Mutual Solubilities: Water + Cyclic Amines, Water + Alkanolamines, and Water + Polyamines

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Mutual solubilities for water + cyclic amines, water + alkanolamines, and water + polyamines have been measured. Of the 24 cyclic amines studied, only furfurylamine and cyclohexylamine were consolute with water. Of 31 alkanolamines studied, 26 were miscible with water in all proportions, 3 were partially miscible between 0 and 90 °C, and 2 had lower critical solution temperatures of 13.6 and 30 °C. Of 27 polyamines studied, 24 were miscible with water in all proportions, only 1 was partially miscible between 0 and 90 °C, and 2 had lower critical solution temperatures of 3 and 57 °C.

Introduction

The cyclic amines, alkanolamines, and polyamines are important industrial chemicals which are produced commercially worldwide. Cyclic amines such as aniline are used to produce rubber chemicals as well as a host of various intermediates and dyestuffs. Alkanolamines are used in water treatment and for the absorption of acid gases. Polyamines are used as chemical intermediates and for the production of polymers and plastics.

The characteristic feature of the cyclic amines is their low solubility in water. Furfurylamine and cyclohexylamine (Table I) both mix with water in all proportions, but all other cyclic amines studied showed low solubility in water. In contrast, the alkanolamines and polyamines show high solubility in water. It was found experimentally that of a

Table I. Cyclic Amines Miscible with Water in all Proportions

furfurylamine (617-89-0)	cyclohexylamine (108-91-8)

Table II. Mutual Solubility *S* of Water (B) and *N*-Methylcyclohexylamine[a] (A) (100-60-7)

	S/(mass %)			*S*/(mass %)	
t/°C	A in B	B in A	*t*/°C	A in B	B in A
11.6	9.99	79.75	40.0	2.82	41.41
12.5	7.59	74.18	50.0	2.46	37.09
13.7	6.60	72.32	60.0	2.25	29.75
14.5	6.12	71.21	70.0	2.10	26.29
16.0	5.68	70.09	80.0	1.91	21.95
17.2	5.33	64.57	90.0	1.90	18.74
20.0	4.45	60.87	std dev	0.02	0.15
30.0	3.41	50.90			

[a] Purity: 99 mass %. The lower critical solution temperature is 10.6 °C. Below this temperature, A and B are miscible in all proportions.

Table III. Mutual Solubility *S* of Water (B) and (2-Methylcyclohexyl)amine[a] (A) (7003-32-9)

	S/(mass %)			*S*/(mass %)	
t/°C	A in B	B in A	*t*/°C	A in B	B in A
0	4.60	60.4	60.0	1.95	31.7
10.0	3.46	53.6	70.0	1.86	28.5
20.0	2.88	47.7	80.0	1.80	25.6
30.0	2.40	44.0	90.0	1.81	23.5
40.0	2.17	39.3	std dev	0.02	0.3
50.0	1.96	35.4			

[a] Purity: 98+ mass %.

Table IV. Mutual Solubility *S* of Water (B) and *N,N*-Dimethylcyclohexylamine[a] (A) (98-94-2)

	S/(mass %)			*S*/(mass %)	
t/°C	A in B	B in A	*t*/°C	A in B	B in A
0	3.35	48.4	60.0	0.74	5.0
10.0	2.53	39.6	70.0	0.59	4.5
20.0	1.62	21.4	80.0	0.51	4.1
30.0	1.26	13.8	90.0		3.4
40.0	1.00	11.3	std dev	0.03	0.4
50.0	0.82	8.0			

[a] Purity: 99.9 mass %.

Table V. Mutual Solubility *S* of Water (B) and *N*-Ethylcyclohexylamine[a] (A) (5459-93-8)

	S/(mass %)			*S*/(mass %)	
t/°C	A in B	B in A	*t*/°C	A in B	B in A
0	4.62	40.4	60.0	0.99	7.9
10.0	3.30	35.3	70.0	0.87	6.8
20.0	2.44	18.4	80.0	0.82	6.2
30.0	1.72	15.6	90.0	0.75	5.4
40.0	1.37	12.8	std dev	0.07	0.5
50.0	1.14	10.1			

[a] Purity: 99+ mass %.

