Solubilities of Oxygen, Nitrogen, and Carbon Dioxide in Aqueous Alcohol Solutions

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Gas solubilities over the complete range of composition for aqueous alcohol solutions at a partial pressure of 1 atm and at temperatures ranging from 0° to 40°C were measured. The systems studied were O_2 in methanol–water, O_2 in ethanol–water, O_2 in 1-propanol–water, O_2 in 2-propanol–water, all at 0°, 20°, and 40°C; N_2 in methanol–water, N_2 in ethanol–water, N_2 in 1-propanol–water, N_2 in 2-propanol–water, all at 20° and 40°C; CO_2 in 1-propanol–water, CO_2 in 2-propanol–water, all at 10°, 20°, 30°, and 40°C.

The solubilities of oxygen, nitrogen, and carbon dioxide in pure solvents have been investigated by many workers, but the solubilities of these gases in mixed solvents, especially containing water as one component, have scarcely been reported in the literature.

In this paper the solubilities of oxygen, nitrogen, and carbon dioxide in alcohol–water solutions over the full range of compositions were determined.

Experimental Apparatus and Procedure

The apparatus shown in Figure 1 is similar to that described in a previous paper (*11*). The principle of this method is to bring a measured volume of a solute gas into contact with a measured quantity of gas-free solution, to agitate until equilibrium is established, and to measure the volume of the remaining gas.

The apparatus comprises an absorption chamber A, gas burets (B, C, D), and a manometer E. The absorption chamber has a volume of 100 ~ 300 cc, depending on the solubility of solute gas, and a stirrer of magnet coated with glass in it. The stirrer is rotated by a magnet R, which is connected to a synchronous motor rotating at 60 rpm. There is a mark M on a capillary tube beneath the absorption chamber to indicate a base line for volume measurements.

Solvent mixtures are refluxed for several hours in the degassing flask G to remove dissolved gases. After the air in the capillary tube a is displaced with solute gas, the gas is introduced to the gas burets from the gas cylinder. Then the capillary tube from cock K_2 to point c is filled with mercury, and the absorption chamber is evacuated. The solvent is then transferred to the absorption chamber from the degassing flask, and the mercury in reservoir I is introduced through cock K_2 to fill the absorption chamber completely with solvent and mercury.

After the temperature in A reaches equilibrium, cock K_3 is opened to outlet c, and cock K_1 is turned to the gas burets. The solute gas is allowed to flow from the gas burets into the absorption chamber, the mercury in A being discharged from c. The meniscus of the mercury in A is then adjusted to the mark M, and the discharged mercury is weighed. The volume of discharged mercury is exactly equal to the volume of gas phase in A. At this moment the solute gas is in contact with the solvent, and the gas absorption by the solvent begins. Cock K_1 is closed, and the stirrer is set in operation. Cock K_1 is occasionally opened to the gas buret to ascertain whether equilibrium is established.

When the absorption equilibrium has been attained, the total pressure in the absorption chamber and the volume of the gas remaining in the buret are recorded.

Materials

Oxygen and nitrogen used were extra pure grade from Osaka Oxygen Co. Ltd., and were certified more than 99.9 and 99.99% purity, respectively. Carbon dioxide was super pure grade of 99.96% obtained from Nippon Tansan Co. Ltd.

Methanol, ethanol, 1-propanol, and 2-propanol were guaranteed reagents manufactured by Wako Pure Chemical Ind. These reagents were further purified in a laboratory fractionating column of about 20 theoretical plates packed with ¼-in. single-turn helices. Intermediate fractions were collected and used in making up the test solutions. The physical properties of the solvents are tabulated in Table I.

Physical Properties of Solvents

The vapor pressures of the alcohol–water solutions at each temperature are required for the calculation of the solubility. The vapor pressure p_{12} for methanol–water or 2-propanol–water solutions was calculated from Equation 1:

$$p_{12} = \gamma_1 p_1{}^\circ x_1 + \gamma_2 p_2{}^\circ x_2 \qquad (1)$$

The values of the activity coefficients of each component in methanol–water and 2-propanol–water solutions at each temperature were taken from the literature of Katayama (*4*).

