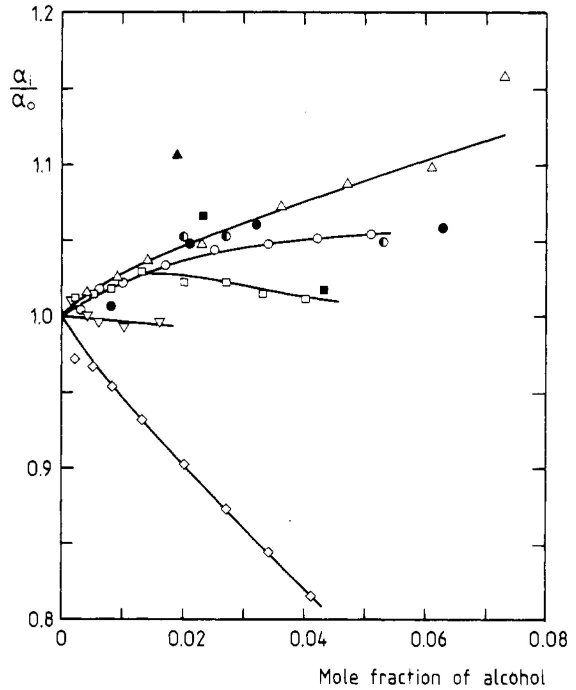

Figure 1. Relative oxygen solubilities at 25 °C as a function of alcohol mole fractions: (△) methanol (▲, Tokunaga (*7*), 20 °C), (○) ethanol (◐, Shchukarev and Tolmacheva (*8*); ●, Cargill (9)), (□) 1-propanol (■, Tokunaga (*7*), 20 °C), (▽) 1-butanol, (◇) glycerol.

Results and Discussion

The values of relative solubility listed in Tables II and III are the mean of two determinations, each. Generally, the values of α_i/α_0 decreased with increasing chain length of the alcohols and with decreasing temperature. The results for 25 °C are depicted and compared to the available literature data in Figure 1. The most extensive studies were reported by Tokunaga (*7*) for temperatures of 0, 20, and 40 °C. His data for low concentrations of methanol and ethanol are high; most of the values are out of the range covered in Figure 1. For ethanol solutions, the results of Shchukarev and Tolmacheva (*8*) for 12 and 25 °C and those of Cargill (*9*) (interpolated for the temperatures applied in this study) agree with the present results. For 1-propanol the data of Tokunaga (*7*) fall in a more reasonable range but show a scatter that renders them useless. The present results show the oxygen solubility to run through a maximum at 1.5–2% mole fraction of 1-propanol. The maximum is most pronounced at 15 °C and almost vanishes at 37 °C. For 1-butanol no previous study has been reported; the present results show no significant effects on the oxygen solubility. The strong decrease of oxygen solubility by glycerol could well be described by eq 2. The relative solubilities at 15 °C are smaller than those reported by Müller (*10*) for 12.2 °C whereas the results for 37 °C are very well represented by $K_i = 4.07 \times 10^{-4}$ L g^{-1} suggested by Zander (*11*). K_i values for all three temperatures are listed in Table III.

It should be emphasized that the reported relative solubilities refer to a fixed oxygen partial pressure (101.3 kPa) whereas the actual dissolved oxygen concentrations at a fixed total pressure are influenced by the partial pressures of alcohol and water. The strongest effect was encountered for 12.2 wt % methanol at 37 °C where $\alpha_i/\alpha_0 = 1.159$ as compared to a ratio of 1.121 of the actual dissolved oxygen concentrations at 101.3-kPa total pressure. Still there is a solubility increase by small-chain alcohols that gives them a unique position as other solutes usually decrease the gas solubilities as compared to water.

Registry No. Glycerol, 56-81-5; methanol, 67-56-1; ethanol, 64-17-5; 1-propanol, 71-23-8; 1-butanol, 71-36-3; oxygen, 7782-44-7.

