R_k, Q_k	UNIFAC volume and area parameter for group k
R	gas constant
R_l	alkyl chain
T	absolute temperature in Kelvin
T_0	reference temperature, usually 298.15 K
v_i^L	liquid molar volume of component i
x,y	nonalkyl UNIFAC groups on a molecule
x_i, y_i	equilibrium liquid- and vapor-phase mole fraction of component i

Greek Letters

δ_{12}	$=2B_{12} - B_{11} - B_{22}$
γ_i^∞	activity coefficient at infinite dilution of component i
ϵ_i^∞	vapor-phase correction
$\nu_k^{(i)}$	coefficient of group k in component i
θ_m	area fraction of group m in a mixture of components
Ψ_{nm}	$=\exp(-a_{nm}/T)$

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Solubility of Nonpolar Gases in Halogenated Compounds. 3. Solubility of Helium, Neon, Argon, Krypton, and Xenon in Chlorocyclohexane and Bromocyclohexane at 263.15–303.15 K and 101.32-kPa Partial Pressure of Gas

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Solubility measurements of noble gases in chlorocyclohexane and bromocyclohexane in the temperature range 263.15–303.15 K and 101.32-kPa partial pressure of gas are reported. Thermodynamic functions for the solution process (Gibbs energy, enthalpy, and entropies) are evaluated. With the Pierotti method, Lennard-Jones 6,12 pair potential parameters for these solvents were determined. For this purpose, we also used the solubilities of ten other nonpolar gases in the same solvents, measured by us, the results of which also appeared in this journal.

Introduction

This study is a continuation of our work on gas solubilities in halogenated solvents (*1*, *2*). We report the solubilities of He, Ne, Ar, Kr, and Xe at 263.15-303.15 K and 101.32-kPa partial pressure of gas in chlorocyclohexane and bromocyclohexane solvents and their thermodynamics properties. In previous papers, we reported the solubilities of the 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 the same solvents, with the same temperature interval and partial molar pressure of gases.

We are interested in the influence of the halogen atom (Cl, Br) of the solvent molecule on the solubility of gases. For this purpose, we compare these results with the experimental solubilities of nonpolar gases in cyclohexane (*3*). Likewise, through a theoretical treatment, it is possible to estimate pair potential parameters for solvent molecules with use of the scaled particle theory (SPT) (*4*). The Pierotti method is an application of SPT to the solubility of gases in liquids; Morel-Desrosiers (*5*) showed that it is coherent to use it for determining the intermolecular potential distance and energy parameters, particularly if they are going to be used to predict the solubility of gases.

We have calculated these parameters by application of the Pierotti method (*4*, *6*) to the solubility of 15 nonpolar gases in chlorocyclohexane and bromocyclohexane, and from them, we have calculated the solubility of gases in these solvents with the objective of comparing the theoretical and experimental results.

Experimental Section

The method used for the solubility measurements was identical with that described earlier (*1*, *2*, *7*). The solvents were chlorocyclohexane (Merck) and bromocyclohexane (Fluka); their purity, >98.5%, was checked by GLC and refraction measurements (*1*, *2*). The gases used were He (99.995%), Ar (99.9990%), Kr (99.95%), and Xe (99.995%), all of them SEO (Sociedad Española del Oxígeno S.A.), and Ne (99.9%) (Baker).

The mole fraction of the dissolved gases 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.

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Table I. Solubility of Gases (10^4x_2) in Chlorocyclohexane and Bromocyclohexane at 101.32-kPa Partial Pressure of Gas between 263.15 and 303.15 K[a]

	10^4x_2								
gas	263.15 K	273.15 K	283.15 K	293.15 K	303.15 K	a	b	c	10^3s
				Chlorocyclohexane					
He	0.545	0.626	0.727	0.829	0.942	-17.3661	-599.8243	1.7629	5
Ne	0.829	0.946	1.064	1.186	1.331	-11.7038	-687.1104	0.8825	5
Ar	10.88	10.81	10.76	10.74	10.69	-8.7715	110.7268	0.2740	1
Kr	44.7	41.3	38.6	36.3	34.0	-7.7923	533.8738	0.0495	2
Xe	269	230	199	174	152	-1.3879	856.2471	-0.9836	1
				Bromocyclohexane					
He	0.427	0.502	0.592	0.687	0.802	-25.4179	-399.4557	3.0275	6
Ne	0.649	0.741	0.839	0.945	1.065	-17.1748	-505.3509	1.6960	3
Ar	8.89	8.92	8.94	8.95	8.97	-7.0381	-14.0655	0.0120	0
Kr	37.7	35.1	32.9	31.1	29.5	-13.5954	749.7196	0.9268	1
Xe	248	211	182	158	140	-12.3215	1362.8443	0.6427	1

