temperatures as well. (In fact, the absolute value of $C_p{}^\circ{}_2$ would have to increase more than 10 times with a temperature increase or decrease of 10 °C to make any sort of contribution.)

The isothermal partial molal compressibilities can thus be calculated as $K_{\phi,s}{}^0 + 2\delta_0(E^0{}_2/\alpha_0)$. The results are given in Table III.

Registry No. KSCN, 333-20-0.

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Solubility of Butane and Isobutane in Butanol, Chlorobenzene, and Carbon Tetrachloride

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Solubilities of butane and isobutane gases are reported for the temperatures 298.15 and 323.15 K and atmospheric pressure for the solvents 1-butanol, chlorobenzene, and carbon tetrachloride. The solubilities were sufficiently high, in the range from 5 to 33 mol % gas in solution, so that special modifications were required for the accurate measurement of these solubilities. Butane was consistently more soluble than isobutane.

Introduction

The solubilities of butane and isobutane were measured in benzene and in normal paraffins from pentane to decane by Jadot (*1*) using a gas-chromatographic technique. Retention times in the chromatographic column were used to estimate Henry's constant at effectively very low gas partial pressures. Henry's constant was also measured by Jadot for butane in carbon tetrachloride so that a comparison with the solubility reported in this paper was possible. Some possible error is introduced when it is assumed that the same Henry's constant applies at atmospheric pressure.

Lenoir et al. (*2*) also utilized a chromatographic technique at low gas partial pressures for measuring the solubilities of butane and isobutane in several highly polar solvents. A more recent modification of the chromatographic technique was reported by Renon and co-workers (*3*) involving stripping of a gas-saturated solution. Solubilities of butane were reported by those workers in C_{16} paraffins. Solubilities of butane and isobutane were reported by Chappelow and Prausnitz (*4*) for high molecular weight solvents to relatively high temperatures using a combined volumetric and material-balanced method to determine Henry's law constants for approximately atmospheric pressure.

Solubilities of propane and butane had previously been measured in this laboratory by Castañeda (*5*) in several paraffin solvents from hexane to hexadecane and also in 1-butanol. The procedure used was similar to that utilized in this work.

For gases of high solubility such as butane and isobutane the normal boiling point temperature of the gas can be considered to be an extension of the solubility curve; that is, as the saturation temperature is reduced, the solution becomes richer in the gas until, at the gas normal boiling point, only the pure gas remains. Propane and butane have previously been shown to exhibit high solubilities at low temperature (*5*). It is expected, therefore, that the order of increasing solubility of a number of gases in a single solvent usually follows the order of increasing boiling point temperatures of the gases.

For nonpolar solvents, a linear extrapolation of all gas solubilities to the solvent critical temperature generally yields a common value or reference solubility. This phenomenon has been used as a basis for determining the temperature coefficient of solubility especially for gases in nonpolar solvents (*6*). Even for highly polar and associating solvents such as water, it was shown that the solubilities of many gases could also be extrapolated to a common solubility at the solvent critical temperature (*7*). Finally, it would appear that this type of extrapolation occurs with sufficient regularity that it may be used as a consistency test for solubility data involving nonpolar gases and liquids.

Experimental Section

The solubility method used in these experiments involved the continuous saturation of a constant flow of degassed solvent fed to the top of a glass absorption spiral by means of a calibrated syringe pump. The pressure in the absorption spiral was observed by means of a small monometer filled with saturated solution and located at the outlet of the spiral. Dry gas was confined in a gas buret over mercury while the pressure was kept constant by using a mercury-lift device driven by a variable-speed motor whose rate could be adjusted as required. The residence time of the solvent in the absorption spiral was approximately 15-30 min during which time saturation was complete. The solubility was determined from the constant solvent feed rate to the apparatus and the absorption rate of the dry gas. The linear relation between the two was confirmed by regular readings for at least 60 min of operation after steady-state conditions prevailed.

