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Low-Volatility Polar Organic Solvents for Sulfur Dioxide, Hydrogen Sulfide, and Carbonyl Sulfide

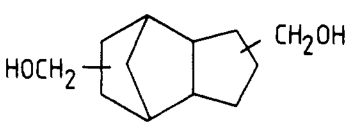
Georg H. Härtel

Lehrstuhl für Technische Chemie an der FAU Erlangen-Nürnberg, 8520 Erlangen, Federal Republic of Germany

The solubility of SO_2, H_2S, and COS in several phosphoric and phthalic acid esters, poly(ethylene glycols), and poly(ethylene glycol) dialkyl ethers was measured at temperatures between 20 and 100 °C and pressures between 0.01 and 1 bar. Henry's and equilibrium constants were determined from experimental solubility data as a function of temperature. Furthermore, selection criteria for the tested organic liquids, like viscosity and vapor pressure data, are also reported.

Introduction

Knowing the solubility of gases in absorbents as a function of temperature, pressure, and composition is an important basis for the design of absorption processes, used for the removal of components from process or waste gases. Recently the use of organic solvents for the gases considered here—sulfur dioxide (SO_2), hydrogen sulfide (H_2S), and carbonyl sulfide (COS)—has been increased (*1–3*). Proper solvents are the esters of phosphoric or phthalic acid (*2*, *4*, *5*), poly(ethylene glycols) (*6–8*), and the dialkyl ethers of poly(ethylene glycols) (*1*, *4*) as well as tricyclodecane derivatives



in mixtures with the mentioned compounds (*4*). The practical value of these solvents is due to their high reversible dissolving capacity and their low vapor pressure, so that, for example, flue gases can be treated, also at elevated temperatures. The published solubility data of SO_2, H_2S, and COS in the solvents are however mostly incomplete and limited to room temperature and atmospheric pressure. In a comparison of organic solvents, vapor pressure, viscosity, and physiological compatibility must be considered beside the solubility of the pollutants. The residual loading of the absorbent in the purified gas stream is limited by commercial considerations and governmental emission regulations. Increasing viscosity leads to increasing mass- and heat-transfer resistance in the liquid phase. A decrease in the plate efficiency, and consequently an increase in the HTU number of packed columns, follows. Therefore, the viscosity of the solvent should not exceed 10 mPa·s.

Selection of the Solvent

Figure 1 shows the loading of the exhaust gas with some absorbents in the equilibrium state at 1-bar overall pressure. In exhaust gas streams greater than 20 000 m^3/h the mass concentration has to be kept below 300 mg/m^3 due to national regulations for the purity of the air in the Federal Republic of Germany (*9*, *10*). As can be seen, the residual loading caused by the partial pressure is below the emission limit for several solvents, e.g., glycols from the triethylene glycol, phosphates from the tri-*n*-butyl phosphate, and phthalates from the diethyl phthalate, if the absorption process is operated under atmospheric pressure below 40 °C (*4*, *11*). However, a residual loading of 300 mg/m^3 in an exhaust gas quantity of 2×10^6 m^3/h for a 750-MW power plant results in a loss of 0.6 t of solvent. This is highly uneconomic. To decrease the emission the absorption temperature can be lowered, but there is a limitation caused by the increase in viscosity. Solvents having a low vapor pressure (Tables I and II and Figure 2) have a high viscosity on the other hand. So glycols within the interesting range of molecular weight have higher viscosities than esters and ethers. Because of their lower vapor pressure they can be used at higher absorption temperatures however. Also there commercial considerations require a solvent recovery, for which the water solubility of glycols or glycol ethers may be advantageous.

Equipment and Operation Procedure

To measure the gas solubiltiy a known mass of degassed solvent is brought in contact with a known volume of gas at a constant temperature. Then the system is well stirred. The dissolution of the gas (Matheson, Heusenstamm, FRG; SO_2, anhydrous, minimum 99.98%; H_2S, c.p., minimum 99.5%; COS, minimum 97.5%) is noted by the decrease in the pressure of the system until equilibrium is reached. The equipment used is schematically represented in Figure 3. The pressure was measured by means of gauge 2 (CMR 100—measuring transducer with Barton-Cell TDZ 224, Schöppe-Faeser GmbH, Minden, FRG). The range of the measured pressure different is from 0 to 250 mbar. When one adjusts the reference pressure with a mercury manometer (0–1067 mbar, degree of accuracy ±0.2 mbar), a survey over the whole range from 0 to 1 bar is possible. The calibration showed that the complete arrangement was accurate to ±0.25 mbar. Constant temperature is provided by an air thermostat.

