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Table III. Water Activity in Poly(ethylene glycol) and Poly(propylene glycol) Solutions (*5*)

wt fraction	a_w exptl	a_w UNIFAC	dev, %	a_w^{new}(UNIFAC)	dev, %
			PEG, 30 °C		
0.012	0.124	0.077	-37.9	0.120	-3.2
0.050	0.309	0.222	-28.2	0.285	-7.8
0.101	0.468	0.464	-0.9	0.481	2.8
0.200	0.648	0.803	23.9	0.716	10.5
0.341	0.789	0.994	26.0	0.870	10.3
0.512	0.900	1.000	11.1	0.947	5.2
0.702	0.956	1.000	4.6	0.979	2.4
			18.9 (av)		6.0 (av)
			PEG, 65 °C		
0.012	0.134	0.095	-29.1	0.088	-3.0
0.049	0.342	0.256	-25.1	0.316	-7.6
0.100	0.520	0.508	-2.3	0.526	1.2
0.199	0.707	0.837	18.4	0.766	8.3
0.338	0.833	1.000	20.0	0.907	8.9
0.511	0.926	1.000	8.0	0.967	4.4
0.701	0.970	1.000	3.1	0.986	1.6
			15.1 (av)		5.1 (av)
			PPG, 30 °C		
0.010	0.208	0.056	-73.1	0.113	-45.7
0.050	0.625	0.339	-45.8	0.463	-25.9
0.099	0.845	0.666	-21.2	0.738	-12.7
0.200	0.955	1.000	4.7	0.994	4.1
0.300	0.978	1.000	2.2	1.000	2.2
0.410	0.985	1.000	1.5	1.000	1.5
			24.8 (av)		15.3 (av)

CH_2O, CH_2, OH, and H_2O were obtained from revised tables published recently (*2*). The results, plotted in Figure 1, deviate significantly from the experimental data. Then a new group, CH_2OH, is introduced.

The interaction parameters were evaluated by a minimization method previously used for silicone compounds (*4*). Their values are listed in Table II. The values of γ_w calculated with the new set of parameters are also depicted in Figure 1. In order to test the applicability of these new parameters to a wider class of materials the activity of water in solutions of low molecular weight polyglycols has been computed. The data of Malcolm and Rowlinson (*5*) on poly(ethylene glycol) (molecular weight 300) at 30 and 65 °C and poly(propylene glycol) (molecular weight 400) at 30 °C were used. The results are depicted in Figure 2 and summarized in Table III. An improved agreement between computed values and experimental data is obtained with the new UNIFAC parameters for all three solutions and over the entire concentration range. The average deviation is reduced by a factor of 3 in the case of PEG. A smaller improvement is obtained for the PPG solution.

The reduced improvement in the case of the PPG solution indicates the smaller role played by the hydroxyl end groups in solutions of this polymer probably due to the shielding effect of the bulky methyl group in its vicinity.

Registry No. TeEG, 112-60-7; H_2O, 7732-18-5.

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Solubility, Density, and Viscosity for Sodium Sulfate–Methanol–Water Systems at 40 °C

Wolfgang Fleischmann* and Alfons Mersmann

Lehrstuhl B für Verfahrenstechnik, Technische Universität München, 8000 München 2, Federal Republic of Germany

The solubility of sodium sulfate in water–methanol mixtures has been determined at 40 °C. Data for densities and viscosities of sodium sulfate–water–methanol systems are presented, covering the whole range from dilute to saturated solutions.

Introduction

Physical data referring to binary salt–water systems are available for nearly all substances of interest. For ternary systems like salt–water–alcohol systems there is a great lack of information. Addition of low alcohols to aqueous salt solu-

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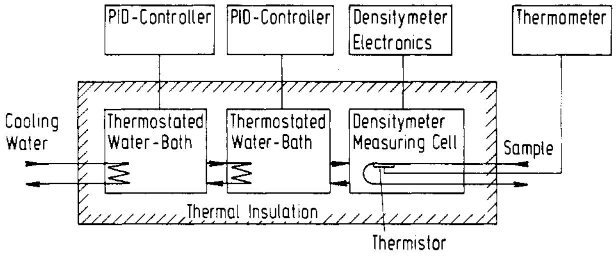

Figure 1. Apparatus for the density measurement.

