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Solubility of Ammonia and Hydrogen Sulfide in Several Polar Solvents

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Solubilities of ammonia and hydrogen sulfide gases are reported for temperatures ranging from 263 to 333 K in acetone, butanol, chlorobenzene, and ethylene glycol solvents, and for hydrogen sulfide in methanol, tetrahydrofuran, and acetic acid as well. These gases and solvents exhibit extreme molecular interactions which are reflected in the corresponding unusual solubility behavior. Whereas, among the solvents utilized, the solubility of hydrogen sulfide is the lowest in ethylene glycol, the solubility of ammonia in that solvent is the highest. This anomaly and other solubility behavior are discussed.

Introduction

The solubilities at 293 K of both ammonia and hydrogen sulfide were reported in the early work of Bell (*1*) in some 12 and 20 solvents, respectively. The procedure used involved first saturating the solvent by bubbling the gas through it in a saturation bulb. Next, the gas was stripped from the saturated solution with purified, dried air and quantitatively adsorbed and reacted in an aqueous solution of hydrogen chloride for ammonia and in aqueous sodium hydroxide and hydrogen peroxide for hydrogen sulfide. The solubilities reported were based on single experimental measurements without replicates and on the assumption that the gases were ideal. Solubilities of both gases were determined by Bell (*1*) in chlorobenzene, one of the solvents used in this work. These data were compiled by Stephen and Stephen (*2*).

The more recent data for the solubilities of hydrogen sulfide as well as three other gases were reported for the temperature range 265-293 K for some 36 different solvents by Gerrard (*3*). A wide range of solvents were used including alcohols, halogenated compounds, and benzene derivatives, and, in particular, chlorobenzene and ethylene glycol, two of the solvents used in this work. The rather simple experimental procedure involved measurement of the increase in mass of a known quantity of solvent during saturation with hydrogen sulfide at atmospheric pressure. The accuracy was considered to be within 4%.

The solubilities of hydrogen sulfide as well as mixtures (*3*) of hydrogen and hydrogen sulfide in methanol were measured at low temperatures and total pressures from 2 to 10 atm by Yorizane et al. (*4*). Even more recently, solubilities of both ammonia and hydrogen sulfide were reported for high temperatures in the solvents hexadecane, bicyclohexyl, and 1-methylnaphthalene and also for hydrogen sulfide in diphenylmethane by Tremper and Prausnitz (*5*). The apparatus was specifically designed to achieve good accuracy even for the high temperatures utilized. A discussion of the phenomena associated with gas solubility may be found in the book by Hildebrand et al. (*6*).

Certain solubility characteristics appear to be common to all solutions of highly soluble gases regardless of how complex the molecular interaction within the solvent or between the gas and solvent. The first is that for highly soluble gases, as the equilibrium temperature is reduced to the boiling point of the gas and provided the solvent does not freeze, the mole fraction solubility tends to become extremely high, approaching a concentration corresponding to that of a pure liquified gas. This is evident for the highly soluble gases such as ammonia and hydrogen sulfide, as this work will show. Other highly soluble gases such as propane and butane have also been shown to exhibit this phenomenon (*7*). Hence, the order of increasing solubility of a number of gases in a single solvent usually follows the order of increasing normal boiling point of the gases.

The other solubility behavior that appears to be common to all solvents is that the solubilities of all gases in a single solvent tend toward a single value as the temperature is increased. When extrapolated, the solubilities of all the gases appear to have approximately the same extrapolated solubility at the solvent critical temperature. Few solubility data are actually available for temperatures above the solvent normal boiling points. These phenomena have been observed for solvents forming regular solutions (*6*) as well as for polar solvents including water (*7-9*).

Hydrogen-bonding factors have been found useful in relating gas solubilities in one hydrogen-bonding solvent to those in other similar solvents (*7*). The hydrogen-bonding factor, α, was based on the ideal gas solubility as follows:

$$\alpha = x_1/x_1^{\mathrm{i}} \qquad (1)$$

$$x_1^{\mathrm{i}} = p_1/p_1^{\circ} \qquad (2)$$

The agreement between the hydrogen-bonding factors for various gases in several chemically similar solvents was found to be more than qualitative and could be used to estimate approximate gas solubilities when solubilities of several other gases were available in both of the solvents. The basic premise for the relationship was that the strong interaction in one solvent to prevent entry of particular solute gas molecules, thus reducing the solubility below the ideal solubility, was related to a similar interaction and reduction in solubility in another solvent of similar chemical nature. One limitation to the prediction of solubility in similar solvents involves solubilities which are much higher than the ideal solubilities. It would appear that a reversible chemical reaction may be occurring in these systems such as for the solution of ammonia in water, for example. Whereas the solubility behavior of various gases in two similar solvents seems to be related, the occurrence of reversible chemical reactions does not.