Table VI. Mutual Solubility *S* of Water (B) and *N*-Isopropylcyclohexylamine[a] (A) (1195-42-2)

	S/(mass %)			*S*/(mass %)	
t/°C	A in B	B in A	*t*/°C	A in B	B in A
0	2.307	33.38	60.0	0.331	2.64
10.0	1.297	12.35	70.0	0.285	2.32
20.0	0.990	7.54	80.0	0.256	2.41
30.0	0.618	5.73	90.0	0.227	2.47
40.0	0.480	3.79	std dev	0.002	0.05
50.0	0.393	3.37			

[a] Purity: 99 mass %.

Table VII. Mutual Solubility *S* of Water (B) and (3,3,5-Trimethylcyclohexyl)amine[a] (A) (15901-42-5)

	S/(mass %)			*S*/(mass %)	
t/°C	A in B	B in A	*t*/°C	A in B	B in A
0	0.72	34.2	60.0	0.35	19.0
10.0	0.58	30.1	70.0	0.31	17.7
20.0	0.51	26.4	80.0	0.35	16.2
30.0	0.35	24.9	90.0	0.35	14.6
40.0	0.36	23.2	std dev	0.01	0.15
50.0	0.35	20.3			

[a] Purity: 99+ mass %.

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Table VIII. Mutual Solubility S of Water (B) and (4-*tert*-Butylcyclohexyl)amine[a] (A) (5400-88-4)

	S/(mass %0			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
40.0	0.22	29.5	70.0	0.16	17.9
50.0	0.20	31.0	80.0	0.18	17.0
60.0	0.21	23.5	90.0	0.21	16.2

[a] Purity: 99+ mass % mixed isomers. Below 40 °C, A and B form a solid complex or hydrate.

Table IX. Mutual Solubility S of Water (B) and *N,N*-Diethylcyclohexylamine[a] (A) (91-65-6)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.42	0.51	60.0	0.19	0.50
10.0	0.29	0.52	70.0	0.19	0.51
20.0	0.20	0.52	80.0	0.14	0.51
30.0	0.19	0.62	90.0	0.17	0.62
40.0	0.20	0.66	std dev	0.01	0.01
50.0	0.15	0.48			

[a] Purity: 99 mass %.

Table X. Mutual Solubility S of Water (B) and *N,N*-Dimethylaniline[a] (A)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.154	0.061	60.0	0.156	0.227
10.0	0.148	0.081	70.0	0.142	0.214
20.0	0.154	0.112	80.0	0.173	0.205
30.0	0.168	0.136	90.0	0.181	0.273
40.0		0.145	std dev	0.002	0.005
50.0	0.165	0.191			

[a] Purity: 99.7 mass %.

Table XI. Mutual Solubility S of Water (B) and *N*-Ethylaniline[a] (A) (103-69-5)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.371	0.327	60.0	0.268	0.540
10.0	0.292	0.373	70.0	0.281	0.593
20.0	0.285	0.420	80.0	0.305	0.564
30.0	0.263	0.425	90.0	0.334	0.588
40.0	0.255	0.412	std dev	0.001	0.013
50.0	0.261	0.550			

[a] Purity: 98 mass %.

Table XII. Mutual Solubility S of Water (B) and 2-Ethylaniline[a] (A) (578-54-1)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
10.0	0.72		60.0	0.74	1.63
20.0	0.75	1.30	70.0	0.76	1.59
30.0	0.70	1.88	80.0	0.84	1.56
40.0	0.65	1.81	90.0	0.87	1.48
50.0	0.66	1.61	std dev	0.01	0.08

[a] Purity: 99+ mass %.

total of 58 compounds studied (Tables XXIII and XXIX), 50 were miscible with water in all proportions between 0 and 90 °C. Of the 8 that show phase separation (Tables XXIV–XXVIII and XXX–XXXII), 4 had lower critical solution temperatures in this temperature range.

No previous literature data could be found for any of the systems studied. Sorensen and Arlt (*1*) give data for several aniline derivatives, but none for the systems reported here. The more than 40 volumes of the *Solubility Data Series* of the International Union of Pure and Applied Chemistry (*2*) do not include these systems.

Table XIII. Mutual Solubility S of Water (B) and 4-Ethylaniline[a] (A) (589-16-2)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
20.0	0.51	3.58	70.0	0.55	3.84
30.0	0.44	3.60	80.0	0.59	3.49
40.0	0.44	3.13	90.0	0.72	2.87
50.0	0.46	3.48	std dev	0.01	0.06
60.0	0.48	3.09			

[a] Purity: 99.5 mass %.