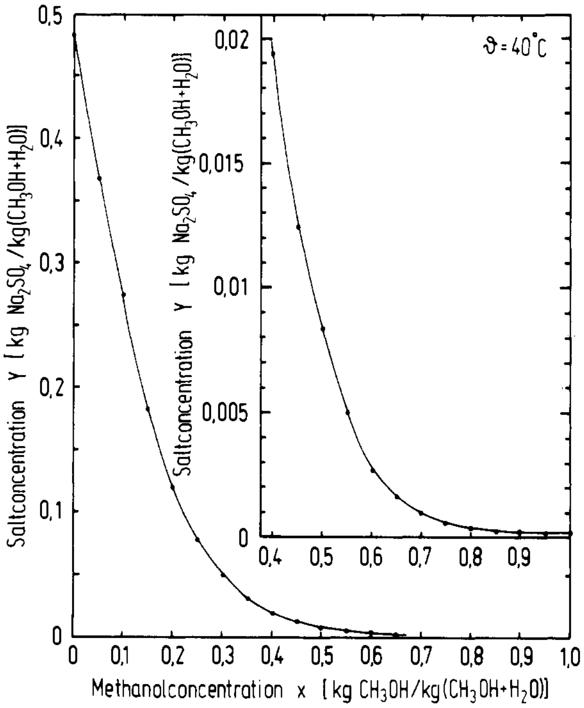

Figure 2. Solubility of sodium sulfate in water–methanol mixtures at 40 °C.

tions is used in salting-out crystallization, thus enhancing product purity and diminishing processing problems (*1–3*). One such crystallization process is the salting-out of anhydrous sodium sulfate from aqueous solution with methanol (*4*, *5*).

The object of the present work is to give accurate data for solubility, density, and viscosity of sodium sulfate–water–methanol mixtures, covering the whole range of possible compositions. The very precise densities enable quick and exact concentration determinations using vibrating-tube density meters.

Experimental Section

The solvents used were analytical-grade methanol (BASF) and deionized water with a conductivity smaller than 1 $\mu\Omega^{-1}$. Commercial pure-grade sodium sulfate was dissolved in water and filtered through a 3-μm multiple tube filter. The filtrate was recrystallized by salting-out with methanol. The product crystals were dried at 110 °C.

The test apparatus was a 500-mL glass vessel, fitted with

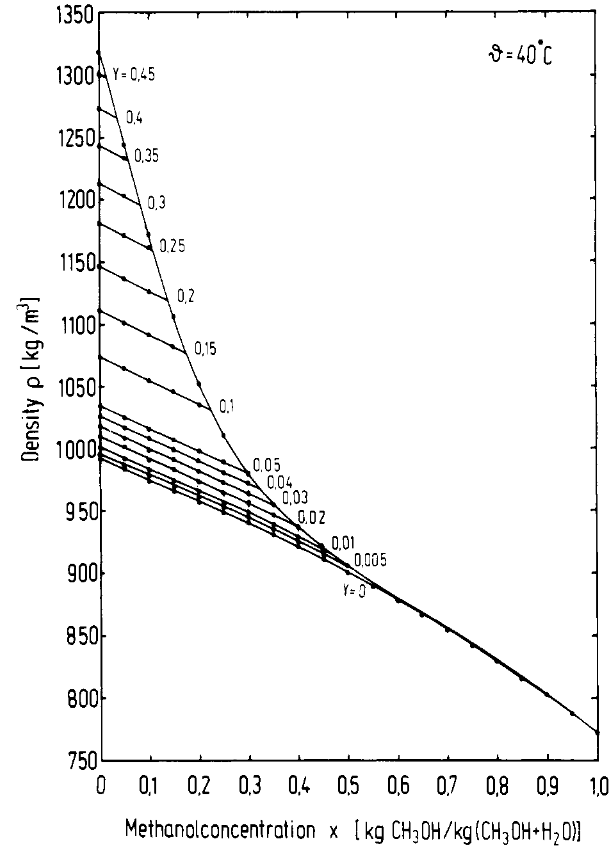

Figure 3. Density of sodium sulfate–water–methanol systems at 40 °C.