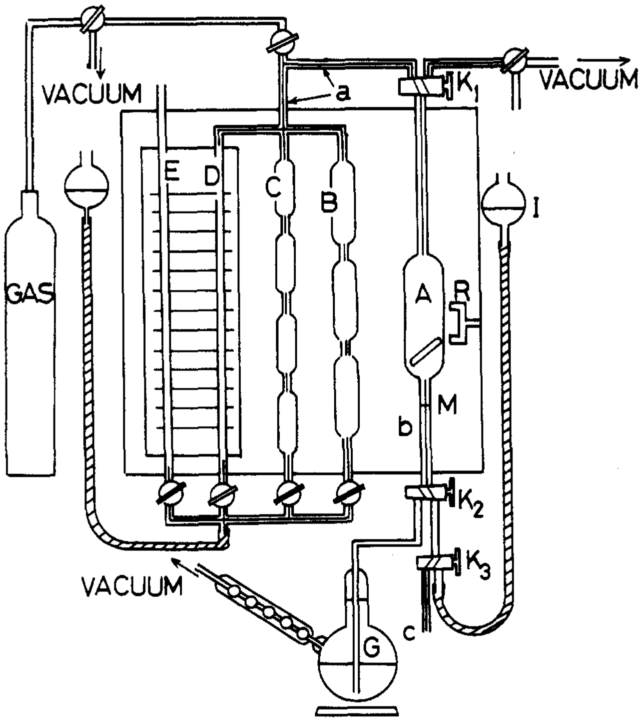

Figure 1. Schematic diagram of apparatus

The activity coefficients of each component in 1-propanol–water solutions at each temperature were calculated by use of both the equilibrium data of Gadwa (*2*) and the heat of mixing data of Bose (*1*).

The vapor-pressure data of ethanol-water solutions were obtained from the International Critical Table (*12*).

Results

Tables II–XI show the experimental solubilities of oxygen in methanol–water, ethanol–water, 1-propanol–water, and 2-propanol–water solutions (at 0°, 20°, and 40°C); nitrogen in methanol–water, ethanol–water, 1-propanol–water, and 2-propanol–water solutions (at 20° and 40°C); and carbon dioxide in 1-propanol–water and 2-propanol–water solutions (at 10°, 20°, 30°, and 40°C).

The solubilities are expressed in terms of the Ostwald coefficients and Henry's constants. The Ostwald coefficient $L_{R,\text{mix}}$ is defined as "the ratio of the volume of gas absorbed to the volume of the absorbing liquid," that is:

$$L_{R,\text{mix}} = V_R/V_s \tag{2}$$

Table I. Properties of Solvent Used

Solvent	Density, 25°C, g/cc		Refractive index, 25°C, —	
	Obsd	Lit	Obsd	Lit
Methanol	0.78670	0.78664 (*9*)	1.32515	1.32652 (*9*)
Ethanol	0.78510	0.78504 (*9*)	1.35945	1.35941 (*9*)
1-Propanol	0.79990	0.79975 (*9*)	1.38345	1.38370 (*9*)
2-Propanol	0.78087	0.78126 (*9*)	1.37500	1.3752 (*9*)

Henry's constant for a solute gas dissolved in the mixed solvent is defined as "the ratio of the fugacity of solute gas to the mole fraction of solute gas in the mixed solvent," that is:

$$H_{R,\text{mix}} = f_R/x_R \tag{3}$$

No correction for gas-phase nonideality was made, and the fugacity was replaced by the partial pressure. In this measurement, Henry's constant was calculated from the Ostwald coefficient using the expression:

$$H_{R,\text{mix}} = \frac{zRT}{L_{R,\text{mix}}\, v_M} + \frac{p_R}{760} \tag{4}$$

The partial pressure p_R was calculated from Equation 5:

$$p_R = \pi - p_{12} - \pi y_{\text{im}} \tag{5}$$

The partial pressure of impurity in the gas phase was calculated by assuming Dalton's law, provided that the impurity in solute gas did not dissolve in the solvents and it remained at the gas phase. As the mole fraction of impurity y_{im} was very small, the partial pressure of impurity gas was negligibly small.