Table XIV. Mutual Solubility S of Water (B) and 2,3-Dimethylaniline[a] (A) (87-59-2)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.90	2.25	60.0	0.70	2.17
10.0	0.70	2.32	70.0	0.81	2.50
20.0	0.64	2.23	80.0	0.73	2.42
30.0	0.50	2.64	90.0	0.81	1.74
40.0	0.51	2.78	std dev	0.02	0.08
50.0	0.56	2.19			

[a] Purity: 99.5 mass %.

Table XV. Mutual Solubility S of WAter (B) and 2,4-Dimethylaniline[a] (A) (95-68-1)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.77	3.86	60.0	0.60	2.55
10.0	0.61	2.96	70.0	0.59	2.60
20.0	0.59	2.60	80.0	0.64	2.59
30.0	0.52	2.53	90.0	0.82	2.98
40.0	0.53	2.50	std dev	0.02	0.06
50.0	0.53	3.19			

[a] Purity: 98.5 mass %.

Table XVI. Mutual Solubility S of Water (B) and 2,5-Dimethylaniline[a] (A) (95-78-3)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.68	2.84	60.0	0.51	1.83
10.0	0.48	1.57	70.0	0.59	1.94
20.0	0.50	1.88	80.0	0.69	1.81
30.0	0.45	2.13	90.0	0.69	
40.0	0.42	1.74	std dev	0.01	0.05
50.0	0.48	1.85			

[a] Purity: 97 mass %.

Table XVII. Mutual Solubility S of Water (B) and 2,6-Dimethylaniline[a] (A) (87-62-7)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.68	1.01	60.0	0.51	1.14
10.0	0.60	0.88	70.0	0.55	1.42
20.0	0.47	0.97	80.0	0.63	1.55
30.0	0.45	1.18	90.0	0.80	1.52
40.0	0.44	1.10	std dev	0.03	0.07
50.0	0.48	1.07			

[a] Purity: 99 mass %.

Experimental Section

To determine whether a particular organic compound mixes completely with water, 10 cm^3 of water at 0 °C were placed in a flask, and successively 1, 1, 2, 2, and 4 cm^3 of the organic

Table XVIII. Mutual Solubility S of Water (B) and 3,5-Dimethylaniline[a] (A) (108-69-0)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.48	2.08	60.0	0.46	2.15
10.0	0.47	2.18	70.0	0.55	1.87
20.0	0.35	1.72	80.0	0.56	2.38
30.0	0.36	2.27	90.0	0.62	2.07
40.0	0.53	2.52	std dev	0.01	0.1
50.0	0.41	2.09			

[a] Purity: 98.5 mass %.

Table XIX. Mutual Solubility S of Water (B) and 2-Methyl-6-ethylaniline[a] (A) (24549-06-2)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.46	0.52	60.0	0.33	0.86
10.0	0.46	0.58	70.0	0.33	0.81
20.0	0.36	0.66	80.0	0.41	0.81
30.0	0.37	0.73	90.0	0.42	0.89
40.0	0.36	0.99	std dev	0.01	0.02
50.0	0.37	0.88			

[a] Purity: 99 mass %.

Table XX. Mutual Solubility S of Water (B) and 2-Isopropylaniline[a] (A) (643-28-7)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
10.0	0.34	0.90	60.0	0.49	1.29
20.0	0.34	1.27	70.0	0.48	1.42
30.0	0.34	0.93	80.0	0.37	1.42
40.0	0.47	1.39	90.0	0.42	1.52
50.0	0.41	1.13	std dev	0.01	0.03

[a] Purity: 99+ mass %.

Table XXI. Mutual Solubility S of Water (B) and N,N-Diethylaniline[a] (A) (91-66-7)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.016	0.028	60.0	0.021	0.073
10.0	0.017	0.022	70.0	trace	0.080
20.0	trace	0.026	80.0	trace	0.108
30.0	trace	0.037	90.0	trace	0.120
40.0	trace	0.047	std dev	0.001	0.002
50.0	trace	0.071			

[a] Purity: 99.7 mass %.

Table XXII. Mutual Solubility S of Water (B) and N,N-Dimethylbenzylamine[a] (A) (103-83-3)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	2.59	12.35	60.0	0.70	1.85
10.0	1.93	5.49	70.0	0.67	1.69
20.0	1.41	3.01	80.0	0.61	1.75
30.0	1.13	2.35	90.0	0.58	1.96
40.0	0.92	1.93	std dev	0.01	0.09
50.0	0.81	1.83			

[a] Purity: 99.9+ mass %.

compound was added with shaking. Possible phase separation was noted after each addition. This was then repeated with 10 cm^3 of water at 90 °C. If there was no evidence of phase separation, it was assumed the organic compound mixes with water in all proportions between 0 and 90 °C.