[a] Coefficients of the equation $\ln x_2 = a + b/T + c \ln T$ and standard deviations (10^3s) as defined in the text.

Solvent vapor pressures were determined by us, and in our temperature interval (263.15–303.15 K), they fit the following equations well:

$$\ln [(P/\mathrm{kPa})(C_6H_{11}Cl)] = -(5.2407 \times 10^3)T^{-1} + 13.0680 \quad (1)$$

$$\ln [(P/\mathrm{kPa})(C_6H_{11}Br)] = -(5.7143 \times 10^3)T^{-1} + 18.2730 \quad (2)$$

The solvent density (chlorocyclohexane and bromocyclohexane) was also measured in our temperature interval and fitted to the following equations:

$$[\rho/(\mathrm{kg{\cdot}m^{-3}})](C_6H_{11}Cl) = -0.9770T + 1.286 \times 10^3 \quad (3)$$

$$[\rho/(\mathrm{kg{\cdot}m^{-3}})](C_6H_{11}Br) = -1.222T + 1.693 \times 10^3 \quad (4)$$

Results and Discussion

Table I gives our experimental data on the solubility of gases in chlorocyclohexane and 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

$$\ln x_2 = a + b/T + c \ln T \quad (5)$$

Parameters a, b, and c and standard deviations

$$s = \{\textstyle\sum(\ln x_2 - a - b/T - c \ln T)/(n - 3)\}^{1/2}$$

are also given in Table I.

With these parameters, the changes in partial molal thermodynamic properties: Gibbs energy, $\Delta G°$, enthalpy, $\Delta H°$, and entropy, $\Delta S°$, for the hypothetical solution process

$$\mathrm{y}(\text{gas, 101.32 kPa}) \rightarrow \mathrm{y}(\text{sol}, x_2 = 1) \quad (6)$$

were calculated. For this purpose, the following equations (*8*) and eq 5 were used

$$\Delta G° = -RT \ln x_2(\text{sat.}) = -RT(a + b/T + c \ln T) \quad (7)$$

$$\Delta H° = RT(\partial \ln x_2(\text{sat.})/\partial \ln T) = R(-b + cT) \quad (8)$$

$$\Delta S° = R\,[(\partial \ln x_2(\text{sat.})/\partial \ln T) + \ln x_2(\text{sat.})] = R\,(a + c + c \ln T) \quad (9)$$

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

The Hildebrand entropy of solution, ΔS_{H}, defined as the change in entropy for the process

$$\mathrm{y}(\text{ideal gas, 101 kPa}) \rightarrow \mathrm{y}(\text{sol}, x_2) \quad (10)$$

was also calculated by means of the equation (*8*)

$$\Delta S_{\mathrm{H}} = R(\partial \ln x_2/\partial \ln T)_{\text{sat.},P} = R(-b/T + c) \quad (11)$$

Table II. Gibbs Energies, Enthalpies, and Entropies of Solution of Gases in Chlorocyclohexane and 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})
		Chlorocyclohexane		
He	23.14	9.36	-0.046	0.031
Ne	22.26	7.90	-0.048	0.026
Ar	16.95	-0.24	-0.058	-0.001
Kr	14.01	-4.48	-0.062	-0.015
Xe	10.21	-9.56	-0.066	-0.032
		Bromocyclohexane		
He	23.57	10.83	-0.042	0.036
Ne	22.82	8.41	-0.048	0.028
Ar	17.39	0.15	-0.057	0.000
Kr	14.38	-3.94	-0.061	-0.013
Xe	10.44	-9.45	-0.066	-0.031

