Solubility of Butane in Several Polar and Nonpolar Solvents and in an Acetone–Butanol Solvent Solution

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Solubilities of butane are reported at 101.325 kPa and for temperatures ranging from 283.15 to 313.15 K in the nine solvents benzene, cyclohexane, methanol, ethanol, 1-propanol, 1-butanol, acetone, methyl ethyl ketone, and aniline, and also in two-component, acetone–1-butanol, mixed solvent solutions. The solubility was determined by utilizing the increase in mass resulting from the saturation of solvent with butane gas at constant temperature and pressure.

Introduction

Butane gas is of particular interest to research workers because of its wide range of solubility in different solvents. For example, butane solubility in hexane is very high, approaching the ideal. Its Oswald coefficient at 278 K is 48.0. This corresponds to a gas solubility at atmospheric pressure of 0.737 mole fraction butane (*1*). In this case the solute gas is the major component in the saturated solution. In contrast, butane solubilities in highly polar associated solvents are extremely low. Its solubility in water at 278 K and 1 atm is 0.000 023 mole fraction (*2*), some 32 000 times lower than in hexane. Apparently the strong cohesive forces in highly polar associated solvents tend to "squeeze out" organic or hydrophobic molecules (*3*). If this is correct, the solubilities of butane in benzene and cyclohexane might be expected to be similar to those in hexane. Furthermore, butane solubilities in solvents such as the alkanols, acetone, methyl ethyl ketone, and aniline, having molecular interactions between those of hexane and water, should be expected to be between those in hexane and water.

Accurate methods for determining gas solubility are usually volumetric, in which it is possible to measure the change in volume of gas as it dissolves in a measured volume of degassed solvent. Such experimental methods have been used successfully by many workers, one of the first of whom was Horiuti (*4*) who made his extremely accurate measurements over 50 years ago. Especially for highly soluble gases it appears equally possible to utilize a method in which the *mass* of degassed solvent and subsequently of saturated solution, and hence of absorbed gas, is measured. Such a method was used by Gerrard (*5*) for a wide range of solvents. A method based on the determination of mass of solvent and saturated solution was utilized in this work but special precautions were taken to prevent possible errors that may be associated with it. A bubbling process for saturating the solvent was avoided for a number of reasons; instead, mechanical agitation of the solubility cell was employed to achieve saturation. The bubbling process in which a relatively large volume of gas contacts the solvent leads to the possibility that impurities of low volatility in the gas are preferentially accumulated in the solvent and/or some solvent is lost by entrainment or vaporization in the effluent gas. In addition, supersaturation of solvent is considered possible if solubility occurs mainly from small bubbles because of the unusually high internal pressure in small bubbles. Because the masses of the materials involved can be determined with high accuracy, the weighing method was considered to give accurate results especially for highly soluble gases such as butane.

The solubility of butane was measured in benzene and in alkane solvents from pentane to decane by Jadot (*6*) using a gas chromatographic technique. Retention times in the chromatographic column were used to estimate Henry's constants at effectively very low partial pressures. Lenoir et al. (*7*) used a similar technique for measuring solubilities of butane in several highly polar solvents including aniline. It is considered, however, that especially for highly soluble gases, Henry's law constants evaluated at very low partial pressures cannot be accurately applied at atmospheric pressure. Hence, the results of Jadot and Lenoir et al. may not be directly comparable to those reported in this work. Kretschmer and Wiebe (*8*, *9*) reported solubilities of butane in alcohols including methanol and ethanol at several pressures approaching atmospheric. They used an apparatus in which the amount of solvent was determined by weight while the amount of gas dissolved was determined by a combination of readings for volume of gas trapped over mercury and pressure by means of manometer. Solubilities of butane in 1-butanol were also previously reported by Castañeda (*1*) and Blais (*10*) who used a volumetric method which utilized a constant flow of degassed solvent through a glass absorption spiral connected to a buret for measuring the volume of gas dissolved.