For those organic compounds showing phase separation, the organic compound and water were brought into equilibrium in a thermostat at a given temperature, and samples of each layer were removed with a syringe for analysis by GLC. Standard solutions of the organic compound and water were made by mass with use of an analytical balance, and used to calibrate the GLC. From these, standard deviations were calculated on the basis of an average composition, and are listed in Tables II–XXII, XXIV–XXVIII, and XXX–XXXII.

Table XXIII. Alkanolamines Miscible with Water in All Proportions

ethanolamine (141-43-5)
4-ethylmorpholine (100-74-3)
2,6-dimethylmorpholine (141-91-3)
3-(diethylamino)-1-propanol (622 93-5)
(2-methoxyethyl)amine (109-85-3) (bp 90 °C)
3-amino-1-propanol (156-87-6) (fp 11.5 °C)
2-(dimethylamino)-2-methyl-1-propanol (7005-47-2)
2-(ethylamino)ethanol (110-73-6)
2-(2-aminoethoxy)ethanol (929-06-6)
(3-ethoxypropyl)amine (6291-85-6)
1-(dimethylamino)-2-propanol (108-16-7)
3-(dimethylamino)-1-propanol (3179-63-3)
N-methylethanolamine (109-83-1)
(2-ethoxyethyl)amine (110-76-9)
2-amino-2-methyl-1-propanol (124-68-5)
N-butylethanolamine (111-75-1)
4-(dimethylamino)-1-butanol (1330-96-6)
6-(dimethylamino)-1-hexanol (1862-07-3)
2-(isopropylamino)ethanol (109-56-8)
2-amino-1-methoxybutane (63448-63-5)
(3-butoxypropyl)amine (16499-88-0)
2-amino-2-ethyl-1,3-propanediol (115-70-8) (mp 39 °C)
(3-methoxypropyl)amine (5332-73-0)
2-(dimethylamino)ethanol (108-01-0)
(3-isopropoxypropyl)amine (2906-12-9)
N-*tert*-butyldiethanolamine (2160-93-2)

Table XXIV. Mutual Solubility S of Water (B) and N-Isobutylmorpholine[a] (A) (10315-98-7)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	8.29		60.0	1.12	1.23
10.0	5.43	1.06	70.0	1.03	1.28
20.0	3.53	1.08	80.0	0.93	1.35
30.0	2.39	1.10	90.0	0.92	1.40
40.0	1.79	1.10	std dev	0.02	0.01
50.0	1.44	1.21			

[a] Purity: 99.7 mass %.

Table XXV. Mutual Solubility S of Water (B) and 2-(Dibutylamino)ethanol[a] (A) (102-81-8)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	1.41	8.55	60.0	0.14	4.16
10.0	0.86	6.44	70.0	0.18	4.14
20.0	0.44	5.94	80.0	0.14	3.97
30.0	0.46	6.05	90.0	0.17	4.00
40.0	0.34	5.80	std dev	0.01	0.10
50.0	0.18	4.41			

[a] Purity: 99.5 mass %.

Table XXVI. Mutual Solubility S of Water (B) and N,N-Diethylhydroxylamine[a] (A) (3710-84-7)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	39.4		60.0	29.6	15.3
10.0	38.2	17.7	70.0	28.9	16.1
20.0	36.3	14.8	80.0	28.1	16.6
30.0	35.2	14.0	90.0	27.4	17.6
40.0	32.5	14.6	std dev	0.1	0.2
50.0	30.5	14.8			

[a] Purity: 99.2 mass %.

Table XXVII. Mutual Solubility S of Water (B) and 2-(Diisopropylamino)ethanol[a] (A) (96-80-0)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
13.6	30.12	40.19	50.0	4.03	8.30
15.0	25.04	33.72	60.0	3.00	7.08
16.0	20.20	27.40	70.0	2.46	6.88
18.0	16.04	21.94	80.0	2.15	5.73
20.0	15.01	19.33	90.0	1.89	5.29
30.0	8.67	13.32	std dev	0.12	0.12
40.0	5.44	9.27			

[a] Purity: 99.8 mass %. The lower critical solution temperature for this system is 13.6 °C. Below this temperature, A and B are miscible in all proportions.