Correction for the small increase of liquid volume by gas absorption was made by using the value of 0.002 for carbon dioxide for the coefficient of dilatation by absorption from the work of Horiuchi (*3*). For the absorption of oxygen and nitrogen, no correction was made, because gas solubilities were very small.

Gas solubilities in pure solvents are the averages of four or five measurements. They are compared with the literature values (*5*) in Table XII. The solubilities of each

Table II. Ostwald Coefficients and Henry's Constants of Oxygen in Methanol (1)-Water(2) Solutions at 760 mm Hg Partial Pressure

0°C			20°C		
Mole fraction alcohol x_1	*L*, —	*H*, atm	Mole fraction alcohol x_1	*L*, —	*H*, atm
0	0.0490	25400	0	0.0347	38400
0.0150	0.0511	24000	0.0188	0.0384	34000
0.0612	0.0535	21800	0.0492	0.0435	29100
0.1051	0.0526	21300	0.0907	0.0472	25700
0.1423	0.0503	21600	0.1103	0.0449	26600
0.1978	0.0488	21200	0.1564	0.0411	27800
0.3068	0.0533	17700	0.2066	0.0418	26100
0.3813	0.0606	14700	0.3054	0.0540	18500
0.5057	0.0777	10300	0.3976	0.0689	13400
0.6328	0.104	7030	0.4895	0.0859	9990
0.8097	0.154	4200	0.5927	0.112	7050
1.0000	0.237	2390	0.7046	0.144	5050
	40°C		0.8041	0.173	3930
0	0.0272	50700	0.8923	0.205	3120
0.0569	0.0358	37200	0.9426	0.221	2790
0.0972	0.0328	39000	1.0000	0.246	2400
0.2106	0.0428	26800			
0.2974	0.0577	18400			
0.4357	0.0820	11500			
0.5052	0.0962	9240			
0.5848	0.116	7170			
0.7009	0.148	5180			
0.8010	0.182	3900			
0.8905	0.213	3140			
1.0000	0.255	2440			

Table III. Ostwald Coefficients and Henry's Constants of Oxygen in Ethanol(1)-Water(2) Solutions at 760 mm Hg Partial Pressure

0°C			20°C		
Mole fraction alcohol x_1	*L*, —	*H*, atm	Mole fraction alcohol x_1	*L*, —	*H*, atm
0	0.0490	25400	0	0.0347	38400
0.0056	0.0485	25400	0.0810	0.0420	27400
0.0089	0.0512	23900	0.1058	0.0409	27000
0.0176	0.0487	24700	0.2057	0.0456	20800
0.0353	0.0489	23800	0.3085	0.0663	12400
0.0552	0.0467	24100	0.4052	0.0890	8100
0.0715	0.0444	24700	0.5280	0.118	5320
0.1065	0.0403	25800	0.5978	0.137	4260
0.1376	0.0372	26600	0.7171	0.165	3170
0.1762	0.0364	25700	0.8065	0.189	2550
0.2384	0.0437	19500	0.9382	0.225	1930
0.3646	0.0689	10500	1.0000	0.244	1690
0.4350	0.0912	7260		40°C	
0.5464	0.111	5290	0	0.0272	50700
0.6676	0.142	3650	0.0158	0.0430	31900
0.8981	0.206	2060	0.0465	0.0383	33800
1.0000	0.238	1660	0.1022	0.0366	32100
			0.2014	0.0483	20700
			0.3063	0.0675	12900
			0.3924	0.0885	8700
			0.4940	0.114	5980
			0.5817	0.137	4540
			0.6915	0.163	3420
			0.7984	0.193	2630
			0.8723	0.213	2240
			0.9317	0.230	1980
			1.0000	0.247	1760