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 an absorption spiral by means of a calibrated syringe pump. The pressure in the absorption spiral was observed by means of a small manometer 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

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Table I. Solvent Density and Vapor Pressure at 298.15 K

solvent	density, kg m^{-3}	vapor press., kPa
acetic acid	1044.4	2.04
acetone	784.9	29.3
butanol	805.8	0.93
chlorobenzene	1100.9	1.52
ethylene glycol	1110.1	0.017
methanol	787.3	16.2
tetrahydrofuran	880.0	24.8

regular readings for at least 60 min of operation after steady-state conditions prevailed. 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. The solubility measurements were performed at atmospheric pressure; hence, the partial pressure of the solute gas was always less than atmospheric. For the calculation of results it was assumed that the Ostwald coefficient remained constant on an increase in gas partial pressure to atmospheric pressure. It was considered that this application of Henry's law over a pressure interval corresponding to the solvent vapor pressure introduced a relatively small possible error in the calculated results.

The solubility apparatus was of a design previously used (*10*) although three different sizes of apparatus were actually used having gas storage burets of 50, 100, and 250 cm^3 in volume. To allow for the corresponding large variability in solubilities, a range of solvent flows was obtained by means of a 20-cm^3 gas-tight syringe with six constant-speed motors for the syringe pump of 1, 2, 3, 6, 12, and 30 revolutions per hour. The syringe pump was calibrated by using distilled water. Solvent rates between 0.5 and 10 cm^3 L^{-1} were used.

It was found that the syringe pump could be readily calibrated to an accuracy of at least 0.1%, the temperature within the apparatus controlled to within 0.1 °C, and the volume in the gas buret read to within 0.2%. The overall reproducibility usually attained was within 1% while the overall accuracy for this method of solubility measurement is considered to be at least 2%.

For experiments involving hydrogen sulfide, the complete solubility apparatus was mounted in a large fume hood for safety (and environmental) reasons. For ammonia, such a precaution was not necessary although venting was to an exhaust system.

The solvents were all purchased from Canlab and were of the Baker Analyzed grade with specified minimum purities as follows: acetone, 99.5%; acetic acid, 99.7%; butanol, 99.0%; chlorobenzene, 99.0%; ethylene glycol, 99.8%; methanol (absolute), 99.5%; and tetrahydrofuran, 99.0%. The solvent density data were obtained from several sources including from Timmermans (*11*). Densities for butanol and ethylene glycol were as reported by Miyano (*12*). The densities of tetrahydrofuran and chlorobenzene were from the data of Schornack and Eckert (*13*). Vapor pressure data were taken from Reid et al. (*14*).

The gases, ammonia and hydrogen sulfide, were obtained from Liquid Carbonic, Canada, and were of the highest purity available. These purities were 99.99% for ammonia and 99.5% for hydrogen sulfide. The volumetric behavior of hydrogen sulfide was taken to be as reported by Reamer et al. (*15*) and that for ammonia as reported by Din (*16*). At 298.2 K the compressibility factors for hydrogen sulfide and ammonia are 0.992 and 0.990, respectively.

The solvent densities and vapor pressures at 298.15 K are listed in Table I. The Ostwald coefficient is calculated from the volume of dry gas, corrected to the equivalent volume of saturated gas, dissolved in a unit volume of solvent:

$$L = mp/(\theta r p_1) \qquad (3)$$

Table II. Solubility of Ammonia and Hydrogen Sulfide at Atmospheric Pressure Expressed as the Ostwald Coefficient (L) and Mole Fraction (x)

