

red indicator for the sodium hydroxide determinations.

Results and Discussion

Tables I through VII present total pressure data as a function of the salt concentration for the seven salts studied. For comparison purposes Figure 1 presents a plot of the activity value

$$a = P/P^s \quad (1)$$

(P is total pressure, P^s is vapor pressure of solvent) vs. molality for the system LiCl-methanol along with the data of Skabichievski (11) at 25 °C. The agreement between the two sets of data is satisfactory.

An examination of the vapor pressure depression

$$\Delta P = P^s - P \quad (2)$$

for the two salts with I^- as common ion (NaI, KI) indicates that increased ΔP values (NaI > KI) follow decreasing values of cation crystallographic radii ($Na^+ < K^+$). For the three salts with Na^+ as common ion (NaOH, NaI, NaBr), however, increased values of ΔP (NaOH > NaI > NaBr) do not correspond to decreasing values of anion radii ($OH^- < Br^- < I^-$). Finally, to establish the order of increasing ΔP values for the three salts with Cl^- as common ion (LiCl, $CuCl_2$, $CaCl_2$) consider Figure 2 where ΔP is plotted against the ionic strength, I

$$I = \frac{1}{2} \sum_i m_i z_i^2 \quad (3)$$

where m_i = molality of ion i , z_i = charge of ion i , and N = number of ion types per molecule.

Use of I , instead of m , is made in this case to take into account the fact that LiCl is a 1-1 salt and $CuCl_2$ and $CaCl_2$ are 2-1 salts. The plots indicate that increasing ΔP effects (LiCl

> $CaCl_2$ > $CuCl_2$) again do not follow decreasing ionic radii ($Li^+ < Cu^{2+} < Ca^{2+}$). Similar observations can be found in the literature. For example, while Tsiparis and Smorigaite (12) report that the salting-out effects of acetic acid in mixtures with water increases with decreasing ionic radius, the results of Sada et al. indicate that this is not the case for tetrahydrofuran-water mixtures (9) or for the solubility of toluene in aqueous salt solutions (10). Apparently, the ion solvation, which determines the P effect, cannot be related in a simple fashion to the ionic crystallographic radii (6).

An attempt to correlate vapor pressure depression effects to salt solubilities in methanol (5) provided also inconclusive. For the three salts with Na^+ as common ion, and the two with I^- , increased ΔP effects correspond to increased salt solubilities. However, this was not the case for the three salts with Cl^- as common ion.

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Solubility of Carbon Dioxide in Aqueous Electrolyte Solutions

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The solubility of CO_2 in aqueous solutions of 16 electrolytes has been determined by the gas volumetric method at 1 atm and temperatures of 15, 25, and 35 °C. The maximum concentration of each aqueous electrolyte solution was above 60 wt % of saturation. For the solubility of CO_2 over the wide ranges of electrolyte concentration, it was found that the empirical Setschenow equation was not applicable to some systems. The data of those systems were correlated by a two-parameter equation within a deviation of 2%.

The solubility of carbon dioxide in aqueous electrolyte solutions has been investigated by many workers. However, there have been few data which were measured over wide ranges of electrolyte concentration with a sufficient number of points to investigate the effect of electrolyte concentration on the solubility of gas for each solution.

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The empirical Setschenow equation has often been used to correlate between the activity coefficient of the nonelectrolyte solute and the concentration of the electrolyte up to the moderate concentrations and has in many cases given sufficient results for correlation, though this equation is a first approximation valid at low electrolyte concentrations. As was shown by Markham and Kobe (6) and Clever and Reddy (2), however, the equation was not valid in some systems. Markham and Kobe (6) proposed a two-parameter equation to fit the data of these systems.

The method of van Krevelen and Hoftijzer (11) based on the empirical Setschenow equation has widely been used to estimate the solubilities of gases in electrolyte solutions. The estimated results by this method are often poor, however.

In this experiment, solubilities of carbon dioxide in a number of aqueous electrolyte solutions over wide ranges of concentration were determined to inspect the applicabilities of the correlating and estimating methods.

