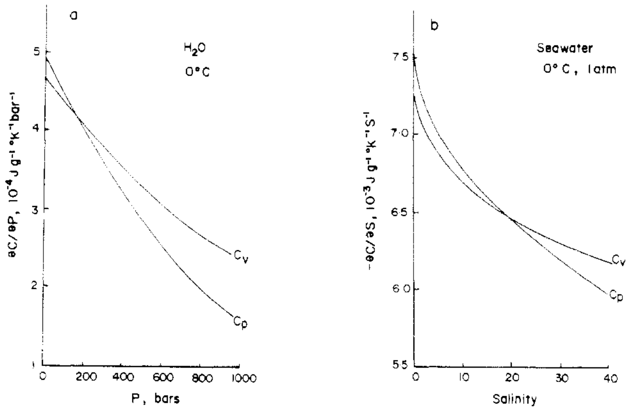

Figure 3. Plots of (a) $\partial C_p/\partial P$ and $\partial C_v/\partial P$ for pure water at 0 °C, and (b) $\partial C_p/\partial S$ and $\partial C_v/\partial S$ vs. salinity for seawater at 0 °C and 1 atm.

to within ±0.026% over the measurement ranges of 20–100 °C and up to 500 bar.

Glossary

C_p	specific heat capacity at constant pressure, J g^{-1} K^{-1}
C_v	specific heat capacity at constant volume, J g^{-1} K^{-1}
J	joules
P	absolute pressure
T	absolute temperature, K
t	temperature, °C
V	specific volume

Registry No. H_2O, 7732-18-5.

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Solubility of Nonpolar Gases in Halogenated Compounds. 1. 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 Chlorocyclohexane at 263.15–303.15 K and 101.32 kPa of Partial Pressure of Gas

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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 chlorocyclohexane have been determined from 263.15 to 303.15 K at a partial pressure of gas of 101.32 kPa. Experimental results are compared with those obtained from Hildebrand's semiempirical approach. Partial molal Gibbs energy, partial molal enthalpy, and partial molal entropies of solution at 298.15 K and 101.32 kPa of partial pressure of gas are evaluated.

Introduction

As is well-known, gas solubility in liquids plays an important role both from the theoretical and the practical point of view. In fact, it is a suitable base for studying liquid structure and for characterizing molecular interactions.

This paper is a part of a more extensive study of solubility of nonpolar gases in halogenated derivatives of benzene and cyclohexane. We report here 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 chlorocyclohexane between 263.15 and 303.15 K, at a partial pressure of gas of 101.32 kPa. Similar experimental measurements on other systems, together with a more detailed discussion of them, will be presented in subsequent papers.

Experimental Section

The solubility apparatus, similar to that used by Ben Naim and Baer (*1*) was housed in a thermostat within ±0.1 K. Its detailed

Table I. Experimental Solubility of Gases (10^4x_2) in Chlorocyclohexane, 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							
gas	263.15	273.15	283.15	293.15	303.15	a	b	c
H_2	2.26	2.45	2.66	2.89	3.10	−13.9505	−297.6	1.1994
D_2	2.35	2.53	2.75	2.96	3.18	−15.8478	−191.6	1.4745
N_2	4.71	4.87	5.06	5.23	5.38	−7.3582	−238.7	0.1083
O_2	9.07	9.10	9.13	9.18	9.26	−12.9610	219.6	0.9189
CH_4	29.6	27.9	26.5	25.4	24.4	−16.7210	784.7	1.4202
C_2H_4	237	200	171	148	129	−11.6539	1348.0	0.5004
C_2H_6	321	267	224	192	166	−15.2763	1606.8	1.0284
CF_4	5.88	5.93	5.98	6.05	6.13	−14.1898	217.8	1.0627
SF_6	39.1	35.7	32.7	30.4	28.4	−16.3507	995.0	1.2605
CO_2	197	163	137	117	101	−15.3774	1608.8	0.9575

description is made elsewhere (*2*). The reliability of the experimental method is demonstrated by comparing our results for Ar + H_2O (*2*) with those obtained by Battino and Clever for the same mixture at 292.85 and 298.85 K (*3*). Both sets of values differ only by about 0.3 and 0.7% respectively. Comparison is also made in the same paper (*2*) of our data for He + and SF_6 + *p*-xylene with those obtained by Byrne et al. (*4*) at 298.15 K; for these less favorable systems the deviations were 2.3 and 1.6%, respectively.

