Solubility of Argon Gas in Aqueous Alkali Halide Solutions

Temperature Coefficient of the Salting Out Parameter

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Solubilities of argon at 1 atm. are reported for aqueous solutions of LiCl at 23°, 35°, and 40° C., NaI at 23°, 30°, and 40° C., and NaCl, NaBr, and KCl at 30° C. up to concentrations of 2.5 molal. The results are combined with other literature values to show that the salting out parameter probably goes through a minimum value with temperature as predicted by the internal pressure theory. The heat capacity change on transferring dissolved gas from water to 1 molal salt solution is calculated from the temperature coefficient of the salting out parameter. Values of the heat capacity change between 10° and 60° are compared graphically for nine gases in NaCl solution and some of the gases in LiCl, NaI, and KI solutions. At 30° C. the heat capacity of transfer to NaCl solution decreases in the order $H_2 > C_2H_4 > CO_2 > C_4H_{10} > C_3H_8 > C_2H_6 > CH_4 > N_2 >$ Ar.

THE EFFECT of aqueous salt solutions on the activity coefficients of nonelectrolyte solutes was reviewed in 1952 (*13*). A summary of developments to 1964 and an extension of the theory were recently published (*5*). The nonelectrolyte activity coefficient is a function of all solute species, and when the nonelectrolyte is dilute, the log of its activity coefficient is a linear function of nonelectrolyte and salt concentrations;

$$\log \gamma_2 = K_2 m_2 + K_3 m_3 \tag{1}$$

Here subscript 2 refers to solute gas and 3 to the dissolved salt. For a nonelectrolyte dissolved in water and dissolved in salt solution at the same pressure and temperature;

$$\log \frac{\gamma_2}{\gamma_2^\circ} = \log \frac{S_2^\circ}{S_2} = K_3 m_3 + K_2(S_2 - S_2^\circ) \tag{2}$$

where γ_2 and γ_2° are the dissolved nonelectrolyte activity coefficents, S_2 and S_2° are the nonelectrolyte solubilities (Bunsen coefficients) in salt solution and in pure water, respectively, K_3 is the salting out parameter, K_2 is the nonelectrolyte salt interaction parameter, and m_3 is the electrolyte molal concentration. For nonelectrolytes of low solubility, such as gases, the last term is usually negligible and the resulting equation is of the same form as the empirical Setchenow equation, $\log S^\circ/S = Km_3$.

This paper presents new data on the solubility of argon gas at 1 atm. in the aqueous alkali halide solutions of LiCl, NaCl, KCl, NaBr, and NaI up to concentrations of 2.5 molal salt. LiCl and NaI solutions were studied at several temperatures. These and other data from the literature are used to calculate values of the enthalpy change, ΔH_t°, and heat capacity change, $\Delta C_{p^\circ t}$, of transferring nonelectrolyte gas from pure water to 1 molal salt solutions at several temperatures.

EXPERIMENTAL

Apparatus. A modification of an apparatus described by Markham and Kobe (*15*) was constructed. Modifications included use of Trubore tubing of 0.4643-sq. cm. cross section in the buret system, incorporation of a sensitive reference pressure device, and a vertical bulb arrangement so that the solvent did not have to stream continuously through a stopcock of small bore. The solvent bulb was calibrated at 30° C. with mercury and it had a volume of 141.8 cc., which was assumed independent of temperature.

Degassing. Water and aqueous alkali halide solutions were degassed by boiling under reduced pressure, cooling under the solvent vapor pressure, and transfer to the solvent bulb without contact with the atmosphere.

Chemicals. The argon was Matheson Co. product stated to be 99.99% pure. The salts were either J. T. Baker or Merck and Co. reagent grade, used without further purification. Solution compositions and densities were determined after the gas solubility measurement. Composition of the alkali halide was determined in most cases by a Volhard titration. Some gravimetric determinations as silver halide were made. Densities were determined by weighing solution delivered from a previously calibrated pipet.

RESULTS

Bunsen coefficients of argon in water and in the salt solutions are given in Table I. Argon solubilities in water were recently reviewed (*2*); the solubilities reported here agree well with other workers' values (*3, 6, 12*).

The salting out parameters, K_3, the slope of $\log S^\circ/S$ against composition, were determined by a least square technique which forced the straight line through the origin. The values of S° used to determine the S°/S ratios were 0.0323 at 23° and 0.0313 at 25° C. At other temperatures the solubilities in Table I were used. Salting out parameters for both molality and molarity plots are given in Table II. All systems salted out. The activity coefficient of argon was increased by the presence of the alkali halide in the order LiCl < KCl < NaBr < NaCl < NaI at 30° C.

