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Gas Chromatographic Determination of Henry's Constants of 12 Gases in 19 Solvents

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Henry's constants determined by gas-liquid chromatography are reported for gaseous solutes in 16 polar solvents and 3 heavy hydrocarbons. A direct measurement of the solubility of air gives the best determination of the dead volume of the chromatographic system and increases the accuracy of the data for the light gases.

Efficient separation of gaseous mixtures by absorption requires that the solvent have a high selectivity for one gas relative to another. Henry's constants of gaseous solutes have been measured by gas-liquid chromatography for many polar and nonpolar solvents.

Chromatographic techniques, first suggested by Martin (*9*), have been considerably utilized by many authors (*1, 11, 14*) in attempting to measure activity coefficients at infinite dilution of liquid solutes. Nevertheless, the data of gas solubilities are relatively scarce (*13, 14*).

EXPERIMENTAL

The apparatus used is very similar to a conventional gas-liquid chromatographic unit. The chromatograph is an IGC 12 M Intersmat model, equipped with a thermal conductivity detector. The columns are immersed in a liquid bath, which allows control of the temperature within ±0.1° C. The pressure drop in the column is measured by means of a mercury manometer. Helium is used as carrier gas, and flow rate is regulated by needle valves and measured when it leaves the column by a soap-bubble flow meter at atmospheric pressure. The response impulse of the detector is recorded on a Sefram recorder.

The columns consist of coiled ¼-in. stainless steel pipe and are 2 or 3 m long. Fluoropak is used as inert solid support. A preliminary experiment has shown that all gases, especially polar gases, are not retained by a column filled only with Fluoropak.

Before the columns are loaded, acetone is added to the solvent. This provides a uniform dissolution of the solvent on the solid support. Acetone is evaporated slowly under the effect of a small nitrogen flow. Columns are weighed before and after the experimental runs to check any loss of solvent. The vapor pressure of the solvent never exceeds 2 mm Hg in the experimental conditions.

The carrier gas and all the gaseous solutes were provided by l'Air Liquide with a stated minimum purity of 99.9%. No further purification was deemed necessary.

The solvents were provided by Touzart & Matignon and Serlabo with a minimum purity of 99% and were further purified (by distillation) when necessary. Refractive index was measured for each of them as an indication of component purity. Maximum relative deviation with values of literature was 10^{-3}. All light impurities, especially water, were expected to be finally eliminated by elution of helium passing through the column during several hours before experimental runs.

In chromatographic measurements, the difference between the absolute retention volume of the solute and the dead volume of the apparatus must be determined. When this difference, generally called the reduced retention volume, is large, one can take the absolute retention volume of air as the value of the dead volume. But, if the solubility of the solute, for instance methane or ethane, is not large enough compared to the solubility of air, the reduced volume is very small, and the dead volume must be measured with a greater accuracy. All the methods (*2, 3*) proposed by authors for the direct determination of the dead volume are not precise enough.

In this work, the solubility of air is obtained at atmospheric pressure in a cell by measurement of the volume of air absorbed in degassed solvent. Another method consists of a quantitative chromatographic analysis of a solvent sample entirely saturated with air. The differences between the values given by the two methods do not exceed 10%. From the measurement of air solubility, the reduced retention volume of air is easily deduced and the dead volume obtained with great precision.

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Injections are made with microsyringes. The volume of the samples does not exceed 10 μl. It has been shown (*5*) that for most systems, retention time is not significantly affected by such a sample size. However, when the activity coefficient is expected to vary rapidly with the solute concentration in the liquid phase, the experiment must be carried out for various sample sizes. Retention time is then plotted vs. sample volume so that a smooth curve can be drawn. The correct value of the retention time at infinite dilution is obtained by an extrapolation to a zero sample volume.

OBTAINMENT OF HENRY'S CONSTANTS

Henry's constant of a solute 2 in a solvent 1 is defined by

$$H_{21} = \lim_{x_2 \to 0} \frac{f_2(P,T)}{x_2} \qquad (1)$$

x_2 is the molar liquid fraction, and $f_2(P,T)$ the fugacity of the solute in the equilibrium conditions of pressure P and temperature T. H_{21} is related to experimental chromatographic parameters (*16, 17*).

$$H_{21} = \frac{RTN_1}{(t_{R_2} - t_m)u_s \cdot j} z_g \cdot \varphi_{2V} \qquad (2)$$

N_1 is the number of moles of solvent in the column, t_{R_2} is the absolute retention time of the solute, and t_m the dead time. The factor j takes into account the variation of the flow rate in the column and is expressed as a function of the inlet pressure p_e and the outlet pressure p_s of the column.

$$j = 1.5 \frac{(p_e/p_s)^2 - 1}{(p_e/p_s)^3 - 1} \qquad (3)$$

The outlet flow rate, u_s, is related to the flow rate, u_a, measured in the soap-bubble flow meter:

$$u_s = u_a \frac{p_a - p_{sw}}{p_s} \frac{T}{T_a} \qquad (4)$$

p_a and T_a are the atmospheric pressure and the ambient temperature, respectively, p_{sw}, is the partial pressure of water in the flow meter, and T the column temperature.

