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Gas Solubilities in Aqueous Solutions of Organic Substances

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The solubilities of He, N_2, O_2, CH_4, and CO_2 in aqueous solutions of glycerol, acetic acid, glucose, sucrose, and lactose were measured at 303.2 K. Additional data were generated for CO_2 at 293.2 K and 323.2 K. The present results and literature data were analyzed to develop an empirical model. The parameter set allows predictions for 15 gases and 63 organic substances at temperatures between 273 K and 343 K.

Introduction

Gas solubilities in mixed aqueous solutions of salts and organic substances are important in many areas of chemical and biochemical engineering. Various models have been developed to predict the effect of dissolved substances on gas solubility.

The salting-out of gases by electrolytes can be described in the form of the Sechenov relation:

$$\log(c_{G,o}/c_G) = \log(H_G/H_{G,o}) = K_S c_S \qquad (1)$$

Here $c_{G,o}$ ($H_{G,o}$) and c_G (H_G) denote the gas solubility (Henry's constant) in pure water (index o) and the salt solution, respectively, and c_S is the molar concentration of the salt. The Sechenov constant K_S is nearly always positive; i.e. the solubility decreases with increasing salt concentration. For the estimation of Sechenov constants, various empirical models have been developed. Recently, Weisenberger and Schumpe (1996) have extended the model of Schumpe (1993) to a temperature range of 273 K to 363 K:

$$c_{G,o}/c_G) = \sum(h_i + h_{G,o} + h_{G,T}(T/\mathrm{K} - 298.15))c_i \qquad (2)$$

Here c_i is the molar concentration of ion i, h_i is an ion-specific parameter and $h_{G,o}$ as well as $h_{G,T}$ are gas-specific parameters. The model allows the prediction of salting-out effects for systems where no experimental data are available (e.g. when a chemical reaction occurs), and it is applicable to mixed electrolyte solutions.

Organic substances in aqueous solution may decrease (e.g. sugars, glycerol) or increase (e.g. short-chain alcohols) the solubilities of gases. At low concentrations, the effect can often be described in the form of eq 1 using the nonelectrolyte concentration c_n in place of the salt concentration c_S:

$$\log(c_{G,o}/c_G) = K_n c_n \qquad (3)$$

Mixed solutions are more relevant in biochemical engineering than solutions of only one substance. Microbial culture media are composed of various salts and at least one organic substance as the carbon source. The individual effects of the components on the gas solubility have been observed to be "log-additive" at sufficiently low concentrations (Schumpe and Deckwer, 1979; Popovic et al., 1979; Schumpe et al., 1982). Introducing eq 2 for the effect of electrolytes, the following relation can be used to estimate gas solubilities in mixed solutions of ions (i) and organic substances (j):

$$\log(c_{G,o}/c_G) = \sum_i(h_i + h_{G,o} + h_{G,T}(T/\mathrm{K} - 298.15))c_i + \sum_j K_{n,j}c_{n,j} \qquad (4)$$

Unfortunately, much less experimental results are available (Kertes, 1979−90) on the K_n values for nonelectrolytes as compared to the Sechenov constants K_S and there is no comparable model for the prediction of K_n values. In this paper, the results of a systematic experimental study for selected substances are presented and it is attempted to develop an empirical model for the effect of organic solutes on gas solubility.

Experimental Section

The gas solubilities were measured with a barometric saturation method described previously (Schumpe et al., 1982; Lühring and Schumpe, 1989). The absorber was made of glass and consisted of chambers for the gas and the liquid with about the same volume (V_L/V_G = 1.013). The chambers were partly separated by a horizontal glass plate to define the liquid level and to minimize the contact area (without stirring). The apparatus was placed in an air bath thermostated to ±1 K; the vessel temperature was controlled to ±0.1 K by pumping thermostated liquid through its jacket. The chemicals were "for biochemistry/microbiology" grade obtained from Merck (except for sucrose: Fluka); all gases were supplied by Linde. In the case of carbon dioxide, a few drops of sulfuric acid were added to make the solution slightly acidic. (The salting-out effect of the acid was negligible, as checked with other gases.)