The electrolytes used were NaCl, $NaNO_3$, KCl, KNO_3 , NH_4Cl , $(NH_4)_2SO_4$, Na_2SO_4 , K_2SO_4 , $MgCl_2$, $Mg(NO_3)_2$, $MgSO_4$, $CaCl_2$, $Ca(NO_3)_2$, $BaCl_2$, $AlCl_3$, and $Al_2(SO_4)_3$.

Table I. Comparison of Experimental Solubility of Carbon Dioxide in Pure Water with Literature Values (Ostwald Coefficient)

temp, °C	experimental solubility			lit. (δ)
	av value	no. of determinations	av dev, ^a %	
15	1.0634	4	0.06	1.075
25	0.8264	10	0.11	0.828
35	0.6675	5	0.24	0.671

^a This means the average deviation of individual observed values from their averaged values.

Experimental Section

The experimental apparatus and procedure are essentially the same as those described by Tokunaga (10). The absorption chamber used in this study was 30 cm³ in volume. The apparatus was housed in a constant-temperature air bath controlled within ± 0.05 °C.

The aqueous electrolyte solutions as the solvent were made by weighing the proper amount of guaranteed grade reagent and dissolving in a weighed amount of deionized water. The concentration of each solution was determined by chemical analysis or by evaporating a known weight of salt solution and then weighing the dry salt.

Carbon dioxide used was superpure grade, 99.96%, from Nippon Tansan Co. Ltd.

Results

The solubilities were evaluated by the Ostwald coefficient, L , being defined as the ratio of the volume of gas absorbed at the observed temperature and pressure, V_G , to the volume of the absorbing liquid, V_L , that is

$$L = V_G/V_L \quad (1)$$

A small increase of liquid volume due to gas absorption was evaluated from the value of the coefficient of dilatation, 0.0016, estimated from the partial molal volume of carbon dioxide in water, 35 cm³ (3).

In order to evaluate L , the data of water vapor pressure for the aqueous electrolyte solutions at the experimental temperatures are needed. The data of vapor pressure were taken from literature (8, 9).

The accuracy and reliability of the equipment and procedure were determined by measurement of the solubility of carbon dioxide in pure water. These data are summarized in Table I. The values agree quite well with the values in the literature (5).

Solubility data obtained in this experiment are given in Table II. For the systems investigated by Kobe and Williams (4), Markham and Kobe (6), and Onda et al. (7) at 25 °C, the results obtained in this experiment agree well with their results.

Discussion

The empirical Setschenow Equation is represented as follows

$$\log L_0/L = KC_s \quad (2)$$

where L_0 is the Ostwald coefficient of the gas in pure water, C_s is the molarity of electrolyte, and K is an empirical constant dependent upon the particular gas and electrolyte pair. Figure 1 shows the plots of $\log L_0/L$ against molarity for the systems of sodium nitrate and ammonium sulfate, as examples of the measurements in this work. In the figure, broken lines show the straight line representing eq 2. It is, then, apparent that eq 2 is well applicable to the sodium nitrate system but not to the ammonium sulfate system.

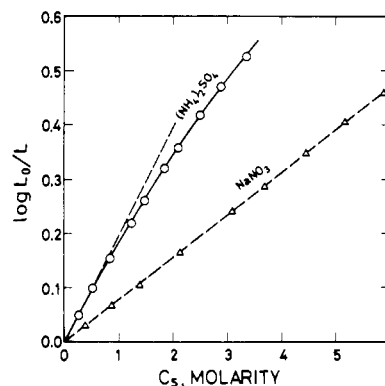


Figure 1. Plots of $\log L_0/L$ against molarity of sodium nitrate and ammonium sulfate at 25 °C.

Over the whole ranges of electrolyte concentration, the Setschenow equation fitted fairly well the data for the systems of NaNO_3 , KNO_3 , Na_2SO_4 , K_2SO_4 , BaCl_2 , AlCl_3 , and $\text{Al}_2(\text{SO}_4)_3$ and fitted approximately for NaCl , KCl , MgCl_2 , $\text{Mg}(\text{NO}_3)_2$, MgSO_4 , and $\text{Ca}(\text{NO}_3)_2$.

Using the experimental data, the value of K has been found for each system mentioned above by the method of least squares. These values are given in Table III.

