

and 4. Good agreement was obtained between the data presented in this investigation and those of Sage et al. (13). It appears that the data reported by Hirata et al. (11) and Akers et al. (1) do not follow the trend as shown in the graphs in the lower pressure range.

#### Acknowledgment

The authors thank J. Argo for his assistance in the preparation of the manuscripts.

#### Nomenclature

$a, b$  = constants of the Redlich-Kwong equation of state  
 $E$  = measuring error  
 $G$  = molal Gibbs free energy  
 $k_{ij}$  = binary interaction constant  
 $P$  = total pressure  
 $R$  = universal gas constant  
 $T$  = temperature  
 $V$  = molal volume  
 $x$  = liquid-phase mole fraction  
 $y$  = vapor-phase mole fraction  
 $\Omega_a, \Omega_b$  = parameters of the Redlich-Kwong equation of state  
 $\varphi$  = fugacity coefficient  
 $\gamma$  = activity coefficient

#### Superscripts

$\hat{\phantom{x}}$  = property in solution  
 $E$  = excess property

$\bar{\phantom{x}}$  = partial molal quantity  
 $\circ$  = standard state

#### Subscripts

$i, j$  = component identification  
 $ij$  =  $i$ - $j$  pair  
 $L$  = liquid phase  
 $v$  = vapor phase  
 $c$  = critical property

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Received for review June 10, 1975. Accepted December 13, 1975. Work supported by the National Research Council of Canada.

## Solubility of Butane in Water and Salt Solutions at Low Temperatures

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**Additional data on the solubility of *n*-butane in water and 3.5 and 7 wt % NaCl solutions for temperatures ranging from 0 to 20 °C are presented. These data, together with those of Umano and Nakano up to 10 wt % salt, are correlated with an expected error of 3% by a single equation.**

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Butane has often been suggested as a refrigerant for the freezing process of desalting seawater (2) since it has a low solubility in water, boils at  $-0.5$  °C at 1 atm, and is relatively inexpensive. Almost all work on the solubility of butane, however, has been for pure water at temperatures above 15 °C and not for salt solutions at lower temperatures. The notable exception is the work of Umano and Nakano (6) who determined the solubility of butane in water and in both 4.79 and 10 wt % NaCl solutions in the temperature range of 0-20 °C. The results reported here supplement those of Umano and Nakano at 0% salt and add butane solubility data for NaCl solutions of 3.5 and 7 wt % and for synthetic sea salt solutions of 3.5 and 7 wt %. In addition, butane solubilities were measured under different total butane pressures to check the validity of Henry's law.

#### Equipment and Experimental Procedure

The equipment used in these experiments consisted of an equilibrium cell in a constant temperature bath and a total carbon analyzer used to analyze the butane concentration in the liquid.

The cell was a heavy walled pyrex vessel with a volume of 1 l. The top was 1-in. thick Plexiglas with ports for sampling, pressure connection, vacuum line, and introduction of gas. The sampling port consisted of a well which extended down into the vessel below the liquid surface and had a septum for the insertion of a hypodermic syringe.

The cell was totally immersed in a constant temperature water bath controlled via a thermoregulator to  $\pm 0.02$  °C. The liquid in the cell was mixed by a Teflon-coated magnetic stirring bar driven by a submersible, air operated, magnetic stirrer underneath the cell. The experimental apparatus is shown schematically in Figure 1.

At the beginning of an experiment, the reaction vessel was filled with about 700 ml of water or salt solution, sealed, and submerged in the water bath. While being stirred, the system was evacuated to the vapor pressure of water for about an hour to remove dissolved air from solution. The vessel, now devoid of air, was charged with *n*-butane of instrument purity, 99.5%.

Approximately 70% of the quantity of butane necessary to bring the solution to equilibrium was dissolved in about 12 h after a change in the temperature or pressure. For a typical change in the equilibrium butane concentration corresponding to a change in temperature or pressure of about 20 ppm, 91–99% of change in butane concentration would occur in 24–48 h allowed between changes in the temperature and

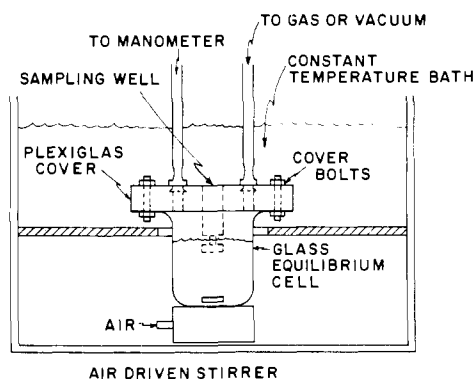


Figure 1. Schematic of equilibrium cell

Table I. Sea Salt Composition (5)

Salts	Concn, ppm
NaCl	24,067
MgCl <sub>2</sub>	5,107
Na <sub>2</sub> SO <sub>4</sub>	4,016
CaCl <sub>2</sub>	1,130
KCl	680
Total	35,000 ppm = 3.5 wt %