solvent		temp, K 263.15^a	 298.15^b	 333.15^c
		Ammonia		
acetone	L	70.9	30.1	
	x	0.1906	0.0842	
butanol	L	213.1	73.0	32.0
	x	0.472	0.217	0.1007
chlorobenzene	L	21.9	10.10	5.24
	x	0.0924	0.0409	0.0200
ethylene glycol	L	727	296.2	120.3
	x	0.652	0.406	0.202
		Hydrogen Sulfide		
acetone	L	57.7	24.6	
	x	0.1607	0.0698	
acetic acid	L		12.47	6.97
	x		0.0287	0.01507
butanol	L	22.8	8.58	3.65
	x	0.0873	0.0315	0.0126
chlorobenzene	L	24.9	12.62	7.78
	x	0.1039	0.0505	0.0294
ethylene glycol	L	13.34	5.36	3.44
	x	0.0332	0.0122	0.00718
methanol	L	40.2	26.93	
	x	0.0689	0.0276	
tetrahydrofuran	L	76.9	33.4	
	x	0.222	0.1014	

[a] −10 °C. [b] 25 °C. [c] 60 °C.

Based on the assumption that Raoult's law can be applied to the solvent in the solution, the gas partial pressure at equilibrium with the solution is given by

$$p_1 = 101.325(p - p_2^\circ)/[p(101.325 - p_2^\circ x_1)] \qquad (4)$$

The mole fraction solubility is

$$x_1 = [1 + V_1/(LV_2)]^{-1} \qquad (5)$$

If the gas molar volume is expressed in terms of a compressibility factor, the mole fraction solubility is

$$x_1 = [1 + ZRT/(101.325LV_2)]^{-1} \qquad (6)$$

An approximate check on the solvent infusion rate is 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.

Results and Discussion

The solubility results for both ammonia and hydrogen sulfide are reported in terms of the Ostwald coefficient and mole fraction solubility in Table II. These data are also shown as the mole fraction vs. temperature on log scales in Figures 1 and 2. In these figures the mole fraction solubility is extrapolated to a mole fraction corresponding to pure ammonia and pure hydrogen sulfide at the temperatures corresponding to the boiling points at atmospheric pressure for these gases. The boiling point of the solvent is indicated by a break in the solid line.

The data reported here confirm former measurements only very approximately. The differences in the data of Gerrard (*3*) for the solubilities of hydrogen sulfide in ethylene glycol and in chlorobenzene, when compared with those reported in this paper, range from −5% to 17% for the former solvent and from 4% to 24% for the latter solvent, as shown in Figure 1. On the other hand, the solubilities of Bell (*1*) for hydrogen sulfide and ammonia in chlorobenzene at 293.15 K are approximately 40% and 9% lower, respectively, than those obtained in this

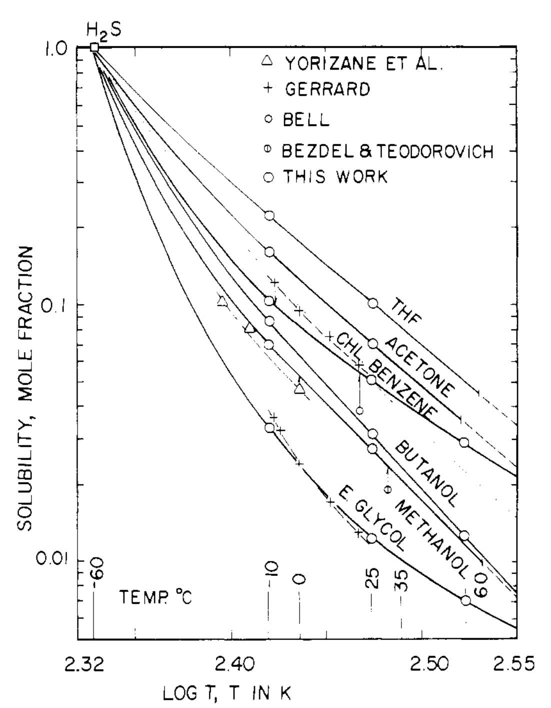

Figure 1. Solubility of hydrogen sulfide in various solvents at atmospheric pressure.

