	38.4	90.0	0.16	22.3	
60.0	0.27	33.4	std dev	0.02	1.0	
70.0	0.35	28.1				

<sup>a</sup> Purity: 99 mass %. Forms gelatinous hydrates below 40 °C.

Table XVIII. Mutual Solubility S of Water (B) and Dibutylamine<sup>4</sup> (A) (111-92-2)

	S/(mass %)			$S/({ m mass}~\%)$	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	1.20	11.14	60.0	0.23	3.06
10.0	0.82	8.40	70.0	0.24	2.64
20.0	0.57	6.36	80.0	0.22	2.71
30.0	0.43	4.85	90.0	0.22	2.12
40.0	0.35	3.70	std dev	0.01	0.11
50.0	0.32	3.43			

<sup>a</sup> Purity: 99 mass %.

Table XIX. Mutual Solubility S of Water (B) and Di-sec-butylamine<sup>4</sup> (A) (626-23-3)

	S/(mass %)			$S/({ m mass}~\%)$	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	1.822	2.08	60.0	0.168	1.15
10.0	1.020	1.74	70.0	0.156	1.13
20.0	0.625	1.29	80.0	0.089	0.92
30.0	0.399	1.19	90.0	0.032	1.05
40.0	0.279	1.17	std dev	0.002	0.02
50.0	0.209	1.07			

<sup>a</sup> Purity: 99.9 mass %.

Table XX. Mutual Solubility S of Water (B) and Diisobutylamine<sup>4</sup> (A) (110-96-3)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.78	2.04	60.0	0.15	1.22
10.0	0.41	1.46	70.0	0.12	1.54
20.0	0.27	1.34	80.0	0.13	1.41
30.0	0.20	1.24	90.0	0.15	0.91
40.0	0.13	1.16	std dev	0.03	0.1
50.0	0.16	1.36			

<sup>a</sup> Purity: 99 mass %.

Table XXI. Mutual Solubility S of Water (B) and (2-Ethylhexyl)amine<sup>4</sup> (A) (104-75-6)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.540	34.7	60.0	0.241	20.2
10.0	0.467	28.8	70.0	0.236	15.2
20.0	0.351	22.2	80.0	0.216	14.3
30.0	0.266	26.4	90.0	0.263	12.2
40.0	0.238	23.3	std dev	0.003	0.3
50.0	0.254	24.2			

<sup>a</sup> Purity: 98 mass %.

Table XXII. Mutual Solubility S of Water (B) and (1,5-Dimethylhexyl)amine<sup>4</sup> (A) (543-82-8)

	$S/({ m mass}~\%)$			$S/({ m mass}~\%)$	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.41	53.4	60.0	0.18	19.1
10.0		41.4	70.0	0.18	16.8
20.0	0.27	35.1	80.0	0.19	14.2
30.0	0.25	30.6	90.0	0.17	13.2
40.0	0.27	27.0	std dev	0.01	0.1
50.0	0.22	22.7			

<sup>a</sup> Purity: 99.9 mass %.

# Table XXIII. Mutual Solubility S of Water (B) and N,N-Diisopropylethylamine<sup>4</sup> (A) (7087-68-5)

	$S/({ m mass}~\%)$			$S/({ m mass}~\%)$	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.99	0.17	60.0	0.14	0.12
10.0	0.58		70.0	0.12	0.16
20.0	0.36	0.14	80.0	0.13	0.19
30.0	0.22	0.11	90.0	0.08	0.18
40.0	0.17	0.10	std dev	0.01	0.01
50.0	0.16	0.14			

<sup>a</sup> Purity: 99.9 mass %.

# Table XXIV. Mutual Solubility S of Water (B) and (1,1,3,3-Tetramethylbutyl)amine<sup>4</sup> (A) (107-45-9)

t/°C	$S/({ m mass}~\%)$			$S/({ m mass}~\%)$	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	1.85	39.23	60.0	0.53	12.85
10.0	1.31	32.28	70.0	0.49	10.15
20.0	1.01	28.02	80.0	0.48	8.74
30.0	0.81	22.92	90.0	0.44	7.11
40.0	0.66	18.47	std dev	0.01	0.12
50.0	0.58	15.94			

<sup>a</sup> Purity: 95.4 mass %.

Table XXV. Mutual Solubility S of Water (B) and Tripropylamine<sup>4</sup> (A) (102-69-2)

	$S/({ m mass}~\%)$			$S/({ m mass}~\%)$	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.071	0.098	60.0	trace	0.121
10.0	0.070	0.112	70.0	trace	0.182
20.0	0.022	0.113	80.0	trace	0.141
30.0	0.017	0.113	90.0	trace	0.193
40.0	trace	0.148	std dev	0.01	0.004
50.0	trace	0.132			

<sup>a</sup> Purity: 98 mass %.

# Table XXVI. Mutual Solubility S of Water (B) and Triallylamine<sup>4</sup> (A) (102-70-5)

	$S/({ m mass}~\%)$			$S/({ m mass}~\%)$	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.53	0.55	60.0	0.19	0.47
10.0	0.43	0.54	70.0	0.21	0.47
20.0	0.29	0.49	80.0	0.18	0.50
30.0	0.23	0.46	90.0	0.24	0.53
40.0	0.21	0.48	std dev	0.05	0.1
50.0	0.22	0.45			

<sup>a</sup> Purity: 99 mass %.

