χ_S is significantly more positive, and χ_H less so. The asymmetry of χ_H and χ_S is even more dramatic for quinoline. Flory (*10*) has shown that χ_S is determined predominantly by equation-of-state contributions; χ_H also consists primarily of these contributions when the mixture species are similar in molecular nature. The effect of such contributions is to increase χ_S and decrease χ_H. Therefore our results show that differences in liquid-state properties become more important for CO_2–aromatic hydrocarbon mixtures compared to CO_2–alkane mixtures.

The significant decrease in χ_H noted here for 1-methylnaphthalene compared to values for the paraffinic solvents is not observed for gas solubilities of simple hydrocarbon gases (CH_4, C_2H_6, and C_3H_8) in these solvents (*6*). In fact, for these gases, χ_H becomes somewhat more positive when the solvent is 1-methylnaphthalene. This suggests that intermolecular-force interactions are more important for CO_2 in the aromatic solvent. The decrease in χ_H observed for this system implies that CO_2–1-methylnaphthalene solutions exhibit solvation effects. The CO_2–quinoline system with a negative χ_H exhibits stronger solvation effects, as expected. Therefore, in modeling the phase equilibrium behavior of mixtures containing CO_2 and complex aromatic hydrocarbons, consideration must be given to increased importance of both these solvation effects and effects due to differences in liquid-state properties of CO_2 and the aromatic constituent.

Acknowledgment

We are grateful to Stan Sandler, who gave us permission to use his experimental equipment as well as modify it for our particular experiments.

Glossary

f	fugacity
H_{21}	Henry's law constant for solute 2 in solvent 1
R	gas constant
T	absolute temperature
x	liquid-phase mole fraction
$\Delta\bar{h}^R$	partial molar residual enthalpy of mixing
$\Delta\bar{s}^R$	partial molar residual entropy of mixing

Greek Letters

γ	activity coefficient
χ	Flory parameter
χ_H	enthalpic part of the Flory parameter
χ_S	entropic part of the Flory parameter

Subscripts

1	solvent
2	solute

Superscripts

c	combinatorial
OL	pure liquid phase
∞	infinite dilution

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Solubility of Carbon Dioxide in Molten Alkali Halides and Nitrates and Their Binary Mixtures

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The solubilities of carbon dioxide in molten alkali halides and nitrates and their binary mixtures were determined at 1 atm by the elution method. The solubility values predicted by the Blander model showed fairly good agreement with the experimental values for alkali halides but were far lower than the experimental values for alkali nitrates. Linear relations between the mole fraction of the salts and the logarithm of the Henry's-law constants of the gas were observed in binary mixtures of $NaNO_3$–$RbNO_3$ and NaCl–KCl.

In investigating the kinetics of gas–molten salt reactions, it is necessary to measure solubilities of gases in molten salts. The solubility data of nonpolar gases, such as He, Ar, N_2 and O_2, have been reported (*3*, *4*). Little is known, however, about solubilities of polar or triatomic gases in pure molten slats and their mixtures (*2*, *7*, *9*). In the previous work (*8*), solubilities of carbon dioxide in four molten salts were measured by a simplified elution method. In the present work, solubilities of carbon dioxide in pure alkali halides and nitrates and their binary mixtures, which are widely used as reaction media in gas–molten salt systems, were determined at 1 atm by the same elution method as part of a systematic investigation of the solubility of gas in molten salts. The alkali halides and nitrates used were NaCl, KCl, RbCl, KBr, $LiNO_3$, $NaNO_3$, KNO_3, $RbNO_3$, and $CsNO_3$, and the binary systems were $NaNO_3$–$LiNO_3$, $NaNO_3$–$RbNO_3$, and NaCl–KCl.

Experimental Section

The experimental apparatus and procedure are essentially as described in the previous paper (*8*). The absorption and elution chamber used in this work was made of quartz glass and was 13 mm in inside diameter and 48 mm in height. The gas inlet, the gas outlet, and the bubbling tube attached to the chamber were also made of quartz glass. The temperature of the chamber was kept constant within ±1 °C.