Phase Equilibrium

At low pressures for the physical solution of a supercritical gas in a liquid the partial pressure p_i of the component i is proportional to the Henry coefficient H and the mole fraction x_i.

$$p_i = Hx_i \tag{1}$$

As proved in IR-spectroscopical investigations (*4*, *5*) strong interacting forces between polar gases, for example, SO_2, and polar organic solvents lead to the formation of associates.

$$nA(g \rightarrow l) + B(l) \rightarrow B_mA_n(l) \tag{2}$$

This reaction is incomplete although B is stoichiometrically in excess. Therefore, a measurable partial pressure of A, according to Henry's law, results from the part of A physically dissolved. The part of the gas there in the form of an associate is given by the law of mass action. Following Dolezalek's (*12*) assumption that the three species form an ideal solution and therefore the activity of each species is equal to its true mole fraction Z_i and assuming that the ratio of the activity coefficients is constant, the liquid-phase equilibrium constant K is given by

$$K = Z_{B_mA_n}/(Z_A{}^nZ_B{}^m) \tag{3}$$

Equation 1 becomes for chemical absorption

$$p_A = HZ_A \tag{4}$$

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Table I. Properties of Selected Solvents

compd	formula	mol wt, g/mol	ρ_{20},[a] g/cm^3	(10^4)(dρ/dt), g/(cm^3 °C)	bp$_{\mathrm{bar}}$, °C	η,[b] mPa·s 40 °C	60 °C	80 °C
triethylene glycol	$HO(C_2H_4O)_3H$	150	1.119	7.666	276	19.8	9.6	5.6
poly(ethylene glycol) 400	$HO(C_2H_4O)_xH$	400	1.128	7.666	300	50.7	23.1	12.4
triethylene glycol dimethyl ether	$CH_3(OCH_2CH_2)_3OCH_3$	178	0.986	11.050	216	1.5	1.1	0.89
Selexol[c]	$O((CH_2CH_2O)_2CH_3)_2$	222	1.009	8.667	$176_{0.05}$	2.5	1.8	1.36
Sepasolv MPE[d]	$CH_3O(CH_2CH_2O)_x$ $CHCH_3CH_3$	316	1.003	8.333	$90_{10^{-4}}$	4.9	3.2	2.31
triethyl phosphate	$O{:}P(OC_2H_5)_3$	182	1.070	9.480	216	1.7	1.3	1.06
triisopropyl phosphate	$O{:}P(OC_3H_7)_3$	214	0.969	8.120	$64_{0.01}$	1.7	1.3	1.02
tri-*n*-butyl phosphate	$O{:}P(O(CH_2)_3CH_3)_3$	266	0.977	8.900	$180_{0.03}$	2.5	1.8	1.35
triisobutyl phosphate	$O{:}P(OCH_2CH(CH_3)_2)_3$	266	0.964	8.425	$115_{0.03}$	3.0	2.0	1.44
bis(2-ethylhexyl) phosphate	$O{:}P(O(CH_2)_6CH_2CH_3)_2OH$	323	1.022	6.250	$209_{0.01}$	124.1	56.8	29.21
tris(2-ethylhexyl) phosphate	$O{:}P(O(CH_2)_6CH_2CH_3)_3$	435	0.920	7.075	$220_{0.07}$	7.9	4.2	2.51
tricresyl phosphate	$O{:}P(OC_6H_4CH_3)_3$	368	1.172	8.125	410	29.3	13.6	7.00
benzyl butyl phthalate	$(C_6H_4CO_2)(C_6H_4C_4H_9)$	312	1.118	7.833	$250_{0.03}$	25.4	12.0	6.42
dibutyl phthalate	$(C_6H_4CO_2)(C_4H_9)_2$	278	1.045	7.875	$206_{0.03}$	9.4	5.1	2.82
diisobutyl phthalate	$(C_6H_4CO_2)(CH_2CH(CH_3)_2)_2$	278	1.036	7.975	320	16.8	7.8	2.08
diisodecyl phthalate	$(C_6H_4CO_2)(C_{10}H_{11})_2$	447	0.963	6.775	$257_{0.01}$	40.0	19.0	8.98
dibutyl glycol phthalate	$(C_6H_4CO_2)(C_2H_4OC_4H_9)_2$	366	1.057	7.950	$270_{0.03}$	15.8	8.7	5.30
dimethyl glycol phthalate	$(C_6H_4CO_2)(C_2H_4OCH_3)_2$	282	1.174	8.500	$230_{0.03}$	21.7	12.4	6.53

[a] Density. [b] Viscosity. [c] Registered trademark of Allied Chemical Corp. for tetraethylene glycol dimethyl ether. [d] Registered trademark of BASF for pentaethylene glycol methyl isopropyl ether.

