

# Solubility Studies in Liquid 2-Oxazolidones

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**A solubility study of alkali metal and ammonium halides in 3-methyl and *t*-butyl oxazolidones is made. Solubility ratios are calculated, and data are presented.**

When substituted in the three position, 2-oxazolidones will likely be utilized as useful and versatile nonaqueous solvents in part because of their high polarities, high dielectric constants (ranging from 42.6 to 77.5), and good working liquid ranges. With this perspective, a solubility study of alkali metal and ammonium halides in 3-methyl (3Me20x) and *t*-butyl oxazolidones (*t*Bu20x) was undertaken to add to the already existing fundamental data for these interesting substances (Figure 1).

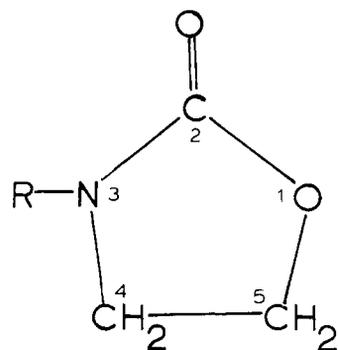
## Experimental

**Procedure.** Four determinations of approximately 1-, 2-, 3-, and 4-g samples of salt plus about 30 ml of the respective substituted oxazolidone were immersed in a thermostatic bath assembly (either a Haake Model ED Unitherm or Sargent Model S-84860), filled with water, and stirred at  $25.00^\circ \pm 0.05^\circ\text{C}$  for 18–24 hr.

The stirred solutions were filtered into separate preweighed medium porosity fritted crucibles. These, along with the original sample containers, were then washed with reagent grade carbon tetrachloride and dried in vacuo at approximately  $50^\circ\text{C}$  for 1–2 hr. Recoveries from the carbon tetrachloride washings showed negligible losses of salt due to washing with it. The dried crucibles and sample containers were reweighed, the total undissolved salt was determined, and the solubility ratio as presented in Table I was calculated. Determinations using both a Mettler Model H-18 analytical balance and a Mettler Model P162 top loader proved to give comparable results for several of the salts.

**Reagents.** Fisher Scientific reagents were used for  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{Br}$ , and  $\text{NaCl}$ . Ventron ultrapure reagents were used for

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R = CH<sub>3</sub>: 3-Me-2-Ox

R = *tert*-butyl: 3-*t*-Bu-2-Ox

Figure 1. Structure of 3-methyl and *t*-butyl-2-oxazolidone

$\text{LiCl}$ ,  $\text{RbCl}$ ,  $\text{CsCl}$ ,  $\text{LiBr}$ ,  $\text{RbBr}$ ,  $\text{CsBr}$ ,  $\text{LiI}$ ,  $\text{RbI}$ , and  $\text{CsI}$ .  $\text{NH}_4\text{I}$ ,  $\text{NaBr}$ ,  $\text{NaI}$ ,  $\text{KCl}$ , and  $\text{KI}$  were J. T. Baker Analyzed reagents. All reagents were dried in vacuo at  $50^\circ\text{C}$  for about 2 hr and were used without further purification. The iodides discolored to a yellow tinted salt upon heating and were therefore, after heating, washed with ether; then they were air dried under suction.

Solvent synthesis and purification have been adequately described previously (1, 3, 5).

## Results and Discussion

From Table I, for a given cation, solubility generally tends to decrease from Li to Cs. When salts were recovered completely (using concentrations approaching 1 g solute/g solvent) they were termed insoluble. The ammonium ion has the ability to hydrogen bond with these polar solvents; therefore, their solubilities are increased. In switching from 3Me20x to *t*Bu20x, the general decrease in solubility can be attributed in part to a substantial decrease in dielectric constant from 77.5 for 3Me20x to 57.6 for *t*Bu20x. Solubilities were lower in *t*Bu20x by as much as an order of magnitude in many cases. Comparisons with other solvents reveal a general trend of al-

Table I. Solubilities

Compound	g solute/g solvent	Av absolute dev	No. of runs
LiCl	a <sup>a</sup> $2.03 \times 10^{-2}$	$0.14 \times 10^{-2}$	2
	b <sup>b</sup> $1.70 \times 10^{-2}$	$0.22 \times 10^{-2}$	3
NaCl	a $7.07 \times 10^{-5}$	$1.64 \times 10^{-5}$	4
	b $4.38 \times 10^{-5}$	$1.72 \times 10^{-5}$	6
KCl	a $1.49 \times 10^{-4}$	$0.05 \times 10^{-4}$	4
	b Insoluble		4
RbCl	a $1.08 \times 10^{-3}$	$0.02 \times 10^{-3}$	3
	b Insoluble		1
CsCl	a $5.78 \times 10^{-4}$	$0.12 \times 10^{-4}$	4
	b Insoluble		1
$\text{NH}_4\text{Cl}$	a $3.26 \times 10^{-4}$	$0.10 \times 10^{-4}$	4
	b $3.08 \times 10^{-4}$	$0.14 \times 10^{-4}$	4
LiBr	a $>10^{-1}$		4
	b $6.57 \times 10^{-2}$	$0.81 \times 10^{-2}$	3
NaBr	a $1.98 \times 10^{-2}$	$0.25 \times 10^{-2}$	4
	b $2.68 \times 10^{-3}$	$0.03 \times 10^{-3}$	3
KBr	a $3.92 \times 10^{-3}$	$0.14 \times 10^{-3}$	4
	b $3.48 \times 10^{-4}$	$0.26 \times 10^{-4}$	4
RbBr	a $6.33 \times 10^{-3}$	$0.12 \times 10^{-3}$	4
	b $5.19 \times 10^{-4}$	$0.06 \times 10^{-4}$	3
CsBr	a $5.15 \times 10^{-3}$	$0.05 \times 10^{-3}$	3
	b $5.09 \times 10^{-4}$	$0.09 \times 10^{-4}$	4
$\text{NH}_4\text{Br}$	a $1.70 \times 10^{-2}$	$0.05 \times 10^{-2}$	4
	b $1.46 \times 10^{-3}$	$0.16 \times 10^{-3}$	4
LiI	a $>10^{-1}$		4
	b $>10^{-1}$		1
NaI	a $>10^{-1}$		4
	b $>10^{-1}$		4
KI	a $>10^{-1}$		4
	b $3.92 \times 10^{-2}$	$0.14 \times 10^{-2}$	3
RbI	a $>10^{-1}$		4
	b $3.17 \times 10^{-2}$	$0.01 \times 10^{-2}$	4
CsI	a $2.03 \times 10^{-1}$	$0.11 \times 10^{-1}$	2
	b $1.32 \times 10^{-2}$	$0.01 \times 10^{-2}$	4
$\text{NH}_4\text{I}$	a $>10^{-1}$		4
	b $>10^{-1}$		1