The chlorocyclohexane used was Merck (better than 98 mol %); its purity was checked by GLC and by refractive index measurements (experimental $n_D(293.15) = 1.4626$; literature, 1.4619 (*5*)). GLC analysis gave actually a purity of better than 98.5 mol % and showed also that the main impurity (0.4 mol %) was cyclohexane. Since gas solubility in the latter differs not very much from that in chlorocyclohexane, we used the commercial product without further purification.

All the gases were used directly from their tanks. They were from Sociedad Española del Oxígeno, except for CF_4 which was from J. T. Baker; their purities (in mole percent) 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.

Results and Discussion

Table I contains the experimental solubilities in chlorocyclohexane in terms of molar fraction (10^4x_2), between 263.15 and 303.15 K and at partial pressure p_2 = 101.32 kPa. The solubility measurements were carried out on the saturated gases. Density and vapor pressure of the solvent were also measured by us at several temperatures between 263.15 and 303.15 K; the results for both properties are well reproduced by the equations

$$\rho = -9.770 \times 10^{-4}T + 1.2856 \qquad (1)$$

$$\ln P = -5240.7T^{-1} + 13.07 \qquad (2)$$

respectively (P/kPa, T/K).

The results for x_2 (101.32 kPa, T) were fitted to the equation

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

The values of the constants a, b, and c are also given in Table I.

Partial molal Gibbs energy $\Delta\bar{G}^\circ$, partial molal enthalpy $\Delta\bar{H}^\circ$, partial molal entropy $\Delta\bar{S}^\circ$, and partial molal Hildebrand's entropy $\Delta\bar{S}_H$ (Table II) were calculated by means of (see ref *6*)

$$\Delta\bar{G}^\circ = -RT \ln x_2 \qquad (4)$$

$$\Delta\bar{H}^\circ = RT(\partial \ln x_2/\partial \ln T) \qquad (5)$$

$$\Delta\bar{S}^\circ = R(\partial \ln x_2/\partial \ln T + \ln x_2) \qquad (6)$$

$$\Delta\bar{S}_H = R(\partial \ln x_2/\partial \ln T) \qquad (7)$$

Table II. Partial Molal Gibbs Energy, Partial Molal Enthalpy, Partial Molal Entropy, and Partial Molal Hildebrand's Entropy of Solution, at 298.15 K and 101.32 kPa Partial Pressure of Gas

gas	$\Delta\bar{G}^\circ$/ kJ mol^{-1}	$\Delta\bar{H}^\circ$/ kJ mol^{-1}	$\Delta\bar{S}^\circ$/ kJ mol^{-1} K^{-1}	$\Delta\bar{S}_H$/ kJ mol^{-1} K^{-1}
H_2	20.12	5.45	−0.049	0.018
D_2	20.05	5.25	−0.050	0.018
N_2	18.69	2.25	−0.055	0.008
O_2	17.33	0.45	−0.057	0.002
CH_4	14.87	−3.00	−0.060	−0.010
C_2H_4	10.61	−9.98	−0.069	−0.033
C_2H_6	9.98	−10.81	−0.070	−0.036
CF_4	18.35	0.82	−0.059	0.003
SF_6	14.46	−5.15	−0.066	−0.017
CO_2	11.22	−11.00	−0.075	−0.037

Table III. Experimental and Calculated (Hilderbrand Theory) Results of 10^4x_2 at 298.15 K and 101.32 kPa Partial Pressure of Gas, and Partial Molal Volumes of Gases Evaluated from Eq 4

	10^4x_2		
gas	exptl	calcd	$\bar{V}_2$/ cm^3 mol^{-1}
H_2	2.99	3.07	54.3
N_2	5.31	4.65	
O_2	9.22	8.71	
CH_4	24.9	22.1	
C_2H_4	138	111	63.2
C_2H_6	178	159	68.2
CF_4	6.08	7.22	66.2
SF_6	29.3	30.1	84.9
CO_2	108	89.8	53.9

or, taking into account eq 3

$$\Delta\bar{G}^\circ = -RT(a + b/T + c \ln T) \qquad (8)$$

$$\Delta\bar{H}^\circ = R(-b + cT) \qquad (9)$$

$$\Delta\bar{S}^\circ = R(a + c + c \ln T) \qquad (10)$$

$$\Delta\bar{S}_H = R(-b/T + c) \qquad (11)$$

The experimental solubilities were compared with those obtained from the regular solution theory for gas–liquid solutions (*7*). The solubility parameter of the solvent δ_1 was evaluated from its enthalpy of vaporization. For all the gases, except for CF_4 and for SF_6, the solubility parameters were taken from ref *8*; for CF_4 and SF_6 we have used average values deduced from their solubility in cyclohexanone (*9*) and in dioxane (*10*); $\delta_2(CF_4) = 4.60$; $\delta_2(SF_6) = 4.85$.