Table II. Properties of Selected Solvent Mixtures

compd	ρ_{20}, g/cm^3	(10^4)(dρ/dt), g/(cm^3 °C)	η, mPa·s 40 °C	60 °C	80 °C
15 wt % TCD alcohol DM[a] in poly(ethylene glycol) 400	1.119	6.950	66.4	26.3	10.18
15 wt % TCD alcohol DM in Selexol	1.028	8.592	3.9	2.6	1.86
15 wt % TCD alcohol DM in Sepasolv MPE	1.024	8.333	7.6	4.7	3.19

[a] Tricyclodecanedimethanol.

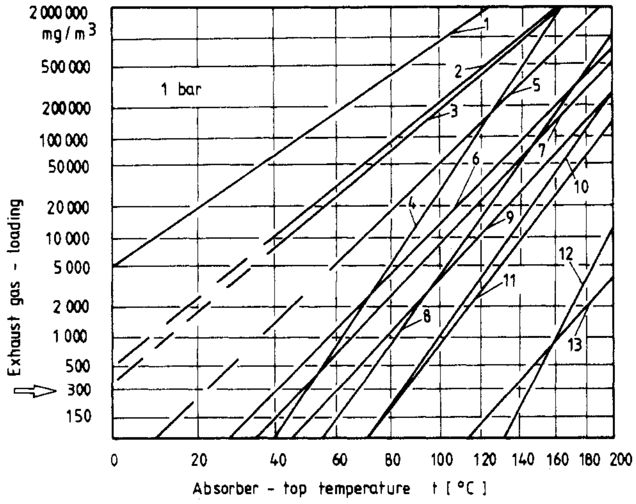

Figure 1. Equilibrium loading of the exhaust gas with organic solvent as a function of the temperature: (1) cyclohexanone, (2) triethyl phosphate, (3) *N*-methylpyrrolidone, (4) poly(ethylene glycol) dimethyl ether (M = 280), (5) ethylene glycol, (6) tri-*n*-butyl phosphate, (7) diethyl phthalate, (8) oligoethylene glycol methyl isopropyl ether (M = 316), (9) triethylene glycol, (10) tricresyl phosphate, (11) dibutyl phthalate, (12) dioctyl sebacinate, (13) dioctyl phthalate.

Assuming the solution consisting of N_2 mol of A and N_1 mol of B, and also the formation of N_3 mol of the complex B·A in the state of equilibrium, the gas partial pressure over the chemically absorbing solution results, by use of the true mole fraction

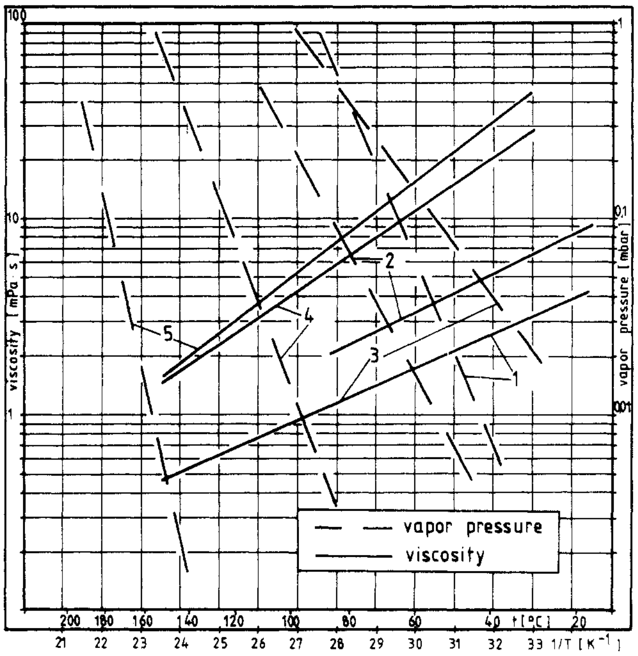

Figure 2. Vapor pressure and viscosity of selected organic solvents as a function of temperature: (1) tetraethylene glycol dimethyl ether, (2) pentaethylene glycol methyl isopropyl ether, (3) tri-*n*-butyl phosphate, (4) dimethyl glycol phthalate, (5) pentaethylene glycol (M = 250).