Table III. Smoothed Values of Experimental Solubilities of Gases (10^4x_2) in Chlorocyclohexane (Table I, Reference 1) and Bromocyclohexane (Table I, Reference 2) and Experimental Solubilities of Gases in Cyclohexane (*3*) at 293.15 K and 101.32-kPa Partial Pressure of Gas

gas	$C_6H_{11}Cl$	$C_6H_{11}Br$	C_6H_{12}
He	0.881	0.743	1.217
Ne	1.26	1.00	1.792
Ar	10.7	8.96	14.80
Kr	35.1	30.3	46.68
Xe	162	148	202.9
H_2	2.99	2.58	4.142
D_2	3.07	2.66	
N_2	5.31	4.18	7.61
O_2	9.22	7.65	12.48
CH_4	24.9	21.5	32.75
C_2H_4	138	123	
C_2H_6	178	158	235.9
CF_4	6.08	4.28	10.34
SF_6	29.3	20.0	54.19
CO_2	108	91.7	76.0

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

In Table III, we present the interpolated values of the solubilities of noble gases in chlorocyclohexane and bromocyclohexane together with those of other nonpolar gases in the same solvents (*1*, *2*) and the solubilities of the gases in cyclohexane (*3*) at 298.15 K. We can see that the solubilities increase in the order

$$C_6H_{11}Br < C_6H_{11}Cl < C_6H_{12}$$

the differences between the halogenated solvents and cyclohexane being considerable in all the systems except for CO_2. This can be attributed to an interaction between halogen and carbon dioxide.

Table IV. Polarizability, α_2, Hard-Sphere Diameter, σ_2, and Energy Parameter, ϵ_2/k, of the Gases at 298.15 K (*12*)

	$10^{10}\sigma_2$/m	(ϵ_2°/k)/K	$10^{30}\alpha_2$/m^3
He	2.63	6.03	0.204
Ne	2.79	35.7	0.393
Ar	3.41	122	1.63
Kr	3.67	169	2.46
Xe	3.96	217	4.00
H_2	2.87	29.2	0.80
D_2	2.87	31.1	0.79
N_2	3.70	95	1.73
O_2	3.46	118	1.56
CH_4	3.70	157	2.70
C_2H_4	4.07	230	3.19
C_2H_6	4.38	236	4.33
CF_4	4.66	134	2.86
SF_6	5.51	201	4.48
CO_2	3.94	195	2.59
hard sphere		2.58	0

The same order is observed in the analogous aromatic solvent series

$$C_6H_5Br\ (9,\ 10) < C_6H_5Cl\ (9,\ 10) < C_6H_6\ (3)$$

but the differences between the solubilities of halogenated and nonhalogenated compounds in the cyclohexane series are higher.

Using the experimental solubilities, intermolecular potential parameters, and polarizability of gases (see Table IV (*11*)) and the necessary properties of liquids (dipole moments (*12*)) and molar volumes (V_1°), we can calculate the Lennard-Jones 6,12 pair potential parameters for the solvent.

The detailed application of the scaled particle theory to the solubility of gases in liquids, developed by Pierotti, is widely explained in the literature (*4*, *6*, *13*, *14*, *15*, *16*). This method implies the calculation of the Henry's law constant at zero polarizability of gases; this can be done by extrapolating the solubilities of the noble gases (spheres) at zero polarizability. In $K_{H,0}$ proves to be 9.76 for $C_6H_{11}Cl$ and 9.96 for $C_6H_{11}Br$.

The distance parameters can be evaluated by means of the equation

$$RT \ln K_{H,0} = G_c + RT \ln (RT/V_1^\circ) \tag{12}$$

where G_c is the partial molal Gibbs energy necessary to create a cavity of the same size as the solute molecule in the solvent and can be evaluated by a method deduced by Reiss (*17*); the value of G_c depends on the solvent density and the distance parameters of solute and solvent, so we can deduce the latter, σ_1. The values found are as follows:

$$\sigma_1(C_6H_{11}Cl) = 5.45 \times 10^{-10}\ \mathrm{m}$$

and

$$\sigma_1(C_6H_{11}Br) = 6.06 \times 10^{-10}\ \mathrm{m}$$

Once the distance parameter is known and by means of the fundamental equation

$$RT \ln K_H = G_c + G_i + RT \ln (RT/V_1^\circ) \tag{13}$$

the energy parameter ϵ_2 can be evaluated.

