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Solubility of Nonpolar Gases in Halogenated Compounds. 2. Solubility of H_2, D_2, N_2, O_2, CH_4, C_2H_4, C_2H_6, CF_4, SF_6, and CO_2 in Bromocyclohexane at 263.15–303.15 K and 101.32 kPa Partial Pressure of Gas

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Solubility measurements of 10 nonpolar gases (H_2, D_2, N_2, O_2, CH_4, C_2H_4, C_2H_6, CF_4, SF_6, and CO_2) in bromocyclohexane in the range 263.15-303.15 K and a gas partial pressure of 101.32 kPa are reported. Thermodynamic functions for the solution process are evaluated. Experimental results are compared with those obtained from Hildebrand's semiempirical approach at 298.15 K, and the partial molal volumes of the gases in the solution are found.

Introduction

Solubility measurements of nonpolar gases in liquids are of great interest not only for practical applications but also for the theoretical study of liquids. This paper continues a study of nonpolar gas solubilities in aliphatic halogenated compounds (*1*).

No general method exists for rigorous gas solubility predictions. Hildebrand's semiempirical approach (*2*), adapted by Prausnitz (*3*, *4*) to gas-liquid solubilities, is the first method that gives an acceptable result, with certain limitations. Other treatments with a sounder theoretical base have since been proposed, for example, Pierotti's theory (*5*) or perturbation methods (*6*-*8*). There are also empirical treatments such as de Ligny (*9*) or UNIFAC (*10*).

We report the solubility measurements of several nonpolar gases (H_2, D_2, N_2, O_2, CH_4, C_2H_4, C_2H_6, CF_4, SF_6, and CO_2) in bromocyclohexane between 263.15 and 303.15 K at a gas partial pressure of 101.32 kPa, and we deduce thermodynamic functions of the solution process from the experimental results. The volume change on mixing for a dissolved gas is an important thermodynamic property, yet only a few workers have given experimental values for the partial molal volumes of gases dissolved in liquids, and these are of limited accuracy. Hildebrand's semiempirical approach is used to estimate these partial molal volumes.

Experimental Section

The solubility apparatus has been described in detail elsewhere (*11*, *12*). It is based on that proposed by Ben Naim and Baer (*13*). It is lodged in an air thermostatic bath whose temperature is controlled within ±0.1 K and essentially consists of a buret system, a Hg manometer, and a solution vessel. This vessel is thermostated in a water bath whose temperature is maintained to ±0.02 K. The mole fraction of the dissolved gas is estimated from both the volume change at constant pressure of saturated gas in the burets and the mass of liquid in the solution vessel, determined by weighing. We assume that the solvent mole fraction in the gas phase is that corresponding to the vapor pressure of bromocyclohexane. Also, we assume ideal behavior of the saturated gas.

Estimated experimental uncertainty is less than 1% for gases of moderate solubility (*1*, *11*). For gases more distant from ideality, such as SF_6 or C_2H_6, the uncertainty is less than 2%.

The gases used were SEO (Sociedad Española del Oxígeno) except for CF_4, which was J.T. Baker. The mole percentage purities were H_2, 99.99%; D_2, 99.4%; N_2, 99.998%; O_2, 99.98%; CH_4, 99.95%; C_2H_4, 99.90%; C_2H_6, 99.0%; CF_4, 99%; SF_6, 99.5%; and CO_2, 99.998%.

The solvent was bromocyclohexane (Fluka, >98%). Its purity was checked by GLC (purity found >99%) and by refractive index measurements [experimental $n_D(293.15) = 1.4957$, literature (*14*) $n_d(293.15) = 1.4954$].

Solvent vapor pressure was determined by us, and in this temperature range it fits the equation

$$\ln P/\text{kPa} = -(5.7143 \times 10^3)T^{-1} + 18.2730 \qquad (1)$$

The density of bromocyclohexane was also measured in the range 263.15-303.15 K and fits the following equation well:

$$\rho/\text{kg·m}^{-3} = -1.222T + 1.693 \times 10^{-3} \qquad (2)$$

Results and Discussion

Table I gives our experimental data on the solubility of gases in bromocyclohexane between 263.15 and 303.15 K, when the gas partial pressure is 101.32 kPa.