For gases of high solubility such as butane it has been shown that the gas normal boiling point can be considered as an extrapolation of the solubility relation; that is, as the saturation temperature is reduced, the solution becomes richer in the gas until as the temperature approaches the gas normal boiling point, the concentration of the saturated solution approaches that of the pure gas. It is hypothesized that this phenomenon occurs only when the solvent and liquefied gas are completely miscible at a temperature below the gas normal boiling point as is the case for butane and hexane. In contrast it appears most *unlikely* that the solubility relation for butane in water can be accurately extrapolated to the butane normal boiling point. The data suggest that as the solution temperature is reduced toward the butane normal boiling point (−0.5 °C) (and the water freezing point) an extrapolated equilibrium solubility very much less than that of pure butane is obtained. It is also hypothesized that when the liquefied solute gas is *immiscible* in the solvent, the gas solubility relation may be extrapolated to the solubility of the liquefied gas in the immiscible solvent. While this appears qualitatively correct for butane and water, we have not substantiated it. Instead, we have measured the solubility of butane in aniline at a temperature of 0.65 °C, within 1.2 °C of the butane normal boiling point, to help clarify this question.

The solubility of a gas in a homologous, two-component, nonpolar solvent solution might be expressed with good accuracy by considering the solution to be ideal. The solubility of acetylene in a mixed hexane–hexadecane solution was successfully expressed by considering the solute gas and mixed

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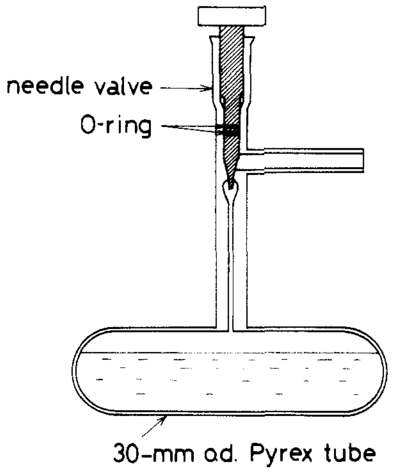

Figure 1. Equilibrium cell.

solvent as an ideal solution (*11*). On the other hand, for solvent mixtures containing highly polar and/or associating solvents, it must be considered that the solubility behavior will be far from ideal, as for acetylene in the 1-butanol–ethylene glycol solvent solutions (*11*). While in this paper we have not been able to contribute to the theoretical explanation of solubilities in polar or associating mixed solvent solutions, we have measured and are reporting here, solubilities of butane at 298.15 K in the complete range of polar mixed solvent solutions composed of acetone–1-butanol. In this work also are reported solubilities of butane at atmospheric pressure and for a range of temperatures (283, 298, and 315 K) in nine solvents of varying polarity. These solvents are benzene, cyclohexane, methanol, ethanol, 1-propanol, 1-butanol, acetone, methyl ethyl ketone, and aniline. Where possible, a comparison is made with previously reported data. A comparison is also made between the butane solubility and hydrogen-bonding parameters for the various solvents. The supposition is that for higher degrees of molecular association in the solvent, the butane solubility is accordingly reduced.

Experimental Section

An equilibrium cell having a volume of approximately 70 cm^3 was constructed of Pyrex glass (Figure 1) and attached to a mechanical shaking device. The cell was installed in a constant temperature bath in a horizontal orientation exposing a large surface area to the dissolving gas when partially filled with solvent. While in operation, gas was supplied to the equilibrium cell to keep the pressure constant. Rubber connectors which could be easily disconnected were used to attach the cell to the gas supply system. The stopcocks used were the Teflon–glass type which were essentially leakproof. The complete arrangement is shown in Figure 2. The procedure for a solubility determination consisted in first determining the tare weight of the cell, then charging the cell with approximately 60 cm^3 of solvent, and degassing the solvent by boiling under vacuum for at least 15 min. This period of time was found sufficient for yielding highly consistent solubility results. After the quantity of degassed solvent was determined by weight, the cell was attached to the mechanical agitator and the gas supply manifold. The cell contents were equilibrated for at least 15 min while subjected to vigorous agitation. Periods of time for agitation in excess of 15 min were found to give no change in the quantity of gas dissolved. The quantity of gas dissolved was determined from a final weight of cell and contents, the combination of which weighed approximately 120 g. The actual quantities of dissolved gas which ranged from 1 to 20 g, depending on the solubility, could be determined very precisely. The distribution of solute between the gas phase in the cell and that actually dissolved could be determined from the volume of the cell and the residual gas volume, V:

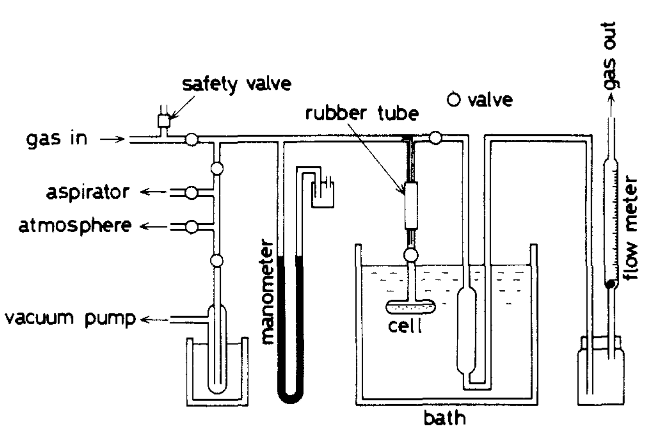

Figure 2. Schematic diagram of gas solubility apparatus.

$$V = V_{\text{cell}} - (W_2 + W_1)/\rho_2 \qquad (1)$$

A more accurate estimate of the solution volume, and hence of the volume of gas in the cell, could have been made, but it was found to be entirely unnecessary. The masses of gas and solvent vapor in the gas phase of the cell were calculated to be so small that corrections for them could have been omitted entirely and thereby introducing an error in solubility of no more than 0.1%. When estimating the gas partial pressure, Raoult's law was considered to apply to the solvent:

$$p_1 = P - x_2P_2 \qquad (2)$$

In determining the mole fraction dissolved gas in solution, although small, corrections to the respective masses were made for the amounts that remained in the gas phase of the cell. The ideal gas law was used in estimating these masses:

$$w_i = p_iVM_i/(RT) \qquad (3)$$

The mole fraction solubility at the partial pressure of gas for the experiment was given by

$$x_p = (W_1 - w_1)/M_1[(W_1 - w_1)/M_1 + (W_2 - w_2)/M_2]^{-1} \qquad (4)$$

An initial estimate of x_p was obtained by ignoring the correction to the mass of gas and solvent vapor in the gas phase; the accurate value was subsequently obtained by repetition of the calculation as required. The solubility corresponding to a gas partial pressure of 1 atm was determined from

$$x = 101325x_p/p_1 \qquad (5)$$

The method for solubility determinations for the mixed solvent solutions of acetone and 1-butanol required some modification. The solvent with the lower volatility (1-butanol) was charged first into the equilibration cell and degassed there. A degassing buret was used for the more volatile solvent (acetone) as shown in Figure 3. After the acetone was degassed by boiling at its vapor pressure within the inverted buret, the buret was sealed, inverted, and connected to the equilibration cell. The interconnecting line was evacuated, and then filled with degassed acetone. Finally the cell was charged with a predetermined quantity of acetone as measured approximately by the volume reading of the buret. An accurate determination of the acetone charged was made by weight. Excess acetone in the charging line of the cell was removed by evaporation under vacuum. Although it was not possible to reproduce individual results exactly, by carefully charging suitable quantities of solvents it was possible to cover the complete composition range of the two solvent components. The calculation of solubility was similar to that for pure solvents.

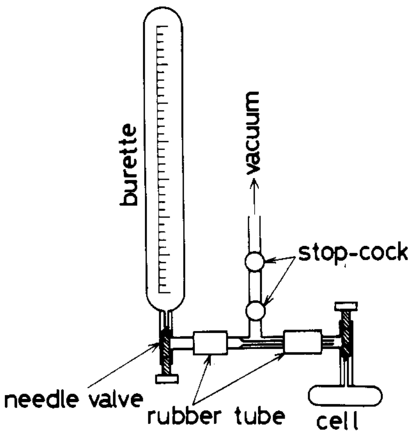

Figure 3. Apparatus for determining solubilities in mixed solvent solutions.

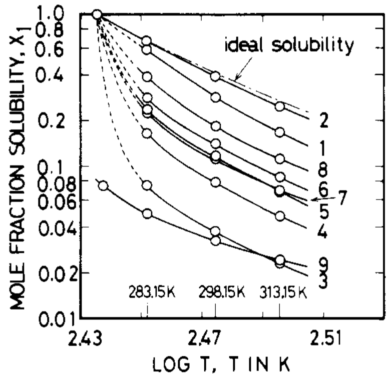

Figure 4. Solubility of butane in various solvents at atmospheric pressure. The solvent numbers are as shown in Table I.