G_i is the partial molal energy of interaction between solute and solvent and consists of two terms, a dispersion term and an induction term:

$$G_i = G_{i,\mathrm{dis}} + G_{i,\mathrm{ind}} \tag{14}$$

$$G_{i,\mathrm{dis}} = -3.555\pi\rho R\sigma_{12}^3(\epsilon_1/k)^{1/2}(\epsilon_2/k)^{1/2} \tag{15}$$

ρ is the density number of the solvent and ϵ_1/k and ϵ_2/k the energy parameters of solvent and solute, respectively.

$$G_{i,\mathrm{ind}} = -1.333\pi\rho N_A(\mu_1^2\alpha_2/\sigma_{12}^3) \tag{16}$$

where μ is the solvent dipole moment and α_2 the polarizability of gases.

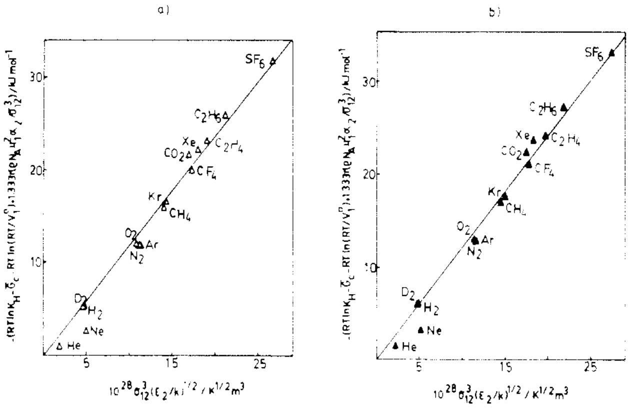

Figure 1. Plot of the left-hand side of eq 17 against a Lennard-Jones distance parameter of nonpolar gases in (a) chlorocyclohexane and (b) bromocyclohexane.

Table V. Solubilities of Gases (10^4x_2) in Chlorocyclohexane and Bromocyclohexane at 298.15 K and 101.32-kPa Partial Pressure of Gas Evaluated by Pierotti's Method

gas	$C_6H_{11}Cl$	$C_6H_{11}Br$	gas	$C_6H_{11}Cl$	$C_6H_{11}Br$
He	1.25	1.06	O_2	15.4	13.8
Ne	3.82	3.38	CH_4	30.5	27.6
Ar	19.0	17.3	C_2H_4	114	104
Kr	40.1	36.8	C_2H_6	118	105
Xe	93.3	86.1	CF_4	6.59	5.17
H_2	2.69	2.34	SF_6	26.2	29.5
D_2	2.90	2.52	CO_2	58.2	53.0
N_2	6.52	5.57			

Equation 16 can be rewritten in the following form:

$$RT \ln K_H - G_c - RT \ln (RT/V_1^\circ) - 1.333\pi\rho N_A(\mu_1^2\alpha_2/\sigma_{12}^3) = G_{i,\mathrm{dis}} = -3.555\pi\rho R\sigma_{12}^3(\epsilon_1/k)^{1/2}(\epsilon_2/k)^{1/2} \tag{17}$$

When the left-hand side of eq 17 is plotted against $(\epsilon_2/k)^{1/2}\sigma_{12}^3$ for each gas, a straight line will be obtained, whose slope allows us to estimate the energy parameter for a solvent. Figure 1 shows this plot for (a) $C_6H_{11}Cl$ and (b) $C_6H_{11}Br$. The values of the energy parameters are

$$(\epsilon_1/k)(C_6H_{11}Cl) = 664\ \mathrm{K}$$

and

$$(\epsilon_1/k)(C_6H_{11}Br) = 707\ \mathrm{K}$$

Once σ_1 and ϵ_1/k are known, the calculations can be reversed to obtain the value of ΔG° and, therefore, the solubilities.

Table V gives the solubilities evaluated by Pierotti's method with these parameters; the agreement between the calculated and experimental solubilities is in many instances acceptable: Kr, H_2, D_2, N_2, CH_4, C_2H_4, C_2H_6, and fluorinated gases. However, for other gases like Ar and CO_2, these solubilities are in considerable disagreement. This behavior has been observed in other solvents (*15*, *18*, *19*, *20*).