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Mutual Solubility of Water and Aliphatic Alcohols

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Mutual solubilities of water and aliphatic alcohols were measured at atmospheric pressure and for the temperature range of 0–90 °C by using the method of standard additions. Binary liquid–liquid equilibrium concentrations for the two liquid layers are given for mixtures of water and the following alcohols: 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 2-methyl-2-butanol, 3-methyl-1-butanol, 3-methyl-2-butanol, 2,2-dimethyl-1-propanol, 1-hexanol, 2-hexanol, 3-hexanol, 2-methyl-1-pentanol, 3-methyl-3-pentanol, 4-methyl-2-pentanol, 1-heptanol, 2-heptanol, 2,4-dimethyl-3-pentanol, 1-octanol, and 2-ethyl-1-hexanol.

Accurate liquid–liquid solubility data are needed to check theoretical solubility relationships and to determine solubility parameters for liquid–liquid mixtures. Also the chemical and petroleum industries have a very strong interest in liquid–liquid solubilities, particularly the solubility of organics in water and water in organics. Such information is necessary for the design of liquid–liquid extractors and the design of decanters in distillation systems. It is of particular importance in these days of higher energy costs.

There are two recent surveys of available liquid–liquid solubility data. Sorensen and Arlt (*1*) give binary data for many systems and critically evaluated "smoothed" values. The International Union of Pure and Applied Chemistry (*2*) is spon-

Table I. Mutual Solubility of Water and 1-Pentanol

	solubility, wt %			solubility, wt %	
temp, °C	A in B[a]	B in A[a]	temp, °C	A in B[a]	B in A[a]
0	3.31	9.54	50.0	1.83	11.66
10.2	2.59	9.75	60.3	1.83	12.30
20.2	2.25	10.21	70.0	1.95	13.08
30.6	2.02	10.56	80.0	1.99	14.01
40.2	1.87	11.09	90.7	2.21	14.98

[a] A: 1-Pentanol (99%). B: Water.

Table II. Mutual Solubility of Water and 2-Pentanol

	solubility, wt %			solubility, wt %	
temp, °C	A in B[a]	B in A[a]	temp, °C	A in B[a]	B in A[a]
0	7.29	10.68	50.0	3.32	12.20
10.1	5.77	10.93	60.0	3.12	12.61
19.5	4.64	11.04	70.1	3.07	13.25
30.6	3.94	11.39	79.9	3.13	13.68
40.0	3.56	11.69	90.3	3.06	14.62

[a] A: 2-Pentanol (99%). B: Water.

soring a Solubility Data Series which will eventually consist of 80–100 volumes issued over approximately the next 10 years. Volumes on liquid–liquid solubility are now in press.

However, an examination of the available literature shows that even in the case of commercially produced chemicals, liquid–liquid solubility data are often very limited, inconsistent, and of dubious accuracy. Sometimes data are available on the solubility of an organic in water, but practically nothing is available on the equally important question of the solubility of water in the organic. The purpose of the present research is to study systems where data are either lacking or inconsistent.

A major problem in obtaining accurate solubility data has been the difficulty of analyzing an organic layer containing a few percent of water and a water layer containing a few tenths of a percent of organic. However, gas chromatography combined with the method of standard additions (*3*) offers a quick and reliable way to measure liquid–liquid solubilities. This method involves the addition of a known quantity of a third component to serve as a standard to which the unknown material is compared. It has the tremendous advantage that roughly equal-sized GC peaks are obtained.

Experimental Section

To evaluate a particular system, water and alcohol were brought into equilibrium in a thermostat, and samples of each layer were removed for analysis. A weighed quantity of acetonitrile was added to the organic layer, and the ratio of the water to the acetonitrile peak was measured by using a Gow-Mac Series 550 thermal conductivity GC, Chromosorb 101 packing, and a Hewlett-Packard 3390A recorder–integrator. The amount of water present in the sample could then be immediately calculated from the weight of acetonitrile added and the GC scale factors for water and acetonitrile determined from a GC analysis of known water and acetonitrile solutions.