<sup>a</sup> 3-Methyl-2-oxazolidone. <sup>b</sup> 3-*t*-Butyl-2-oxazolidone.

kali metal and ammonium halide solubilities decreasing with solvent in the order: ethylenediamine (4) > DMF (6) > 3Me2Ox > 3tBu2Ox > acetonitrile (4).

These data show that 3Me2Ox and tBu2Ox may be suitable media for conductance (2), spectroscopy, and acid-base equilibrium studies. Due to their relatively high dielectric constants and large polarities, these cyclic urethanes have promise as electrolytic solvents for a wide variety of applications.

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## Solubility of Methane in Distilled Water and Seawater

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**Bunsen solubility coefficients for methane in distilled water and in seawater at three salinities were determined with an estimated accuracy of 0.5%. The experimental data were fit by the least-squares method to an equation established by Weiss. A table of Bunsen solubility coefficients covering the temperature range -2° to 30°C and the salinity range 0-40 parts per thousand was calculated from the fitted equation. For seawater of salinity 34‰, the Bunsen coefficients ranged from 0.04489 at 0°C to 0.02368 at 30°C. Solubility values for distilled water were in agreement with those reported by Bunsen and Claussen and Polglase but were 3-5% higher than those of Winkler and Morrison and Billet.**

During the past several years, there has been increasing interest in the oceanic distribution of methane (1, 11, 12, 15). Concentrations of methane in the atmosphere and seawater were measured by Swinnerton and his coworkers (11), but they were unable to conclude from their observations whether the ocean is acting as a source or sink for this gas. More recently, Swinnerton and Lamontagne (12) proposed an empirical relationship involving the ratio of the measured methane concentration and its baseline concentration in seawater and similar ratios for ethane and propane as an index of contamination for hydrocarbon pollution. Proper interpretation and use of such information require accurate values for the solubility of methane in seawater. This paper reports the measurement of Bunsen solubility coefficients of methane in distilled water and in seawater at three salinities.

Methane solubilities in distilled water have been reported by a number of workers (2, 3, 9, 18). The results of Bunsen (2) and Claussen and Polglase (3) are about 3-5% higher than those of Winkler (18) and Morrison and Billet (9). Measurements were made in NaCl solutions by Morrison and Billet (9) and by Mishnina et al. (7, 8). The latter workers made measurements in NaCl solutions ranging from 1.00 to 5.31M which is considerably higher than the range of salinities encountered in seawater. Measured solubilities of methane in

seawater have not been reported previously. Calculated solubilities were reported by Atkinson and Richards (1), and Weiss (14) made measurements at one salinity and one temperature.

#### Experimental

Research grade methane gas (Linde Specialty Gas, 99.99% purity) was used for all measurements. The gas was passed through a tube of Ascarite to remove CO<sub>2</sub> prior to use. Seawater was collected, prepared, and degassed as described by Crozier and Yamamoto (4).

Solubility measurements were made by the Scholander microgasometric technique (10) as modified by Douglas (5), using the procedure described previously (4). Measurements were made at several temperatures for waters of a given salinity. Saturation halftimes for distilled water at 11°C was 2.5 min, and for seawater (27.8‰) at 30°C, 4 min. The solution was allowed to equilibrate at least 45 min to ensure complete mixing.

The volumes of absorbed gas and of the water were measured. Bunsen solubility coefficients,  $\beta$ , were calculated from the observed volumes (5).  $\beta$  is defined as the volume of gas (corrected to standard temperature and pressure) absorbed in a unit volume of water at the measurement temperature when the partial pressure of the gas is 760 mm. The calculated solubilities were corrected for the effect of dissolved gas on the volume of the aqueous phase by using a value of 37 cm<sup>3</sup> for the partial molal volume of methane (6). The corrections increased the solubility coefficients by about 0.16%.

#### Results and Discussion

The experimental Bunsen solubility coefficients for methane in distilled water and seawater at three salinities are given in Table I.

The Bunsen solubility coefficient can be expressed as a function of temperature and salinity as follows (13):

$$\ln \beta = A_1 + A_2(100/T) + A_3 \ln (T/100) + S[B_1 + B_2(T/100) + B_3(T/100)^2] \quad (1)$$

where  $A$  and  $B$  are constants,  $T$  is temperature in degrees Kelvin, and  $S$  is salinity in parts per thousand. The constants

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