Table IV. Ostwald Coefficients and Henry's Constants of Oxygen in 1-Propanol(1)–Water(2) Solutions at 760 mm Hg Partial Pressure

0°C			20°C		
Mole fraction alcohol x_1	L, —	H, atm	Mole fraction alcohol x_1	L, —	H, atm
0	0.0490	25400	0	0.0347	38400
0.0240	0.0507	23000	0.0230	0.0370	33800
0.0477	0.0446	24700	0.0432	0.0353	33700
0.0719	0.0411	25400	0.0847	0.0401	26800
0.1007	0.0417	23400	0.1057	0.0446	22900
0.1248	0.0454	20300	0.2050	0.0703	11800
0.1982	0.0647	12300	0.3133	0.0970	7060
0.2852	0.0840	8090	0.4175	0.119	4910
0.4223	0.106	5190	0.5103	0.138	3760
0.6208	0.154	2830	0.6020	0.152	3080
0.7842	0.173	2130	0.6953	0.169	2500
0.8784	0.187	1810	0.7987	0.184	2080
1.0000	0.209	1480	0.9085	0.202	1710
	40°C		1.0000	0.221	1450
0	0.0272	50700			
0.0225	0.0305	42300			
0.0428	0.0265	46100			
0.0657	0.0294	39200			
0.0834	0.0347	32700			
0.1043	0.0393	27500			
0.2044	0.0707	12000			
0.3034	0.0983	7180			
0.4033	0.122	4990			
0.5056	0.142	3740			
0.6063	0.159	2950			
0.6972	0.173	2470			
0.8010	0.188	2060			
0.8955	0.205	1730			
1.0000	0.226	1440			

Table V. Ostwald Coefficients and Henry's Constants of Oxygen in 2-Propanol(1)–Water(2) Solutions at 760 mm Hg Partial Pressure

0°C			20°C		
Mole fraction alcohol x_1	L, —	H, atm	Mole fraction alcohol x_1	L, —	H, atm
0	0.0490	25400	0	0.0347	38400
0.0096	0.0495	24500	0.0220	0.0392	32000
0.0168	0.0491	24200	0.0408	0.0346	34600
0.0467	0.0430	25600	0.0733	0.0334	33100
0.0851	0.0352	28700	0.0943	0.0346	30400
0.1116	0.0329	29000	0.1994	0.0605	13800
0.1602	0.0431	19900	0.2985	0.0917	7600
0.2779	0.0751	9130	0.3920	0.115	5220
0.3591	0.102	5900	0.5950	0.162	2860
0.4838	0.126	4000	0.7836	0.204	1860
0.5417	0.142	3310	1.0000	0.246	1270
0.6902	0.173	2300		40°C	
0.7936	0.197	1820	0	0.0272	50700
1.0000	0.231	1300	0.0791	0.0368	31200
			0.0993	0.0390	28000
			0.1496	0.0524	18500
			0.1984	0.0690	12700
			0.3003	0.105	6960
			0.3952	0.131	4790
			0.5000	0.156	3500
			0.5978	0.179	2700
			0.6995	0.199	2170
			0.7930	0.220	1790
			0.8950	0.238	1510
			1.0000	0.255	1280

Table VI. Ostwald Coefficients and Henry's Constants of Nitrogen in Methanol(1)–Water(2) Solutions at 760 mm Hg Partial Pressure

20°C			40°C		
Mole fraction alcohol x_1	L, —	H, atm	Mole fraction alcohol x_1	L, —	H, atm
0	0.0179	74500	0	0.0147	96600
0.0274	0.0188	68800	0.0225	0.0168	82700
0.0514	0.0197	64100	0.0478	0.0164	82300
0.0670	0.0198	62700	0.0664	0.0177	73500
0.0967	0.0183	66000	0.1009	0.0186	68800
0.1653	0.0202	56000	0.2036	0.0219	53300
0.2084	0.0217	50200	0.2971	0.0279	38400
0.2931	0.0261	38800	0.4278	0.0433	22200
0.4050	0.0318	28900	0.5200	0.0534	16700
0.5038	0.0448	19000	0.6712	0.0805	9850
0.6088	0.0598	13100	0.7074	0.0867	8910
0.6784	0.0723	10300	0.7897	0.101	7190
0.7630	0.0910	7670	0.8957	0.117	5790
0.8973	0.118	5390	1.0000	0.146	4250
1.0000	0.138	4310			