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Isothermal Vapor–Liquid Equilibrium Data for Binary Systems at High Pressures: Carbon Dioxide–Methanol, Carbon Dioxide–Ethanol, Carbon Dioxide–1-Propanol, Methane–Ethanol, Methane–1-Propanol, Ethane–Ethanol, and Ethane–1-Propanol Systems

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Isothermal vapor–liquid equilibrium data for binary systems carbon dioxide–methanol, carbon dioxide–ethanol, carbon dioxide–1-propanol, methane–ethanol, methane–1-propanol, ethane–ethanol, and ethane–1-propanol were measured by a new static phase equilibrium apparatus at 313.4 and 333.4 K.

Introduction

Production of C_1 to C_6 alcohols from syngas is one of the most promising developments in C_1 chemistry. The reactions are

main reactions

$$n\mathrm{CO} + 2n\mathrm{H_2} \rightarrow \mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{OH} + (n-1)\mathrm{H_2O}$$

side reactions

$$n\mathrm{CO} + (2n+1)\mathrm{H_2} \rightarrow \mathrm{C}_n\mathrm{H}_{2n+2} + n\mathrm{H_2O}$$

$$\mathrm{CO} + \mathrm{H_2O} \rightleftharpoons \mathrm{CO_2} + \mathrm{H_2}$$

And as a result, the separation of the ten-component system, H_2, CO, CO_2, CH_4, C_2H_6, C_3H_8, H_2O, CH_3OH, C_2H_5OH, and C_3H_7OH, becomes important in process design. Although there are much data available in some literature for the binary components of the system, little or no data exist at the conditions of interest for the CO_2–alcohol binaries, methane–alcohol binaries, and ethane–alcohol binaries. Furthermore, no multicomponent phase equilibria data exist for the above mentioned multicomponent system at any conditions.

In this work, we report on the design of a new static phase equilibrium apparatus and also report isothermal high-pressure vapor–liquid equilibrium data for the CO_2–methanol, CO_2–ethanol, CO_2–1-propanol, methane–ethanol, methane–1-propanol, ethane–ethanol, and ethane–1-propanol systems in the 313–333 K temperature range.

Experiment

Apparatus. The vapor–liquid equilibrium apparatus is shown in Figure 1 and was designed to accommodate the ten-component system. It is a static type of apparatus in which the coexisting phases are recirculated, sampled, and analyzed.

The apparatus is made up of two sections: (i) an equilibration section that consists of an equilibrium cell, 1, enclosed in an air bath, 23, at the temperature of interest and (ii) an analysis section that consists of a homogenizing system enclosed by an air bath, 24, kept at a temperature much greater than the equilibrium temperature. The air bath of each section was controlled to ±0.1 K by a Pt sensor PID controller (REX-C1000, REK Co.). The temperature in the equilibrium cell could be measured by a platinum resistance probe (Shimaden SD-10) with digital readout to ±0.1 K. Pressure in the equilibrium cell could be measured by either a Bourdon gauge (GP35, Nagano Co.), 0–250 kg/cm^2 marked in 0.5 divisions, or a $4^1/_2$ digital gauge, 0–200 kg/cm^2 (GC-11, Nagano).

Equilibrium Cell. The equilibrium cell consisted of a two-piece autoclave with a titanium delta-ring and was designed to carry a maximum pressure of 25 MPa at 453 K. Three pairs of diametrically opposed windows of 12-mm o.d. with Vespal gaskets (Du Pont Co.) allowed viewing of the sample and liquid level. Further details of the cell design are given in Figure 2.

Sampling Valves. Details of the sampling valves are given in Figures 3 and 4. Each was constructed from 316-type stainless steel and consisted of two pairs of two-way valves placed at 90° angles from each other and two holes in the body that allowed for heating with cartridge heaters. The internal volume of the liquid sampler was 0.75 cm^3. The internal volume of the vapor sampler could be varied from 1 to 10 cm^3 by manually changing a stainless steel insert.

Chromatograph Arrangement. The gas chromatographs (Shimadzu GC-8A) were fitted with thermal conductivity detec-

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