$$z_A = \frac{N_2 - N_3}{N_1 + N_2 - N_3} \tag{5}$$

and the method suggested by Prausnitz (*13*) as

$$p_A = H\frac{N_2 - N_1 + \left[(N_1 + N_2)^2 - 4\dfrac{KN_1N_2}{K+1}\right]^{1/2}}{N_1 + N_2 + \left[(N_1 + N_2)^2 - 4\dfrac{KN_1N_2}{K+1}\right]^{1/2}} \tag{6}$$

For the correlation of the experimental data a least-squares

Table III. Results of the Regression for the System Poly(ethylene glycol)/Sulfur Dioxide and Calculated Enthalpy of Solution

	temp, °C									
	20	40	60	80	100	*C*	*D*	*E*	*F*	$-\Delta H_s$, kJ/mol
				Poly(ethylene glycols) 200 and 400/SO_2 (*15*)						
H	1275	2001	3225	5209	8249	2557	15.8	2519	6.8	21.3
K	7.93	2.65	1.66	1.33	1.19					
				Poly(ethylene glycol) 400/SO_2 (This Work)						
H	1368	2036	2890	3941	5935	1826	13.5	4118	10.9	15.2
K	23.5	9.1	4.1	2.1	1.5					

Table IV. Results of the Regression for the System Phosphoric Acid Ester/Sulfur Dioxide and Calculated Enthalpy of Solution

phosphate	*C*	*D*	*E*	*F*	$-\Delta H_s$, kJ/mol
triethyl	2451	16.8	3947	9.3	20.4
triisopropyl	2200	16.0	2333	4.2	18.3
tri-*n*-butyl	3127	18.4	1184	1.4	26.0
triisobutyl	1396	14.1	3751	8.0	11.6
bis(2-ethylhexyl)	3978	20.9	617	1.9	33.1
tris(2-ethylhexyl)	3994	20.9	1456	1.2	33.2
tricresyl	1714	13.8	3688	7.5	14.3

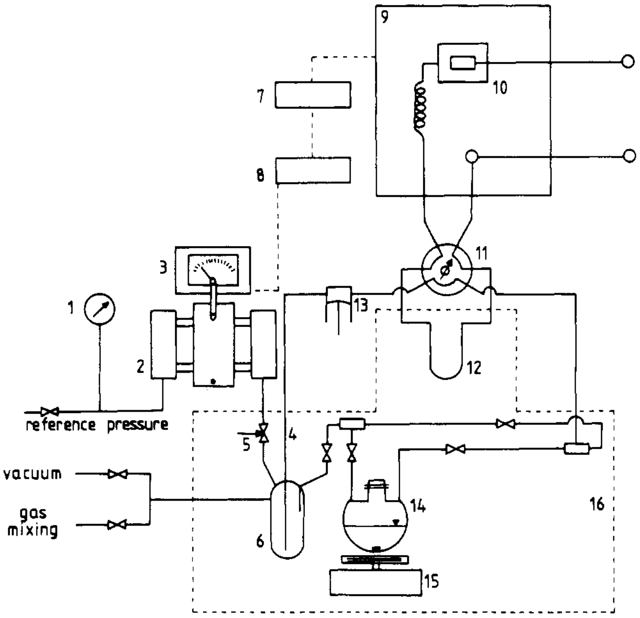

Figure 3. Determination of the absorption coefficient using the vapor pressure method—scheme of the experimental apparatus: (1) manometer, (2) Barton cell, (3) transmitter, (4) valve, (5) evacuation screw, (6) gas tank, (7) integrator, (8) plotter, (9) gas chromatograph, (10) detector, (11) six-way valve, (12) measuring loop, (13) membrane pump, (14) saturation tank, (15) stirrer motor, (16) air thermostat.

estimation of nonlinear parameters according to Marquardt (*14*) was used. The Henry coefficient H and the equilibrium constant *K* fit the model equations

$$\mathrm{H} = \mathrm{H}_0 \exp(-C/T) \tag{7}$$

$$K = K_0 \exp(E/T) \tag{8}$$

for which H_0 and K_0 are denoted as exp *D* and exp(−*F*), respectively, for better handling.