The product $z_g \cdot \varphi_{2V}$ of the compressibility factor of the gas phase by the vapor fugacity coefficient of the solute in the gas phase, can be calculated by means of a correlation proposed by O'Connell and Prausnitz (*10*). For all the solutes used in this work, this term is equal to unity within 5.10^{-3}. Therefore, in the final values of Henry's constants, it is taken as unity.

Activity coefficients were calculated using as reference state, zero pressure and experimental temperature. If $f^0_{2L}(P_0 = 0,T)$, the liquid fugacity of the pure solute at $P_0 = 0$, is taken as the reference fugacity, the activity coefficients at infinite dilution are given by the following expression:

$$\gamma^{\infty}_{21}(0,T) = \frac{H_{21}}{f^0_{2L}(P_0 = 0,T)} \qquad (5)$$

The Poynting term which should appear in this expression does not differ from unity by more than 5.10^{-3}.

For nonpolar gases, the reference fugacity can be evaluated as a function of the reduced temperature, the acentric factor of Pitzer and the critical pressure (*7*). For carbon dioxide, hydrogen sulfide, and sulfur dioxide, experimental *PVT* data (*4, 12, 15*) allow the determination of this fugacity. (Activity coefficients are given in ref. *6*.)

RESULTS

Experimental values of Henry's constants are given in Table I for 12 solutes and 19 solvents.

Many authors give values of activity coefficients determined by gas-liquid chromatography with an expected precision of 4 or 5%. Ng et al. (*13*) pointed out that uncertainties are considerably larger for light gases such as methane, carbon dioxide, and ethane. These uncertainties

Table I. Henry's Constants in Atm

Solvents	*T*, °C	Methane	Ethane	Propane	Butane	Isobutane	Ethylene	Propylene	1,3-Butadiene	Propylene	Carbon dioxide	Hydrogen sulfide	Sulfur dioxide
Aniline	25	1580	183	70.5	25.3	43.6	208	43.5	8.21	8.93	127	15.1	
Benzyl alcohol	25	1030	146	50.8	15.7	31.2	160	37.5	8.82	11.8	128	24.0	2.08
Decahydronaphthalene	25	348	44.7	12.1	3.57	5.40	72.2	14.1	4.05	12.8	110	29.8	18.8
Decahydronaphthalene	50	437	54.4	16.4	4.91	7.53	84.9	16.5	5.87	17.8	136	37.6	25.6
Dimethylsulfoxide	25	2440	386	186	64.9	141	312	92.3	16.4	9.20	106	10.9	0.117
Dipropylene glycol	25	1450	197	71.5	23.0	42.4	204	51.7	9.98	14.1	121	22.9	
Dipropylene glycol	50	1800	246	85.0	30.7	53.7	254	67.3	16.7	20.2	154	30.7	
Dipropylene glycol	70	2230	287	119	37.4	74.3	295	96.2	27.4	33.4	212	74.3	
Ether triglycol	25	528	98.0	34.0	10.1	18.4	88.3	22.5	4.20	4.39	47.4	7.04	
Ethylene glycol	25	5800	620	409	268	320	764	205	45.0	55.5	262	52.9	3.41
Heptadecane	50		35.1	12.5	3.75	6.20	52.0	12.8	4.29		72.2		16.4
Hexadecane	25	209	26.4	7.41	2.02	3.24	42.8	8.62	2.38	7.85	62.5	18.7	12.9
Hexamethyl phosphoric triamide	25	471	57.6	19.9	6.09	10.5	52.9	13.4	2.18	1.73	30.4	1.61	
1-Methyl-2-pyrrolidinone	25	1020	149	57.2	18.4	33.3	126	31.0	4.77	3.95	59.1	5.56	
Nitrobenzene	25	940	128	44.1	13.6	24.3	126	30.6	5.77	7.94	76.7	18.7	1.64
Phenol	50	1990	270	101	37.5	67.0	259	80.7	20.1	24.8	214	50.0	7.07
Propylene carbonate	25	1140	232	107	38.5	66.3	192	55.5	10.4	9.13	67.7	20.9	1.20
Propylene carbonate	50	1340	280	135	56.9	94.3	235	79.8	19.0	16.5	103	33.8	3.17
Propylene carbonate	70	1430	314	150	67.9	110	271	97.5	24.4	22.7	124	40.1	
Tributyl phosphate	52	224	46.4	15.1	6.10		52.5		3.82		43.0	9.07	
Triethyl phosphate	52	705	92.4	37.2	14.2	21.8	87.0	28.6	6.50		54.4	28.6	1.41
Trisobutyl phosphate	52	190	42.5	14.4	5.44	8.36	48.7	13.8	3.72		38.4	8.89	0.695
Trimethyl phosphate	52		250	114	49.6	75.2	199	68.8	15.4		87.1	18.4	
Tripropyl phosphate	25	257	39.0	13.1	4.04	6.23	41.1	9.91	1.92	2.42	28.1	4.19	
Tripropyl phosphate	50	306	51.1	20.2	7.19	10.7	57.3	16.6	3.93	5.04	42.4	7.96	0.621
Tripropyl phosphate	70	325	68.0	28.2	10.6	15.8	71.1	23.7	6.62	8.45	59.5	12.6	1.45