Alcohol in the water layer was determined in a similar way by using a higher alcohol as standard; for example, 1-pentanol was determined by using 1-hexanol as standard. In some cases temperature programming was needed, since the very large water peak sometimes interfered with the later alcohol peaks. Some samples phase separated and had to be brought into solution by heating or by the addition of a solvent such as methanol, acetone, or dimethyl sulfoxide. All measurements were done at atmospheric pressure.

To check the general accuracy of the method, wherever possible our data were compared with recommended values given by Sorensen and Arlt. The average error was less than 5%, and much of this was probably the result of differences

Table III. Mutual Solubility of Water and 3-Pentanol

	solubility, wt %			solubility, wt %	
temp, °C	A in B[a]	B in A[a]	temp, °C	A in B[a]	B in A[a]
0	8.31	7.01	50.0	4.23	9.23
10.2	6.96	7.52	60.0	3.55	9.99
20.0	5.86	7.94	70.0	3.45	9.99
30.0	5.32	8.29	80.0	3.31	11.03
40.0	4.14	8.51	90.0	3.44	11.64

[a] A: 3-Pentanol (98%). B: Water.

Table IV. Mutual Solubility of Water and 2-Methyl-1-butanol

	solubility, wt %			solubility, wt %	
temp, °C	A in B[a]	B in A[a]	temp, °C	A in B[a]	B in A[a]
0.5	3.91	6.90	49.6	2.21	9.52
9.7	3.39	6.82	59.3	2.07	9.43
19.6	2.83	8.30	69.5	2.24	10.73
29.6	2.51	8.38	79.7	2.30	11.14
39.3	2.36	8.94	90.8	2.46	11.82

[a] A: 2-Methyl-1-butanol (98%). B: Water.

Table V. Mutual Solubility of Water and 2-Methyl-2-butanol

	solubility, wt %			solubility, wt %	
temp, °C	A in B[a]	B in A[a]	temp, °C	A in B[a]	B in A[a]
0.5	15.8	25.5	49.0	7.23	18.4
9.8	14.8	24.2	60.0	6.25	19.4
20.8	11.5	20.5	70.2	5.97	17.6
29.5	9.94	19.1	80.1	5.70	17.7
39.5	8.15	19.5	90.2	5.47	17.5

[a] A: 2-Methyl-2-butanol (99%). B: Water.

Table VI. Mutual Solubility of Water and 3-Methyl-1-butanol

	solubility, wt %			solubility, wt %	
temp, °C	A in B[a]	B in A[a]	temp, °C	A in B[a]	B in A[a]
0	3.73	9.29	49.9	2.03	11.55
10.1	3.14	9.37	59.8	2.19	11.97
19.8	2.64	9.62	70.0	2.11	12.88
30.2	2.29	10.28	80.0	2.20	13.50
40.0	2.18	10.47	90.0	2.27	14.45

[a] A: 3-Methyl-1-butanol (98%). B: Water.

Table VII. Mutual Solubility of Water and 3-Methyl-2-butanol

	solubility, wt %			solubility, wt %	
temp, °C	A in B[a]	B in A[a]	temp, °C	A in B[a]	B in A[a]
0	8.38	11.3	50.0	4.05	12.3
10.1	7.19	11.9	60.0	3.39	12.5
20.0	5.96	12.0	70.0	3.66	13.0
30.0	5.13	12.4	79.5	3.60	13.5
40.0	4.45	12.2	90.0	3.60	13.9

[a] A: 3-Methyl-2-butanol (98%). B: Water.

Table VIII. Mutual Solubility of Water and 2,2-Dimethyl-1-propanol[a]

	solubility, wt %			solubility, wt %	
temp, °C	A in B[b]	B in A[b]	temp, °C	A in B[b]	B in A[b]
12.0	3.70	7.71	60.0	2.51	10.46
18.8	3.49	7.89	70.2	2.16	10.94
30.0	2.93	8.74	80.0	2.59	11.74
40.0	2.70	9.20	90.0	2.38	11.96
50.0	2.36	9.86			

[a] Freezes at 11 °C. [b] A: 2,2-Dimethyl-1-propanol (99%). B: Water.