With some simplifying assumptions the temperature function of the solubility is given by eq 9. The values for the enthalpy of solution ΔH_s given in Tables III–VIII are determined by this equation, where the apparant mole fraction x_A is given by

$$(\delta \ln x_A/\delta(1/T))_p = -\overline{\Delta H_s}/R \tag{9}$$

Table V. Results of the Regression for the System Phthalic Acid Ester/Sulfur Dioxide and Calculated Enthalpy of Solution

solv	*C*	*D*	*E*	*F*	$-\Delta H_s$, kJ/mol
benzyl butyl phthalate	900	11.9	3636	9.6	7.5
dibutyl phthalate	2300	15.6	4946	14.7	19.1
diisobutyl phthalate	1760	14.6	2817	7.4	14.6
diisodecyl phthalate	2240	15.5	1580	4.5	18.6
dibutyl glycol phthalate	2580	16.0	1499	4.2	21.5
dimethyl glycol phthalate	2420	16.1	3902	10.8	20.1

Table VI. Results of the Regression for the Systems Polyethylene Glycol Dialkyl Ether/Sulfur Dioxide and Calculated Enthalpy of Solution

solv	*C*	*D*	*E*	*F*	$-\Delta H_s$, kJ/mol
triethylene glycol dimethyl ether	2025	15.7	1456	2.1	16.8
tetraethylene glycol dimethyl ether	2241	14.8	1461	2.7	18.6
pentaethylene glycol methyl isopropyl ether	2622	15.8	3434	9.3	21.8
tetraethylene glycol dimethyl ether/tricyclodecane-dimethanol (85/15 wt %)	4779	23.1	4852	14.5	39.7

Table VII. Henry Coefficient H (mbar/Mole Fraction) as a Function of Temperature and Calculated Enthalpy of Solution for the Systems Poly(ethylene glycol)/Hydrogen Sulfide

H					
60 °C	80 °C	100 °C	*C*	*D*	$-\Delta H_s$, kJ/mol
		Poly(ethylene glycol) 200/H_2S			
23 958	5169	12 097	12 097	15 464	21 551
21 989	33 121	44 812	2218	16.7	18.4 (this work)
		Poly(ethylene glycol) 400/H_2S			
11 378	2804	4 859	6 667	11 739	17 921
9 498	15 023	20 598	2412	16.4	20.1 (this work)

$$x_A = N_2/(N_1 + N_2) \tag{10}$$

Experimental Results and Discussion

In Figures 4 and 5 the experimental data for the systems SO_2/tri-*n*-butyl phosphate and SO_2/tetraethylene glycol dimethyl ether are presented. The solid lines are calculated from the experimental data of this work, by using eq 6–8 with parameters listed in Tables IV and VI. As can be seen from Figures 4 and 5 the experimental results of Cooper (*5*) and Albright (*1*) can also be represented by the same coefficients. On the other hand, the results of Gestrich and Reinke (*15*) for the SO_2/poly(ethylene glycol) 400 system are only reproduced with moderate agreement (Tables III and IX). For the H_2S/poly(ethylene glycol) systems (Table VII) the measured data fit, within the experimental error, the data of the named authors.

Table VIII. Henry Coefficient H (mbar/Mole Fraction) as a Function of Temperature and Calculated Enthalpy of Solution for Hydrogen Sulfide and Carbonyl Sulfide over Various Solvents

gas	H 20 °C	40 °C	60 °C	80 °C	100 °C	C	D	$-\Delta H_s$, kJ/mol
			Tri-n-butyl Phosphate					
H_2S	3540	5429	8571	10084	16304	2000	15.0	16.7
COS	7672	11725	15080	24819	33691	2023	15.8	16.8
			Tetraethylene Glycol Dimethyl Ether					
H_2S	3390	6179	8310	11321	16901	2016	15.2	17.2
COS	9643	15392	21231	32762	41976	2027	16.1	16.9
			Pentaethylene Glycol Methyl Isopropyl Ether					
H_2S	2804	4859	6667	11739	17921	2500	16.4	20.7
COS	8521	13017	13838	27063	43640	2170	16.4	18.0
			Tetraethylene Glycol Dimethyl Ether/Tricyclodecanedimethanol (85/15 wt %)					
H_2S	5169	8487	12097	15464	21551	1910	15.3	16.0
COS	13610	21731	31847	37401	44088	1606	15.1	13.3