Figure 1 shows the salting out parameter *vs.* temperature for LiCl and NaCl solutions. Included are salting out parameters from the literature (*4, 9, 17, 19*). Some of the earlier literature values do not fit the plot (*1*). Others (*4*) were calculated assuming a 1 molal solution, although apparently the solutions were not corrected for concentration changes during degassing. Values of dK/dT at 30° C. followed the order LiCl < NaCl < NaI.

DISCUSSION

The theoretical approaches to the influence of an electrolyte on the activity of a dissolved nonelectrolyte are classed (*13*) as ionic, electrostatic, van der Waals, and internal pressure. The internal pressure concept developed in modern

Table I. Solubility of Argon in Water and in Aqueous Alkali Halide Solutions

Salt	Temp., °C.	Molality	No. of Detns.	Bunsen Coefficient × 10^3
None	25		5	31.5 ± 0.6
	30		4	28.8 ± 0.3
	35		10	26.9 ± 0.5
	40		4	25.2 ± 0.3
LiCl	23	0.4186	4	28.5 ± 0.3
		1.2311	5	23.9 ± 0.3
		2.5340	3	18.0 ± 0.1
	35	0.4378	3	24.5 ± 0.2
		0.6325	6	23.5 ± 0.5
		1.2581	6	19.9 ± 0.5
		1.9735	3	17.2 ± 0.2
	40	0.4378	3	23.3 ± 0.1
		0.9986	5	20.6 ± 0.4
		1.2311	5	18.6 ± 0.3
		1.2581	4	19.4 ± 0.2
NaCl	30	0.5083	3	24.5 ± 0.5
		1.0337	3	21.2 ± 0.3
		2.1119	3	15.6 ± 0.0
KCl	30	0.3702	4	25.2 ± 0.4
		0.7627	4	22.3 ± 0.4
		1.0210	4	21.3 ± 0.2
		1.6778	4	18.2 ± 0.1
NaBr	30	0.4910	5	24.3 ± 0.4
		0.9867	4	21.3 ± 0.2
		2.0440	5	16.1 ± 0.2
NaI	23	0.6712	7	26.1 ± 0.4
		1.0773	3	22.4 ± 0.4
		2.2264	3	15.5 ± 0.1
	30	0.5016	4	24.1 ± 0.5
		1.0840	3	20.9 ± 0.2
		2.0180	5	15.2 ± 0.3
		3.8766	5	8.3 ± 0.3
	40	0.6712	4	20.4 ± 0.4
		1.0773	3	17.7 ± 0.1
		2.2264	3	12.6 ± 0.1

Table II. Salting Out Parameters, K_s

Salt	Temp., °C.	Salting Out Parameter, K_s	
		Molality	Molarity
LiCl	23	0.102	0.107
	35	0.099_5	0.102_5
	40	0.097_5	0.100
NaCl	30	0.127	0.132
KCl	30	0.125_5	0.130_5
NaBr	30	0.126_5	0.132_5
NaI	23	0.143_5	0.155
	30	0.138_5	0.155
	40	0.136_5	0.147_5

terms (*14*) correlates well with the present results. The internal pressure theory is based on a calculation of the free energy of transfer of a nonpolar nonelectrolyte from pure water to the salt solution, assuming the neutral molecules merely occupy volume. The theories-limiting expression for the salting out parameter is;

$$K_s = \frac{\bar{V}_2^\circ\,(V_3 - \bar{V}_3^\circ)}{2.303\,K_t RT} \tag{3}$$

where $\bar{V}_2^\circ$ and $\bar{V}_3^\circ$ are partial molar volumes at infinite dilution of nonelectrolyte and electrolyte, respectively, V_3 is the molar volume of pure liquid electrolyte, and K_t is the isothermal compressibility of the pure solvent.

Differentiation of Equation 3 with respect to temperature gives several terms, of which