The binary mixtures were prepared by weighing the two salts and then melting them in a chamber at a temperature which

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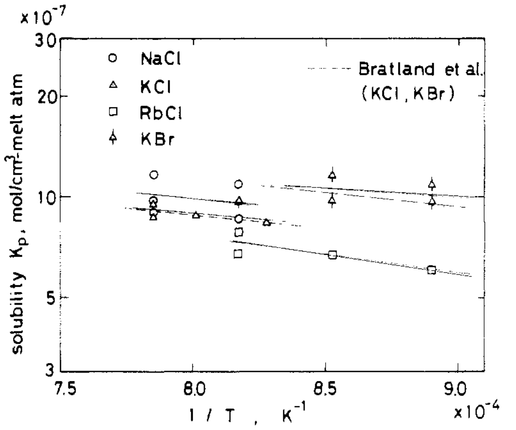

Figure 1. Solubility of CO_2 in molten alkali halides.

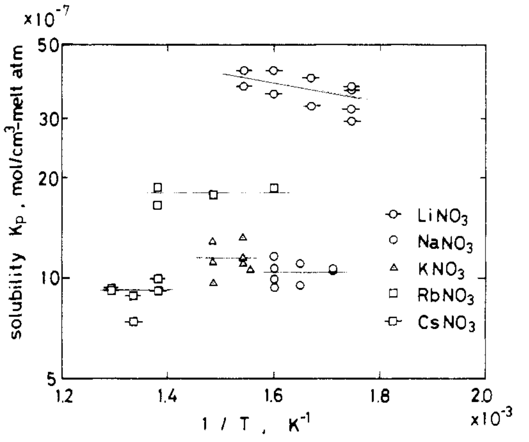

Figure 2. Solubility of CO_2 in molten alkali nitrates.

exceeded the higher of the melting points of either component.

The salts used were of reagent grade, and the effect of impurities in the salts on the solubility data was neglected (*8*). Carbon dioxide was superpure grade, 99.96%, and free from water.

Results and Discussion

The solubilities of carbon dioxide in the molten alkali halides are shown in Figure 1. The solubilities, K_p, are expressed as moles of carbon dioxide per cubic centimeter per atmosphere of molten salt at the observed temperature. Density, vapor-pressure, and surface-tension data for the molten salts were taken from the literature (*5*, *6*), and the effects of vapor pressure on the solubility data were neglected because of their low values (the maximum value 15 mmHg, KCl at 1000 °C). The solubilities increase slightly with an increase in temperature and with a decrease in the radius of alkali cations. The values of solubility in molten KCl and KBr measured by Bratland et al. (*2*) are shown in Figure 1 by broken lines and agree well with the results in this work. On the other hand, their values for molten NaCl are ~30% lower than those in this work.

The solubilities of carbon dioxide in molten alkali nitrates are shown in Figure 2. Some of the data for $NaNO_3$ were reported in the previous paper (*8*). The solubilities are little affected by temperature except in $LiNO_3$ and do not vary with the radius of alkali cations. The averaged values of the solubilities are shown in Table I.

Blander et al. (*1*) used the Uhlig model to estimate solubilities in molten salts. The solubility of carbon dioxide in molten salts is given by the following equation:

$$-\ln K_pRT = NA\gamma/RT \qquad (1)$$

where *N* is Avogadro's number, *R* the gas constant, *T* the temperature, *A* the surface area of the carbon dioxide molecule, and γ the surface tension of the salt. The surface area *A* was calculated to be 4.5 × 10^{-15} cm^2/molecule by representing the carbon dioxide molecule as two hemispheres joined by a cylinder. The values of K_p predicted with the use of the Blander model (eq 1) are compared with the measured values