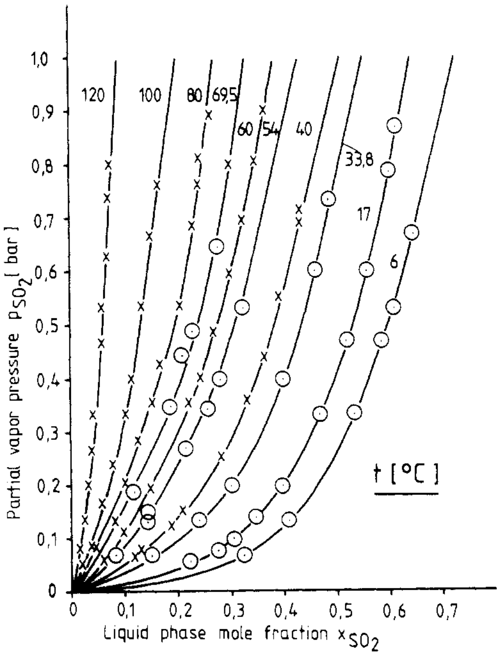

Figure 4. Absorption isotherms for sulfur dioxide in tri-n-butyl phosphate: (⊙) Cooper (*5*), (×) this work, (—) calculated.

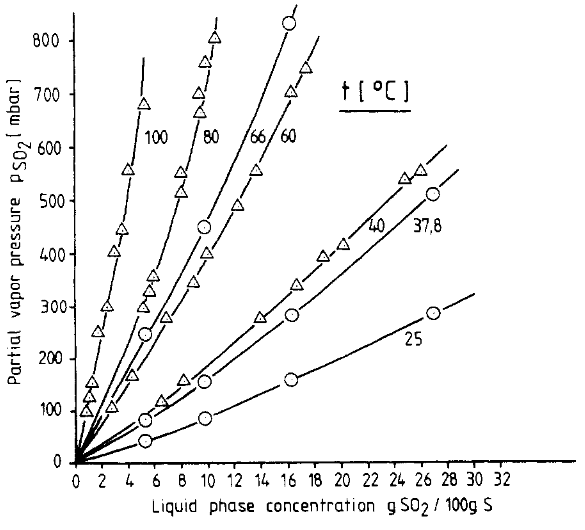

Figure 5. Solubility isotherms of sulfur dioxide in tetraethylene glycol dimethyl ether: (⊙) Albright (*1*), (△) this work, (—) calculated.

Table IX. Technical Absorption Coefficient at Partial Pressure of 0.98 bar in N m³/(t•bar)

gas	temp, °C 20	40	60	80	100
		Poly(ethylene glycol) 400			
H_2S (*15*)			5.2	3.8	2.8
H_2S	15.7	9.4	6.0	3.9	2.8
SO_2 (*15*)	170	81	42	24	14
SO_2	190	95	69	32	20
		Tri-n-butyl Phosphate			
COS	11.7	7.7	5.9	3.7	2.7
H_2S	18.9	15.7	12.3	8.8	6.4
SO_2	86.4	47.1	27.5	18.4	13.2
		Tetraethylene Glycol Dimethyl Ether			
COS	11.0	6.7	5.0	3.3	2.6
H_2S	23.7	12.9	10.4	8.0	5.8
SO_2	246	153		50.3	30.0
		Pentaethylene Glycol Methyl Isopropyl Ether			
COS	9.1	6.0	4.6	2.8	1.8
H_2S	28.9	17.9	10.1	7.3	5.1
SO_2	237	118		36.0	22.0
		15 wt % TCD Alcohol DM in Tetraethylene Glycol Dimethyl Ether			
COS	7.9	5.1	3.3	2.9	2.6
H_2S	22.7	12.8	9.2	6.6	5.1
SO_2	273	114		48.0	30.7

The results of the other H_2S and COS systems can be represented by eq 6–8 with correlation coefficients better than 0.99. The parameters which were evaluated from the experiemental data are listed in Tables IV–IX. In these tables the enthalpy of solution determined by using eq 9 is also reported.