Table XXVII. Mutual Solubility S of Water (B) and Decylamine<sup>a</sup> (A) (2016-57-1)

S/(mass %)				S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
20.0	0.430	73.9	70.0	trace	18.0
30.0	trace	64.6	80.0	trace	15.5
40.0	trace	35.5	90.0	trace	12.9
50.0	trace	27.6	std dev	0.01	0.33
60.0	0.059	23.5			

<sup>a</sup> Purity: 96 mass %. Forms a hydrate with water at room temperature with a freezing point of 17 °C. Solid hard to melt.

Table XXVIII. Mutual Solubility S of Water (B) and Dipentylamine<sup>a</sup> (A) (2050-92-2)

S/(mass %)				$S/({ m mass}~\%)$	
t/°C	A in B	B in A	t/°C	A in B	B in A
10.0	0.103	2.97	60.0	trace	1.69
20.0	0.080	2.53	70.0	trace	1.65
30.0	0.04	2.20	80.0	trace	1.67
40.0	trace	2.10	90.0	trace	1.54
50.0	trace	2.10	std dev	0.01	0.05

<sup>a</sup> Purity: 99 mass %.

Table XXIX. Mutual Solubility S of Water (B) and N,N-Dimethyloctylamine<sup>4</sup> (A) (7378-99-6)

$S/({ m mass}~\%)$				S/(m)	<b>158</b> %)
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.063	2.79	60.0	trace	0.82
10.0	0.044	1.45	70.0	trace	0.71
20.0	0.036	0.99	80.0	trace	0.82
30.0	trace	0.87	90.0	trace	0.86
40.0	trace	0.76	std dev	0.002	0.03
50.0	trace	0.71			

<sup>a</sup> Purity: 95 mass %.

Table XXX. Mutual Solubility S of Water (B) and Dodecylamine<sup>4</sup> (A) (124-22-1)

$S/({ m mass}~\%)$				S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
40.0	0.064		80.0	0.090	9.1
50.0		20.4	90.0	0.161	7.9
60.0		16.6	std dev	0.02	1.0
70.0	0.084	12.6			

<sup>a</sup> Purity: 98 mass %. Melting point 28-30 °C.

Table XXXI. Mutual Solubility S of Water (B) and Dihexylamine<sup>e</sup> (A) (143-16-8)

	S/(m	ass %)	<b>S</b> /+		mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A	
20.0	traceb	1.41	70.0	trace	1.00	
30.0	trace	1.24	80.0	trace	1.02	
40.0	trace	1.15	90.0	trace	0.95	
50.0	trace	1.10	std dev		0.01	
60.0	trace	1.02				

<sup>a</sup> Purity: 97 mass %. Freezes at 16 °C. <sup>b</sup> Less than 0.1% dihexylamine.

Table XXXII. Mutual Solubility S of Water (B) and Tributylamine<sup>4</sup> (A) (102-82-9)

	$S/({ m mass}~\%)$			$S/({ m mass}~\%)$	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.095		60.0	0.050	0.156
10.0	0.090	0.087	70.0	0.049	0.133
20.0	0.096	0.100	80.0	0.039	
30.0	0.105	0.101	90.0		0.162
40.0	0.103	0.119	std dev	0.006	0.003
50.0	0.050	0.084			

Table XXXIII. Mutual Solubility S of Water (B) and Triisobutylamine<sup>4</sup> (A) (1116-40-1)

$S/({ m mass}~\%)$				$S/({ m mass}~\%)$	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	traceb	0.20	60.0	trace	0.50
10.0	trace	0.21	70.0	trace	0.58
20.0	trace	0.36	80.0	trace	0.56
30.0	trace	0.47	90.0	trace	0.71
40.0	trace	0.43	std dev		0.01
50.0	trace	0.45			

<sup>a</sup> Purity: 99.4 mass %. <sup>b</sup> Less than 0.1% triisobutylamine.

All experimental measurements were done at atmospheric pressure. Most organics came from laboratory supply houses such as Aldrich or TCI America. A few samples were supplied by commercial producers of the compound. Materials were used directly in the research, without any attempt at further purification.

Most organics had purities of 98% or better, although a few had purities ranging down to 95 mass %. Since water is the most common impurity in an organic, and since other impurities may be isomers having no major effect on solubility, data are simply given as measured. However, the purity of the material used is always given, and the reader may choose to discount measurements on those materials having purities less than 98 mass %.

In some instances samples phase separated and had to be brought into solution by heating or by the addition of a solvent such as methanol. 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 the tables of data. 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, often including a lower critical solution temperature. These were simply analyzed directly with the GC, using scale factors determined from an analysis of standard solutions.

#### Summary of Data

Like all organics, the chief characteristic of the amines is the great decrease in solubility with an increase in the molecular weight. All amines up to the  $C_4$ 's are miscible with water in all proportions from zero to the boiling point of the amine (Table I). Five of the  $C_5$  amines (Table I) are also miscible with water in all proportions between zero and the boiling point. Five other  $C_5$  amines are only partially miscible with water at higher temperatures (Tables II–VI), but have lower critical solution temperatures and are completely miscible with water at lower temperatures.

Solubility does not seem to be strongly affected by whether the amine is primary, secondary, or tertiary. For example, hexylamine, dipropylamine, and triethylamine (Tables VII, VIII, and X) all show similar solubilities.

As the molecular weight of the amine increases to  $C_{12}$ (Tables XXX–XXXIII), the solubility of the amine in water becomes extremely low, in some cases below the sensitivity of the GC used in the analysis. However, even under these conditions, there may be moderate solubility of water in the amine. Note that the primary amines such as decylamine (Table XXVII) show a much higher solubility for water than a secondary amine such as dipentylamine (Table XXVIII) or a tertiary amine such as N,N-dimethyloctylamine (Table XXIX).

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