Table VII. Ostwald Coefficients and Henry's Constants of Nitrogen in Ethanol(1)–Water(2) Solutions at 760 mm Hg Partial Pressure

20°C			40°C		
Mole fraction alcohol x_1	L, —	H, atm	Mole fraction alcohol x_1	L, —	H, atm
0	0.0179	74500	0	0.0147	96600
0.0070	0.0193	68100	0.0195	0.0163	84100
0.0199	0.0200	64100	0.0385	0.0161	82000
0.0558	0.0212	56700	0.0509	0.0159	80200
0.0815	0.0214	53800	0.0574	0.0159	80200
0.1015	0.0217	51300	0.0734	0.0170	73100
0.1558	0.0240	42600	0.1087	0.0186	63100
0.2757	0.0363	23600	0.2237	0.0278	35200
0.3206	0.0421	19100	0.3120	0.0432	20000
0.4628	0.0622	10900	0.4162	0.0554	13700
0.5952	0.0846	6930	0.5061	0.0707	9680
0.7130	0.102	5150	0.6062	0.0852	7230
0.8746	0.126	3620	0.6946	0.100	5650
0.9140	0.134	3320	0.7751	0.115	4570
1.0000	0.151	2730	0.8814	0.136	3490
			0.9702	0.151	2920
			1.0000	0.156	2760

Table VIII. Ostwald Coefficients and Henry's Constants of Nitrogen in 1-Propanol(1)-Water(2) Solutions at 760 mm Hg Partial Pressure

20°C			40°C		
Mole fraction alcohol x_1	*L*, —	*H*, atm	Mole fraction alcohol x_1	*L*, —	*H*, atm
0	0.0179	74500	0	0.0147	96600
0.0247	0.0210	59300	0.0247	0.0170	77700
0.0349	0.0180	67400	0.0480	0.0163	76400
0.0758	0.0202	54300	0.0717	0.0205	57300
0.0987	0.0234	44400	0.1008	0.0283	38600
0.1997	0.0371	22500	0.1395	0.0365	27300
0.3020	0.0541	12900	0.2903	0.0616	12100
0.4045	0.0636	9390	0.4107	0.0798	7770
0.5014	0.0712	7380	0.4955	0.0882	6280
0.6058	0.0846	5490	0.6135	0.0989	4880
0.7775	0.101	3880	0.6993	0.108	4110
0.8640	0.109	3310	0.8251	0.118	3310
1.0000	0.123	2650	0.8761	0.122	3050
			1.0000	0.132	2570

Table IX. Ostwald Coefficients and Henry's Constants of Nitrogen in 2-Propanol(1)-Water(2) Solutions at 760 mm Hg Partial Pressure

20°C			40°C		
Mole fraction alcohol x_1	*L*, —	*H*, atm	Mole fraction alcohol x_1	*L*, —	*H*, atm
0	0.0179	74500	0	0.0147	96600
0.0709	0.0168	65900	0.0480	0.0136	91300
0.1585	0.0246	37100	0.1046	0.0205	52700
0.3288	0.0511	13000	0.1620	0.0299	31700
0.4000	0.0636	9350	0.2200	0.0395	21400
0.5351	0.0773	6410	0.3249	0.0586	12000
0.6396	0.0939	4680	0.4174	0.0732	8330
0.7125	0.0986	4130	0.5300	0.0921	5700
0.8147	0.117	3160	0.6031	0.0990	4860
0.9031	0.119	2860	0.7743	0.117	3420
1.0000	0.133	2390	0.8487	0.126	2970
			0.9535	0.140	2450
			1.0000	0.146	2210