Solubility of Sulfur Dioxide

It is known from the literature that phosphoric acid esters dimerize at moderate temperatures (*16*), and the ester oxygen atoms P–OR form complexes with the SO_2 beside the phosphoryl oxygen atoms —P=O, at higher SO_2 partial pressure (*17*). Nevertheless, the assumed model of the temperature dependence of the Henry coefficient H and the equilibrium constant K describes the experiental phase equilibrium data with an average deviation of ±4.2%, also at low temperatures.

The investigated phthalic acid esters show good solubility properties for sulfur dioxide. Though the IR analysis of the SO_2-saturated phthalic acid esters shows only a slight change of the —(C=O)—O— stretch oscillation at 1285 and 1220 cm^{-1}, the experimental results follow eq 6. The average deviation of the calculated partial pressures from the experimental values is ±3.9%.

The polyethylene dialkyl ethers show essentially higher solubilities for sulfur dioxide (Tables VI and IX). The IR spectrum gives a hint of the interaction between the SO_2 and the ether-bridge atoms from 600 to 400 cm^{-1}. Also interference in the area of the free symmetry and asymmetric valence oscillations of the SO_2 (1345 and 1335 cm^{-1}, respectively) can be observed. The average deviation of the experimental partial pressures from the calculated values (eq 6) and parameters of Table VI) is ±0.4%.

Solubility of Hydrogen Sulfide and Carbonyl Sulfide

The solution properties of the investigated solvents for H_2S and COS, both less polar than SO_2 (dipole moments (debyes): SO_2, 1.63; H_2S, 0.97; and COS, 0.71), show only gradual differences and differ only slightly in temperature behavior. The experimental data for the partial pressure of the dissolved gas p_i as a function of the mole fraction in the solution x_i fit Henry's law according to eq 1 within the investigated concentration range ($x_{H_2S}^{max}$ = 0.16 and x_{COS}^{max} = 0.10), with correlation coefficients better than 0.99.

Registry No. H_2S, 7783-06-4; SO_2, 7446-09-5; COS, 463-58-1; $HO(C_2H_4O)_3H$, 112-27-6; $HO(C_2H_4O)_xH$, 25322-68-3; $CH_3(OCH_2CH_2)_3OCH_3$, 112-49-2; $O((CH_2CH_2O)_2CH_3)_2$, 143-24-8; $CH_3O(CH_2CH_2O)_xCHCH_3CH_3$, 71495-18-6; $O{:}P(OC_2H_5)_3$, 78-40-0; $O{:}P(OC_3H_7)_3$, 513-02-0; $O{:}P(O(CH_2)_3CH_3)_3$, 126-73-8; $O{:}P(OCH_2CH(CH_3)_2)_3$, 126-71-6; $O{:}P(O(CH_2)_6CH_2CH_3)_2OH$, 298-07-7; $O{:}P(O(CH_2)_6CH_2CH_3)_3$, 78-42-2; $O{:}P(OC_6H_4CH_3)_3$, 1330-78-5; $(C_6H_4CO_2)(C_6H_4C_4H_9)$, 85-68-7; $(C_6H_4CO_2)(C_4H_9)_2$, 84-74-2; $(C_6H_4CO_2)(CH_2CH(CH_3)_2)_2$, 84-69-5; $(C_6H_4CO_2)(C_{10}H_{11})_2$, 26761-40-0; $(C_6H_4CO_2)(C_2H_4OC_4H_9)_2$, 117-83-9; $(C_6H_4CO_2)(C_2H_4OCH_3)_2$, 36339-61-4; tricyclodecanedimethanol, 26896-48-0.