Solubility in mole fraction (x_2) as a function of temperature, was fitted by least squares to an equation of the form

$$\ln x_2 = a + b/T + c \ln T \qquad (3)$$

The parameters a, b, and c are given in Table I.

With these parameters, the changes in thermodynamic properties Gibbs energy, $\Delta\bar{G}°$; enthalpy, $\Delta\bar{H}°$; and entropy, $\Delta\bar{S}°$, for the hypothetical solution process

$$\text{y(gas, 101.32 kPa)} \rightarrow \text{y(sol,} x_2 = 1)$$

were calculated. For this purpose, eq 4, 5, and 6, given in ref *15*, and eq 3 were used:

$$\Delta\bar{G}° = -RT \ln x_2(\text{sat}) = -RT(a + b/T + c \ln T) \qquad (4)$$

$$\Delta\bar{H}° = RT(\partial \ln x_2(\text{sat})/\partial \ln T) = R(-b + cT) \qquad (5)$$

$$\Delta\bar{S}° = R[(\partial \ln x_2(\text{sat})/\partial \ln T) + \ln x_2(\text{sat})] = R(a + c + c \ln T) \qquad (6)$$

where R is the gas constant and x_2(sat) refers to a solution in equilibrium with gaseous y.

Hildebrand entropy of solution, ΔS_H, defined as the change in entropy for the process

$$\text{y(ideal gas, 101 kPa)} \rightarrow \text{y(sol,} x_2)$$

was also calculated by means of the equation (*15*)

$$\Delta\bar{S}_H = R(\partial \ln x_2/\partial \ln T)_{\text{sat},P} = R(-b/T + c) \qquad (7)$$

The results thus obtained for 298.15 K are given in Table II.

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Table I. Solubility of Gases (10^4x_2) in Bromocyclohexane at 101.32 kPa Partial Pressure of Gas between 263.15 and 303.15 K and Coefficients of the Equation $\ln x_2 = a + b/T + c \ln T$

	T/K					parameter		
gas	263.15	273.15	283.15	293.15	303.15	a	b	c
H_2	1.91	2.09	2.29	2.49	2.68	-6.4840	-660.6356	0.0770
D_2	2.03	2.21	2.39	2.57	2.76	-8.1281	-529.2115	0.2934
N_2	3.61	3.77	3.93	4.10	4.28	-15.0812	22.9199	1.2681
O_2	7.42	7.47	7.54	7.59	7.70	-13.4474	206.6357	0.9790
CH_4	25.2	23.9	22.8	21.9	21.1	-13.6519	623.0242	0.9509
C_2H_4	209	176	151	131.7	115.6	-17.0486	1545.9236	1.3105
C_2H_6	283	235	199	169	147	-16.1328	1628.4908	1.1445
CF_4	3.88	4.01	4.12	4.23	4.33	-6.2045	-252.3418	-0.1237
SF_6	25.3	23.4	21.9	20.6	19.5	-15.7884	855.0286	1.1771
CO_2	162	135.5	114.7	98.4	85.7	-16.3539	1654.9720	1.1017

Table II. Gibbs Energies, Enthalpies, and Entropies of Solution of Gases in Bromocyclohexane at 298.15 K and 101.32 kPa Partial Pressure of Gas

gas	$\Delta G°$/kJ·mol^{-1}	$\Delta H°$/kJ·mol^{-1}	$\Delta S°$/kJ·mol^{-1}·K^{-1}	ΔS_H/kJ·mol^{-1}·K^{-1}
H_2	20.48	5.99	-0.049	0.020
D_2	20.40	5.38	-0.050	0.018
N_2	19.28	2.94	-0.055	0.010
O_2	17.79	0.83	-0.057	0.003
CH_4	15.23	-2.71	-0.060	-0.009
C_2H_4	10.90	-9.44	-0.068	-0.032
C_2H_6	10.29	-10.56	-0.070	-0.035
CF_4	19.23	1.91	-0.058	0.006
SF_6	15.40	-4.05	-0.065	-0.014
CO_2	11.63	-10.35	-0.074	-0.035

Table III. Partial Molal Volumes of Gases at 298.15 K Obtained by Means of Eq 9 and Prausnitz Partial Molar Volumes