The maximum deviation of the observed data from the solubilities calculated by eq 2 with values of K in Table III was about 1% for each system of NaNO_3 , KNO_3 , Na_2SO_4 , K_2SO_4 , BaCl_2 , AlCl_3 , and $\text{Al}_2(\text{SO}_4)_3$, 1.7% for NaCl , $\text{Mg}(\text{NO}_3)_2$, MgSO_4 , and $\text{Ca}(\text{NO}_3)_2$, and 2.5% for KCl and MgCl_2 .

The following empirical equations proposed by van Krevelen and Hoftijzer (11) have been used to estimate the solubilities of gases in aqueous electrolyte solutions

$$\log L_0/L = kI \quad (3)$$

$$I = \frac{1}{2} \sum_i c_i z_i^2 \quad (4)$$

$$k = i_+ + i_- + i_g \quad (5)$$

where parameters i_+ , i_- , and i_g are the contributions to the salting-out parameter k referring to the species of positive and of negative ions and to the species of gas, respectively. Values of i_+ , i_- , and i_g have also been given by Onda et al. (7) and Barrett (1). The values of K calculated by eq 5 and 6 using the values of i given by Onda et al. (7) are given in Table III, column 5

$$K = kI/C_s \quad (6)$$

where I is the ionic strength corresponding to C_s . The maximum deviations of the solubilities calculated by eq 2 with the values of K in Table III, column 5, from the observed data are also given in column 6. It is apparent that the solubilities estimated by the method mentioned above give the comparable values to the corresponding data observed for the systems of NaNO_3 , Na_2SO_4 , K_2SO_4 , BaCl_2 , AlCl_3 , NaCl , and MgCl_2 but not for the others.

When the allowable range of electrolyte concentration to apply the estimation method by van Krevelen and Hoftijzer (11) is limited to an ionic strength of 2 mol/L, however, the deviation of the estimated solubilities from the observed data is within 5% for all systems summarized in Table III.

The Setschenow equation could not be used for the systems of NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$, and CaCl_2 and used only approximately for those of NaCl , KCl , MgCl_2 , $\text{Mg}(\text{NO}_3)_2$, MgSO_4 , and $\text{Ca}(\text{NO}_3)_2$.

Table III. Comparison of Experimental Salting-Out Coefficients with Values Estimated by the Method of van Krevelen and Hofstijzer for CO₂ Solubility

electrolyte	temp, °C	obsd		calcd	
		$C_{s,max}^a$, mol/L	K , L/mol	K^b , L/mol	max dev, ^c %
NaNO ₃	15	5.93	0.084	0.0825	2.4
	25	7.26	0.078	0.0770	-2.3
	35	5.19	0.071		
KNO ₃	25	1.63	0.044	0.0591	-5.7
	35	1.77	0.039		
Na ₂ SO ₄	15	1.06	0.344	0.3123	7.0
	25	2.21	0.297	0.2958	1.4
	35	1.76	0.274		
K ₂ SO ₄	25	0.45	0.240	0.2421	0.4
BaCl ₂	25	1.56	0.214	0.1998	4.2
AlCl ₃	25	2.57	0.245	0.2478	-2.4
Al ₂ (SO ₄) ₃	25	0.85	0.747	0.6645	14.8
NaCl	15	4.72	0.104	0.1011	3.9
	25	5.10	0.100	0.0956	4.2
	35	4.86	0.095		
KCl	25	4.13	0.062	0.0777	-16.1
	35	4.11	0.061		
MgCl ₂	15	3.77	0.184	0.1878	-3.7
	25	3.96	0.179	0.1713	5.5
	35	3.74	0.174		
Mg(NO ₃) ₂	25	3.37	0.136	0.1155	20.6
MgSO ₄	25	2.27	0.269	0.2404	14.5
Ca(NO ₃) ₂	25	3.58	0.150	0.1218	28.8

^a Maximum salt concentration observed in this experiment.

^b Values calculated by the method of van Krevelen and Hofstijzer (*I*) with values of contributions of positive ion, negative ion, and gas to salting-out parameter *k* evaluated by Onda et al. (7).