Table IX. Mutual Solubility of Water and 1-Hexanol

	solubility, wt %			solubility, wt %	
temp, °C	A in B[a]	B in A[a]	temp, °C	A in B[a]	B in A[a]
0	0.964	6.50	50.0	0.497	7.58
10.2	0.759	6.70	60.0	0.518	8.11
20.0	0.666	6.82	70.3	0.577	8.69
29.7	0.558	6.93	80.3	0.625	9.19
39.8	0.514	7.41	90.3	0.638	9.54

[a] A: 1-Hexanol (98%). B: Water.

Table X. Mutual Solubility of Water and 2-Hexanol

	solubility, wt %			solubility, wt %	
temp, °C	A in B[a]	B in A[a]	temp, °C	A in B[a]	B in A[a]
0	2.06	6.60	50.0	0.96	7.65
10.1	1.68	6.52	60.2	0.91	7.81
19.8	1.29	7.04	70.0	0.98	8.29
29.9	1.18	7.08	80.1	1.13	8.89
40.0	1.09	7.40	90.2	0.94	8.67

[a] A: 2-Hexanol (99%). B: Water.

Table XI. Mutual Solubility of Water and 3-Hexanol

	solubility, wt %			solubility, wt %	
temp, °C	A in B[a]	B in A[a]	temp, °C	A in B[a]	B in A[a]
0	2.75	3.43	50.0	1.10	5.48
10.1	1.96	4.05	60.1	1.02	5.74
20.0	1.67	4.35	70.2	1.02	6.24
30.0	1.39	4.69	80.2	1.07	6.52
39.8	1.23	5.09	90.3	1.10	6.81

[a] A: 3-Hexanol (99%). B: Water.

Table XII. Mutual Solubility of Water and 2-Methyl-1-pentanol

	solubility, wt %			solubility, wt %	
temp, °C	A in B[a]	B in A[a]	temp, °C	A in B[a]	B in A[a]
0	1.301	4.78	60.1		6.35
10.0	1.036	4.85	60.3	0.758	
19.3		4.91	70.1	0.770	
19.6	0.878		70.2		6.70
30.8	0.791		79.8		7.14
30.9		5.28	80.3	0.838	
40.0		5.41	90.5		7.20
40.3	0.772		90.7	0.921	
50.0	0.751	5.96			

[a] A: 2-Methyl-1-pentanol (95%). B: Water.

Table XIII. Mutual Solubility of Water and 3-Methyl-3-pentanol

	solubility, wt %			solubility, wt %	
temp, °C	A in B[a]	B in A[a]	temp, °C	A in B[a]	B in A[a]
9.8	4.58	10.76	59.5	2.02	9.19
19.5	3.54	10.59	70.1	1.91	9.68
29.8	3.45	10.29	80.1	1.86	9.50
39.8	2.78	9.76	90.4	1.68	9.26
49.7	2.44	9.94			

[a] A: 3-Methyl-3-pentanol (99%). B: Water.

Table XIV. Mutual Solubility of Water and 4-Methyl-2-pentanol

	solubility, wt %			solubility, wt %	
temp, °C	A in B[a]	B in A[a]	temp, °C	A in B[a]	B in A[a]
0	2.82	5.08	50.0	1.19	6.90
9.7	2.09	5.61	60.1	1.11	7.08
20.0	1.63	5.90	70.2	1.13	7.34
30.0	1.53	6.00	80.2	1.24	7.87
40.3	1.29	6.63	90.2	1.17	8.50

[a] A: 4-Methyl-2-pentanol (99%). B: Water.