Table I. Solubility of CO_2 in Molten Alkali Halides and Nitrates

salt	temp, °C	density, g/cm^3	solubility K_p,[a] mol/cm^3	SD
NaCl	950	1.475	0.99 × 10^{-6}	0.18 × 10^{-6}
	1000	1.448	1.01 × 10^{-6}	0.12 × 10^{-6}
KCl	935	1.432	8.33 × 10^{-7}	
	950	1.423	9.78 × 10^{-7}	
	970	1.411	8.74 × 10^{-7}	
	1000	1.394	9.08 × 10^{-7}	0.40 × 10^{-7}
RbCl	850	2.129	6.09 × 10^{-7}	
	900	2.085	6.63 × 10^{-7}	
	950	2.041	7.31 × 10^{-7}	0.57 × 10^{-7}
KBr	850	2.032	1.02 × 10^{-6}	0.06 × 10^{-6}
	900	1.991	1.08 × 10^{-6}	0.10 × 10^{-6}
	950	1.950	0.97 × 10^{-6}	
$LiNO_3$	300	1.755	3.39 × 10^{-6}	0.33 × 10^{-6}
	325	1.742	3.64 × 10^{-6}	0.35 × 10^{-6}
	350	1.728	3.86 × 10^{-6}	0.33 × 10^{-6}
	375	1.714	3.96 × 10^{-6}	0.24 × 10^{-6}
$NaNO_3$	310	1.916	1.07 × 10^{-6}	0.01 × 10^{-6}
	330	1.902	1.03 × 10^{-6}	0.08 × 10^{-6}
	350	1.888	1.04 × 10^{-6}	0.09 × 10^{-6}
KNO_3	370	1.846	1.06 × 10^{-6}	
	375	1.843	1.20 × 10^{-6}	0.09 × 10^{-6}
	400	1.824	1.12 × 10^{-6}	0.13 × 10^{-6}
$RbNO_3$	350	2.443	1.88 × 10^{-6}	
	400	2.395	1.78 × 10^{-6}	
	450	2.346	1.77 × 10^{-6}	0.12 × 10^{-6}
$CsNO_3$	450	2.778	9.60 × 10^{-7}	0.40 × 10^{-7}
	475	2.749	8.10 × 10^{-7}	0.70 × 10^{-7}
	500	2.719	9.30 × 10^{-7}	0.10 × 10^{-7}

[a] mol/cm^3 of CO_2 in molten salt at 1 atm.

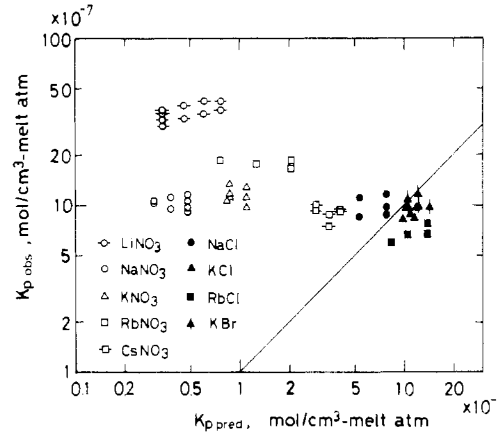

Figure 3. Comparison between experimental and calculated values of solubility.

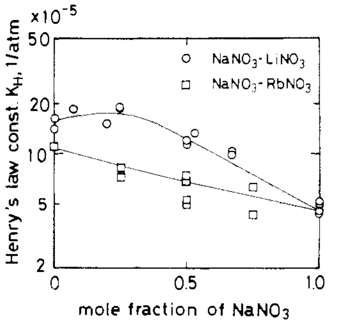

Figure 4. Solubility of CO_2 in $NaNO_3$–$LiNO_3$ and $NaNO_3$–$RbNO_3$.

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Table II. Solubility of CO_2 in Binary Mixtures

system	mole fraction of A	K_p,[a] mol/cm^3	K_H,[b] 1/atm
$NaNO_3$(A)-$LiNO_3$(B) (350 °C)	0	3.86×10^{-6}	1.54×10^{-4}
	0.07	4.70×10^{-6}	1.89×10^{-4}
	0.20	3.68×10^{-6}	1.52×10^{-4}
	0.25	4.67×10^{-6}	1.93×10^{-4}
	0.50	2.79×10^{-6}	1.19×10^{-4}
	0.52	3.18×10^{-6}	1.37×10^{-4}
	0.66	2.34×10^{-6}	1.03×10^{-4}
	1.00	1.04×10^{-6}	4.68×10^{-5}
$NaNO_3$(A)-$RbNO_3$(B) (350 °C)	0	1.88×10^{-6}	1.13×10^{-4}
	0.25	1.36×10^{-6}	7.66×10^{-5}
	0.50	1.18×10^{-6}	6.15×10^{-5}
	0.75	1.07×10^{-6}	5.27×10^{-5}
	1.00	1.04×10^{-6}	4.68×10^{-5}
NaCl(A)-KCl(B) (1000 °C)	0	9.08×10^{-7}	4.85×10^{-5}
	0.25	7.24×10^{-7}	3.65×10^{-5}
	0.50	8.17×10^{-7}	3.86×10^{-5}
	0.75	9.66×10^{-7}	4.23×10^{-5}
	1.00	1.01×10^{-6}	4.07×10^{-5}