The solubility apparatus was similar to that used previously (*8*) but with appropriate modifications for accurate measure-

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ment of the solubilities of the highly soluble gases having Ostwald coefficients ranging from approximately 14 to 120 cm^3 of gas (cm^3 of solvent)$^{-1}$. The modifications involved using very low solvent infusion rates, reducing the solvent holdup in the absorption spiral, and providing a preheater for the solvent. The relatively low solvent injection rates were required to keep the volume of gas utilized reasonably small and to ensure that the solvent was saturated at the outlet of the absorption spiral. The tube of the absorption spiral itself was reduced in diameter to approximately 5-mm outside diameter, but the pitch was increased to reduce the quantity of solvent held in the spiral; the quantity of solvent within the spiral was reduced because both the spiral tube was smaller in diameter and the solvent effective velocity was increased because of the greater slope of the spiral tube. A low holdup of solvent was useful for achieving a steady-state solvent flow in the absorption spiral in less than 30 min, thus reducing the total time required for a single experimental measurement. The syringe needle itself was sheathed in a plastic heat exchanger along its length. Through the heat exchanger constant-temperature water was circulated; hence, the solvent was initially at the temperature of the experiment in spite of the low solvent flows utilized.

A 5-cm^3 gas-tight Hamilton syringe was used for the injection of degassed solvent, in conjunction with a Harvard Apparatus syringe pump equipped with one of three constant-speed motors with shafts turning at 1/20, 1/10, and 1/5 rpm. The infusion rates ranged from approximately 0.004 to 0.017 cm^3 min^{-1} and were accurately measured by using distilled water. The solubility apparatus contained a gas buret of 25-cm^3 capacity and the volume was readable to 0.01 cm^3. Although the temperature in the constant-temperature circulator was controlled within a much narrower temperature range, the temperature within the apparatus was controlled to ±0.1 K.

The butanol and carbon tetrachloride solvents were obtained from Canlab and were supplied by the J. T. Baker Chemical Co. These solvents were specified as the spectrophotometric grade having minimum purities of 99.5% and 99.9% for the butanol and carbon tetrachloride, respectively. The chlorobenzene was supplied by Matheson Coleman and Bell and had a specified minimum purity of 98.0%. Solvent densities (*9*) and vapor pressures (*10*) were taken from the literature.

The butane and isobutane were obtained from Liquid Carbonic and were specified as the pure grade having minimum purities of 99.0%. The gas molar volumes were obtained from Perry and Chilton (*11*). The Ostwald coefficient was calculated from the volume of dry gas, corrected to the equivalent volume of saturated gas, dissolved in a unit volume of solvent:

$$L = vp/(\theta r p_1) \qquad (1)$$

Based on the assumption that Raoult's law can be applied to the solvent in the solution and considering the concentration of dissolved gas, the gas partial pressure is given by

$$p_1 = 101.325(p - p_2{}^\circ)/[p(101.325 - p_2{}^\circ x_1)] \qquad (2)$$

The Ostwald coefficient is converted to the mole fraction solubility by utilizing the gas and liquid molar volumes:

$$x_1 = [1 + V_1/(LV_2)]^{-1} \qquad (3)$$

An approximate check on the solvent infusion rate was available by observing the accumulated volume of solution in the liquid-solution buret. For highly soluble gases the solution volume is measurably higher than the initially injected solvent volume. Calculated solubilities were based on the regression line of the relation between the gas and solvent volumes, solvent density and vapor pressure, and gas molar volume. Whereas the reproducibility for the three results obtained at each condition was within 1%, it is considered that the overall accuracy was 2%.

Table I. Solubility of Butane and Isobutane in 1-Butanol, Chlorobenzene, and Carbon Tetrachloride

solvent	temp, K	*L*	*x*	Δ, %
		Butane		
butanol	298.15	41.6	0.139	
	298.15	42.4 (*5*)	0.141 (*5*)	+1.4
	323.15	21.5	0.0725	
	323.15	20.3 (*5*)	0.0686 (*5*)	−5.7
chlorobenzene	298.15	85.4	0.269	
	323.15	37.3	0.131	
carbon tetrachloride	298.15	122.7	0.339	
	298.15		0.359 (*1*)	+5.9
	323.15	52.0	0.167	
		Isobutane		
butanol	298.15	25.3	0.0889	
	323.15	14.1	0.0486	
chlorobenzene	298.15	45.1	0.162	
	323.15	23.1	0.0853	
carbon tetrachloride	298.15	76.5	0.238	
	323.15	39.9	0.132	