Table II. Solubility Data for *n*-Butane in Water and Salt Solutions

Wt %	Temp, °C	Solubility in ppm at 1 atm partial press <sup>a</sup>	
0	3	182.4	
	6	152.4	
	9	134.5	
	14	109.6	
	19	91.9	
	19	61.3 ( $p_B = 0.667$ atm)	
	3.5	0.5	137.2
		3	113.4
		7	92.9
		11	84.1
15		74.7	
19		63.8	
7.0	0.3	99.3	
	3	79.8	
	3	56.9 ( $p_B = 0.721$ atm)	
	3	40.9 ( $p_B = 0.513$ atm)	
	7	65.5	
	11	55.0	
	14	50.1	
	19	46.0	
3.5	3	114.1	
	11	83.1	
	15	75.0	
	19	63.5	
7.0	3	78.5	
	11	54.8	
	19	45.5	

<sup>a</sup> All of the above data represent the average values obtained from three to nine separate injections into the total carbon analyzer, and in some cases represent the combination of data taken from different runs.

pressure. Longer times were allowed for the larger changes, and the solution was taken to be at equilibrium when no change in butane partial pressure could be detected in 4 h. Detectable changes would correspond to changes in butane concentrations of about 0.2 ppm or about 1% of the total change. Longer periods of time were also necessary to bring a fresh solution to equilibrium with butane at ambient temperatures since the change in concentration under these conditions would be as much as five times higher. Additionally, to assure that equilibrium concentrations were achieved, dual measurements were made for each temperature, one approaching the equilibrium from a previous higher temperature and one from a lower. No significant difference was found in the observed equilibrium concentrations, and the average of the dual measurements is reported.

A liquid sample was taken by inserting a microliter syringe into the sample port, through the septum, and directly into the

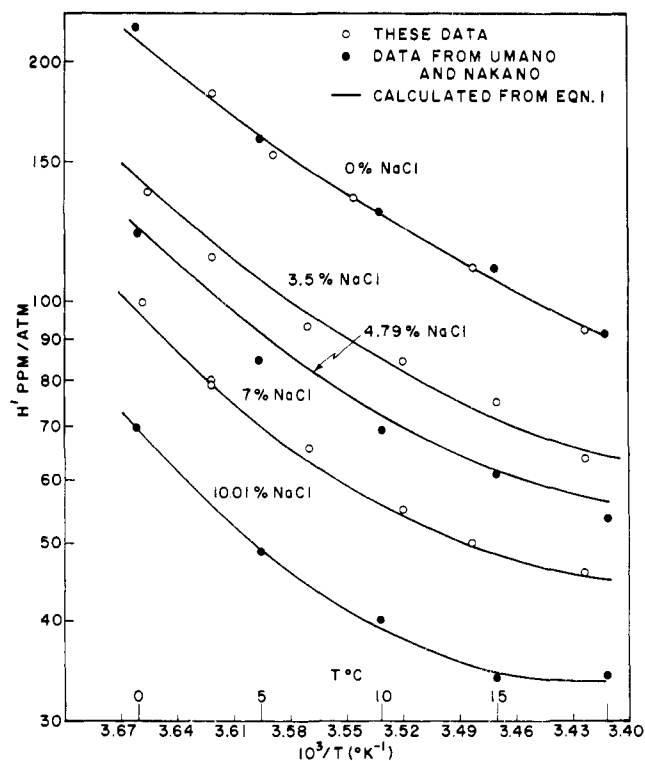


Figure 2. Butane solubility vs. temperature and NaCl concentration

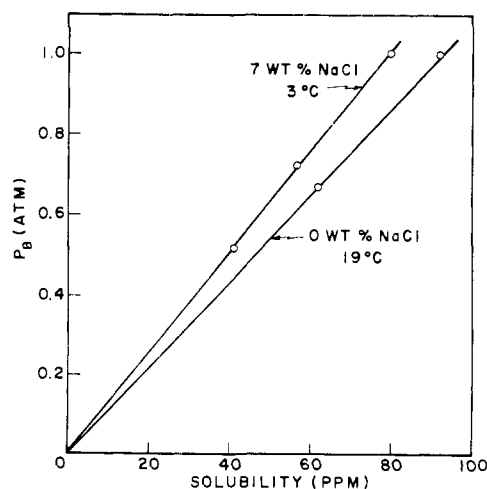


Figure 3. Butane partial pressure vs. butane solubility

**Table III. Calculated Solubility of *n*-Butane in Water and NaCl Solution**

Figures in table give solubility in ppm for 1 atm partial pressure *n*-C<sub>4</sub>H<sub>10</sub>.