	V_2/cm^3·mol^{-1}	
gas	eq 9	Prausnitz
H_2	35	60.9
N_2	32.4	65.2
O_2	33.0	56.2
CH_4	52.0	62.2
C_2H_4	65.0	66.7
C_2H_6	70.0	71.3
CF_4		81.6
SF_6		97.4
CO_2	55.0	56.5

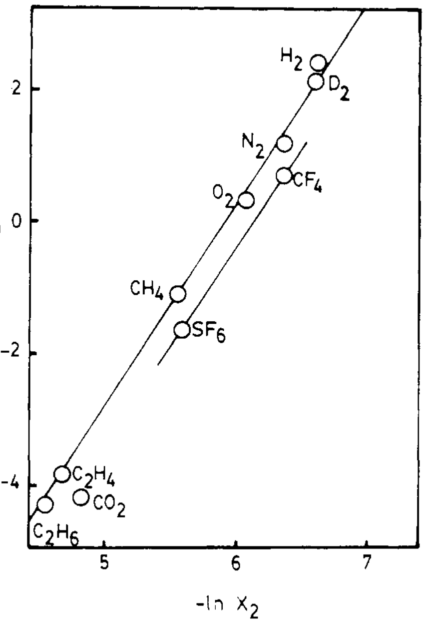

Figure 1. Plot of $(\partial \ln x_2/\partial \ln T)$ for the gases in bromocyclohexane at 298.15 K vs $-\ln x_2$ to evaluate the Δ parameter.

Table IV. $-\ln x_2$ According to Hildebrand's Theory at 298.15 K

gas	$(-\ln x_2)_{V_2}$[a]	$(-\ln x_2)_{V_2}$[b]	$(-\ln x_2)_{\mathrm{exptl}}$[c]
H_2	8.304	7.511	8.261
N_2	10.415	7.877	7.779
O_2	8.334	7.209	7.176
CH_4	6.522	6.289	6.144
C_2H_4	4.665	4.643	4.397
C_2H_4	4.318	4.301	4.140
CF_4	7.609		7.756
SF_6	6.234		6.214
CO_2	4.884	4.885	4.692

[a] $-\ln x_2$ with the V_2 evaluated by us according to eq 9. [b] $-\ln x_2$ with Prausnitz's V_2. [c] Experimental $-\ln x_2$.

The experimental solubilities were compared with those obtained from the regular solution theory for gas-liquid solutions (*3*, *4*). It comes from the combination of two concepts, the idea of corresponding states and that of regular solution.

For gas solubility the theory gives (*16*, *17*)

$$-\ln x_2 = \ln f_{2,1} + \frac{V_2(\delta_1 - \delta_2)^2}{RT}\Phi_1^2 \qquad (8)$$

x_2 is the mole fraction of gas in a saturated solution, and $f_{2,1}$ is the fugacity of solute as a hypothetical liquid at 101.32 kPa, evaluated from the Prausnitz plots (*3*).

V_2 is the partial molal volume of solute as a hypothetical liquid. It can be evaluated (*18*-*20*) by means of the equation

$$V_2 = \frac{-(\Delta - 1)}{(\partial P/\partial T)_v} R \ln x_2 + V_{2,b} \qquad (9)$$

where $V_{2,b}$ is the molar volume of the solute at its boiling temperature, $(\partial P/\partial T)_v$ can be calculated from the isobaric expansion and the isothermic compressibility coefficients, and $(\Delta - 1)$ is a simple entropy expansion term (*18*). The parameter Δ can be evaluated from the experimental $(\partial \ln x_2/\partial \ln T)$ vs $-\ln x_2$ plot; see Figure 1. The partial molal volumes thus calculated are given in Table III together with those reported by Prausnitz (*3*, *18*).

δ_1 and δ_2 are the solubility parameters of solvent and solute respectively. δ_1, the solubility parameter of bromocyclohexane, was obtained from ref *16*.

$$\delta_1 = \{(\Delta H_{\mathrm{vap}} - RT/V°_1\}^{1/2}$$

ΔH_{vap} and $V°_1$ were evaluated from their vapor pressure and density measurements, respectively. The value found was δ_1 = 19 137 (J·m^{-3})$^{1/2}$. δ_2, solubility parameters of the gases, were taken from the literature (*3*, *18*). For CF_4 and SF_6 we have used average values deduced from experimental solubility of each gas in other solvents (*12*, *21*): $\delta_2(CF_4)$ = 9405 (J·

$m^{-3})^{1/2}$; $\delta_2(SF_6) = 9916\ (J{\cdot}m^{-3})^{1/2}$. Finally, Φ_1 is the molar volume fraction of solvent, which for very dilute solutions approaches unity (17).

