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Solubility of CO_2 in Aqueous Solutions of Saccharose, Glucose, Fructose, and Glycerin

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The solubility of carbon dioxide at 101.3 kPa has been measured in aqueous solutions of glucose, fructose, and glycerin at 298.1 K and saccharose from 293.1 to 313.1 K. The concentration range was from 0 to 150 g·dm^{-3}.

Introduction

Gas−liquid mass transfer rates depend on the mass transfer coefficients, the area of the gas−liquid interface, and the rate constants of any chemical reactions accompanying the physical absorption process. Calculation of these parameters from experimental gas−liquid mass transfer data in conjunction with absorption equations, and application of the latter once the transfer parameters are known, requires prior knowledge of various physical properties of the liquid phase (density, surface tension, and viscosity) and of the solubility and diffusivity of the gas in the liquid. However, such values are not always available in sufficient detail in the literature, especially for systems in which surfactants, sugars, or glycerin have been included so as to allow investigation of the behavior of the gas−liquid interface when surface tension or viscosity are altered (*1−3*).

The measurement of solubilities has been extensively dealt with in the literature (*4−9*), but the available data for the solubility of CO_2 in water present some dispersion (*10*) and in aqueous solutions of sugars or glycerin (*11, 12*) exhibit considerable lacunae in the temperature−concentration region of interest to us. For future correlation of mass transfer data we required sets of solubilities determined under uniform conditions throughout the region of interest. Rather than using existing solubility prediction methods, which are too inaccurate except for use as a last resort, we decided to determine a series of solubilities experimentally. In this paper we describe the apparatus constructed for this purpose and report solubilities of CO_2 in aqueous solutions of saccharose, glucose, fructose, and glycerin.

Theory

The solubility of a gas in a liquid is the partition coefficient describing the distribution of the gaseous solute (A) between the gaseous and liquid phases at equilibrium. It is calculated from the partial pressure of A in the gas phase and its concentration in the liquid phase (B). If the gas phase contains only A and vapor from the liquid, then it is sufficient to know the total pressure of the gas phase and the vapor pressure of the liquid at the working temperature. The concentration of A in the liquid phase can be determined by chemical analysis of samples, or by physical methods involving measurement of pressure, mass, or volume changes. By conservation of mass, these results allow calculation of the quantity of A transferred to the liquid phase at equilibrium. Note that it is the number of moles of species A itself that is required; any chemical reaction between A and the absorbent liquid must be taken into account in the mass balance.

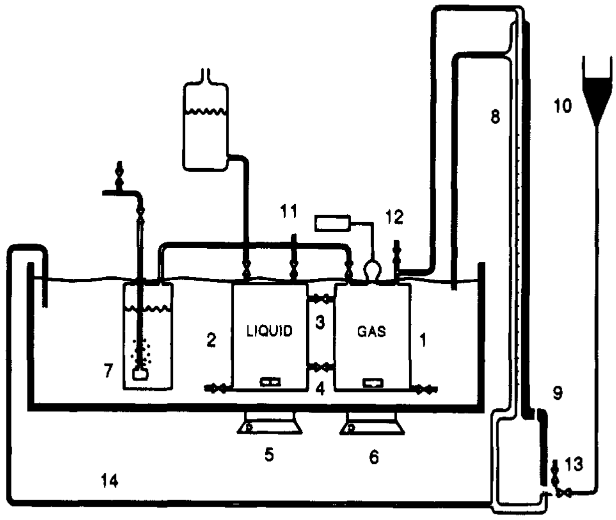

Figure 1. Schematic drawing of the experimental apparatus.

For a gas−liquid system at constant temperature and pressure, it suffices to determine the volume of gas absorbed by a known mass of liquid (*13−15*). The apparatus constructed in our laboratory measures the volume of absorbed gas as the volume of mercury that must be supplied to the system in order to restore the initial pressure. This apparatus combines previous designs (*15, 16*) to achieve a more accurate determination of the volume of the absorbent liquid. The raw solubility data are gas/liquid volume ratios (or mole or mass ratios, if ideal behavior is assumed for the gas phase).

Experimental Section

Apparatus. The apparatus used (Figure 1) consists of two glass cells, one for the gas (1) and the other for the liquid (2), which communicate via two stopcocks (3, 4) and are equipped with magnetic stirrers (5, 6). The gas cell has a volume of about 500 cm^3, and the liquid cell has a precisely determined volume of 243 cm^3. Commercial gas from a bottle is saturated with water vapor by passage through a humidifier (7) before entering the gas cell. The latter contains a calibrated pressure transducer connected to a digital display, which together measure pressure to within ±0.1 kPa over the range 0−0.16 MPa. The gas cell is connected to a 150 cm^3 graduated buret (8) with a bulb of precisely known volume (9) at its lower end; the bulb communicates with a graduated mercury reservoir of variable height (10). Three valves (*11−13*) allow the

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Table 1. Density ϱ at Mass Fraction w

saccharose	w	0.02690	0.05280	0.07486	0.09805	0.12069	0.14283
	$\varrho/(\mathrm{kg{\cdot}m^{-3}})$	1.007	1.017	1.021	1.027	1.037	1.050
glucose	w	0.02486	0.04934	0.07327	0.09688	0.12092	0.14390
	$\varrho/(\mathrm{kg{\cdot}m^{-3}})$	1.006	1.013	1.023	1.033	1.035	1.044
fructose	w	0.02489	0.04952	0.07329	0.09668	0.11970	0.14208
	$\varrho/(\mathrm{kg{\cdot}m^{-3}})$	1.006	1.010	1.023	1.034	1.044	1.056
glycerin	w	0.02528	0.05316	0.07481	0.09856	0.12243	0.14858
	$\varrho/(\mathrm{kg{\cdot}m^{-3}})$	1.002	1.009	1.014	1.018	1.025	1.031

Table 2. Solubilities s of CO_2 in Aqueous Solutions of Saccharose, Glucose, Fructose, and Glycerin of Various Concentrations at Various Temperatures[a]

		$10^5 s/(\mathrm{mol{\cdot}cm^{-3}})$					
	T/K	w = 0.0296 90	w = 0.052 80	w = 0.074 86	w = 0.098 05	w = 0.120 69	w = 0.142 83
saccharose	293.1	3.68	3.59	3.49	3.38	3.31	3.23
	298.1	3.29	3.19	3.11	3.05	2.94	2.89
	303.1	2.91	2.87	2.80	2.74	2.69	2.63
	308.1	2.63	2.57	2.51	2.45	2.40	2.34
	313.1	2.37	2.34	2.28	2.22	2.18	2.13

		$10^5 s/(\mathrm{mol{\cdot}cm^{3}})$					
	T/K	w = 0.024 86	w = 0.049 34	w = 0.073 27	w = 0.096 88	w = 0.120 92	w = 0.143 90
glucose	298.1	3.26	3.18	3.13	3.05	2.96	2.86

		$10^5 s/(\mathrm{mol{\cdot}cm^{3}})$					
	T/K	w = 0.024 89	w = 0.049 52	w = 0.073 29	w = 0.096 68	w = 0.119 70	w = 0.142 08
fructose	298.1	3.27	3.18	3.11	3.02	2.96	2.91

		$10^5 s/(\mathrm{mol{\cdot}cm^{3}})$					
	T/K	w = 0.025 28	w = 0.053 16	w = 0.074 81	w = 0.098 56	w = 0.122 43	w = 0.148 58
glycerin	298.1	3.26	3.19	3.13	3.05	2.96	2.89

[a] partial pressure of CO_2 is 101.3 kPa.

system to be purged. The buret and bulb are jacketed and are thermostated to within ±0.05 K by circulating water (14) from the water bath containing the gas and liquid cells and the humidifier.

Procedure. With valves 3 and 4 shut, the liquid cell is purged by filling it completely, and then isolated by closure of all its valves. After attainment of the working temperature, the gas circuit is purged and checked to ensure that there are no leaks, and the working pressure is established in the isolated gas cell, buret, and bulb.

The absorption process is initiated by opening valves 3 and 4 to communicate the gas and liquid cells. The resulting drop in pressure is countered by allowing mercury to enter the bulb and buret; successive corrections of this kind are effected until the attainment of equilibrium is signaled by the pressure remaining stable at the desired value for at least 20 min. The total volume of mercury introduced into the bulb and buret is the volume of gas absorbed under the working conditions, and is measured with a relative error of less than 1%.

Systems Investigated. We investigated the solubility of CO_2 (>99.9% pure) in aqueous solutions of saccharose, glucose, fructose, or glycerin (all from Merck; the nominal purity of the sugars was >99.95% in each case, and that of the glycerin >99.5%). Prior to use, the sugars were dried until their weight remained constant. The solutions were prepared as follows: distilled water was desgassed (by boiling), stoppered immediately, and weighed; a known mass of solute was added; and the stoppered mixture was shaken until all the solute had dissolved, and was used immediately. In preliminary work, the solubility of CO_2 in degassed distilled water was determined.

The mass of absorbent solution in the liquid cell (of known volume) was determined by measuring the density of the solution in a BOSCH S 2000/30 densimetric balance with a precision of $\pm 10^{-4}$ $\mathrm{g{\cdot}cm^{-3}}$. Table 1 lists the densities (at 298 K) and concentrations (mass fraction) of the absorbent solutions used.

The influence of solution concentration on the solubility of CO_2 at 298.1 K was studied for all four solutes. The saccharose systems were also studied at 293.1, 303.1, 308.1, and 313.1 K to allow analysis of the influence of both concentration and temperature. The partial pressure of CO_2 was 101.3 kPa for all experiments, and the total pressure of the vapor-saturated gas phase therefore dependent on temperature. On average, a complete experiment took 3–4 h.

Results

Since the mole fractions of sugar or glycerin used in the absorbent solutions were very small (never more than 0.03), the corresponding change in the vapor pressure of water was treated as negligible (*17*); the estimated error that this introduced in the total pressure measurements was less than 0.2%. The variation in the volume of the absorbent liquid due to temperature over the range 293.1–313.1 K was less than 0.7% (if desired, this error can be circumvented by working with the mass of the liquid), and the mole fraction of absorbed gas in the absorbent solution never exceeded 0.001 (*18*). In view of the foregoing, solubility data are presented in Table 2 as (mol of CO_2)/(cm^3 of absorbent solution), the number of moles of CO_2 having been calculated from the measured absorbed volume and the known working temperature and pressure.

The experimental apparatus and procedure were tested by determining the solubility of CO_2 in degassed distilled water at various temperatures and with a partial pressure of CO_2 of 101.3 kPa. Under these conditions the reaction between CO_2 and water is negligible, so that all the gas absorbed can be treated as molecular CO_2 (*8*). The results

Table 3. Solubility s_0 of CO_2 in Water According to Various Sources

	$10^5 s_0$/(mol·cm^{-3})								
T/K	288.1	293.1	298.1	303.1	308.1	311.1	313.1	318.1	323.1
experimental		3.79	3.33	2.96	2.66		2.39		
calculated (eq 1)		3.77	3.34	2.97	2.65		2.38		
Doods (*10*)	4.54	3.90	3.38	2.96			2.37		1.95
	4.47	3.83	3.29	2.85			2.19		1.71
Seidell (*11*)	4.55	3.92	3.39	2.97			2.37		1.95
	4.53		3.38						
	4.56		3.36			2.44			
Stephen (*12*)	4,46	3,65							
Haimour (*13*)	4.55	3.90	3.35	2.90	2.52	2.32	2.20	1.93	1.70
Houghton (*19*)	4.42	3.82	3.35		2.59				1.87

Table 4. Parameters of Eq 2 (with n = 1.2)

solution	$10^5 D$/(mol·cm^{-3})	$10^5 E$/(mol·cm^{-3})	solution	$10^5 D$/(mol·cm^{-3})	$10^5 E$/(mol·cm^{-3})
saccharose	3.334	4.748	glycerin	3.320	4.339
glucose	3.322	4.635	all solutes	3.319	4.488
fructose	3.314	4.464			

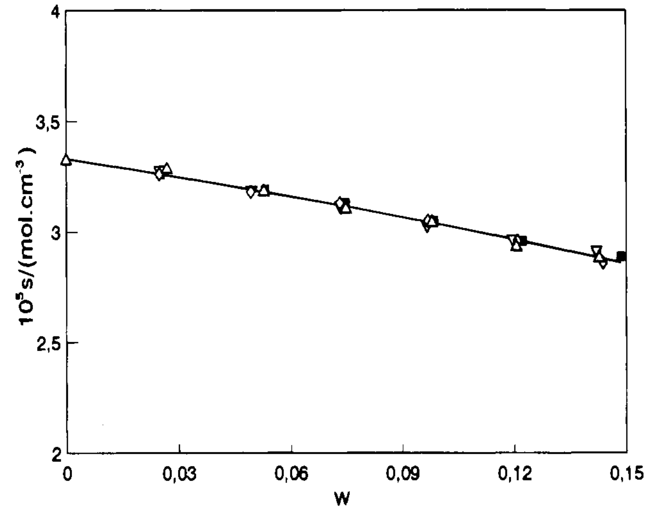

Figure 2. Solubilities of CO_2 in aqueous saccharose, glucose, fructose, and glycerin solutions of various concentrations w (mass fraction) at 298.1 K, together with the result of fitting eq 2 to these values.

agree satisfactorily with reference values (*10–13, 19*) (Table 3) and were fitted to within a relative error of 0.5% by the equation

$$s_0 = (p/101.3)e^{(A/T-B)} \qquad (1)$$

where s_0 is the solubility of CO_2 (mol·cm^{-3}), T is the temperature (*K*), p is the partial pressure of CO_2 (101.3 kPa), and the values of the optimized constants A and B were found to be 2119.05 K and 17.4141, respectively.

The solubilities of CO_2 in aqueous solutions of saccharose, glucose, fructose, or glycerin at 298.1 K and p = 101.3 kPa were found to exhibit very similar concentration dependencies (Figure 2). In view of this, the equation

$$s = D - Ew^n \qquad (2)$$

(where w is the concentration of sugar or glycerin in the absorbent solution (mass fraction) and D, E, and n are constants to be optimized) was first fitted (by Nelder and Mead's method) to the results for all four solutes (Figure 2 and bottom line of Table 4), and the single value of n so obtained (1.2) was then kept fixed while refitting eq 2 to the data for each solute to obtain solute-specific values of D and E (Table 4). The resulting equations fitted the data to within a relative error of 0.7% (in fact, 95% of the data lay within this neighborhood of the equation fitted to the whole data set to obtain n).

Table 5. Solubilities s of CO_2 in Saccharose Solutions: Comparison of the Experimental Results of This Work with Data Available Hitherto for Temperatures and Concentrations within the Rangers Used in This Work

		$10^5 s$/(mol·cm^{-3})	
T/K	*w*	refs 11 and 12	this work
293.1	0.042 27	3.77	3.64
	0.083 35	3.62	3.49
298.1	0.026 15	3.32	3.28
	0.050 87	3.26	3.20
	0.094 02	3.13	3.07
	0.118 73	3.04	2.96

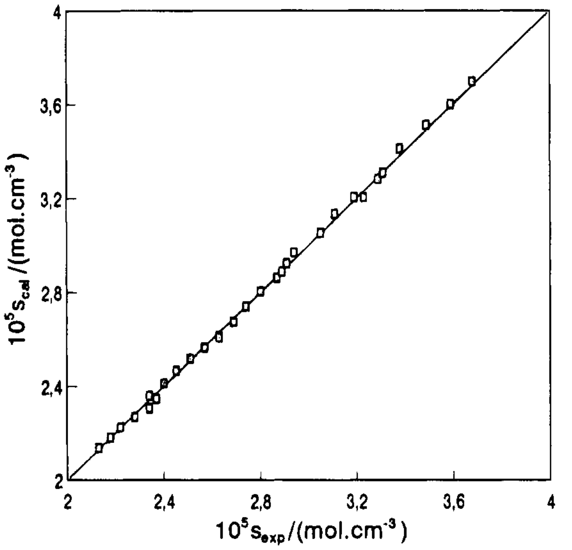

Figure 3. Regression of the CO_2 solubility (s) values given by eq 4 against the experimental values for solutions of saccharose of various concentrations and at various temperatures.

Table 5 compares our experimental results with published (*11, 12*) values for the solubility of CO_2 in saccharose solutions within the range of temperatures and concentrations used in this work. We have found no such results for solutions of glucose, fructose, or glycerin.

Equation 2, with n = 1.2, also satisfactorily fitted the solubility–concentration data at each of the temperatures at which experiments were performed with saccharose solutions. For each given concentration, solubility varied with temperature in accordance with an equation of the form

$$s = s_0 - Ke^{(a/T-b)} \qquad (3)$$

where s_0 is the s of water given by eq 1. Combining eqs 2 and 3 and fitting the result to the whole data set for saccharose solutions of all concentrations and temperatures yielded

$$s = s_0 - w^{1.2} e^{(3958.91/T - 23.2453)} \qquad (4)$$

Regressing s as given by eq 4 against the experimental values (Figure 3) confirmed the adequacy of this equation.

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