Wt % NaCl	Temperature, °C										
	0	2	4	6	8	10	12	14	16	18	20
0	212	189	170	153	140	128	118	109	102	95.6	90.2
1	189	168	151	136	124	114	105	97.6	91.4	86.1	81.7
2	169	150	134	121	110	101	93.4	87.1	81.9	77.6	74.1
3	152	134	119	107	97.6	89.7	83.1	77.8	73.4	69.9	67.1
4	136	119	106	95.3	86.7	79.7	74.0	69.4	65.8	63.0	60.8
5	121	106	94.2	84.6	76.9	70.8	65.9	62.0	59.0	56.7	55.1
6	109	94.7	83.8	75.1	68.3	62.9	58.6	55.4	52.9	51.1	50.0
7	97.1	84.4	74.5	66.7	60.6	55.9	52.2	49.4	47.4	46.0	45.3
8	86.9	75.2	66.2	59.2	53.8	49.6	46.5	44.1	42.5	41.5	41.0
9	77.7	67.0	58.9	52.6	47.8	44.1	41.4	39.4	38.1	37.4	37.2
10	69.5	59.8	52.3	46.7	42.4	39.2	36.8	35.2	34.1	33.7	33.7

liquid phase of the reaction cell. It was then injected directly into the total carbon analyzer. The procedure was repeated several times to obtain multiple peaks on the recorder chart. Injecting the sample taken from the reaction cell directly into the carbon analyzer with no intervening storage time insures no loss of dissolved *n*-butane to the atmosphere or contamination from other sources of carbon.

All solutions of NaCl or sea salts were made up volumetrically with reagent grade chemicals. In the case of NaCl solutions, the NaCl was dried overnight, cooled, and then weighed on an analytical balance. The sea salt solutions were made up similarly, and their composition is given in Table I. This recipe uses five salts, four of which are stable in anhydrous form and were dried, cooled in a desiccator, and weighed analytically. The fifth salt, MgCl<sub>2</sub>, is not stable in its anhydrous form, and the stable hexahydrate was used directly from a newly opened bottle.

### Results

All of the results are listed in Table II. These results, together with those of Umamo and Nakano (6), are also presented in Figure 2, in which the natural log of the butane solubility (parts per million) divided by the butane partial pressure in atm (*H'*) is plotted against reciprocal temperature (K) at constant salt concentrations, and in Figure 3 which is a plot of the butane solubility vs. butane partial pressure at two sets of values of temperature and salt concentration.

### Analysis and Discussion of Results

Figure 3 shows that for the two sets of values of temperature and salt concentration, the butane solubility in water and salt solutions is directly proportional to the partial pressure of butane. Since the maximum nonideality for butane vapor at these temperatures and pressures is 3%, Henry's law is valid for butane-salt water solutions. This confirms the work at 25 °C by Denton et al. (3) who found that Henry's law held down to much lower concentrations (0.02 ppm). A comparison of the butane solubilities in sea salt solutions to NaCl solutions of equal wt % shows that they are the same within an average of 0.8%, which is within the precision of the data.

Because Henry's law is valid, all of the butane-water data reported here, along with those of Umamo and Nakano, were correlated together. The following equation was the result:

$$\ln H' = -671.5248 + 31,696.51/T + 99.97065 \ln T + (-145.3127 + 6,137.061/T + 21.8756 \ln T) \times W \quad (1)$$

where *H'* = (solubility in ppm)/(butane partial pressure in atm), *T* = K, and *W* = wt % NaCl. The constants for this equation were determined by a nonlinear least-squares procedure. The maximum absolute value of deviation of any of the data from the equation is 8 ppm with an estimated stan-

dard deviation of 3%. A comparison of the predictions of the equation with the experimental data is shown in Figure 2. In Table III the solubility values predicted by Equation 1 are tabulated for values of NaCl concentrations of 0–10% and temperatures from 0 to 20 °C. The solubility of butane decreases with increasing temperature and with increasing salt concentration. The reduction in butane solubility with increasing salt concentration is consistent with the effect of salt addition on the solubility of gases in water observed by others [Morrison and Billet (4)]. Apparently, the salt ions associate with several water molecules, effectively reducing the number of water molecules available for dissolving the butane.

The heat of solution of butane in water and salt solutions is obtained by differentiating Equation 1 with respect to reciprocal temperature:

$$-\Delta H_s/R = 31,696.51 - 99.97065 \times T + (6137.061 - 21.87756 \times T) \times W \quad (2)$$

The heat of solution is negative (heat is liberated upon solution), but its magnitude decreases with increasing temperature and salt concentration. In pure water at 0 °C and 1 atm of butane, the heat of solution is -8728 cal/g-mol, while its heat of condensation is only -5340 cal/g-mol.

Although little work has been done on the solubility of butane in water and salt solutions in the temperature range of 0–20 °C, many workers have measured butane solubilities in pure water at higher temperatures. The measurements of these workers have been critically examined by Bajolle et al. (7) and correlated by the equation:

$$\ln H' = 18.2914 - 11.5149 \times (1000/T) + 2.18249 \times (1000/T)^2 \quad (3)$$

for the temperature range 10–70 °C. This equation predicts a solubility at 20 °C which is 8.7% lower (8 ppm) than does Equation 1. This difference probably arises because Bajolle's correlation considered only three data points below 20 °C, with most of the data in the range from 20 to 70 °C, while Equation 1 considers data only in the range of 0–20 °C.

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Received for review July 7, 1975. Accepted December 15, 1975.