Mutual Solubility of Water and Nitriles

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Mutual solubilities of 21 nitriles in water have been measured from 0 to 90 °C. All nitriles except malononitrile exhibited partial miscibility over this temperature range. Aromatic nitriles have higher solubilities than aliphatic nitriles, and an unsaturated nitrile (acrylonitrile) shows higher solubility than a saturated nitrile (propionitrile). In general, mutual solubilities decrease with an increase in the molar mass of the nitrile.

Introduction

The nitriles are important industrial chemicals which are produced commercially all over the world. They readily enter into chemical reactions because of the reactive –CN group. Thus, although several of the lower nitriles such as acetonitrile find some use as solvents, the chief use of nitriles is as chemical intermediates for the production of polymer materials and a host of other chemical raw materials.

Very little has been published on the solubility of nitriles in water. Sorensen and Arlt (*1*) give data for propionitrile and 3-methoxypropionitrile. We did not measure the latter. Their data for propionitrile show little agreement with Table 3 except for the solubility of the nitrile in water at the higher temperatures. There is wide disagreement for the solubility of water in the nitrile. Some of the data they have used go back to 1898.

Experimental Section

As before (*2-9*), samples were analyzed using the method of standard additions. Water and an organic were brought into equilibrium at a given temperature in a thermostatically-controlled water bath (Figure 1). Samples of each layer were removed with a syringe for analysis. To determine the amount of water in the organic layer sample, a weighted quantity of a solvent such as propanol was added and the ratio of the water to the propanol peak measured with a Gow-Mac Series 550 thermal conductivity GC, a 1.9-m by 2.2-mm-i.d. 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 propanol added and the gas chromatograph (GC) scale factors for water and propanol as determined from GC analyses of known water and propanol solutions. This calibration was done for each system using at least three standards covering, if possible, the composition range of the unknown solutions.

The amount of the organic in the water layer was determined in a similar way using a standard which appears at a different place on the GC diagram. For example, benzyl cyanide was determined using 2-butoxyethanol as the standard. As in the case of the water layer, the calibration was done for each system using at least three standard solutions.

All experimental measurements were done at atmospheric pressure. Most organics came from laboratory supply houses such as Aldrich or TCI America. A few were supplied by commercial producers of the compounds.

In some instances, the sample separated into two phases on cooling and had to be brought into solution 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 were calculated on the basis of an average composition and are listed in Tables 1–21. The temperature of the thermostat was controlled by a Braun Thermomix 1480 or a Lauda Brinkmann RM 20 water bath for the lower temperatures.

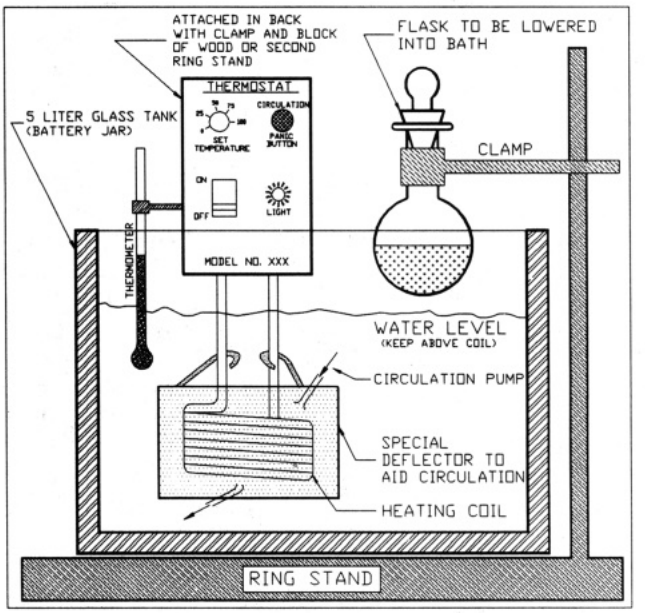

Figure 1.

Table 1. Mutual Solubility *S* of Water (B) and Chloroacetonitrile[a] (A) (107-14-2)

	S/(mass %)			*S*/(mass %)	
t/°C	A in B	B in A	*t*/°C	A in B	B in A
0	5.27	1.27	60.0	7.45	4.21
10.0	5.36	1.38	70.0	8.36	5.47
20.0	5.82	1.79	80.0	12.73	6.81
30.0	6.39	2.24	90.0	14.85	8.59
40.0	6.91	2.54	std dev	0.05	0.04
50.0	7.47	3.28			

[a] Purity: 99+ mass %.

Table 2. Mutual Solubility *S* of Water (B) and Trichloroacetonitrile[a] (A) (545-06-2)

	S/(mass %)			*S*/(mass %)	
t/°C	A in B	B in A	*t*/°C	A in B	B in A
0	0.230	0.100	50.0	0.098	0.131
10.0	0.130	0.078	60.0	0.120	0.174
20.0	0.124	0.100	70.0	0.108	0.213
30.0	0.072	0.141	80.0	0.081	0.259
40.0	0.095	0.087	std dev	0.008	0.006

[a] Purity: 97 mass %. Boiling point: 83–84 °C.