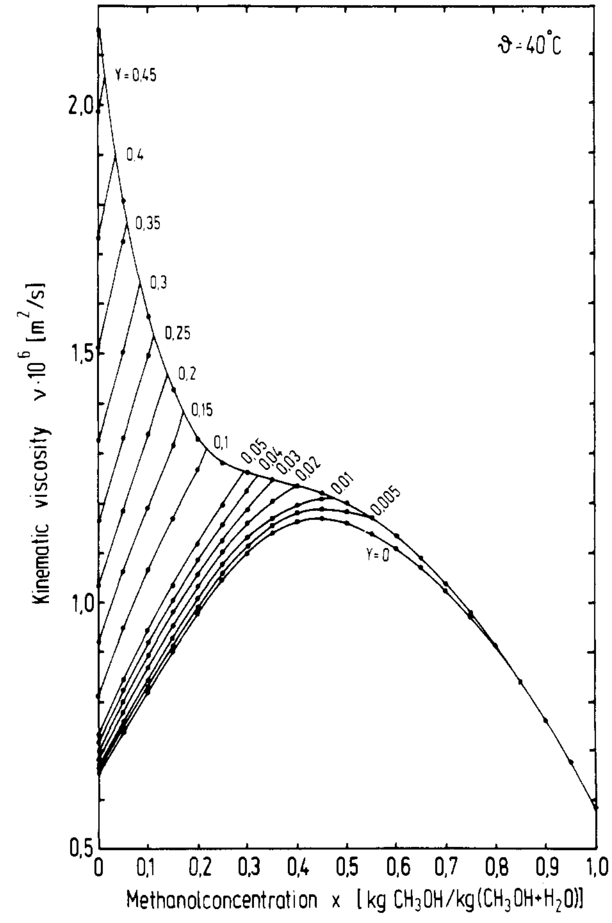

Figure 4. Kinematic viscosity of sodium sulfate–water–methanol systems at 40 °C.

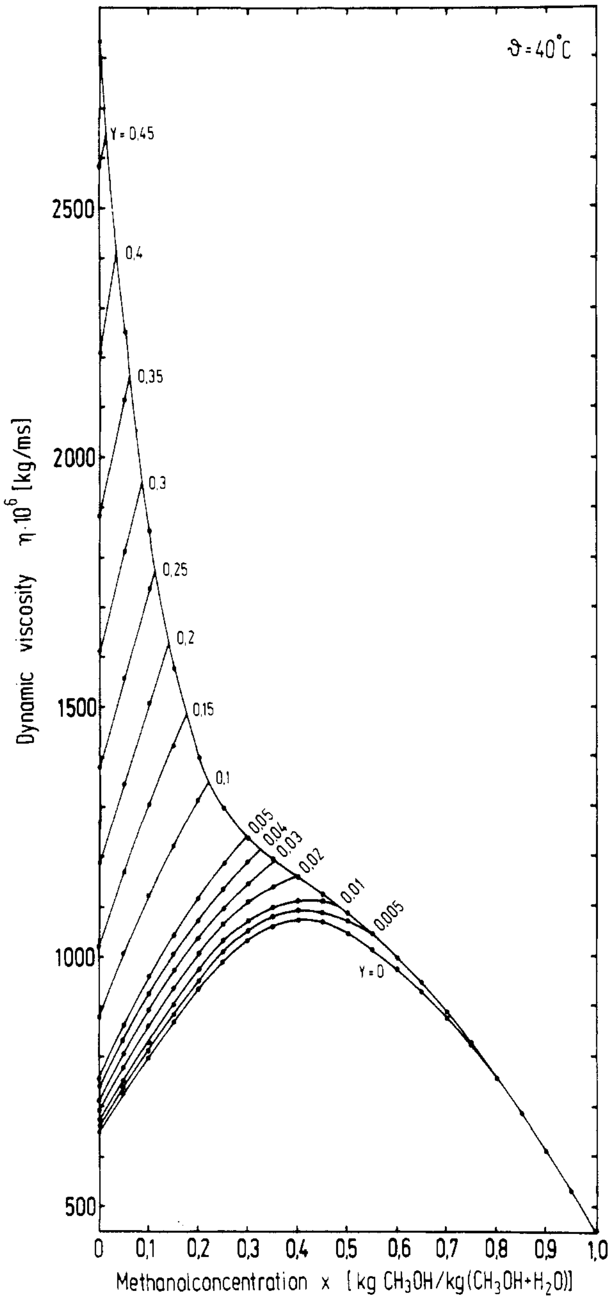

Figure 5. Dynamic viscosity of sodium sulfate–water–methanol systems at 40 °C.

a sealed glass stirrer and a Pt 100 resistance thermometer. The equipment was immersed in a thermostated water bath controlled to ±0.01 °C.

Solvent (200 g) composed of weighed quantities of water and methanol was added to a weighed quantity of sodium sulfate. Dissolution was observed by eye and after disappearance of the last crystals agitation was continued for 5 min. In the case of saturation measurements salt was added in excess and agitation was performed for 24 h.