The liquid was degassed by evacuation after adding surplus water to compensate for evaporation losses. Evacuation was terminated when the correct liquid level was reached again. After thermal equilibration, the vapor pressure P_L of the liquid was read. Then dry gas was slowly introduced into the head space via a coiled metal tube in a constant-temperature bath. At a pressure P_0

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Table 1. Henry's Constants at 303.2 K

	H/kPa m^3 mol^{-1}				
c_n/kg m^{-3}	He	N_2	O_2	CH_4	CO_2
		Water			
0	263	168.7	88.5	78.2	3.45
(lit. data)	263[a]	165.5[a]	86.3[b]	78.0[a]	3.39[b]
		Glycerol			
23.4	283	182.5	90.0	81.5	3.53
46.8	300	191.1	94.5	84.4	3.60
92.7	313	199.3	98.8	85.9	3.71
138	318	205.7	99.7	87.6	3.88
209	326	213.2	107.0	93.4	3.96
492	499	349	149.7	112.6	5.04
691	751	546	203.5	142.1	5.91
		Acetic Acid			
15.4	262	166.7	85.8	76.5	3.44
30.6	264	165.6	87.9	77.1	3.39
61.8	275	168.4	85.4	75.9	3.37
121	273	168.8	83.5	73.7	3.24
302	262	145.9	76.4	59.6	2.70
600	213	84.8	47.9	31.9	1.74
1450	96.2	21.8	13.9	7.20	0.609
		D(+)-Glucose			
166.5	349	211.1	109.4	95.4	4.05
333	435	296.3	142.3	123.1	4.91
500	552	477	182.2	192.1	6.22
		Sucrose			
200	328.7	220.8	107.7	96.8	4.02
281.4				105.6	
400	412	272.6	135.4		4.78
600	796	425.4	199.2	167.6	5.94
		Lactose Monohydrate			
60.1	282.5	183.7	94.5	83.7	3.59
120	295.5	198.5	99.1	89.1	3.80
180.2	331.5	211.8	106.3	92.5	4.01

Kertes (1979−90). [b] Schumpe et al. (1982).

close to atmospheric pressure, the gas supply line was closed and a magnetic stirrer was started. The liquid then overflowed the glass plate and the isothermal and isochoric absorption process started. The steady equilibrium pressure P_∞, usually read after 5 min, was used to calculate Henry's constant H:

$$H = \frac{P_\infty - P_L}{P_0 - P_\infty} RT \frac{V_L}{V_G} \tag{5}$$

The standard deviation of repeated measurements was 0.05%. The reported solubilities are mean values of at least two measurements differing by less than 1%.

Results

The solubilities of five gases (He, N_2, O_2, CH_4, CO_2) in aqueous solutions of glycerol, acetic acid, glucose, sucrose, and lactose were studied in wide concentration ranges at 303.2 K (Table 1). Equation 3 was found to apply well except for high acetic acid concentrations where the gas solubilities increase strongly and become much higher than in pure water. Additional measurements were taken for CO_2 at 293.2 K and 323.2 K in solutions of sugars and complex bio-media (Table 2).

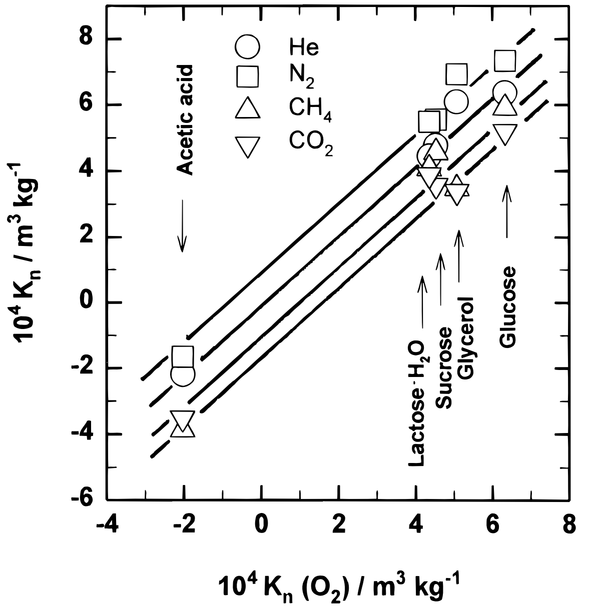

Figure 1. Comparison of the solubility parameters, K_n (eq 3), fitted to the results in Table 1.

Irregularities in the gas absorption capacity of bio-media have led to the suspicion that pH-dependent adsorption to proteins might be considerable (Schumpe et al., 1982). In this study, the oxygen capacity of yeast extract medium (50 kg/m^3) was measured in the pH range of 2.5−8.5. The overall oxygen capacity was not affected by the pH value.