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Table 3. Mutual Solubility S of Water (B) and Propionitrile[a] (A) (107-12-0)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	6.2	18.4	60.0	9.8	12.2
10.0		13.8	70.0	13.4	12.6
20.0	5.5	12.2	80.0	15.6	13.7
30.0	6.5	12.3	90.0	19.5	14.7
40.0	7.9	11.0	std dev	0.2	0.2
50.0	9.4	11.5			

[a] Purity: 99 mass %.

Table 4. Mutual Solubility S of Water (B) and 3-Chloropropionitrile[a] (A) (542-76-7)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	3.69	1.39	60.0	6.62	4.73
10.0	3.91	1.71	70.0	7.09	5.66
20.0	4.31	2.31	80.0	7.87	7.01
30.0	4.92	4.27	90.0	9.49	8.81
40.0	5.85	5.59	std dev	0.1	0.1
50.0	5.85	6.16			

[a] Purity: 99.7 mass %.

Table 5. Mutual Solubility S of Water (B) and Acrylonitrile[a] (A) (107-13-1)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	6.58	2.08	50.0	7.36	5.33
10.0	6.68	2.57	60.0	7.39	6.57
20.0	6.90	3.28	70.0	8.56	8.16
30.0	6.64	3.81	std dev	0.2	0.05
40.0	6.88	4.68			

[a] Purity: 99+ mass %. Boiling point of A: 77 °C. Inhibited with hydroquinone monomethyl ether.

Table 6. Mutual Solubility S of Water (B) and Butyronitrile[a] (A) (109-74-0)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	3.75	1.72	60.0	3.21	4.65
10.0		1.98	70.0	3.19	5.32
20.0	3.35	1.99	80.0	3.40	5.36
30.0	3.31	2.76	90.0	3.61	6.49
40.0	3.25	3.31	std dev	0.05	0.04
50.0	3.23	3.86			

[a] Purity: 98 mass %.

Table 7. Mutual Solubility S of Water (B) and Isobutyronitrile[a] (A) (78-82-0)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	3.70	1.59	60.0	3.42	4.42
10.0	3.60	1.92	70.0	3.48	5.15
20.0	3.70	2.15	80.0	3.71	5.65
30.0	3.31	2.65	90.0	3.63	6.05
40.0	3.36	3.10	std dev	0.05	0.03
50.0	3.46	3.74			

[a] Purity: 99 mass %.

The absolute temperature was measured by a calibrated thermometer accurate to 0.1 °C.

Summary of Data

All nitriles except malononitrile showed only partial mutual solubility over the temperature range from 0 to 90 °C.

Table 8. Mutual Solubility S of Water (B) and 4-Chlorobutyronitrile[a] (A) (628-20-6)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	2.14	1.03	60.0	3.31	3.32
10.0	1.92	1.24	70.0	3.49	3.60
20.0	2.04	1.72	80.0	3.88	4.60
30.0	2.26	2.15	90.0	4.12	5.28
40.0	2.34	2.16	std dev	0.2	0.05
50.0	2.54	2.74			

[a] Purity: 98.8 mass %.

Table 9. Mutual Solubility S of Water (B) and Allyl Cyanide[a] (A) (109-75-1)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	3.32	1.61	60.0	3.79	4.60
10.0	3.31	1.96	70.0	4.14	5.37
20.0	3.30	2.51	80.0	4.96	5.72
30.0	3.28	2.80	90.0	5.57	6.80
40.0	3.46	3.46	std dev	0.02	0.02
50.0	3.67	4.01			

[a] Purity: 99 mass %.

Table 10. Mutual Solubility S of Water (B) and Methacrylonitrile[a] (A) (126-98-7)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	2.63	0.94	50.0	2.35	2.35
10.0	2.33	1.17	60.0	2.58	2.87
20.0	2.18	1.46	70.0	2.61	3.43
30.0	2.22	1.72	80.0	3.29	3.66
40.0	2.22	1.87	std dev	0.05	0.03

[a] Purity: 99 mass %. Normal boiling point of A: 90 °C.

Table 11. Mutual Solubility S of Water (B) and Crotononitrile[a] (A) (4786-20-3)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	3.23	1.55	60.0	3.24	4.48
10.0	3.17	2.09	70.0	3.68	5.02
20.0	3.00	2.53	80.0	4.39	5.97
30.0	2.99	2.78	90.0	4.19	6.55
40.0	3.04	3.24	std dev	0.05	0.06
50.0	3.16	3.97			

[a] Purity: 99.9 mass %.

Table 12. Mutual Solubility S of Water (B) and Valeronitrile[a] (A) (110-59-8)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	1.54	1.01	60.0	1.45	4.73
10.0	1.51	1.19	70.0	1.69	4.40
20.0	1.30	1.56	80.0	2.16	5.35
30.0	1.32	2.69	90.0	2.09	4.68
40.0	1.32	3.18	std dev	0.03	0.1
50.0	1.39	4.57			

[a] Purity: 98.9 mass %.