At the end of this time samples were taken by a syringe fitted with a 2-μm filter.

The solubility determination was performed by heating a weighed quantity of solution (~100 g) to dryness at 110 °C and weighing again the dry salt. The precision of this method was better than ±0.5%.

Measurement of viscosity was accomplished with a KPG-Ubbelohde viscosimeter, immersed in the same thermostated water bath as the test apparatus. The precision of the viscosity

Table I. Physical Properties of Sodium Sulfate–Water Solutions at 40 °C

Y, kg of Na_2SO_4/kg of (CH_3OH + H_2O)	ρ, kg/m^3	$10^6\eta$, kg/ms	$10^6\nu$, m^2/s
0.005	996.61	661.0	0.6632
0.01	1000.79	671.2	0.6707
0.02	1009.37	692.1	0.6857
0.03	1017.91	713.4	0.7008
0.04	1026.19	735.4	0.7166
0.05	1034.37	758.1	0.7329
0.1	1073.94	880.6	0.8120
0.15	1111.67	1023.0	0.9202
0.2	1147.35	1187.0	1.0346
0.25	1181.94	1379.5	1.1671
0.3	1213.48	1612.0	1.3284
0.35	1244.26	1884.5	1.5145
0.4	1274.15	2209.5	1.7341
0.45	1301.98	2587.0	1.9870
0.4819	1319.37	2837.7	2.1508

Table II. Physical Properties of Methanol–Water Mixtures at 40 °C

x, kg of CH_3OH/kg of (CH_3OH + H_2O)	ρ, kg/m^3	$10^6\eta$, kg/ms	$10^6\nu$, m^2/s
0	992.24	651.5	0.6561
0.05	983.08	724.5	0.7370
0.1	974.51	797.2	0.8181
0.15	965.98	868.7	0.8993
0.2	957.61	936.2	0.9776
0.25	948.98	991.2	1.0445
0.3	940.21	1033.7	1.0994
0.35	930.95	1061.7	1.1404
0.4	921.32	1072.2	1.1638
0.45	911.21	1066.5	1.1704
0.5	900.66	1047.7	1.1633
0.55	889.78	1013.7	1.1393
0.6	878.80	976.0	1.1106
0.65	866.75	930.2	1.0732
0.7	854.65	877.3	1.0265
0.75	842.25	817.7	0.9708
0.8	829.12	757.5	0.9136
0.85	815.78	687.2	0.8424
0.9	801.74	612.5	0.7640
0.95	787.33	533.5	0.6776
1.0	722.54	451.0	0.5838

Table III. Physical Properties of Saturated Sodium Sulfate–Water–Methanol Systems at 40 °C

x, kg of CH_3OH/kg of (CH_3OH + H_2O)	Y, kg of Na_2SO_4/kg of (CH_3OH + H_2O)	ρ, kg/m^3	$10^6\eta$, kg/ms	$10^6\nu$, m^2/s
0	0.4819	1319.37	2837.7	2.1508
0.05	0.3679	1245.12	2250.1	1.8071
0.1	0.2738	1176.46	1852.6	1.5747
0.15	0.1811	1104.54	1577.6	1.4283
0.2	0.1192	1052.84	1400.1	1.3298
0.25	0.0788	1011.39	1297.6	1.2830
0.3	0.0488	980.87	1238.8	1.2630
0.35	0.0310	956.37	1196.3	1.2509
0.4	0.0194	938.26	1159.8	1.2361
0.45	0.0125	921.27	1124.8	1.2209
0.5	0.0081	906.98	1088.3	1.1999
0.55	0.0050	892.78	1047.3	1.1731
0.6	0.0027	880.62	999.8	1.1353
0.65	0.0016	868.27	947.3	1.0910
0.7	0.0010	855.76	889.8	1.0398
0.75	0.0005	844.02	827.3	0.9802
0.8	0.0003	829.62	760.3	0.9164
0.85	0.0002_5	816.57	688.8	0.8435
0.9	0.0002_5	802.11	613.8	0.7652
0.95	0.0002_4	787.56	534.8	0.6791
1.0	0.0002_3	772.82	451.3	0.5840

Table IV. Density ρ (kg/m^3) of Undersaturated Sodium Sulfate-Methanol-Water Solutions at 40 °C