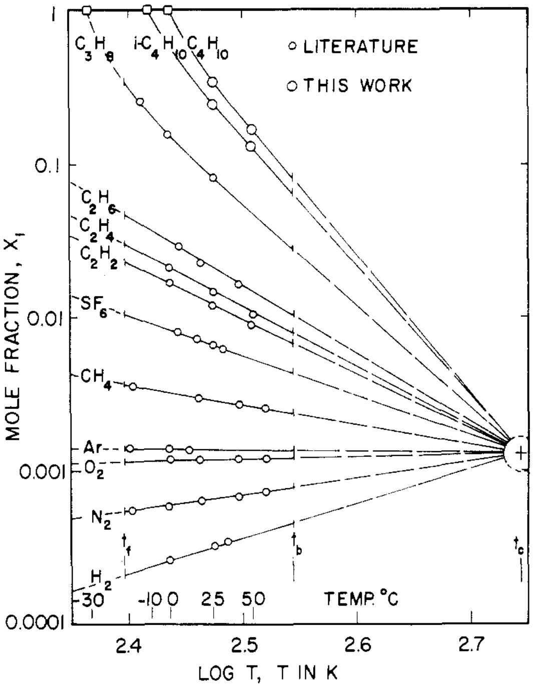

Figure 1. Solubilities in carbon tetrachloride.

Results and Discussion

The solubilities of butane and isobutane are reported as the Ostwald coefficient and the mole fraction in Table I. Comparisons are made with the solubilities reported previously. A good check was obtained with the data of Castañeda (*5*) for the solubility of butane in butanol at 298.15 K with the difference being +1.4%, whereas the comparison was less favorable at 323.15 K with the difference being approximately −6%. A difference of approximately +6% was also obtained for the solubility of butane in carbon tetrachloride at 298.15 K when compared with the data of Jadot (*1*). The latter data, however, were obtained by using a gas-chromatographic technique at effectively very low gas partial pressures and are subject to some uncertainty.

The solubilities of butane and isobutane are also shown for the solvents carbon tetrachloride, butanol, and chlorobenzene in Figures 1–3, respectively, along with solubilities of several other gases in these solvents. Particularly the solubilities in the nonpolar solvents show that a common solubility appears to be obtained when the solubilities of all the gases are extrapolated linearly to the critical temperature of the solvent. It may also be observed that the solubilities for the highly soluble gases may

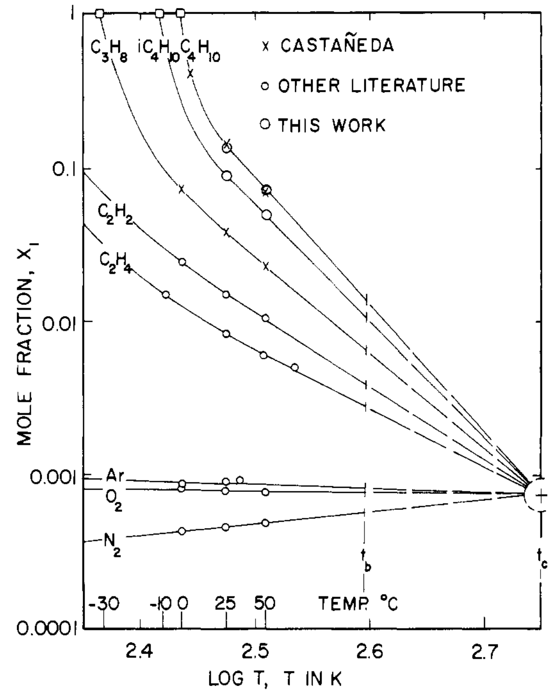

Figure 2. Solubilities in butanol.