The reproducibility for the solubility experiments was usually better than 0.2% and the total error is considered to be less than 0.1%. The bath temperature was controlled to 0.02 K, the pressure was measured to 0.1 mm of mercury, and the weights of the cell and contents were measured to 0.1 mg.

The butane for these experiments had a specified minimum purity of 99.0 vol % and was obtained from Chugoku Kasei. The solvents were obtained from Nakarai Chemicals. The minimum specified purities of cyclohexane, 1-butanol, methyl ethyl ketone, and aniline were all 99.0 vol %. The specified minimum purities for benzene, methanol, ethanol, 1-propanol, and acetone were all 99.5 vol %. The chemicals were used as received. The solvent densities and vapor pressures were obtained from the literature (*12*–*15*).

Results and Discussion

The results for butane solubilities in the nine solvents corresponding to a gas partial pressure of 101.325 kPa are listed in Table I and graphically illustrated in Figure 4. It is noted that comparable data for solubilities in methanol and ethanol at 298.15 K of Kretschmer and Wiebe (*8*, *9*) as well as those in 1-butanol of Castañeda (*1*) and Blais (*10*) all agree within 1% of solubilities obtained in this work. It is of particular interest that the methods for solubility determination used by the above-mentioned research workers were significantly different from that used in this work. On the other hand, the data of Jadot (*6*) for solubilities of butane in benzene and of Lenoir et al. (*7*) for the solubilities in aniline are substantially different from those obtained in this work. We suggest that it may be concluded that Henry's law constants obtained by a gas chromatographic technique at essentially very low gas partial pressures *cannot* be accurately extrapolated to atmospheric pressure. Hence the data of Jadot and Lenoir et al. are simply not directly comparable with ours. Further, it is noted that the butane solubilities of Kretschmer and Wiebe were obtained at several different gas pressures so that it is possible to observe the effect of pressure on the solubility. From their work it is apparent that, particularly for butane, or generally for highly soluble gases, Henry's law is not obeyed even at pressures below atmospheric. Gerrard (*5*) discusses the variation of solubility with pressure for highly soluble gases at some length.

Table I. Butane Solubility at Atmospheric Pressure

no.	solvent	temp, K	x_1	% dev
1	benzene	283.15	0.5904	
		298.15	0.2851	
		298.15	0.207 (6)	−37.7
		313.15	0.1672	
2	cyclohexane	283.15	0.6712	
		298.15	0.3962	
		313.15	0.2490	
3	methanol	283.15	0.04457	
		298.15	0.03763	
		298.15	0.0376 (9)	−0.1
		313.15	0.02322	
4	ethanol	283.15	0.1647	
		298.15	0.07825	
		298.15	0.0788 (8)	+0.7
		313.15	0.04664	
5	1-propanol	283.15	0.2346	
		298.15	0.1138	
		313.15	0.06834	
6	1-butanol	283.15	0.2817	
		298.15	0.1401	
		298.15	0.141 (10)	+0.6
		298.15	0.139 (11)	−0.8
		313.15	0.08534	
7	acetone	283.15	0.2276	
		298.15	0.1108	
		313.15	0.06907	
8	methyl ethyl ketone	283.15	0.3885	
		298.15	0.1824	
		313.15	0.1121	
9	aniline	273.80	0.0744	
		283.15	0.04886	
		298.15	0.03241	
		298.15	0.0395 (7)	+21.9
		313.15	0.02412	

The effect of temperature on the solubility of butane in the various solvents is shown in Figure 4. In Figure 4 may be found support for the statement that the gas normal boiling point is usually an extension of the solubility curve, the exception being when the liquefied gas is immiscible in the solvent. Except for the solubility in aniline it appears that the remaining solubilities may be extrapolated to the butane normal boiling point (272.6 K). Unfortunately data were not obtained for all the solvents at a temperature within one or two degrees of the butane boiling point; however, experiments were performed for the solubility of butane in aniline at an average temperature of 0.65 °C. This latter solubility indicates quite conclusively that for aniline, which is immiscible in liquid butane, extrapolation cannot be made to the butane boiling point. To clarify unequivocally the solubility behavior at temperatures approaching the gas normal boiling point, additional research is required.