^c Maximum deviation of the calculated Ostwald coefficient from the observed data within the maximum salt concentration measured in this experiment.

Table IV. Parameters of Equation 7 for Solubility of CO₂

electrolyte	temp, °C	<i>A</i> , L/mol	<i>B</i> , L/mol
NH ₄ Cl	15	0.0477	0.123
	25	0.0435	0.133
	35	0.0434	0.136
(NH ₄) ₂ SO ₄	15	0.207	0.0787
	25	0.198	0.0752
	35	0.190	0.0770
CaCl ₂	25	0.211	0.0572
	35	0.190	0.0529
NaCl	15	0.112	0.0201
	25	0.105	0.0124
	35	0.0989	0.0112
KCl	25	0.0754	0.0671
	35	0.0731	0.0599
MgCl ₂	15	0.186	0.0051
	25	0.188	0.0172
	35	0.181	0.0191
Mg(NO ₃) ₂	25	0.128	-0.0246
MgSO ₄	25	0.250	-0.0361
Ca(NO ₃) ₂	25	0.145	-0.0127

To correlate the data of these systems, the empirical eq 7 previously proposed (12) has been applied.

$$\log L_0/L = AC_s/(1 + BC_s) \quad (7)$$

in which *A* and *B* are empirical constants dependent upon the particular solute present and *A* corresponds to the limiting value of *K* at an infinite dilution of electrolyte. Using the experimental data, values of *A* and *B* have been found for each system by the method of least squares. These values are given in Table IV. The solid line in Figure 1 shows the plot of eq 7 for the system of (NH₄)₂SO₄.

The maximum deviations of the values estimated by eq 7 from the observed data are about 0.6% for the system of NH₄Cl,

Table V. Maximum Deviation of Estimated Ostwald Coefficient from Observed Data

electrolyte	temp, °C	$C_{s,max}^a$, mol/L	calcd	
			K^b , L/mol	max dev, ^c %
NH ₄ Cl	15	4.21	0.0457	-13.2
	25	5.65	0.0402	-18.0
(NH ₄) ₂ SO ₄	15	3.35	0.1461	16.2
	25	3.36	0.1296	24.5
CaCl ₂	25	4.53	0.1776	7.6

^{a,b,c} Refer to footnotes *a*, *b*, and *c* of Table III.

1.4% for (NH₄)₂SO₄, and 2% for CaCl₂ when the concentration of CaCl₂ is less than 3 mol/L. For the system of CaCl₂, however, the maximum deviation becomes about 6% when eq 7 is applied over the whole range of the salt concentrations observed, because the plot of log *L*₀/*L* against *C*_s curves sharply above 3 mol/L of the salt concentration.

As to these three electrolytes, the values of *K* calculated by eq 3-6 with values of *i* given by Onda et al. (7) and the maximum deviation of the values estimated by eq 2 with the calculated values of *K* from the observed data are summarized in Table V.

The maximum deviation of values estimated by eq 7 from the observed data are about 1% for the systems of NaCl, KCl, Mg(NO₃)₂, MgSO₄, and Ca(NO₃)₂, and 2% for MgCl₂.

Equation 7, therefore, in most cases fits the data of the gas solubility in electrolyte solutions as a function of concentration accurately enough for practical purposes.

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Glossary

<i>A</i> , <i>B</i>	parameters in eq 7, L/mol
<i>C</i> _s	molar concentration of electrolyte, mol/L
<i>c</i> _{<i>i</i>}	concentration of <i>i</i> species, mol/L
<i>I</i>	ionic strength, mol/L
<i>i</i> ₊ , <i>i</i> ₋ , <i>i</i> _g	contributions of positive ion, negative ion, and gas to <i>k</i> , L/mol
<i>K</i>	salting-out parameter in eq 2, L/mol
<i>k</i>	salting-out parameter in eq 3, L/mol
<i>L</i>	Ostwald coefficient
<i>V</i> _G	volume of gas dissolved in liquid at observed temperature and pressure, cm ³
<i>V</i> _L	volume of aqueous salt solution, cm ³
<i>z</i> _{<i>i</i>}	ionic valency of <i>i</i> species

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