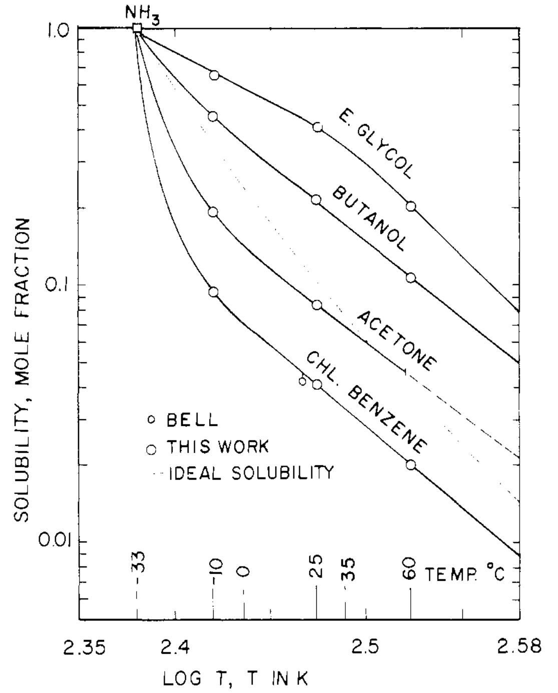

Figure 2. Solubility of ammonia in various solvents at atmospheric pressure.

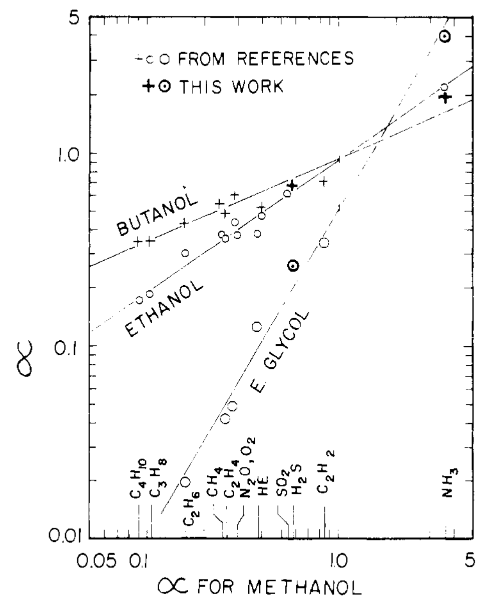

Figure 3. Relation between hydrogen-bonding factors for a number of gases in methanol, ethanol, butanol, and ethylene glycol.

work. The value for the solubility of hydrogen sulfide in methanol at 303.15 K reported by Bezdel and Teodorovich (*17*) is approximately 22% lower than that reported in this work. The former two workers used a rudimentary apparatus designed for making many approximate measurements. It appears possible that there was an inherent error in the results. Bell (*1*) indicated that his experiments were not repeated so that errors could have been large. The experiments of Bezdel and Teodorovich (*17*) were conducted at very low pressures such that extrapolation to atmospheric pressure may have introduced a significant error. The results in this work are based on at least three measurements for every different condition and are considered accurate to within 2%. The results for the solubility of hydrogen sulfide in methanol compare more favorably with those of Yorizane et al. (*4*) when the latter are extrapolated to atmospheric pressure using a Henry's law constant evaluated at 2-atm pressure. The results of Yorizane et al. (*4*) appear to be within 10% of those reported in this work.

It is apparent from Figures 1 and 2 that hydrogen sulfide and ammonia exhibit extreme solubility behavior in the solvent ethylene glycol. Ammonia is extremely soluble in ethylene glycol having solubilities much higher than the ideal solubility. These phenomena may be associated with a reversible chemical reaction between the gas and solvent possibly forming ammonium radicals at the hydroxyl groups of the ethylene glycol. The more common behavior in the highly polar ethylene glycol solvent is that of hydrogen sulfide for which there is observed a low solubility, much below the ideal solubility. The mechanism for the latter behavior may involve such a strong intermolecular hydrogen-bonding effect in the solvent that the solute gas molecules are "squeezed out" and prevented from penetrating the solvent network, thus exhibiting a low solubility. This type of solubility behavior may be observed for many gases in water, for example (*9*).

If one accepts that the cause of the high solubility of ammonia in the alcohols is the result of a reversible chemical reaction with the hydroxyl groups, one may expect the order of solubilities to be related to the ratio of the number of hydroxyl groups to the number of carbons for these alcohols. Thus, a very high solubility would be observed in ethylene glycol and methanol, a lower solubility in ethanol, and respectively lower solubilities in propanol and butanol. The very early data (19th century) tabulated in Stephens and Stephens (*2*), along with the solubilities in ethylene glycol and butanol reported here, confirm this order of ammonia solubilities in the alcohols.