It has further been reported by Baburin et al. (1981) that sunflower seed oil, added as an antifoam agent, increased the oxygen capacity by factors up to 3. This was much more than what could be explained by the higher solubility in the pure organic liquid at the small volume fractions applied (0−0.2 vol %). It was suggested that oxygen adsorbs on the surface of fine oil droplets. Using the same medium as Baburin et al. (150 kg/m^3 molasses, 20 kg/m^3 $(NH_4)_2SO_4$, 5 kg/m^3 KH_2PO_4, 5 kg/m^3 K_2HPO_4), sunflower seed oil (H[O_2, 293.2 K] = 18.4 kPa m^3 mol^{-1}) was added at 0.05 and 0.2 vol %. (Without any oil, excessive foaming during evacuation prevented the measurement.) The oxygen solubilities at the two studied oil fractions were not significantly different, whereas Baburin et al. (1981) had observed the oxygen capacities to differ by a factor of 2.

In the present study neither significant adsorption on proteins nor adsorption on fine antifoam droplets could be observed.

Empirical Model

By fitting eq 3 to the results listed in Table 1 (as far as applicable at lower concentrations), a set of K_n parameters was obtained. (Since the molar mass is not defined for some of the organic "substances", the mass concentration in kg m^{-3} is used throughout for c_n.) The parameters are

Table 2. Henry's Constants *H* for Carbon Dioxide at 293.2 K and 323.2 K

	H/kPa m^3 mol^{-1}								
	D(+)-glucose		sucrose		lactose monohydrate		yeast extract	malt extract	casein peptone
c_n/kg m^{-3}	293.3 K	323.2 K	293.3 K	323.2 K	293.2 K	323.2 K	323.2 K	323.2 K	323.2 K
0	2.58	5.21	2.58	5.21	2.58	5.21	5.21	5.21	5.21
25	2.59	5.31	2.59	5.36	2.59	5.31	5.43	5.31	5.40
50	2.68	5.42	2.65	5.43	2.66	5.43	5.71	5.43	5.50
100	2.82	5.71	2.75	5.65	2.76	5.70	6.26		5.95
150			2.86	5.83					

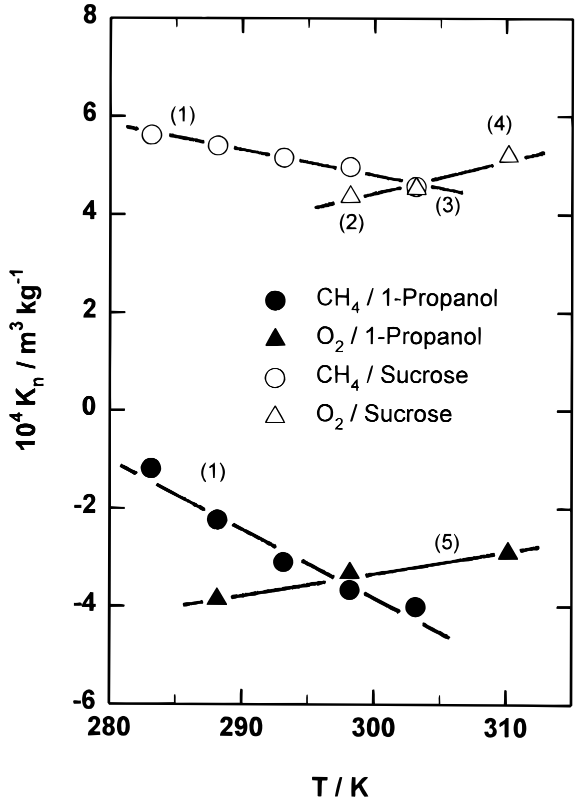

Figure 2. Temperature effect on the solubility parameters K_n: (1) Ben-Naim and Yaacobi, 1974; (2) Quicker et al., 1981; (3) this study; (4) Zander, 1976; (5) Kutsche et al., 1984.