The order of butane solubilities in the alkanols is as expected, with the lowest solubility occurring in methanol and with an increase in solubility with each increase in number of carbons in the normal alcohols. The low solubility in methanol is considered to be the result of a strong associating tendency of this solvent, whereas solubilities in the other alkanols increase as the associating tendency is reduced (*3*). In this regard it is of great interest to compare butane solubilities in all the solvents with their respective hydrogen-bonding parameters as compiled by Martin and Hoy (*16*) for a wide range of solvents. The solvents are listed in order of decreasing butane solubility with corresponding hydrogen-bonding parameter in brackets when

Table II. Solubility of Butane in Acetone-1-Butanol Mixed Solvent Solutions at 298.15 K

acetone[a] vol fraction	solubility x_1	acetone[a] vol fraction	solubility x_1
0.0	0.1401	0.5986	0.1247
0.0464	0.1381	0.7063	0.1221
0.1044	0.1354	0.8003	0.1193
0.1967	0.1328	0.9029	0.1154
0.3034	0.1309	0.9307	0.1138
0.4086	0.1287	0.9660	0.1122
0.4958	0.1270	1.0	0.1108

[a] Butane-free.

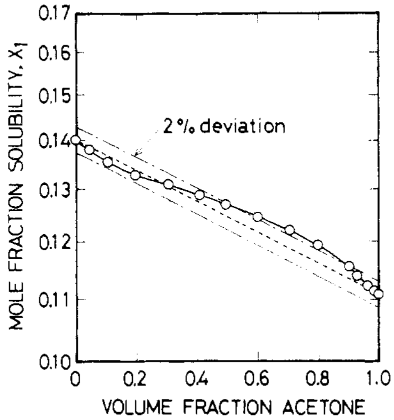

Figure 5. Solubility of butane in acetone-butanol mixtures at 298.15 K and atmospheric pressure.

available: cyclohexane (0), benzene (1.98), methyl ethyl ketone (4.63), 1-butanol (7.55), 1-propanol (8.64), acetone (5.39), ethanol (9.78), methanol (11.73), and aniline (not available). Except for the hydrogen-bonding parameters for acetone and aniline, there appears to be a definite relation between solubilities and hydrogen-bonding parameter. The hydrogen-bonding parameter for aniline was simply not evaluated but wouuld be expected to be high as for other nitrogen-containing compounds. If one had wished to find the order of solubilities in the nine solvents using the hydrogen-bonding parameters, only acetone solvent would have been in the wrong order. There appears to be strong support for the hypothesis that an increasing degree of molecular association in the solvent results in a corresponding reduction in gas solubility.

Solubilities of butane at 298.15 K in the solvent solutions composed of acetone and 1-butanol are given in Table II and shown graphically in Figure 5. When some properties such as density, refractive index, or gas solubility are plotted as a function of *volume* fraction for nonpolar, two-component solvent solutions, an approximately linear relation usually results (*17*). In this case the volumes of solvent components prior to mixing are considered, because a volume change may occur on mixing. It may be observed from Figure 5 that even for the polar solvent solution, acetone-1-butanol, deviations from linearity for the solubilities are relatively small. It would appear that the degree of molecular association on mixing of the acetone and 1-butanol components remains essentially unchanged from that which occurs in the individual solvents.

Acknowledgment

Mr. H. Asatani measured the solubilities of butane in aniline at 0.65 °C at the University of Ottawa.

Glossary

M_i	molecular weight of solvent or solute
p_i	partial pressure of solvent or solute, Pa
P_i	vapor pressure of solvent or solute, Pa
P	total pressure, Pa
R	gas constant, Pa·m^3/(mol·K)
T	temperature, K
V	volume of gas phase in cell, m^3
V_{cell}	volume of cell, m^3
W_i	total mass of solvent or solute in cell, kg
w_i	mass of solvent or solute in gas phase of cell, kg
x_i	mole fraction of solvent or solute in liquid
x_p	mole fraction of solute at a partial pressure of less than 1 atm
x	mole fraction of solute at a partial pressure of 101.325 kPa
ρ_2	density of solvent, kg/m^3

Subscripts

$i = 1$	solute
$i = 2$	solvent

Registry No. Butane, 106-97-8; benzene, 71-43-2; cyclohexane, 110-82-7; methanol, 67-56-1; ethanol, 64-17-5; propyl alcohol, 71-23-8; butyl alcohol, 71-36-3; acetone, 67-64-1; 2-butanone, 78-93-3; benzenamine, 62-53-3.

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