The partial molal volumes of the gases in chlorocyclohexane were calculated from the equation (*11*)

$$(\bar{V}_2 - V_2^\circ)(\partial P/\partial T) = (\Delta - 1) R \ln x_2 \qquad (12)$$

where $(\bar{V}_2 - V_2^\circ)$ is the volume change associated with the mixing process, $(\partial P/\partial T)$ can be calculated from the thermal expansion and the isothermal compressibility coefficients of chlorocyclohexane, and Δ is the slope of experimental $R(\partial \ln x_2/\partial \ln T)$ vs. $-R \ln x_2$ plot, except for N_2, O_2, and CH_4 whose values were taken from the literature (*12*) as they lead to results in better agreement with the experimental ones.

In Table III, experimental and calculated results of $10^4 x_2$ at 298.15 K, and the partial molal volumes of the gases obtained from equation (*12*), are shown.

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; VF_4, 75-73-0; SF_6, 2551-62-4; CO_2, 124-38-9; chlorocyclohexane, 542-18-7.

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Transference Number Measurements in Aqueous Solutions at 25 °C. 3. Lithium Bromide

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Transference numbers for aqueous solutions of LiBr at 25 °C are determined by employing the direct moving-boundary method. Due to the hygroscopic character of this electrolyte, the value of the concentration for each of the solutions studied, with its most probable error included, is obtained from its experimental density. The corrected ionic transference numbers are optimized on the basis of their sum which must equal 1 at each concentration. From the "best" transference numbers thus obtained, C_{best} values are calculated which allow the direct determination of experimental values for such transference numbers that would be coincident with these best ones. The extrapolation to zero concentration of these transference numbers is done by using the 1963 Fuoss and Onsager equation and from such limiting values, $T_\pm^0$, the limiting equivalent conductance for the lithium ion, is also obtained. The density–concentration relationship found for these aqueous solutions of LiBr is also presented.

Introduction

In solutions of hygroscopic electrolytes, the knowledge of their concentration is usually accompanied by a high lack of precision that prevents an accurate calculation of the electrolyte magnitudes which depend on these concentrations as well as a rigorous analysis of their variation with that concentration. Nevertheless, in the case of transference numbers, this situation is not very problematic. In fact, if we take into account that this ionic parameter can be independently obtained for each of the ions present in the solution plus the fact that the sum of the transference numbers for all of these ions must equal 1 (from the definition of the transference number), we have an easy way to optimize the results and thus to minimize the errors derived from the use of that concentration value.

In the present paper we illustrate this assertion by presenting the transference numbers for both Li^+ and Br^- ions in aqueous solutions of LiBr at 25 °C. The hygroscopic character of the LiBr does not permit the preparation of their solutions by the most accurate method of weighing both solvent and solute, but instead uses stock solutions whose concentrations have to be determined by titration. The possibility of optimizing the value of such concentrations on the basis of the transference numbers obtained makes possible the obtainment of more precise values for other thermodynamic parameters of this electrolyte.

Experimental Section

Chemicals. LiBr, Merck "suprapur", was heated in vacuo at 150 °C for 72 h before use. $(C_2H_5)_4NBr$, Carlo Erba for polarography, was used without any previous manipulation but dried by means of a dry nitrogen stream before use. $KOOCCH_3$, Merck analytical reagent grade, was recrystallized twice from a saturated solution with ethanol, dried in an oven at 110 °C for 24 h, and stored in a desiccator. Sodium salt was used instead of the lithium salt because the latter was not available; nevertheless it is well-known (*1*) that the use of the former salt does not introduce any error into the experimental determination of the transference numbers.

Solutions. Determination of Their Concentrations. The following electrolyte solutions were prepared by weighing and correcting to vacuo both conductivity-grade water ($\kappa_0 = 5 \times 10^{-7}$ ohm^{-1} cm^{-1}) and the solute.

LiBr solutions, due to the hygroscopic character of the electrolyte, must be prepared from stock solutions which were obtained as follows: LiBr, after heating to vacuo, was added to a small known quantity of conductivity-grade water, determining by difference the weight of salt added and estimating the concentration of the solution thus prepared (which we will call "initial solution"). From this initial solution, "stock solutions" at different concentrations were prepared by taking portions of it and adding to them different quantities of conductivity-grade water. The concentration of each one of these stock solutions was determined from the value of its experimental density by substituting it into the expression

$$d = (0.997055 \pm 3.4 \times 10^{-5}) + (0.00726 \pm 2.6 \times 10^{-5})p \qquad (1)$$

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