Y, kg of Na_2SO_4/kg of (CH_3OH + H_2O)	x, kg of CH_3OH/kg of (CH_3OH + H_2O)									
	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4	0.45	0.5
0.005	987.54	978.79	970.23	961.87	953.30	944.48	935.19	925.49	915.45	906.78
0.01	991.73	983.18	974.47	966.01	956.49	948.58	939.24	929.52	919.39	
0.02	1000.14	991.41	982.78	974.41	965.53	956.59	947.21			
0.03	1008.63	999.63	991.06	982.34	973.62	964.45	954.96			
0.04	1016.94	1007.86	999.09	990.30	981.60	972.24				
0.05	1024.84	1016.09	1007.16	998.32	989.19					
0.1	1064.84	1054.94	1046.16	1036.51						
0.15	1101.64	1091.73	1082.48							
0.20	1137.11	1127.15								
0.25	1171.00	1160.87								
0.3	1203.26									
0.35	1229.20									

Table V. Kinematic Viscbsity $10^6\nu$ (m^2/s) of Undersaturated Sodium Sulfate-Methanol-Water Solutions at 40 °C

Y, kg of Na_2SO_4/kg of (CH_3OH + H_2O)	x, kg of CH_3OH/kg of (CH_3OH + H_2O)									
	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4	0.45	0.5
0.005	0.7473	0.8307	0.9129	0.9908	1.0600	1.1154	1.1563	1.1824	1.1897	1.1843
0.01	0.7585	0.8434	0.9280	1.0090	1.0785	1.1322	1.1715	1.1980	1.2106	
0.02	0.7802	0.8695	0.9526	1.0335	1.1034	1.1611	1.2053			
0.03	0.8013	0.8950	0.9824	1.0583	1.1268	1.1884	1.2401			
0.04	0.8225	0.9202	1.0059	1.0849	1.1582	1.2261				
0.05	0.8440	0.9447	1.0347	1.1202	1.1979					
0.1	0.9481	1.0670	1.1707	1.2647						
0.15	1.0616	1.1935	1.3171							
0.2	1.1862	1.3403								
0.25	1.3315	1.4979								
0.3	1.5056									
0.35	1.7265									

Table VI. Dynamic Viscosity $10^6\eta$ (kg/ms) of Undersaturated Sodium Sulfate-Methanol-Water Solutions at 40 °C

Y, kg of Na_2SO_4/kg of (CH_3OH + H_2O)	x, kg of CH_3OH/kg of (CH_3OH + H_2O)									
	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4	0.45	0.5
0.005	738.0	813.1	885.7	953.0	1010.5	1053.5	1081.4	1094.3	1089.1	1073.9
0.01	752.2	829.2	904.3	974.7	1031.6	1074.0	1100.3	1113.6	1113.0	
0.02	780.3	862.1	936.2	1007.1	1065.4	1110.7	1141.7			
0.03	808.2	894.7	973.6	1039.6	1097.1	1146.2	1184.2			
0.04	836.4	927.4	1005.0	1074.4	1136.9	1192.1				
0.05	865.0	959.9	1042.1	1118.3	1185.0					
0.1	1009.6	1125.6	1224.8	1316.1						
0.15	1169.5	1303.0	1425.7							
0.2	1348.8	1510.7								
0.25	1559.2	1738.9								
0.3	1811.6									
0.35	2122.2									

measurements was ±0.2%.

Density determination was carried out by a vibrating-tube density meter DMA 60 + DMA 602 from Paar, Austria. A sketch of the experimental apparatus is given in Figure 1. The density meter was thermostated by two cascaded PID-controlled water baths (proportional plus floating plus derivative control). With this arrangement the temperature constancy was better than 0.005 °C. The error of density determination was smaller than 0.01 kg/m^3.

Results

Measured values for the binary systems water-methanol (*6*, *7*) and sodium sulfate-water (*8*, *9*) are in good agreement with published data. For the ternary system sodium sulfate-water-methanol only two rather incomplete papers (*10*, *11*) could be found in the literature.

Saturation solubility of sodium sulfate in water-methanol mixtures is substantially reduced with increasing methanol concentration (Figure 2).

In Figures 3-5 densities and kinematic and dynamic viscosities are shown for the ternary system. The parameter Y is the salt concentration. The dynamic viscosity has been calculated from the measured values of density and kinematic viscosity. Numerical values of the physical properties of the binary systems sodium sulfate-water and methanol-water are given in Tables I and II. The physical properties of the saturated ternary system sodium sulfate-water-methanol are presented in Table III. Tables IV–VI gives the density, the kinematic viscosity, and the dynamic viscosity of the undersaturated ternary system sodium sulfate–water–methanol.

