Oxygen Solubilities in Aqueous Alcohol Solutions

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Oxygen solubilities in aqueous alcohol solutions were investigated by Winkler's method at temperatures of 15, 25, and 37 °C. Methanol, ethanol, 1-propanol, 1-butanol, and glycerol were employed at concentrations up to 18 wt %. The relative solubilities as compared to water decreased with decreasing temperature and with increasing chain length of the alcohols.

For estimation of gas solubilities in mixed aqueous solutions of salts and organic substances, in particular for microbial culture media, an empirical model has been shown to apply (*1*) which is based on "log additivity" of the individual salting-out effects:

$$\log(\alpha_0/\alpha) = \sum_i \log(\alpha_0/\alpha_i) \qquad (1)$$

α_0/α is the ratio of the gas solubility in water to the one in a mixed solution. α_0/α_i is the individual ratio for an equally concentrated aqueous solution of component i alone. Instead of the Bunsen coefficients α (volume of gas, reduced to 0 °C and 101.3 kPa, per unit volume of solvent at a gas partial pressure of 101.3 kPa) any proportional solubility measure could be used. For salts and for some organic substances as well, the concentration dependencies can be described by the Sechenov equation:

$$\log(\alpha_0/\alpha_i) = K_i c_i \qquad (2)$$

Here c_i is the concentration of substance i and K_i is a slightly temperature-dependent constant that is specific to the substance and the gas. For small-chain alcohols eq 2 does not hold as even maxima and minima of gas solubility may be encountered with changing alcohol concentration. However, eq 1 still applies up to 10 wt % alcohol by introducing measured relative gas solubilities (α_i/α_0) for the particular alcohol concentrations (*2*). Unfortunately, literature data on oxygen solubilities in low-concentration alcohol solutions are scarce and the available data disagree strongly (*1*). It is the purpose of this paper to provide reliable solubility data in the low concentration range.

Experimental Section

The solutions were prepared from analytical-grade alcohols and distilled water. They were saturated with air in a short jacketed bubbling tower thermostated to ±0.2 K. Prior to entering the bubbling tower the air passed through another thermostated saturation flask filled with the same solution. Thus, the concentrations as determined by refractometry hardly changed by stripping during the equilibration process. Samples of the saturated solutions were analyzed for their dissolved oxygen content by the Winkler titration method (*3*). Reproducibility was better than by 1%. The measured oxygen concentrations, c (mg L^{-1}), were converted to Bunsen coefficients by the following equation:

$$\alpha = 101.3c/\{10^6\rho_{G_0}(P_b + P_{st} - P_1 - P_2)(0.2094)\}$$
$$= 0.3386c/(P_b + P_{st} - P_1 - P_2) \qquad (3)$$

where ρ_{G_0} (g cm^{-3}) is the density of oxygen gas (0 °C, 101.3 kPa), P_b is the barometric pressure, P_{st} is the mean hydrostatic head in the bubbling tower (1 kPa), and P_1 and P_2 are the partial pressures of alcohol and water, respectively. The partial pressures were obtained from the literature (*4-6*).

Table I. Oxygen Solubilities in Water

temp, °C	α_0 obsd[a]	α_0 lit.[b]	rel dev, %
15.0	0.0338	0.0342	-1.2
25.0	0.0279	0.0284	-1.8
37.0	0.0235	0.0240	-2.1

[a] Mean of eight measurements. [b] Mean of literature data (*1*).

Table II. Relative Oxygen Solubilities (α_i/α_0) in Aqueous Alcohol Solutions

concn, wt %	temp, °C	α_i/α_0 MeOH	EtOH	1-PrOH	1-BuOH
0.8	15.0	1.009	1.024	1.015	
	25.0	1.015	1.004	1.011	1.011
	37.0	1.026	1.009	1.003	1.009
1.6	15.0	1.024	1.027	1.021	
	25.0	1.025	1.018	1.015	1.000
	37.0	1.039	1.017	1.013	1.000
2.4	15.0	1.030	1.024	1.024	
	25.0	1.036	1.022	1.018	0.996
	37.0	1.039	1.030	1.017	1.004
4.0	15.0	1.039	1.027	1.030	
	25.0	1.047	1.033	1.029	0.993
	37.0	1.065	1.043	1.026	0.996
6.1	15.0	1.069	1.042	1.039	
	25.0	1.073	1.043	1.022	0.996
	37.0	1.091	1.052	1.026	
8.0	15.0	1.090	1.039	0.997	
	25.0	1.087	1.047	1.022	
	37.0	1.108	1.067	1.030	
10.2	15.0	1.096	1.039	0.997	
	25.0	1.098	1.051	1.015	
	37.0	1.129	1.082	1.047	
12.2	15.0	1.102	1.033	0.993	
	25.0	1.158	1.054	1.011	
	37.0	1.159	1.091	1.069	

Table III. Relative Oxygen Solubilities (α_i/α_0) in Glycerol Solutions and Coefficients K_i (Eq 2)

concn, wt %	α_i/α_0 15.0 °C	25.0 °C	37.0 °C
1.31	0.982	0.971	0.983
2.52	0.973	0.967	0.978
3.74	0.973	0.953	0.961
6.16	0.943	0.931	0.935
9.18	0.880	0.902	
12.21	0.847	0.873	
15.23	0.808	0.844	
18.26	0.770	0.815	0.853
10^4K_i, L g^{-1}	5.77	4.74	4.07[a]

[a] Value suggested by Zander (*11*).

The oxygen solubilities determined in water were 1-2% smaller than the mean of literature data (Table I). This small systematic error is presumably due to iodine losses during the titration procedure and cancels out in the relative solubilities (α_i/α_0). If absolute solubilities are needed, the reported relative solubilities should preferably be multiplied by the mean α_0 from the literature (*1*).

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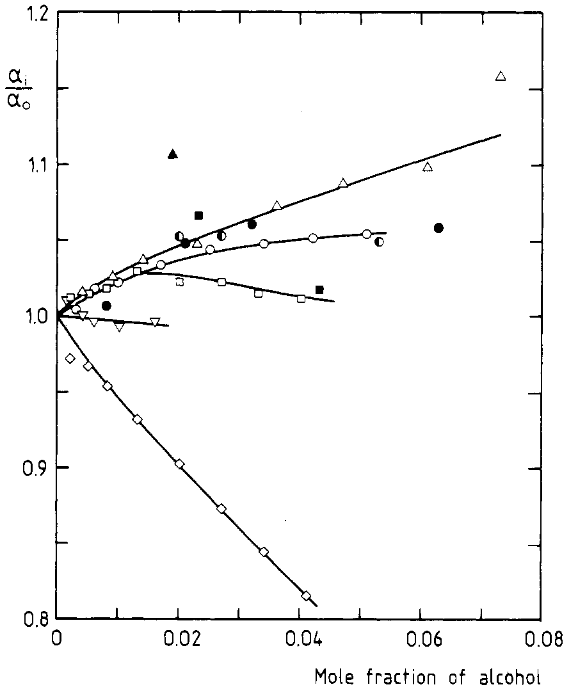

Figure 1. Relative oxygen solubilities at 25 °C as a function of alcohol mole fractions: (△) methanol (▲, Tokunaga (*7*), 20 °C), (○) ethanol (◐, Shchukarev and Tolmacheva (*8*); ●, Cargill (9)), (□) 1-propanol (■, Tokunaga (*7*), 20 °C), (▽) 1-butanol, (◇) glycerol.

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-

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