Table XV. Mutual Solubility of Water and 1-Heptanol

	solubility, wt %			solubility, wt %	
temp, °C	A in B[a]	B in A[a]	temp, °C	A in B[a]	B in A[a]
0	0.236	5.46	50.1	0.162	
9.7		6.22	60.0	0.178	
10.5	0.253		60.1		6.56
19.7		6.63	70.0		6.74
20.2	0.184		70.1	0.204	
29.9		5.76	80.0		7.17
30.6	0.154		80.1	0.217	
39.8	0.166		90.5	0.243	10.18
40.1		5.87			

[a] A: 1-Heptanol (99%). B: Water.

Table XVI. Mutual Solubility of Water and 2-Heptanol

	solubility, wt %			solubility, wt %	
temp, °C	A in B[a]	B in A[a]	temp, °C	A in B[a]	B in A[a]
0	0.647	4.39	49.8		5.33
10.1		4.48	50.0	0.293	
10.2	0.463		60.3	0.288	5.40
19.5	0.424		70.3	0.321	
19.6		4.67	70.4		5.69
30.6		4.84	80.0	0.321	
30.7	0.350		80.6		5.86
39.8		4.84	90.2	0.343	
40.0	0.328		90.7		6.15

[a] A: 2-Heptanol (96%). B: Water.

Table XVII. Mutual Solubility of Water and 2,4-Dimethyl-3-pentanol

	solubility, wt %			solubility, wt %	
temp, °C	A in B[a]	B in A[a]	temp, °C	A in B[a]	B in A[a]
0	1.186	2.53	50.0		3.50
10.0	1.050	2.76	60.0		3.36
20.0		2.68	60.3	0.466	
20.2	0.710		70.0		3.83
30.6	0.642	3.08	70.2	0.441	
39.5	0.533		80.1		4.13
40.0		3.30	80.2	0.428	
49.7	0.506		90.6	0.450	3.82

[a] A: 2,4-Dimethyl-3-pentanol (99+%). B: Water.

Table XVIII. Mutual Solubility of Water and 1-Octanol

	solubility, wt %			solubility, wt %	
temp, °C	A in B[a]	B in A[a]	temp, °C	A in B[a]	B in A[a]
10.0		4.14	60.2		5.33
19.0		4.35	60.3	0.088	
20.5	0.049		70.1		5.43
30.5		4.48	70.3	0.077	
30.6	0.064		80.1	0.087	5.37
40.0		4.81	90.3	0.086	
40.1	0.065		90.5		5.55
50.0	0.105	4.92			

[a] A: 1-Octanol (99%). B: Water.

Table XIX. Mutual Solubility of Water and 2-Ethyl-1-hexanol

	solubility, wt %			solubility, wt %	
temp, °C	A in B[a]	B in A[a]	temp, °C	A in B[a]	B in A[a]
0		2.08	50.0		2.82
9.8		2.24	50.2	0.074	
10.2	0.132		60.2		3.31
19.8	0.125		60.3	0.086	
20.0		2.40	70.1	0.099	
29.6	0.097		70.3		3.49
30.1		2.50	80.0		3.50
39.7		2.72	80.1	0.108	
40.1	0.110		90.3	0.117	4.04

[a] A: 2-Ethyl-1-hexanol (99%). B: Water.

in the purity of the alcohols which were used. Because of the sensitivity of GC analysis, the method was suitable for concentrations of 0.1% or less. Tables I-XIX summarize experimental measurements for systems studied. There are two interesting conclusions from studying the data. First, solubility of water in the alcohol remains quite high, even for C_7 and C_8 alcohols where solubility of alcohol in water becomes small. Second, solubility of alcohol in the water layer first decreases with temperature, goes through a minimum at about 60 °C, and then increases with temperature. Thus, any solubility equation which assumes increasing solubility with temperature will be in error, at least over the temperature range studied here.