may result also from such effect as solute adsorption at the gas-liquid interface. Thus, it seems practically impossible to estimate the experimental error.

One can only compare the data presented here with published values (*1, 11, 13, 14*). It was done for binary systems of paraffins (*8*). It appears that the relative deviation among all these values does not exceed 6.5%, and the average relative deviation is 3%. For polar systems, we did not find enough reliable data to compare with our experimental Henry's constants.

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NOMENCLATURE

$f_2(P,T)$ = fugacity of the solute at pressure P and temperature T, atm
$f^0_{2L}(P_0,T)$ = liquid fugacity of the pure solute at pressure P_0 and temperature, atm
H_{21} = Henry's constant of the solute 2 in the solvent 1, atm
j = James-Martin factor
N_1 = number of moles of solvent introduced in the chromatographic column
p_a = atmospheric pressure, atm
p_e = inlet pressure of the column, atm
p_s = outlet pressure of the column, atm
p_{se} = partial pressure of water at temperature T_a, atm
t_m = dead time, sec
t_{R_2} = absolute retention time of the solute, sec
T = temperature in the column, ° K
T_a = ambient temperature, ° K
u_a, u_s = flow rate of the carrier gas in the flow meter, at the outlet of the column, cm^3/sec
x_2 = liquid molar fraction of the solute
z_g = compressibility factor of the gas phase in the column
$\gamma_{21}^{*}(0,T)$ = activity coefficient at infinite dilution of the solute 2 in the solvent 1, when the reference fugacity is chosen as f^0_{2L} $(P_0 = 0,T)$
φ_{2V} = vapor fugacity coefficient of the solute in the gas phase

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Enthalpy of Dilution of Superphosphoric Acids

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Superphosphoric acids in the concentration range 62–85% P_2O_5 (86–117% H_3PO_4) were diluted and hydrolyzed in an acidic solvent in a solution calorimeter to obtain values for their enthalpies of formation and relative apparent molal heat contents. The results join smoothly with data obtained previously for lower concentrations of acid. With the enthalpy of formation of acid containing 62.04% P_2O_5 (85.66% H_3PO_4), taken as −609.14 kcal/mol P_2O_5, the enthalpies of formation ranged from −607.03 kcal/mol P_2O_5 for acid containing 68.76% P_2O_5 (94.94% H_3PO_4) to −591.83 kcal/mol P_2O_5 for acid containing 85.17% P_2O_5 (117.60% H_3PO_4).

Previous studies (*4*) of the enthalpy of dilution of phosphoric acid were extended only to about 90% H_3PO_4, the concentration at which the amount of condensed phosphate species becomes significant. This study extends the thermal data into the concentration range of the superphosphoric acids, a range of increasing importance in fertilizer technology.

To produce a well-defined final state, a solvent and a temperature were chosen that would hydrolyze the condensed phosphates completely to orthophosphate in a length of time suitable for calorimetric measurements. Exploratory tests showed that 10.35*m* HCl effected complete hydrolysis to orthophosphate in less than 30 min at 40° C. All measurements then were made with this solvent at 40° C, and the results were converted to the standard enthalpies of formation at 25° C. The relative apparent molal heat contents, ϕ_L, that were calculated from the enthalpies of formation may be used to calculate the enthalpy of dilution of phosphoric acid between any two concentrations up to 117% H_3PO_4.

MATERIALS AND PROCEDURE

Superphosphoric acid was prepared by dissolving 2.8 kg of reagent P_2O_5 in 1050 ml of reagent H_3PO_4 (85%) at 145° C, and filtering the hot solution through a coarse glass frit into a phosphoric acid reagent bottle for storage. Portions of the stock acid (117.6% H_3PO_4) were diluted with reagent H_3PO_4 to prepare solutions of nominal concentrations—95, 105, 110, and 115% H_3PO_4—and the

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