Table 3. Gas-Specific Model Parameters (Eq 6)

gas	$10^4 b_{G,o}$/ $m^3 kg^{-1}$	$10^4 b_{G,T}$/ $m^3 kg^{-1} K^{-1}$	temp range/K	no. of K_n values
	−0.71	0.161	288−298	10
	−0.48[a]	n.a.[c]	303.15	5
Ne	2.39	−0.018	283−313	4
Ar	3.67	−0.176	288−343	18
Rn	0.31[b]	n.a.	291.15	1
	0.67	−0.061	293−303	14
	≡0	−0.044	273−313	61
O	−1.84	0.138	288−303	18
$_2$	−1.86	0.010	288−323	24
$_4$	−0.69	−0.120	283−303	24
H_6	−3.69	−0.175	283−303	25
H_8	−4.38	−0.065	278−318	3
$_4H_{10}$	−6.74	−0.112	278−318	3
$_4H_{10}$	−6.68	−0.092	278−318	3
S	−3.04	−0.067	273−298	3

Valid for 303.15 K with $b_{G,T}$ set to zero. [b] Valid for 291.15 K $b_{G,T}$ set to zero. [c] n.a.: not available.

compared graphically in Figure 1 by plotting the values for He, N_2, CH_4, and CO_2 against those for O_2. The results can be approximated by parallel lines, the parameters for nitrogen being on the higher side and those for carbon dioxide being on the lower side. Although the spread is wider for glycerol, the general trend suggests a model where a set of substance-specific parameters is modified by adding a gas-specific constant.

In addition to the present results, literature data were analyzed to obtain a comprehensive set of experimental K_n values. (The full set of 34 references is available from the authors.) In view of the application to bio-media, some frequently used complex additives to microbial culture media were also considered a "substance" although the composition is ill-defined and may vary depending on the manufacturer and the batch. Overall, 216 K_n values were

Table 4. Substance-Specific Model Parameters (Eq 6) and Upper Concentration Limits

substance	$10^4 b_n$/ $m^3 kg^{-1}$	max. conc/ kg m^{-3}	no. of K_n values
	Saccharides		
sucrose	5.85	200−600	21
D-glucose	6.68	330−500	13
lactose	5.47	170−280	10
maltose	5.68	(200)	1
D-fructose	5.03	(180)	1
L-arabinose	6.65	(150)	1
starch	6.88	(200)	1
glycogen	7.12	(250)	1
dextrin	5.55	(200)	1
inulin	6.01	(200)	
glucose-1-phosphate	12.40	(200)	
glucose amine	11.76	(300)	1
gluconic acid	3.92	(500)	1
	Alcohols		
methanol	−5.71	25−160	9
ethanol	−4.78	40−210	13
1-propanol	−3.12	40−100	13
2-propanol	−7.67	(65)	5
1-butanol	0.45	(60)	2
glycol	4.47	(185)	2
polyethylene glycol (PEG) 3000	4.29	(300)	1
PEG 10,000	4.94	(160)	1
PEG 20,000	5.55	(100)	1
glycerol	5.25	180−690	21
1,2,3,4-butane tetrol	5.07	(120)	1
	Amines		
ethanol amine	2.94	70	2
diethanol amine	4.58	110	4
triethanol amine	6.88	320	1
isopropanol amine	3.58	20	1
diisopropanol amine	4.31	180	1
ethane 1,2-diamine	5.60	90	1
choline chloride	6.01	(700)	1
acetylcholine chloride	6.56	(300)	1
	Various Substances		
acetic acid	−1.13	150−300	9
propionic acid	0.97	100−180	2
oxalic acid	3.34	(80)	1
chloracetic acid	5.52	100	1
citric acid	4.81	(200)	2
urea	5.05	120−600	23
chondroitine sulfate	11.64	(200)	1
creatine	6.58	(100)	1
adenosin diphosphate (ADP)	6.13	(200)	1
adenosin triphosphate (ATP)	7.63	(200)	1
chloralhydrate	3.94	320	2
acetamide	2.72	(60)	2
1,4-dioxane	−2.61	(135)	10
	Amino Acids		
glycine	12.10	(200)	3
alanine	10.43	(300)	3
cysteine	23.35	(200)	1
lysine	13.98	(300)	1
hydroxyproline	8.34	(200)	1
	Proteins		
albumin (bovine)	1.97	(200)	2
albumin (chicken)	3.76	(200)	1
α-globulin	3.58	(100)	1
β-globulin	4.25	(150)	1
γ-globulin	3.09	(200)	1
haemoglobin	0.23	(250)	1
	Complex Substances		
pharmamedia	1.50	80	1
corn steep liquor	2.11	(100)	1
malt extract	4.97	50	1
meat extract	5.92	(60)	1
yeast extract	7.90	(100)	2
casein peptone	5.79	(100)	2
molasses	4.03	240	1