Table X. Ostwald Coefficients and Henry's Constants of Carbon Dioxide in 1-Propanol(1)-Water(2) Solutions at 760 mm Hg Partial Pressure

10°C			20°C		
Mole fraction alcohol x_1	*L*, —	*H*, atm	Mole fraction alcohol x_1	*L*, —	*H*, atm
0	1.21	1060	0	0.930	1430
0.0266	1.16	1030	0.0258	0.899	1270
0.0738	1.00	1060	0.0504	0.845	1380
0.1055	1.05	942	0.0772	0.859	1270
0.1416	1.13	809	0.1027	0.926	1105
0.2081	1.32	610	0.2013	1.14	727
0.3082	1.56	429	0.3043	1.39	499
0.4149	1.79	319	0.4024	1.58	379
0.5046	1.96	259	0.5087	1.72	301
0.6195	2.14	208	0.6195	1.90	241
0.7068	2.26	180	0.7190	1.99	207
0.8264	2.43	150	0.7939	2.07	187
0.8903	2.55	135	0.8705	2.13	168
1.0000	2.76	113	0.9558	2.27	147
	30°C		1.0000	2.35	137
0	0.742	1850		40°C	
0.0441	0.742	1640	0	0.618	2290
0.0922	0.761	1420	0.0405	0.615	2050
0.1953	1.01	852	0.0782	0.652	1760
0.3194	1.28	543	0.1088	0.733	1460
0.4505	1.48	388	0.2107	0.971	844
0.5407	1.60	321	0.3112	1.17	613
0.6346	1.72	268	0.4080	1.31	472
0.8041	1.88	207	0.5094	1.46	373
0.9274	2.00	175	0.5811	1.55	323
0.9660	2.05	166	0.7087	1.66	263
1.0000	2.10	157	0.8078	1.75	227
			0.9075	1.81	201
			1.0000	1.88	179

Table XI. Ostwald Coefficients and Henry's Constants of Carbon Dioxide in 2-Propanol(1)-Water(2) Solutions at 760 mm Hg Partial Pressure

10°C			20°C		
Mole fraction alcohol x_1	*L*, —	*H*, atm	Mole fraction alcohol x_1	*L*, —	*H*, atm
0	1.21	1060	0	0.930	1430
0.0720	0.887	1210	0.0238	0.850	1460
0.1319	0.892	1050	0.0765	0.733	1490
0.1811	1.02	828	0.1874	0.919	930
0.2455	1.20	618	0.2445	1.09	703
0.3520	1.47	423	0.3648	1.37	456
0.5121	1.77	282	0.4773	1.59	336
0.6038	1.93	232	0.5973	1.75	264
0.7113	2.10	190	0.6866	1.90	220
0.8215	2.26	158	0.7848	1.98	192
0.9376	2.45	132	0.8786	2.10	166
1.0000	2.53	122	0.9568	2.17	150
	30°C		1.0000	2.18	145
0	0.742	1850		40°C	
0.0460	0.681	1780	0	0.618	2290
0.0843	0.660	1670	0.0339	0.579	2220
0.1035	0.688	1530	0.1013	0.639	1700
0.1976	0.901	953	0.1567	0.760	1260
0.2580	1.03	746	0.2860	1.02	728
0.4142	1.34	447	0.4022	1.23	505
0.4585	1.40	399	0.4670	1.37	414
0.6145	1.63	284	0.5763	1.47	336
0.7079	1.75	240	0.6530	1.57	289
0.8366	1.83	203	0.7090	1.62	264
0.9112	1.91	182	0.9442	1.78	194
1.0000	1.95	166	1.0000	1.86	178

Table XII. Comparison of Experimental Solubilities of Oxygen, Nitrogen, and Carbon Dioxide in Pure Solvents with Literature Values (Ostwald Coefficient)