Table XXVIII. Mutual Solubility S of Water (B) and 1-Diethylamino-2-propanol[a] (A) (4402-32-8)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
30.0	30.77	30.5	70.0	6.36	8.9
32.0	26.34	24.4	80.0	5.49	8.8
40.0	15.55	16.0	90.0	4.88	7.8
50.0	11.14	12.7	std dev	0.12	0.1
60.0	7.91	10.5			

[a] Purity: 99 mass %. The lower critical solution temperature for this system is 30 °C. Below this temperature, A and B are miscible in all proportions.

Table XXIX. Polyamines Miscible with Water in All Proportions

ethylenediamine (107-15-3) (fp 10.9 °C)
1,3-diaminopentane (589-37-7)
2-[(2-aminoethyl)amino]ethanol (111-41-1)
N,N'-dimethyl-1,3-propanediamine (109-55-7)
N-(2-hydroxypropyl)ethylenediamine (123-84-2)
2,2-dimethyl-1,3-propanediamine (7328-91-8) (mp 26 °C)
N,N-bis(3-aminopropyl)methylamine (105-83-9)
4-amino-1-(diethylamino)pentane (140-80-7)
1,4-butanediamine (110-60-1) (mp 26 °C)
N,N'-diethyl-1,3-propanediamine (104-78-9)
N,N,N',N'-tetramethyl-1,3-butanediamine (97-84-7)
N,N'-dimethylneopentanediamine (53369-71-4)
N,N,N',N'-tetramethyl-1,3-propanediamine (110-95-2)
bis(3-aminopropyl)amine (56-18-8)
2-methyl-1,5-pentanediamine (15520-10-2)
N-ethylethylenediamine (110-72-5)
N,N'-dimethylethylenediamine (108-00-9)
1,3-diaminopropane (109-76-2)
1,2-propanediamine (78-90-0)
N,N'-diethylethylenediamine (100-36-7)
N,N,N',N'-tetramethylethylenediamine (110-18-9)
N-methyl-1,3-propanediamine (6291-84-5)
1,6-diaminohexane (124-09-4)
diethylenetriamine (111-40-0)

From three to five standards were made for each system studied. In most cases the water and the organic compound were not completely miscible, so a third solvent was added to form a homogeneous solution. Some judgment was required in selecting the third solvent, since it should not interfere with the other peaks on the GLC.

Analysis was done on a Gow-Mac Series 550 thermal conductivity gas chromatograph GC, a 1.9-m by 2.2-mm-internal-diameter column, Chromosorb 103 packing, and a Hewlett-Packard 3390A recorder–integrator. 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.

All measurements were made at atmospheric pressure. Most of the organic compounds came from laboratory supply houses such as Aldrich or TCI America; a few were supplied by commercial producers of the compounds.

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

Table XXX. Mutual Solubility S of Water (B) and *N,N'*-Dibutylethylenediamine[a] (A) (3529-09-7)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	3.72	61.0	60.0	0.57	21.9
10.0	2.42	53.2	70.0	0.56	18.9
20.0	1.59	44.2	80.0	0.53	14.6
30.0	1.18	37.6	90.0	0.56	10.4
40.0	0.78	26.0	std dev	0.01	0.4
50.0	0.64	25.4			

[a] Purity: 99.4 mass %.

Table XXXI. Mutual Solubility S of Water (B) and [3-(Dibutylamino)propyl]amine[a] (A) (102-83-0)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
3.0	6.20	85.1	50.0	0.58	33.8
5.0	4.41	79.5	60.0	0.53	26.7
10.0	2.09	66.1	70.0	0.51	22.9
20.0	1.46	52.5	80.0	0.45	17.7
30.0	1.03	50.8	90.0	0.37	14.4
40.0	0.74	43.9	std dev	0.01	0.5

[a] Purity: 99.6 mass %. The lower critical solution temperature for this system is 3 °C. Below this temperature, A and B are miscible in all proportions.

Table XXXII. Mutual Solubility S of Water (B) and *N,N,N',N'*-Tetramethyl-1,6-hexanediamine[a] (A) (111-18-2)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
57.0	10.74	59.5	70.0	3.00	28.0
58.0	8.29	57.9	80.0	2.21	17.8
59.0	7.26	53.6	90.0	1.64	10.8
60.0	5.93	47.2	std dev	0.05	0.8

[a] Purity: 99.1 mass %. The critical solution temperature for this system is 57 °C. Below this temperature, A and B are miscible in all proportions.

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