Glossary

x	methanol concentration, kg of CH_3OH/kg of ($CH_3OH + H_2O$)
Y	salt concentration, kg of Na_2SO_4/kg of ($CH_3OH + H_2O$)
ρ	density, kg/m^3
ν	kinematic viscosity, m^2/s
η	dynamic viscosity, kg/ms
ϑ	temperature, °C

Registry No. Na_2SO_4, 7757-82-6; CH_3OH, 67-56-1.

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Solubility of Carbon Dioxide, Hydrogen Sulfide, and Methane in Pure and Mixed Solvents[†]

Florentino Murrieta-Guevara and Arturo Trejo Rodríguez*

Instituto Mexicano del Petrôleo, Subdirectiôn de I.B.P.—Tefetra, Eje Central Lâzaro Cârdenas 152, 07730 Mêxico, D.F.

The solubility of carbon dioxide has been measured at 25 and 50 °C in *N*-methylpyrrolidone and propylene carbonate and in mixtures of these solvents individually with monoethanolamine and diethanolamine at two different concentrations. The solubility of hydrogen sulfide and methane was measured at 25 °C in *N*-methylpyrrolidone and in mixtures of this solvent with monoethanolamine also at two different concentrations. The solubility of methane was also determined at 25 °C in a mixture of *N*-methylpyrrolidone with diethanolamine.

Introduction

The study of the solubility of gaseous solutes in solvents is of great interest from both theoretical and practical points of view. The efficient removal of acid gases (e.g., CO_2 and H_2S) from industrial and natural gases is a continuous need. The design and operation of absorption and stripping equipment require reliable equilibrium data of the solubility of carbon dioxide, hydrogen sulfide, and light hydrocarbons in absorbing liquids, pure or mixed, as a function of temperature and concentration.

Aqueous alkanolamine solutions are used extensively for the removal of acid gases in gas mixtures. However, the present interest in energy conservation and pollution control has led to the search for more efficient and economical methods of removing acid gases. The use of physical solvents may offer some advantages (*1*) over the use of chemical solvents to remove CO_2, H_2S, and other sulfur compounds. There exist several absorption processes which use a physical solvent such as Rectisol (*2*), Purisol (*2*), Fluor Solvent (*3*, *4*), Selexol (*5*), etc.

However, it is also possible to combine the advantages of using a chemical solvent and a physical solvent to remove acid gases with great efficiency at reduced operating costs as in the sulfinol process (*6*, *7*). We report in this work solubility data for carbon dioxide, hydrogen sulfide, and methane in pure physical solvents and in mixtures of physical solvent with a chemical solvent as part of a study to evaluate mixtures of solvents which could be used as substitutes for the ones traditionally used in industry. The physical solvents considered here are *N*-methylpyrrolidone (NMP) and propylene carbonate (PC) whereas the chemical solvents are monoethanolamine (MEA) and diethanolamine (DEA).

Experimental Section

Materials. The pure samples of NMP, PC, MEA, and DEA are the same as those used in a study of liquid densities as a function of temperature (*8*) and their purity was always better than 99.5 mol %. The CO_2 was obtained from Infra S.A. with a reported purity of 99.7 mol %. The H_2S and CH_4 were obtained from Matheson with a reported purity of 99.5 and 99.99 mol %, respectively.

Apparatus and Procedure. The measurements of solubility were carried out in a vapor-liquid equilibrium system with circulation of the vapor phase. Figure 1 is a schematic diagram of the experimental apparatus which consists essentially of equilibrium glass cell 1, magnetic pump 2, gas-storage cylinder 3, pressure gauge 4, pressure transducer 5, digital temperature indicator 6, and proportional temperature controller 7.

The 170-cm^3 equilibrium cell was made of Pyrex glass with an inlet gas tube ending in a fine fritted glass disk to disperse the gas bubbles into the bulk of the solvent. A magnetic Teflon-coated bar was used for continuous agitation of the liquid phase to ensure thermal equilibrium during measurements. Additionally a magnetic pump was used to circulate the vapor phase from the top of the cell into the liquid through the fritted glass disk. The equilibrium cell, the magnetic pump, and the gas-storage cylinder were placed in an air bath controlled within ±0.1 °C by a proportional controller using a thermistor for air

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[†] Presented at the Meeting of the IUPAC, London, England, Sept 1982.

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