The solubilities obtained from eq 8 at 298.15 K are given in Table IV. We give two series of evaluated values: (a) solubilities evaluated with the partial molal volumes, from eq 9, and (b) solubilities evaluated with the Prausnitz partial molal volumes. We also give a series of experimental solubilities. We can see that for H_2, N_2, and O_2 the solubilities are quite different, while they are similar for the rest of gases; the same behavior is found in the study of solubilities of nonpolar gases in chlorocyclohexane (1).

If we compare the results for the solubilities of gases in bromocyclohexane (Table I) with the solubilities of the same gases in chlorocyclohexane given in a previous work (1), we observe that the solubilities of all the gases are greater with chlorinated solvents than brominated solvents. The difference fluctuates between 12% for C_2H_4 and C_2H_6 and >40% for the fluorinated gases. Likewise, we can see that the solubilities of these gases in the two liquids are considerably lower than in cyclohexane (22).

The solubilities of nonpolar gases in these liquids are in inverse order to the vaporization enthalpies of liquids. This agrees with the predictions of eq 8 and with the biggest intermolecular interactions in the sequence cyclohexane > chlorocyclohexane > bromocyclohexane.

Registry No. H_2, 1333-74-0; D_2, 7782-39-0; N_2, 7727-37-9; O_2, 7782-44-7; CH_4, 74-82-8; C_2H_4, 74-85-1; C_2H_6, 74-84-0; CF_4, 75-73-0; SF_6, 2551-62-4; CO_2, 124-38-9; bromocyclohexane, 108-85-0.

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Dynamic Viscosity of Mixtures of Benzene, Ethanol, and *n*-Heptane at 298.15 K

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Experimental dynamic viscosities and densities are reported for the binary and ternary mixtures of benzene, ethanol, and *n*-heptane at 25 °C. The data are correlated with the generalized corresponding states method of Teja and Rice by treating the ternary system as pseudobinary and by using only binary information. A van Laar type mixing rule is used for the pseudocritical temperature of the binary mixtures. Experimental and calculated viscosities for the ternary system are in satisfactory agreement.

Introduction

The viscosities of multicomponent liquid mixtures are required in many chemical engineering calculations involving fluid flow, heat transfer, and mass transfer. It is impractical to measure viscosities at all external conditions of interest, and thus, methods for the estimation of viscosities of multicomponent mixtures are not only of theoretical but also of great practical interest. Such a method is the generalized corresponding states (GCS) method of Teja and Rice, (1) which has been successfully applied to the viscosity of binary liquid mixtures. The method can in principle be extended to multicomponent mixtures by using only binary data. Teja et al. (2) have used the GCS method, even, for the estimation of the viscosity of undefined liquid mixtures. Testing of this method and similar methods requires consistent experimental data for the viscosities of pure components, of their binaries, and of their multicomponent mixtures. In this work we are reporting such data for a highly nonideal system containing one associated component, ethanol, one inert solvent, *n*-heptane, and one active aromatic component, benzene. In a previous work (3) we reported similar data for the system containing acetone, isooctane, and toluene. The two sets of data are used for testing the "predictive" character of the GCS method of Teja and Rice (1).

Table I. Properties of Pure Liquids at 25 °C

	ρ, g/cm^3		η, cP	
liquid	exptl	lit.	exptl	lit.
benzene	0.873 47	0.8737[a]	0.6048	0.6028,[e] 0.606[f]
ethanol	0.785 09	0.7852[b]	1.0832	1.0812[b]
n-heptane	0.679 62	0.6810,[c] 0.680[d]	0.3870	0.386,[e] 0.3967[g]

[a] Reference 8. [b] Reference 9. [c] Reference 4. [d] Reference 10. [e] Reference 11. [f] Reference 12. [g] Reference 13.

Experimental Section

Materials. All pure liquids used in this work were pro analysi grades from MERCK. Their purity was determined by GL

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