Registry No. 1-Pentanol, 71-41-0; 2-pentanol, 6032-29-7; 3-pentanol, 584-02-1; 2-methyl-1-butanol, 137-32-6; 2-methyl-2-butanol, 75-85-4; 3-methyl-1-butanol, 123-51-3; 3-methyl-2-butanol, 598-75-4; 2,2-dimethyl-1-propanol, 75-84-3; 1-hexanol, 111-27-3; 2-hexanol, 626-93-7; 3-hexanol, 623-37-0; 2-methyl-1-pentanol, 105-30-6; 3-methyl-3-pentanol, 77-74-7; 4-methyl-2-pentanol, 108-11-2; 1-heptanol, 111-70-6; 2-heptanol, 543-49-7; 2,4-dimethyl-3-pentanol, 600-36-2; 1-octanol, 111-87-5; 2-ethyl-1-hexanol, 104-76-7.

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Effect of Concentration on Hydrolysis Rate of Tripolyphosphate at 25 °C

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The effect of concentration on the rate of hydrolysis of tripolyphosphate at 25 °C was determined at pH 5-7 in solutions that ranged from 4.76% to 32.3% in P_2O_5 content. The hydrolysis rate constants were found to increase with increasing total P_2O_5 content and decreasing pH. A general linear equation was developed for calculating rate constants and half-lives when the pH and the P_2O_5 content of tripolyphosphate solutions are known.

The hydrolytic degradation of tripolyphosphate has been studied previously (*1-11*). In a previous paper (*11*) it was indicated that concentration had little effect on the first-order rate constants for the hydrolysis of tripolyphosphate. This finding was contrary to that of previous investigators (*12*). However, later work (*13*) showed that there is an effect of concentration upon the specific rate of tripolyphosphate hydrolysis. To quantify this relationship, the rate of hydrolysis of ammonium tripolyphosphate was studied at five P_2O_5 concentrations and three pH levels.

Experimental Section

The solutions to be studied were prepared by making three stock solutions that were almost saturated with $(NH_4)_4HP_3O_{10}$ at pH 5, 6, or 7. Portions of each stock solution were diluted with distilled water in the following proportions of stock solution:water: 3:1, 1:1, 1:3, and 1:7. These diluted solutions were adjusted to the desired pH level with gaseous ammonia or cation-exchange resin in the hydrogen form. The diluted solutions, along with the stock solutions, were placed in a water bath at 25 ± 0.2 °C and agitated at 4 rpm. The solutions were sampled at various times (up to 1227 days) to determine the extent of tripolyphosphate (P_3O_{10}) hydrolysis, phosphate distribution, and pH.

Total P_2O_5 was determined gravimetrically (*14*) and the ammoniacal nitrogen determined by distillation into standard acid followed by back-titration with NaOH. The pH was measured with a glass electrode. One-dimensional paper chromatography (*15*) was used to determine the phosphate distribution as a function of reaction time.

Results and Discussion

The hydrolytic degradation of the tripolyphosphate ion proceeds according to the following model:

$$P_3O_{10} \xrightarrow[H_2O]{k_3} P_2O_7 + PO_4 \xrightarrow[H_2O]{k_2} PO_4 + PO_4 \qquad (1)$$

where P_3O_{10} represents the tripolyphosphate anionic species, and P_2O_7 and PO_4 are the corresponding pyro- and orthophosphates, respectively. The hydrolysis of tripolyphosphate follows first-order kinetics (*16*) in the pH and P_2O_5 concentration ranges studied, as shown by the plots of log % P (as P_3O_{10}) vs. time in Figures 1-3.

The hydrolysis rate constants were calculated as described previously (*16*). The rate constants for P_3O_{10}, k_3, at each pH and P_2O_5 concentration were determined by a nonlinear regression (NLIN) of the data fitted to the equation

$$P_3O_{10} = (P_3O_{10})_0 \exp(-k_3 t) \qquad (2)$$

where P_3O_{10} = percent phosphorus present as P_3O_{10} at time t, days; $(P_3O_{10})_0$ = a constant (% P as P_3O_{10} initially present in solution); k_3 = first-order rate constant for P_3O_{10} hydrolysis, day^{-1}.

The rate constants for P_2O_7 hydrolysis, k_2, at each pH and total P_2O_5 concentration were determined by a NLIN computation method in which the data were fitted to the consecutive