Solubilities of Hydrogen and Nitrogen in Alcohols and *n*-Hexane

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Solubilities of hydrogen and nitrogen in methanol, ethanol, *n*-propanol, isopropanol, *n*-butanol, and *n*-hexane were measured at atmospheric pressure and temperatures of 25, 0, −20, −40, and −60 °C, except for the hydrogen–isopropanol system. Differences in the partial molar excess entropies of the gases (*R*) in alcohols (*A*) and those in *n*-hexane (*B*) $\bar{s}^E_{R,A} - \bar{s}^E_{R,B}$, calculated from the experimental solubility data, were within the values of −2.4 and −3.7 cal/mol·K.

Solubilities of gases in liquids are fundamental properties for designs of gas absorption and stripping columns in chemical industries. In addition, solubility results over a wide range of temperature are useful in studying the solution properties. The entropies of solution of a gas in alcohols have been known to be smaller than those in nonpolar solvents (*5*). However, there have been few data of gas solubilities in alcohols over a wide range of temperature. In this experiment, solubility measurements of hydrogen and nitrogen in aliphatic alcohols at temperatures of 25, 0, −20, −40, and −60 °C have been performed. Solubility data in *n*-hexane have also been obtained as reference solubilities in an inert solvent. The experimental entropies of solution of a gas are calculated from the temperature dependence of experimental solubilities.

Apparatus and Procedure

The solubility apparatus and procedures were the same as previously described (*9*), which were similar to those of Horiuti (*4*). The dissolution vessels used in this experiment were 80 cc for nitrogen solubility measurements and 150 cc for hydrogen. The gas buret was maintained at 25 °C in an air thermostat, and the dissolution vessel was immersed in a water bath or an *n*-heptane Dewar flask (at lower temperatures than 0 °C). The solubility measurements at atmospheric pressure were performed continuously by lowering the temperature of the dissolution vessel thermostat as 25, 0, −20, −40, and −60 °C. The thermostat was regulated within 0.05 °C except at −60 °C where it was within 0.12 °C.

Temperature determination was made by means of a thermistor thermometer, which was calibrated with the sublimation point of dry ice (−78.5 °C), the melting point of mercury (−38.87 °C), the triple point of ice (0.01 °C), and thermostat temperatures of 25 and 50 °C determined by a Toshiba reference thermometer.

Materials

The alcohols were guaranteed reagents from Nakarai Chemicals Ltd. Methanol, ethanol, and isopropanol were used without further purification, but *n*-propanol and *n*-butanol were fractionated in a laboratory column. Their purity was considered to be higher than 99.9% for each alcohol by measurements of densities and refractive indices and by gas chromatographic analyses. Merck Uvasol spectral-grade chemical was used for *n*-hexane without further purification.

Nitrogen gas was super-pure grade of 99.9995% obtained from Osaka Oxygen Co. Ltd., and hydrogen gas was research grade of 99.99% from Takachiho Chemical Industry Co. Ltd. The gases were used without further purification.

Solubility Expression and Physicochemical Property

The solubility was expressed in two ways: the Ostwald coefficient L and Henry's constant H as follows:

$$L = C_R^L/C_R^G \tag{1}$$

$$H = p_R/x_R \tag{2}$$

No correction for vapor-phase nonideality was made. Because the experimental pressure was low and $x_R \ll 1$, the partial pressure p_R was evaluated by means of Raoult's law as:

$$p_R = P - P^s_{\text{solvent}}(1 - x_R) \tag{3}$$

A small increase of liquid volume due to gas absorption was evaluated from the average values of the coefficients of dilatation, determined by Horiuti (*4*): 0.0022 for nitrogen and 0.0016 for hydrogen.

The evaluation of L and H necessitates the data of vapor pressure and density of pure solvents at the experimental temperatures. Vapor-pressure data were taken from Timmermans' tables (*10*). Density data at 25 °C were also taken from Timmermans, and those at lower temperatures were measured in this experiment by means of similar devices to those of Horiuti (*4*). Density values determined are recorded in Table I.

Solubility Data

Solubility data of hydrogen and nitrogen obtained in this experiment are summarized in Tables II and III, respectively. Solubility measurements were made several times for each system, and reproducibility was within ±1% for nitrogen and within ±1.5% for hydrogen. Table IV shows comparisons between experimental and literature solubilities for each system. Agreements within 2% were obtained except for the two cases, hydrogen–*n*-hexane and nitrogen–*n*-butanol systems. Figures 1 and 2 show the plots of Henry's constant H against the absolute temperature T. Experimental points of hydrogen gas are nearly on straight lines for each solvent, but those of nitrogen are on curves, slightly upward convex,

Table I. Densities of Alcohols and *n*-Hexane, g/cc

Temp, °C	MeOH	EtOH	*n*-PrOH	*i*-PrOH	*n*-BuOH	*n*-Hexane
25	0.78654[a]	0.78508[a]	0.79985[a]	0.78087[a]	0.80567[a]	0.65481[a]
0	0.8099	0.8063	0.8193	0.8013	0.8243	0.6771
−20	0.8284	0.8232	0.8347	0.8174	0.8390	0.6943
−40	0.8472	0.8402	0.8503	0.8340	0.8539	0.7113
−60	0.8663	0.8575	0.8661	0.8476	0.8692	0.7282

[a] Literature value taken from Timmermans' tables (*10*).