The reduced solubilities of gases which do not react with the alcohol solvents may result from the high intermolecular attraction between solvent molecules or hydrogen bonding. Then the order of gas solubilities would be reversed. That is, the solubility of an unreacting gas would be least in ethylene glycol and would successively increase in methanol, ethanol, and butanol. The hydrogen-bonding parameter is considered to be a measure of the effect of molecular association on gas solubility. The influence of molecular association on gas solubility in one solvent might be expected to be related to an equivalent influence in another similar solvent. Hence, hydrogen-bonding factors for a number of gases in one polar solvent may be

Table III. Sources of Solubility Data for Ammonia for Determination of Hydrogen-Bonding Factors

butanol	C_4H_{10}, C_3H_8 (*7*); C_2H_6, CH_4 (*18*), C_2H_4 (*19*); O_2 (*20*); C_2H_2 (*12*); H_2S, NH_3, this work
ethanol	C_4H_{10}, C_3H_8, CH_4, C_2H_4, CO_2, N_2O, He, NH_3 (*2*); C_2H_6 (*18*); O_2 (*20*)
ethylene glycol	C_2H_6 (*21*); C_2H_4 (*19*); C_2H_2 (*12*); CO_2 (*22*); H_2S, NH_3, this work
methanol	C_4H_{10}, C_3H_8, C_2H_4, CH_4, SO_2, He, N_2O, NH_3, CO_2 (*2*); C_2H_6 (*18*); C_2H_2 (*12*); O_2 (*20*); H_2S, this work

related to those in another polar solvent.

In Figure 3 hydrogen-bonding factors for various gases in ethanol, butanol, and ethylene glycol are shown as a function of the hydrogen-bonding factor in methanol. It is evident that there is a close relation between the hydrogen-bonding factors in one of the alcohols and those of the other alcohol solvents. Although it is difficult to predict solubilities accurately from graphs such as that shown in Figure 3, the relation is at least semiquantitative. For all four solvents it would appear that some degree of chemical reaction occurs with ammonia, yielding hydrogen-bonding factors in excess of 1. On the other hand, the hydrogen-bonding factors for hydrogen sulfide in three of the alcohols are less than 1 and are generally consistent with the hydrogen-bonding factors for the other gases for which solubilities are available. Data for the hydrogen-bonding factors shown in Figure 3 are from sources given in Table III.

Glossary

L	Ostwald coefficient, cm^3 of gas (cm^3 of solvent)$^{-1}$
m	volume of dry gas absorbed, cm^3
p_1	partial pressure of gas, kPa
p	total pressure, kPa
p_1°	vapor pressure of pure liquified gas, kPa
p_2°	vapor pressure of pure solvent, kPa
r	solvent injection rate, cm^3 s^{-1}
R	gas constant
T	absolute temperature, K
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
x_1^i	ideal gas solubility defined by eq 2
Z	gas compressibility factor
α	hydrogen-bonding factor defined by eq 1
θ	elapsed time for solubility measurement, s

Registry No. Acetone, 67-64-1; butanol, 71-36-3; chlorobenzene, 108-90-7; ethylene glycol, 107-21-1; methanol, 67-56-1; tetrahydrofuran, 109-99-9; acetic acid, 64-19-7; ammonia, 7664-41-7; hydrogen sulfide, 7783-06-4.

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Ultrasonic Speeds and Isentropic Compressibilities for Binary Mixtures of 1-Hexanol with Hexane Isomers at 298.15 K[†]

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The effect of isomeric variations of one of the components of a binary mixture on its thermodynamic properties was studied by measuring ultrasonic speeds for mixtures of 1-hexanol with the four isomers of *n*-hexane. Isentropic compressibilities were calculated from the results by using excess volumes reported previously.

An earlier study (*1*) of binary mixtures of 1-hexanol with *n*-alkanes showed that the speed of sound and the excess isentropic compressibility varied regularly as the number of carbon atoms in the hydrocarbon increased from 5 to 10. Moreover, the behavior of these properties in the region of high dilution of 1-hexanol was characterized by the appearance of unusual extrema or points of inflection for all of the mixtures. In order to investigate the effect of changes in the molecular configuration of the hydrocarbon, we have measured the speed of ultrasound in binary mixtures of 1-hexanol with the four isomers of *n*-hexane: 2-methylpentane (2-MP), 3-methylpentane (3-MP), 2,2-dimethylbutane (2,2-DMB), and 2,3-dimethylbutane (2,3-DMB). A priori, the results for these systems were expected to fall between those for mixtures of 1-hexanol with *n*-pentane and with *n*-hexane.

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