	Oxygen			Nitrogen			Carbon dioxide		
Solvent	Temp, °C	Obsd	Lit	Temp, °C	Obsd	Lit	Temp, °C	Obsd	Lit
Water	0	0.0490	0.0477 (5)[a]				10	1.21	1.25 (5)
	20	0.0347	0.0333 (5)[a]	20	0.0179	0.0172 (5)[a]	20	0.930	0.941 (5)
	40	0.0272	0.0265 (5)[a]	40	0.0147	0.0138 (5)[a]	30	0.742	0.748 (5)
							40	0.618	0.614 (5)
Methanol	0	0.237	0.245 (5)						
	20	0.246	0.248 (5)	20	0.138	0.166 (5)			
	40	0.255	0.252 (5)[a]	40	0.146	0.174 (5)			
Ethanol	0	0.238	0.242 (5)						
	20	0.244	0.244 (5)	20	0.151	0.146 (5)			
	40	0.247	0.244 (5)	40	0.156	0.156 (5)[a]			
1-Propanol	0	0.209	...				10	2.76	...
	20	0.221	0.214 (5)	20	0.123	...	20	2.35	...
	40	0.226	...	40	0.132	...	30	2.10	...
							40	1.88	...
2-Propanol	0	0.231	0.244 (5)				10	2.53	...
	20	0.246	0.247 (5)	20	0.133	0.144 (5)[a]	20	2.18	...
	40	0.255	0.251 (5)[a]	40	0.146	0.155 (5)[a]	30	1.95	...
							40	1.86	...

[a] Interpolated values.

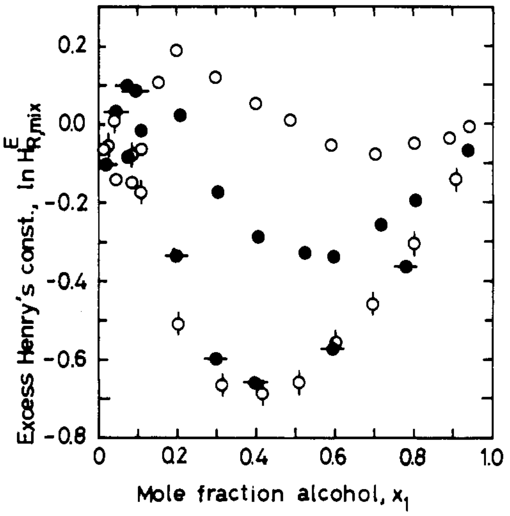

Figure 2. Excess Henry's constants of oxygen in methanol(1)-water(2), ○; ethanol(1)-water(2), ●; 1-propanol(1)-water(2), ϕ; and 2-propanol(1)-water(2), -●-, solutions at 20°C

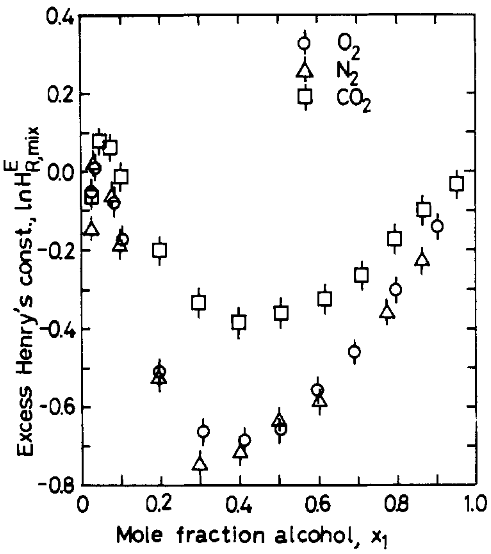

Figure 3. Excess Henry's constants of oxygen, nitrogen, and carbon dioxide in 1-propanol(1)-water(2) solutions at 20°C

gas for pure solvents obtained in this work agree well with the ones in the literature (5), except for nitrogen in methanol.

No data for the solubilities of gases in aqueous alcohol solutions are available in the literature to compare with the results obtained in this work. The reproducibility of the experimental solubilities was about 1% in the average.