Table II. Experimental Data of Hydrogen Solubility in Aliphatic Alcohols and in *n*-Hexane

Temp, °C	L, —	H, atm	L, —	H, atm
	Methanol		Ethanol	
25	0.0975	6160	0.0852	4900
0	0.0797	7110	0.0696	5640
−20	0.0675	7960	0.0580	6400
−40	0.0557	9090	0.0480	7270
−60	0.0442	10710	0.0372	8750
	n-Propanol		*n*-Butanol	
25	0.0763	4270	0.0709	3750
0	0.0615	4970	0.0577	4320
−20	0.0520	5550	0.0493	4770
−40	0.0426	6360	0.0398	5530
−60	0.0336	7510	0.0324	6340
	n-Hexane			
25	0.130	1430		
0	0.105	1670		
−20	0.0873	1920		
−40	0.0710	2230		
−60	0.0550	2690		

Table III. Experimental Data of Nitrogen Solubility in Aliphatic Alcohols and in *n*-Hexane

Temp, °C	L, —	H, atm	L, —	H, atm
	Methanol		Ethanol	
25	0.164	3660	0.149	2800
0	0.152	3720	0.138	2840
−20	0.145	3700	0.131	2830
−40	0.139	3640	0.125	2800
−60	0.134	3520	0.121	2700
	n-Propanol		*i*-Propanol	
25	0.131	2490	0.147	2170
0	0.121	2520	0.135	2210
−20	0.115	2500	0.128	2210
−40	0.111	2450	0.121	2190
−60	0.107	2360	0.118	2090
	n-Butanol		*n*-Hexane	
25	0.123	2170	0.256	727
0	0.114	2190	0.235	749
−20	0.107	2200	0.219	764
−40	0.101	2180	0.206	766
−60	0.0954	2150	0.195	758

having each maximum point in the experimental temperature region.

Experimental Excess Entropy of Solution

Consider two mixtures of solute R (gas component) − solvent A (alcohol) and the same solute R − solvent B (nonpolar substance, *n*-hexane). The difference of the logarithmic Henry's constants $\ln H_{R,A} - \ln H_{R,B}$ is interrelated to the differences of the partial molar excess enthalpies $\bar{h}^E_{R,A} - \bar{h}^E_{R,B}$ and entropies $\bar{s}^E_{R,A} - \bar{s}^E_{R,B}$ in thermodynamics as

$$\ln H_{R,A} - \ln H_{R,B} = (\bar{h}^E_{R,A} - \bar{h}^E_{R,B})/RT - (\bar{s}^E_{R,A} - \bar{s}^E_{R,B})/R \quad (4)$$

Plots of the experimental values of $\ln H_{R,A} - \ln H_{R,B}$ against $1/T$ are linear for each alcohol (R = hydrogen or nitrogen). Table V shows the experimental differences of the partial molar excess entropies $\bar{s}^E_{R,A} - \bar{s}^E_{R,B}$ calculated from the intercepts. They are negative values in the range of −2.4 to −3.7 cal/mol·K, and the absolute values decrease in order of methanol > ethanol > *n*-propanol > isopropanol ≃ *n*-butanol. This order is corresponding to that of the decrease of self-association strengths.

Table IV. Comparison Between Experimental and Literature Values of Gas Solubilities, Ostwald Coefficient L

Gas	Liquid	Temp, °C	This work	Lit	
N_2	*n*-Hexane	25	0.256	0.261 (*2*)	0.232 (*3*)
N_2	Methanol	25	0.164	0.1645 (*6*)	0.167 (*1*)
		0	0.152	0.1532 (*6*)	
N_2	Ethanol	25	0.149	0.1489 (*6*)	0.149 (*1*)
		0	0.138	0.1391 (*6*)	
N_2	*n*-Propanol	25	0.131	0.132 (*2*)	0.133 (*1*)
N_2	*i*-Propanol	25	0.147	0.1465 (*6*)	
		0	0.135	0.1353 (*6*)	
N_2	*n*-Butanol	25	0.123	0.1225 (*6*)	
		0	0.114	0.1075 (*6*)	
H_2	*n*-Hexane	0	0.105	0.0926 (*11*)	
H_2	Ethanol	25	0.0852	0.0856 (*8*)	