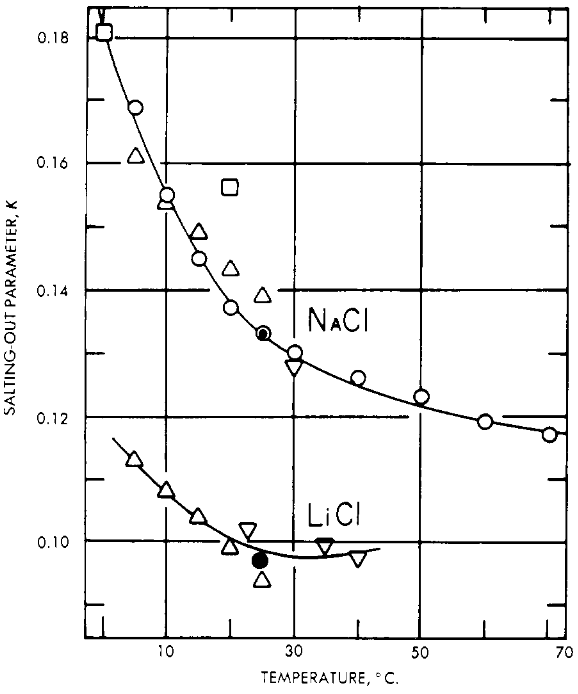

Figure 1. Salting out parameter vs. temperature

Ar-NaCl. △(*4*), □(*9*), ○(*17, 19*), ▽this work
Ar-LiCl. △(*4*), ●(*19*), ▽ this work

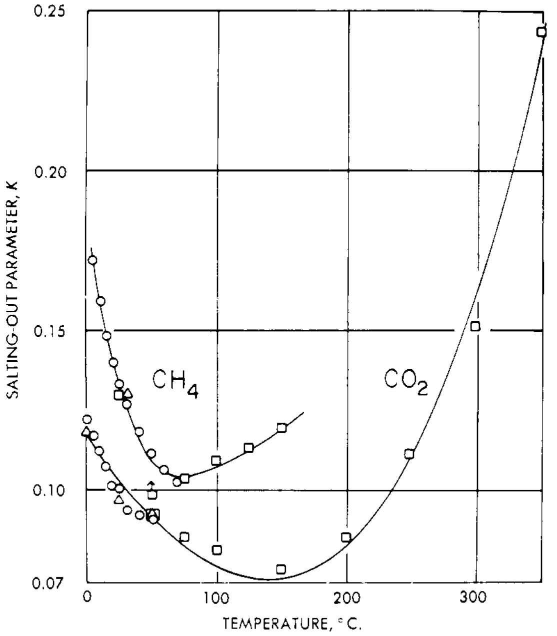

Figure 2. Salting out parameter vs. temperature

Methane-NaCl. △(*7*), □(*16*), ○(*17*)
Carbon dioxide-NaCl. □(*8*), △(*15*), ○(*17*)

$$\frac{dK}{dT} = -\frac{\bar{V}_2^\circ}{2.303\,RT}\,\frac{d\bar{V}_2^\circ}{dT} \qquad (4)$$

is the dominant one.

Equation 3 predicts the order of the salting out parameter in alkali halides to be $\text{Li}^+ < \text{K}^+ < \text{Na}^+$ for a common anion and $\text{I}^- < \text{Br}^- < \text{Cl}^-$ for a common cation. The alkali metal chlorides show the expected order, but the sodium halides do not at 30° C. However, at about 15° C. there appears to be a crossover, and NaCl salts out more below 15° C. than does NaI.

Equation 4 shows that the slope dK/dT should be opposite in sign to the slope $d\bar{V}_2^\circ/dT$. Plots (not shown) of the apparent molar volumes of the alkali halides (*11*) against temperature give the predicted correlation between dK/dT and $-d\bar{V}_2^\circ/dT$ in the order LiCl<NaCl<NaI as observed. The plots of $\bar{V}_2^\circ$ against T go through a maximum for LiCl at about 40° C. and KCl at about 60° C. and are so shaped for the other alkali halides that one expects them to show a maximum at higher temperatures (*11*). Thus, one would predict that the salting out parameter reaches a minimum value at some higher temperature. Literature data on the salting out of methane and carbon dioxide in NaCl solutions show such a minimum (Figure 3). The methane data are from three sources (*7, 16, 17*). The authors calculated the salting out constants from the solubility data in the latter two papers.

The carbon dioxide salting out parameters show a definite concentration dependence. The plotted values are for 1 molal salt solutions and the three workers' (*8, 15, 17*) values agree within 1% at 50° C. One set of data (*17*) is a compilation of earlier workers' results. The minimum in the salting out parameter comes at about 80° C. for methane and 135° C. for carbon dioxide. Equation 4 would predict all gases to show a minimum in K at the same temperature for a common electrolyte. However, the 55° C. difference in temperature of minimum K for methane and carbon dioxide is not surprising, since Equation 4 has assumed that certain terms cancel and since carbon dioxide and water react in a rather complicated temperature-dependent equilibrium themselves. For gases that obey a Setschenow-like equation of the form $\log S^\circ/S = \log \gamma/\gamma^\circ = