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SOLUBILITIES OF GASES IN H_2O AND ^2H_2O

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SUMMARY

The solubilities of various gases in H_2O and ^2H_2O are reported over a temperature range of 5–40°C. A gas chromatographic technique which allows the simultaneous determination of the gas solubility in both solvents is employed. The technique described allows the saturation solubility to be determined by a direct comparison to a pure gas calibration curve obtained under conditions identical to those used in the analysis of the dissolved gas.

INTRODUCTION

The use of a gas chromatographic (GC) technique to determine amounts of dissolved gas in a known volume of solvent is widely reported[1–4]. Choosing appropriate chromatographic conditions, small solvent samples can be analysed and amounts of dissolved gas down to 10^{-8} moles can be accurately determined.

For removal and analysis of the dissolved gas, most workers have adopted a "stripping" technique whereby the preferentially dissolved gas solution sits above a fritted glass disc and the chromatograph carrier gas is bubbled rapidly through the solution. The dissolved gas is then stripped from the solution by the carrier gas and transferred to a chromatographic detector. This technique, however, has required the adoption of a relative, rather than an absolute, measurement for the quantification of the dissolved gas.

In this paper we report a GC method whereby the amount of dissolved gas in solution is determined by comparison to a pure gas calibration curve obtained under conditions matching those used in the stripping and analysis of the dissolved gas. The solute gas response is thus directly compared to the pure gas reponse, circumventing the need for a relative comparison with "another gas" dissolved under conditions wherein the saturation solubility is already well established.

EXPERIMENTAL

A 20-ml volume of degassed solvent (sublimation technique) is transferred to a

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previously evacuated (10^{-4} Torr) saturation cell immersed in an insulated, thermostatically controlled (± 0.01°C) water-bath. The gas under study, at 1 atm* pressure, is dispersed through the constantly stirred solution by a coarse, fritted glass disc. Prior to analysis, the gas solution is allowed to sit under 1 atm of gas for 1 h to equilibrate. Saturation is obtained within a few hours.

A saturated sample is then withdrawn from the saturation cell through the rubber serum cap on the cell using a greaseless, gas-tight (2.500 $\pm$ 0.001 ml) Gilmont micrometer syringe. The barrel of the syringe is designed so that it can be filled very slowly, thus preventing the sample from being placed under a reduced pressure.

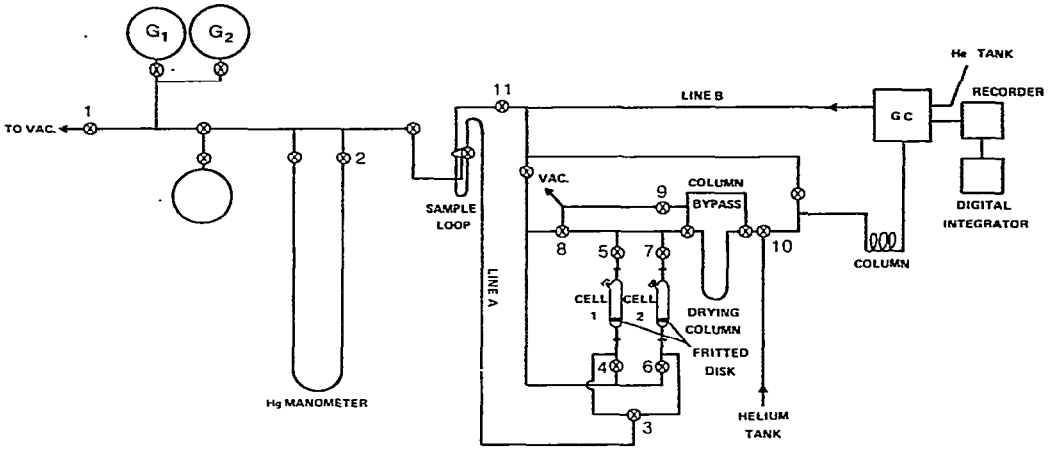

Fig. 1. Gas stripping line.

Prior to injection of the solution into the stripping cells, a pure-gas calibration curve is obtained using the gas stripping line shown diagramatically in Fig. 1 (ref. 5). The stripping cells (Fig. 1) are initially evacuated (10^{-6} Torr) through stopcocks 8 and 9 and the line purged with helium through stopcock 10. The pure-gas calibration plot is obtained by using a gas sampling loop[6]. Initially, the gas sampling loop and the mercury manometer are evacuated and maintained under 10^{-6} Torr. Stopcock 1 is shut to isolate the system from the vacuum pump and stopcock 2 is shut to utilize the mercury U-tube as a closed-end manometer. The pure gas is introduced into the sampling loop at room temperature from one of the gas bulbs (G_1 and G_2). The temperature of the gas is read (± 0.01°C) and the pressure measured on the closed-end manometer (± 0.004 cmHg). Prior calibration of the volume of the sampling loop (0.708 $\pm$ 0.001 ml) thus allows the number of moles of gas contained in the sampling loop to be determined. Rotation of the sampling loop stopcock through 90° allows the carrier gas from line B (with stopcock 11 open) to transfer the known number of moles of pure gas via line A through the stripping cell, the drying column and the chromatographic column, to the GC detector (Varian Model 90P) where the response is recorded on an electronic digital integrator (CMC Model 707 BN). The gas sampling loop stopcock is then rotated back 90°, stopcocks 1 and 2 are opened to the vacuum and the system is re-evacuated. This process is repeated for different numbers

* 1 atm = 101.325 kPa; Torr = atm/760.

of moles of pure gas until the desired number of calibration points are obtained. In practice, a calibration curve is obtained prior to the analysis of the dissolved gas samples and again after the analyses have been completed.

Upon completion of the calibration curve, the carrier gas is directed preferentially through cell 2 or cell 1 by closing stopcocks 4 and 5 or stopcocks 6 and 7, respectively. The loaded syringe needle is introduced into the appropriate stripping cell through a rubber serum cap, with the helium carrier gas flowing.

Initially, 0.250 ml of the sample are injected into the cell to "wet" the frit, since it would appear that some adsorption of dissolved gas occurs in the frit. After this sample has been "stripped", four 0.500-ml samples are injected sequentially into the cell. The dispensed, dissolved gas samples are maintained above the fritted disc by means of the dry, flowing helium carrier-gas pressure.

Sufficient time is allowed between each injection for the previous sample to be "stripped" and analysed on the gas chromatograph. The five injections are made without the syringe being withdrawn from the stripping cell, thus ensuring that no air leaks or air contamination has occurred.

The stripped gas is then dried by passage through a 50% $CaCl_2$ and 50% $CaSO_4$ drying tube before entering the chromatographic column. Appropriate columns are used for each gas investigated, the main intention being to achieve separation of O_2 and N_2 from the selected gas to monitor possible air leaks or other sources of contamination. The dry gas is then analysed on the dual-filament thermal conductivity detector and the response of the stripped gas compared directly to the previously obtained calibration plot, the variation in response being no more than $\pm 0.5\%$ amongst the four injected samples.

After analysis, a "wet" calibration curve is obtained, which requires a known number of moles of the dry gas from the sampling loop to be passed through the 2.5 ml of solvent remaining in the stripping cells. These "wet" calibration points serve to show that no instrumental factors have altered during the time taken for sample analyses and that the presence of the solvent on top of the fritted discs in the stripping cells has not caused changes in chromatographic response through a change in carrier-gas flow-rate.

Our experiments have shown that the calibration plot is independent of the cell used and also that the introduction of approximately 2.5 ml of sample into the stripping cell is not sufficient to retard the carrier-gas flow-rate and change the response of the detector. The calibration curve that is obtained prior to the introduction of the solution to be stripped must be identical to the wet calibration curve obtained after the sample has been introduced and stripped. Hence, by direct comparison of the integrator response of the four stripped samples to that of the pure-gas calibration curve, the number of moles of dissolved gas in each 0.500 ml of solution can be determined. For low-solubility gases, the injected sample size can be increased to 1.000 ml (and decreased to 0.2 ml for higher-solubility gases, as is the case for organic solvents).

RESULTS

To illustrate the reliability of this technique, we report gas solubility data for a range of gases dissolved in both H_2O and ^2H_2O. The saturation of the gas into each

TABLE I

MOLE FRACTION SOLUBILITY, χ_2, OF GASES DISSOLVED IN H_2O AND ^2H_2O

T (°K)	*Argon ($\chi \cdot 10^4$)*				
	H_2O			*^2H_2O*	
	Ref. 9	*Ref. 8*	*Present study*	*Present study*	*Ref. 8*
278.15	–	0.3787	0.3785	0.4271	0.4270
283.15	0.3352	0.3367	0.3333	0.3731	0.3750
288.15	0.2953	0.3025	0.2988	0.3333	0.3341
293.15	0.2697	0.2746	0.2722	0.3048	0.3003
298.15	0.2482	0.2516	0.2520	0.2680	0.2724
303.15	0.2284	0.2326	0.2316	0.2497	–
	Krypton ($\chi \cdot 10^4$)				
	H_2O			*^2H_2O*	
	Ref. 9	*Ref. 8*	*Present study*	*Present study*	
278.15	–	0.7526	0.7533	0.8624	
283.15	0.5989	0.6498	0.6577	0.7264	
288.15	0.5317	0.5680	0.5740	0.6472	
293.15	0.4799	0.5025	0.5113	0.5544	
298.15	0.4305	0.4494	0.4526	0.4803	
303.15	0.3955	0.4062	0.4180	0.4451	
308.15	0.3606	0.3708	–	–	
313.15	0.3345	0.3417	0.3649	0.3809	
	Nitrogen ($\chi \cdot 10^4$)				
	H_2O			*^2H_2O*	
	Ref. 10	*Ref. 8*	*Present study*	*Present study*	
278.15	0.1680	0.1695	0.1692	0.1862	
283.15	0.1507	0.1519	0.1513	0.1691	
288.15	0.1371	0.1379	0.1372	0.1561	
293.15	0.1254	0.1265	0.1275	0.1467	
298.15	0.1162	0.1173	0.1175	0.1335	
303.15	0.1086	0.1098	0.1116	0.1249	
308.15	–	0.1038	0.1062	0.1170	
313.15	–	0.09894	0.09986	0.1069	

T (°K)	*Oxygen* ($\chi \cdot 10^4$)				
	H_2O			^2H_2O	
	Ref. 11	*Ref. 8*	*Present study*	*Present study*	
278.15	0.3416	0.3458	0.3446	0.3729	
283.15	0.3025	0.3071	0.2963	0.3332	
288.15	0.2708	0.2759	0.2678	0.2950	
293.15	0.2445	0.2505	0.2496	0.2673	
298.15	0.2221	0.2298	0.2264	0.2459	
303.15	0.2035	0.2127	0.2081	0.2263	
308.15	–	0.1988	0.1985	0.2101	
313.15	–	0.1873	0.1853	0.2000	
	CH_4 ($\chi \cdot 10^4$)				
	H_2O			^2H_2O	
	Ref. 12	*Ref. 8*	*Present study*	*Present study*	*Ref. 8*
278.15	0.3977	0.3979	0.3978	0.4371	0.4349
283.15	0.3457	0.3483	0.3467	0.3732	0.3782
288.15	0.3096	0.3086	0.2940	–	0.3328
293.15	0.2754	0.2767	0.2720	0.3006	0.2962
298.15	0.2527	0.2507	0.2485	0.2655	0.2664
303.15	0.2341	0.2295	0.2278	0.2382	–
308.15	0.2143	0.2121	0.2140	0.2176	–
313.15	–	0.1978	0.1943	0.2080	–
318.15	–	0.1860	0.1899	0.1854	–
	C_2H_6 ($\chi \cdot 10^4$)				
	H_2O			^2H_2O	
	Ref. 12	*Ref. 8*	*Present study*	*Present study*	*Ref. 8*
278.15	0.6445	0.6488	0.6483	0.7010	0.6983
283.15	0.5226	0.5359	0.5226	0.5775	0.5748
288.15	0.4469	0.4506	0.4438	0.4869	0.4808
293.15	0.3849	0.3852	0.3832	0.4121	0.4082
298.15	0.3321	0.3345	0.3330	0.3520	0.3514
303.15	0.2922	0.2948	0.2916	0.3024	–
308.15	0.2609	0.2633	–	–	–
313.15	–	0.2384	–	–	–

(Continued on p. 166)

TABLE I *(continued)*

T (°K)	SF_6 ($\chi \cdot 10^4$)				
	H_2O			^2H_2O	
	Ref. 13	*Ref. 8*	*Present study*	*Present study*	
278.15	0.09123	0.09164	0.09164	0.1106	
283.15	0.07340	0.07335	0.07340	0.07812	
288.15	0.06041	0.06032	0.06035	0.06505	
293.15	0.05056	0.05088	0.05143	0.05465	
298.15	0.04393	0.04394	0.04426	0.04829	
303.15	0.03842	0.03881	0.03872	0.04280	
308.15	0.03469	0.03499	0.03486	0.03960	
313.15	0.03232	0.03218	0.03226	0.03584	
323.15	—	—	—	0.03311.	
	CF_4 ($\chi \cdot 10^4$)				
	H_2O			^2H_2O	
	Ref. 8	*Ref. 14*	*Present study*	*Present study*	*Ref. 14*
293.15	0.04265	0.04160	0.04174	0.04874	0.0479
298.15	0.03819	0.03740	0.03750	—	0.0436
303.15	0.03477	0.03370	0.03492	0.03719	0.0383

solvent was carried out simultaneously. The analysis of the amount of gas dissolved was made using one stripping cell for H_2O and one for ^2H_2O, effectively creating an internal reference system for ^2H_2O by monitoring the "established" H_2O values. Two sets of four 0.500-ml injections were performed on each dissolved gas solution. A comparison of the data obtained with that reported in the literature is made in Table I. The comparison is seen to be excellent.

Some years ago, Maharajh and Walkley[7] presented data for the saturation solubilities of binary gas mixtures in H_2O. The "lowering" of the solubility of each gas from the expected (Henry's law) value was reported. These data were shown to be incorrect by several workers[8], and this present investigation arose from an attempt to discover the cause of the error. The most likely explanation lies in the occurrence of an intermittent lowering of carrier-gas flow-rate during the stripping operation. A

TABLE II

MOLE FRACTION SOLUBILITY, χ_2, OF N_2/O_2 DISSOLVED IN H_2O AT 298°K

Gas	P_{χ_2} *(atm)*	$\chi \cdot 10^4$	
		Obs.	*Calc. (Table I)*
N_2	0.486	0.05694	0.0571
O_2	0.514	0.1207	0.1164

stripping technique that purposely avoided the use of fritted discs was employed at that time. As is seen in Table II, by employing our new experimental technique, values obtained for the solubility of N_2/O_2 mixtures in H_2O are in agreement with predicted, Henry's law values. It is also noted that the dry-gas sample cell allows excellent analysis of the composition of the N_2/O_2 gas mixture.

DISCUSSION

Table I shows the solubility data obtained by the reported technique to be in excellent agreement with that reported by other workers. H_2O and ^2H_2O present two of the most difficult systems to study due to extremely low gas solubilities. This technique, however, is versatile in that one can study these low solubility systems as well as high organic solubility systems without loss of accuracy.

It is emphasized that the gas sampling loop and calibration curve have been shown to be linear over a solvent sample size of 0.2 ml to 1 ml. However, for organic solvents, the gas sampling loop volume must be adjusted to account for the much larger gas solubilities, often a factor of 10^2 greater than their H_2O counterparts. Furthermore, this technique allows one to completely recover the solvent used allowing solubility studies to be made using only small solvent samples, something particularly important when studying "exotic" solvents. A complete temperature study using as little as 20 ml of solvent (allowing four 0.5-ml samples per temperature) has been made, in which most of the solvent is recovered.

In particular, the effects of added salts and other solvents, "salting in" and "salting out" can be readily studied using this technique. The two stripping cells allow a simultaneous analysis with the pure solvent acting as an internal reference.

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