[a] mol/cm^3 of CO_2 in molten salt at 1 atm. [b] mol of CO_2/mol of salt at 1 atm.

of K_p in Figure 3. The solubility data for the alkali halides in this work show fairly good agreement with the values predicted by eq 1. The data for the alkali nitrates, by contrast, are much larger than the predicted values. These deviations in the alkali nitrates may be attributed to the nonspherical shape of the NO_3^- ion, the negative energy of interaction between the ions and the CO_2 quadrupole, and the low temperature range of the measurements.

Figure 4 shows Henry's-law constants K_H mol of gas/(mol of salts atm) plotted against the mole fraction of $NaNO_3$ on semilogarithmic coordinates for the $NaNO_3$-$LiNO_3$ and $NaNO_3$-$RbNO_3$ systems. The Henry's-law constant of a gas in a binary solvent is expressed by the following equation (*9*):

$$\ln K_{H(a+b)} = X_a \ln K_{H(a)} + X_b \ln K_{H(b)} - \alpha_{ab} X_a X_b \qquad (2)$$

where X_a and X_b are mole fractions of a and b components, respectively. In the case of an ideal mixture, α_{ab} is equal to zero, and a plot of ln K_H against the mole fraction of one component of the mixture gives a straight line. Such a linear relation is observed in the $NaNO_3$-$RbNO_3$ system. The $NaNO_3$-$LiNO_3$ system, however, shows a slight positive deviation from ideal behavior, especially at high mole fraction of $LiNO_3$. This might be attributed to the small ionic radius of Li^+ in comparison with those of Na^+, Rb^+, and NO_3^-. A linear relation is also observed in the NaCl-KCl system at 1000 °C. These results are summarized in Table II.

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Vapor–Liquid Equilibrium in Ternary Mixtures of Hydrogen + Carbon Dioxide + Tetralin

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Vapor–liquid equilibrium was determined for the ternary system hydrogen + carbon dioxide + tetralin at 543 and 663 K, and 50–250 atm. The relative concentrations of hydrogen to carbon dioxide were systematically varied from 75 to 95 mol % of hydrogen at each condition of temperature and pressure. The effect of composition upon the *K* values was studied.

Introduction

Recent developments in coal hydrotreating processes have created a need for phase-equilibrium data of mixtures containing hydrogen and heavy hydrocarbons at high temperatures and pressures. We report in this work experimental data on vapor–liquid equilibrium in ternary mixtures of hydrogen + carbon dioxide + tetralin at the two temperatures of 543 and 663 K and pressures to 250 atm. The relative concentrations of hydrogen to carbon dioxide were varied, and three observations were made at each condition of temperature and pressure in order to determine the response of the *K* values to changing compositions.

The equilibrium data for this ternary system are not available in the literature. However, the constituent binary mixtures of hydrogen + tetralin (*2*) and carbon dioxide + tetralin (*1*) have been reported.

Experimental Section

For the study of binary mixtures of a light gas and a heavy solvent, the experimental apparatus and procedure have been described (*2*) in detail. Modification has been made of the apparatus and procedure for the study of ternary mixtures of two light gases and a heavy solvent such as the present mixture system. The modification has also been described (*3*). Briefly, a mixed gas stream is prepared of the two light gases at a specified composition. The binary gas mixture is compressed and mixed with a liquid stream of the heavy solvent. The combined gas and liquid heterogeneous mixture is heated to the desired temperature. The saturated phases are separated in

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