Discussion

The excess Henry's constant, $H_{R,\mathrm{mix}}^E$, defined in Equation 6 has been used to correlate gas solubilities in mixed solvents by many investigators (*6–8, 10*).

$$\ln H_{R,\mathrm{mix}}^E = \ln H_{R,\mathrm{mix}} - (x_1 \ln H_{R,1} + x_2 \ln H_{R,2}) \tag{6}$$

Figures 2 and 3 show the relations between the excess Henry's constants of the solute gases and the alcohol mole fractions in the solutions.

Figure 2 shows the effects of different kinds of alcohols on the excess Henry's constants of oxygen in binary solutions of water with methanol, ethanol, 1-propanol, or 2-propanol. The values of excess Henry's constants decrease in the order methanol > ethanol > 2-propanol ≃ 1-propanol. The excess Henry's constants for 1-propanol-water and 2-propanol-water are approximately equal.

The values of excess Henry's constants of nitrogen or carbon dioxide in the four kinds of alcohol-water solutions decrease in the same order as for oxygen.

Figure 3 shows the difference of excess Henry's constants of solute gases in 1-propanol-water solutions. In other alcohol–water solutions studied, the excess Henry's constants of oxygen and nitrogen are approximately equal and are smaller than the values of carbon dioxide.

Regardless of the kinds of solute gases, the excess Henry's constants in alcohol–water solution do not converge to zero with temperature rising but increase in a negative direction.

Whether the observed excess Henry's constants could be fitted to a polynomial equation of the Redlich-Kister type or not was examined. However, the observed excess Henry's constants could not be expressed by a Redlich-Kister equation with four constants within experimental errors.

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Nomenclature

f = fugacity, atm
H = Henry's constant, atm
L = Ostwald coefficient, –
p = pressure, mm Hg
R = gas constant, atm cc/mol K
T = absolute temperature, K
v_M = molar volume of solvent, cc/mol
V = volume, cc
x = mole fraction in liquid phase, –
y = mole fraction in gas phase, –
z = compressibility factor, –
γ = activity coefficient, –
π = total pressure, mm Hg

Superscripts

E = excess quantity
$^\circ$ = pure component

Subscripts

im = impurity gas in solute gas
R = solute gas
R,mix = solute gas (R) in mixed solvent
s = solvent
1 = alcohol
2 = water

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Viscosity of Ten Binary and One Ternary Mixtures

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The viscosity of 10 binary systems, including polar and nonpolar components, was determined at 20° and 25°C. The viscosity of the ternary system heptane–iso-octane–toluene was also determined at 25°C. Experimental data were correlated by means of the method of McAllister and that of Heric.

The literature dealing with systematic studies of the viscosity of mixtures is rather limited. In this paper experimental data on a number of binary systems, including mixtures of strong polar components and a limited number of experimental data on the viscosity of the ternary system heptane–iso-octane(2,2,4-trimethylpentane)–toluene are published. The binary data have been correlated by means of the method of McAllister (*3*) and that of Heric (*1*). Both approaches apply to ternary systems. The extended equations contain the binary parameters of the related binary systems and one term containing a ternary parameter. The experimental ternary data have been correlated by this method. The ternary parameter has been determined by a least-squares method applied to the differences of the experimental value and the computed value, taking into account all terms except the term containing the ternary parameter.

Experimental

The systems which are studied in this work are listed in Table I. The materials were purified by fractionation and dried afterward; the hydrocarbons were dried on sodium, and the other materials on molecular sieves. Methylcyclohexane contained some toluene. This toluene was first removed by sulfonation by means of a concentrated solution of sulfuric acid. The ethanol was first dehydrated by calcium oxide. The purity of the materials was checked by means of gas chromatographic analysis on two different columns: apiezon L on chromosorb P, 80–100 mesh and porapak Q, 80–100 mesh and by comparison of the value of the specific gravity and refractive index of the used materials with critically chosen values from the literature. Values are listed in Table II.

A Hoppler viscosimeter was used for determining the viscosities of the binary and ternary systems. The viscosimeter was calibrated against known viscosities of solu-

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