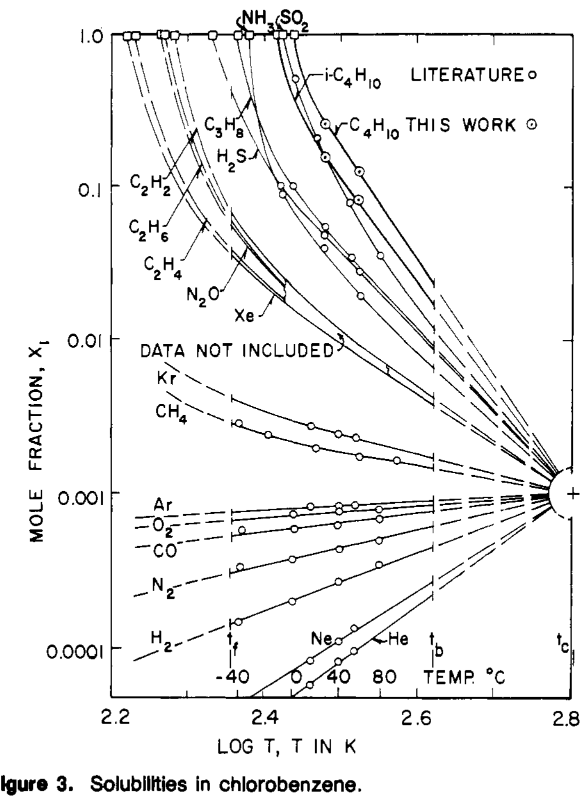

Figure 3. Solubilities in chlorobenzene.

be extrapolated to the gas normal boiling points. The gas normal boiling points do indeed seem to indicate the order of gas solubilities, although this relation is not consistently observed; the solubilities of ammonia and sulfur dioxide are below those of gases with lower boiling points. One might speculate that the polar nature of those gases reduces their solubility in chlorobenzene except that the solubilities of neither hydrogen sulfide nor nitrous oxide seem to be similarly affected.

In the diagrams straight lines have been drawn through the data points for the slightly soluble gases when the gas normal boiling points have been much lower than the scale shown. One could consider that even the slightly soluble gases show fictitious minimum solubilities at temperatures below the chlorobenzene freezing point as they do in water (*7*), which then increase as the temperature is reduced further. For the highly soluble gases the curvature in the solubility data is apparent so that extrapolation to the gas normal boiling points appears justified.

Table II. Sources of Solubility Data

solvent	gas (lit. source)
butanol	C_4H_{10} (*5*, this work); C_3H_8 (*5*); C_2H_2 (*13*); C_2H_4 (*14*); Ar (*15*); O_2, N_2 (*16*)
carbon tetrachloride	C_4H_{10} (this work); C_3H_8 (*17*); CH_4, O_2, N_2, H_2, C_2H_6 (*18*); C_2H_4 (*14*); C_2H_2 (*13*); SF_6 (*19*); Ar (*20*)
chlorobenzene	C_4H_{10} (this work); C_3H_8 (*5*); NH_3, H_2S (*12*); C_2H_4 (*14*); SO_2, C_2H_6, C_2H_2, N_2O, CH_4, O_2, CO, N_2, H_2 (*18*); Xe, Kr, Ar, Ne, He (*21*)

It is of interest to note that all the gases for which a comparison is possible are less soluble in butanol that in carbon tetrachloride save one, and that is acetylene. It may be the result of its high reactivity and consequent reversible reaction with butanol (possibly forming vinyl butyl ether), enhancing its solubility in that solvent. These complexities frustrate any simple explanation of the solubility behavior of gases.

The limits of the solid lines in Figure 1–3 indicate the solvent freezing and normal boiling temperatures. Although it is possible to obtain solubilities at temperatures above the normal boiling point at elevated pressures, few such solubilities have actually been reported. Table II indicates the sources of data shown in Figures 1–3.

Glossary

L	Ostwald coefficient, cm^3 of gas (cm^3 of solvent)$^{-1}$
v	volume of dry gas absorbed, cm^3
p_1	partial pressure of gas, kPa
p	total pressure, kPa
$p_2{}^0$	vapor pressure of pure solvent, kPa
r	solvent injection rate, cm^3 s^{-1}
V_1	molar volume of gas at 101.325 kPa pressure, m^3 mol^{-1}
V_2	molar volume of solvent, m^3 mol^{-1}
x_1	mole fraction gas solubility at a gas partial pressure of 101.325 kPa
θ	elapsed time for solubility measurement, s

Registry No. Butane, 106-97-8; isobutane, 75-28-5; 1-butanol, 71-36-3; chlorobenzene, 108-90-7; carbon tetrachloride, 56-23-5.

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