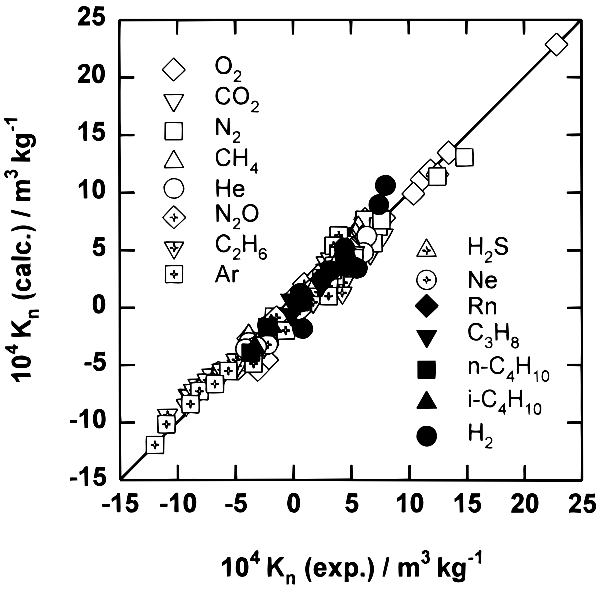

Figure 3. Parity plot for eq 6 with the parameter values listed in Tables 3 and 4.

evaluated for 15 gases and 63 substances in the temperature range of 273 K to 343 K. The strongest solubility increase was found for 2-propanol; the strongest "salting-out" effects were reported for amino acids. Usually, eq 3 could be applied in the full concentration range covered experimentally. When the data allowed an upper limit to be identified, this turned out to be mainly substance-specific rather than gas-specific.

The temperature dependence was close to linear. As exemplified in Figure 2, the slope in a plot of K_n against temperature is clearly gas-specific but to some extent also substance-specific. The scatter is considerable for other systems, particularly when the results of different studies have to be combined. To avoid insignificant results, it was found necessary to ignore any substance-specificity of the temperature effect. The following relation was applied to describe the experimental data:

$$K_n = b_n + b_{G,o} + b_{G,T}(T/K - 298.15) \qquad (6)$$

The structure of eq 6 was kept analogous to eq 2, suggested for electrolytes, by using 298.15 K as the reference temperature. (A particularly large number of data points is available for this temperature.) The $b_{G,o}$ parameter for oxygen was arbitrarily set to zero to obtain one parameter set out of an unlimited number of equivalent sets. Nonlinear regression analysis (Marquardt's method) was used to arrive at the parameter set listed in Tables 3 and 4 for the gas-specific and for the substance-specific parameters, respectively. It is interesting to note that the hydrocarbon gases, while showing the strongest salting-out behavior in electrolyte solutions (highest $h_{G,o}$ values reported by Weisenberger and Schumpe, 1996), have the smallest $b_{G,o}$ values. The model describes the experimental K_n values with a standard deviation of 0.75 × 10^{-4} m^3/kg. A parity plot is provided in Figure 3.

It should be noted that many parameters are based just on one system studied experimentally (cf. number of K_n values listed in Tables 3 and 4). To indicate the concentration range where the model applies, the respective upper limits for a particular substance (with some variation depending on the gas and the source of information) are listed in Table 4. In many cases the limit just corresponds to the highest concentration studied (as indicated by brackets) and some extrapolation might be possible. With respect to the temperature range for the $b_{G,T}$ parameter, some extrapolation may also be justified. Gas solubilities in pure water at the considered temperature can be found in the Solubility Data Series (Kertes, 1979−90) or calculated from Wilhelm et al. (1977).

Conclusions

Based on the present results and comprehensive literature data, an empirical model could be developed for the prediction of gas solubilities in aqueous solutions of organic substances (eq 6). The model may be combined with a previously suggested model for salting-out by electrolytes (eq 2) to estimate gas solubilities in mixed solutions, e.g. microbial culture media (eq 4). The data set for organic substances is much less comprehensive than for salts. More data are needed to check and adjust the model. However, when no experimental data are available, the suggested model is a convenient way to access the effects of dissolved organic substances on the solubility of gases.

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