Literature Cited

(1) Albright, L. F.; Shannon, P. T.; Yu, Sun-Nieu; Chueh, Ping Lin. *Chem. Eng. Prog., Symp. Ser.* **1963**, *59*, 66–74.
(2) Peter, S. German Patent DE-OS 1948253, April 1971.
(3) Judd, D. K. *Hydrocarbon Process.* **1978**, *57*, 122–4.
(4) Härtel, G. Dissertation, Universität Erlangen-Nürnberg, 8520 Erlangen, FRG, 1980.
(5) Cooper, D. F.; Smith, J. W. *J. Chem. Eng. Data* **1974**, *19*, 133–6.
(6) Hirai, M.; Odello, R.; Shimamura, H. *Chem. Eng.* (*N.Y.*) **1972**, *79*, 78–9.
(7) Davis, J. C. *Chem. Eng.* (*N.Y.*) **1972**, *79*, 66–8.
(8) Deschamps, A.; Renault, P. US Patent 3598529, 1971.
(9) "Technische Anleitung zur Reinhaltung der Luft". *Umwelt* **1974**, *No. 33*, 6.
(10) Langner, G. "Vorschriften zur Reinhaltung der Luft"; Bundesanzeiger-Verlag: 5000 Köln 1, FRG, 1983.
(11) Block, U. *VDI-Ber.* **1978**, *No. 253*, 71–6.
(12) Dolezalek, F. *Z. Phys. Chem.* **1908**, *64*, 727.
(13) Prausnitz, J. M. "Molecular Thermodynamics of Fluid-Phase Equilibria"; Prentice-Hall: Englewood Cliffs, NJ, 1969; p 331.
(14) Marquardt, D. W. *J. Soc. Ind. Appl. Math.* **1963**, *11*, 431–41.
(15) Gestrich, W.; Reinke, L. *Chem.-Ing.-Tech.* **1963**, *55*, 629.
(16) Petkovic, Dj. *J. Inorg. Nucl. Chem.* **1963**, *30*, 603.
(17) Albertson, N. F.; McReynolds, J. P. *J. Am. Chem. Soc.* **1943**, *65*, 1687–91.

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Thermodynamics of Nucleoside–Solvent Interactions. Uridine and Cytidine in Pure Water and in 3 *m* Ethanol between 17 and 37 °C

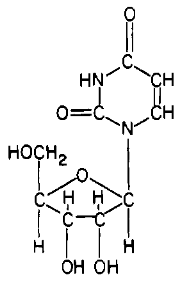
John H. Stern* and Lisa P. Swanson

Department of Chemistry, California State University—Long Beach, Long Beach, California 90840

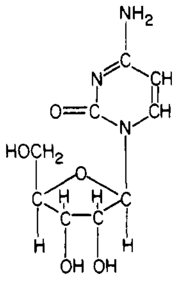
Enthalpies of solution of the nucleosides uridine and cytidine in water and in 3 *m* ethanol were measured between 17 and 37 °C. From these were calculated positive enthalpies of transfer from water to 3 *m* ethanol. Heat capacities of solution obtained from the temperature variation of the enthalpies of solution and combined with estimated heat capacities of the solids yielded partial molal heat capacities of the nucleosides. In pure water these are 96 and 93 cal/(mol deg) for uridine and cytidine, respectively. The small difference between the values indicates that the partial molal heat capacities in pure water are almost independent of the interchange of the base groups uracil and cytosine. In 3 *m* ethanol the values are 98 and 84 cal/(mol deg) and show that ethanol tends to reduce the leveling effect observed in water.

Introduction

The structural stabilities of DNA and RNA depend in part on the interaction of their repeating nucleoside components with the solvent, and thermodynamic studies may provide useful information on these poorly understood systems. This is the second contribution on the thermodynamics of nucleoside–solvent interactions in aqueous solutions and follows a study of enthalpies and heat capacities of solution of inosine and adenosine in pure water, $\Delta H°$, and in 1 *m* ethanol, ΔH, from 25 to 35 °C (*1*). The present work is concerned with the enthalpies of solution of the major pyrimidine nucleosides uridine and cytidine in water and in 3 *m* ethanol between 17 and 37 °C. The results allow calculation of enthalpies of transfer from water to the mixed aqueous solvent, $\Delta \bar{H}$, from $\Delta \bar{H} = \Delta H - \Delta H°$.



uridine



cytidine

Enthalpies of transfer to aqueous ethanol reflect the complicated disturbing effects of ethanol on the solvent properties of water (*2*). It may be noted that the presence of alcohol also has a profound effect on the double-helical structure of DNA, since one form is favored in water, transforming to another form in aqueous alcohol (*3*).

The temperature variation of the enthalpies of solution yields the heat capacity of solution in pure water, $\Delta C_p°$, in 3 *m* ethanol, ΔC_p, and the heat capacity of transfer $\Delta \bar{C}_p = \Delta C_p - \Delta C_p°$, where $\Delta \bar{C}_p$ in part reflects the difference in the ordering or structuring of solvent molecules around the solutes upon transfer.

Experimental Section

The calorimeter and calorimetric procedure have been described elsewhere (*4*). Uridine and cytidine were obtained from

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