Solubility increased or in some cases remained essentially constant with temperature. Aromatic nitriles such as benzyl cyanide and the three tolunitriles (Tables 17–20) showed higher solubility than the aliphatic nitrile (Table 16). Acrylonitrile (Table 5), an unsaturated nitrile, had higher solubility than saturated propionitrile (Table 3), but unsaturated crotononitrile (Table 11) had about the same solubility as saturated butyronitrile (Table 6). As expected, solubility

Table 13. Mutual Solubility S of Water (B) and 3-Pentenenitrile[a] (A) (4635-87-4)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	1.09	1.10	60.0	1.12	2.86
10.0	1.01	1.29	70.0	1.24	3.49
20.0	0.90	1.61	80.0	1.68	3.98
30.0	0.89	1.91	90.0	1.43	4.74
40.0	0.99	2.22	std dev	0.02	0.04
50.0	0.99	2.54			

[a] Purity: 96.8 mass %.

Table 14. Mutual Solubility S of Water (B) and Isocapronitrile[a] (A) (542-54-1)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.40	0.83	60.0	0.35	1.83
10.0	0.34	0.92	70.0	0.41	2.03
20.0	0.32	1.10	80.0	0.43	2.37
30.0	0.32	1.10	90.0	0.50	3.10
40.0	0.34	1.51	std dev	0.01	0.03
50.0	0.34	1.54			

[a] Purity: 99.9 mass % mixed isomers, 79.6 mass % isocapronitrile.

Table 15. Mutual Solubility S of Water (B) and Benzonitrile[a] (A) (100-47-0)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.35	0.85	60.0	0.42	1.62
10.0	0.33	0.78	70.0	0.60	2.05
20.0	0.40	1.21	80.0	0.95	2.31
40.0	0.45	1.40	90.0	0.91	2.62
50.0	0.38	1.56	std dev	0.01	0.03

[a] Purity: 99+ mass %.

Table 16. Mutual Solubility S of Water (B) and Octanenitrile[a] (A) (124-12-9)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	trace	0.58	60.0	trace	1.29
10.0	trace	0.57	70.0	trace	1.47
20.0	trace	0.97	80.0	0.033	1.50
30.0	trace	0.96	90.0	0.033	1.57
40.0	trace	1.12	std dev	0.001	0.02
50.0	trace	1.10			

[a] Purity: 98.3 mass %.

Table 17. Mutual Solubility S of Water (B) and Benzyl Cyanide[a] (A) (140-29-4)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.17	1.16	60.0	0.33	1.92
10.0	0.14	1.17	70.0	0.39	1.76
20.0	0.14	1.65	80.0	0.61	2.45
30.0	0.18	1.84	90.0	0.51	2.31
40.0	0.22	1.73	std dev	0.01	0.05
50.0	0.28	2.00			

[a] Purity: 99+ mass %.

decreased substantially as the molar weight of the nitrile increased.

Malononitrile (Table 21) showed a particularly interesting solubility relationship with temperature. The mutual solubility in both layers is high and increases with temperature. At 61 °C, there is an upper critical solution temperature, and malononitrile and water are miscible in all proportions above this temperature.

Table 18. Mutual Solubility S of Water (B) and o-Tolunitrile[a] (A) (529-19-1)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
10.0	0.092		60.0	0.153	1.71
20.0	0.108	0.83	70.0	0.170	1.62
30.0	0.095	1.07	80.0	0.237	1.47
40.0	0.113	0.97	90.0	0.268	2.50
50.0	0.191	1.17	std dev	0.002	0.02

[a] Purity: 99.5 mass %. Melting point of A: 16 °C.

Table 19. Mutual Solubility S of Water (B) and m-Tolunitrile[a] (A) (620-22-4)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
0	0.10	0.41	60.0	0.18	1.19
10.0	0.11	0.50	70.0	0.18	1.31
20.0	0.10	0.63	80.0	0.21	1.58
30.0		0.74	90.0	0.23	1.63
40.0	0.14	0.94	std dev	0.01	0.02
50.0	0.15	1.08			

[a] Purity: 99.2 mass %.

Table 20. Mutual Solubility S of Water (B) and p-Tolunitrile[a] (A) (104-85-8)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
30.0	0.078	0.80	70.0	0.152	1.53
40.0	0.083	0.90	80.0	0.226	1.68
50.0	0.162	1.08	90.0	0.211	1.92
60.0	0.139	1.40	std dev	0.002	0.02

[a] Purity: 99.8 mass %. Freezing point of A: 26.5 °C.

Table 21. Mutual Solubility S of Water (B) and Malononitrile[a] (A) (109-77-3)

	S/(mass %)			S/(mass %)	
t/°C	A in B	B in A	t/°C	A in B	B in A
40.0	14.5	12.9	60.0	32.1	33.4
50.0	23.3	19.9	std dev	0.5	0.4

[a] Purity: 99.9 mass %. Melting point of A: 32 °C. Upper critical solution temperature for this system: 61 °C. Above this temperature, A and B are miscible in all proportions.

Registry numbers in this paper were supplied by the author.

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