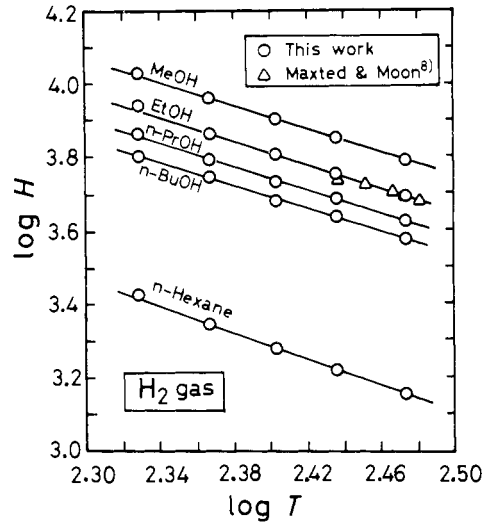

Figure 1. Experimental Henry's constants of hydrogen against absolute temperature

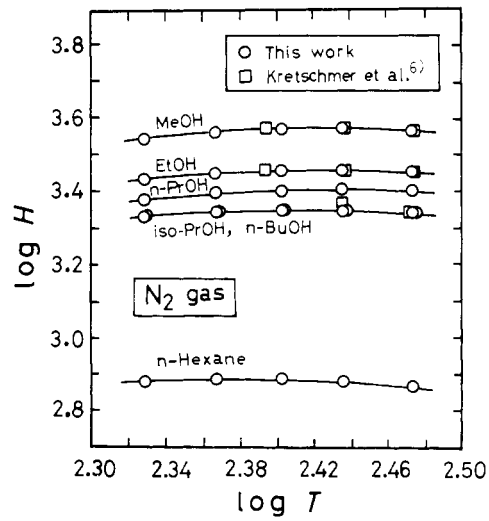

Figure 2. Experimental Henry's constants of nitrogen against absolute temperature

Table V. Difference of Partial Molar Excess Entropies of Gas in Alcohols and in *n*-Hexane

Alcohol	$\bar{s}^E_{R,A} - \bar{s}^E_{R,B}$, cal/mol·K	
	Hydrogen	Nitrogen
MeOH	−3.28	−3.66
EtOH	−2.78	−3.03
n-PrOH	−2.50	−2.93
i-PrOH	...	−2.54
n-BuOH	−2.41	−2.54

As Henry's constant is interrelated to the activity coefficient of solute, the theoretical expression for $\bar{s}^E_{R,A} - \bar{s}^E_{R,B}$ is given by means of suitable activity coefficient equations. Qualitative explanation of experimental values for $\bar{s}^E_{R,A} - \bar{s}^E_{R,B}$ is obtained when the Kretschmer-Wiebe equation (*7*) is assumed for component *A* and the Flory-Huggins equation with the Scatchard-Hildebrand equation for component *B*.

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Nomenclature

C = molar concentration, mol/cc
H = Henry's constant, atm
$\bar{h}$ = partial molar enthalpy, cal/mol
L = Ostwald coefficient, −
P = total pressure, atm
p = partial pressure, atm
R = gas constant, cal/mol·K
$\bar{s}$ = partial molar entropy, cal/mol·K
T = absolute temperature, K
x = mole fraction, −

Subscripts

A = alcohol
B = inert solvent (*n*-hexane)
R = gas component (H_2 or N_2)
R, α = refer to R in binary mixture of R and α

Superscripts

E = excess quantity
G = gas phase
L = liquid phase
s = quantity at saturation

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Isothermal Liquid-Vapor Equilibria for System Methanol–Water

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Gibbs free energies of mixing of methanol–water mixtures in the range of 35–65 °C and densities of the mixtures at 25 °C are measured. The enthalpies and free energies of mixing are thermodynamically consistent within the limits to which the gas imperfections are known. Earlier liquid-vapor equilibrium measurements are reanalyzed, using only total pressure and liquid composition data, and with corrections for gas imperfections. Of the previously reported free energies of mixing, only the single set of transpiration measurements at 25 °C by Butler et al. is to any degree consistent with our data.

The recent renewal of interest in alcohol–water systems prompts us to report measurements of free energies of mixing at 35, 50, and 65 °C and densities of mixtures at 25 °C, which we have hitherto hesitated to publish for lack of a detailed theoretical interpretation. Although there are some recent isobaric studies at atmospheric pressure (*8, 14, 15*), there have been few new isothermal data (*4, 22*) reported in the past few years.

A precise evaluation of the free energy of mixing from vapor-pressure data requires a knowledge of the gas imperfections of both the pure components and of their mixtures. Second virial coefficients are known fairly precisely for water (*9a*), imprecisely for methanol (*16, 17*), and not at all for their mixtures. It is frequently assumed (*13*) that the cross term, B_{12}, is given by the arithmetic mean of the virial coefficients of the pure components. Such an approximation is, however, highly suspect for mixtures with strong interactions between the components. An alternative approach is to assume that the vapor pressures and phase compositions are consistent with the Gibbs-Duhem equation, which allows an estimate of B_{12} to be made (*19*). Both approaches are considered here.

Thermodynamic consistency between enthalpy and free energy measurements has often been tested by estimating the heat of mixing from the temperature coefficient of the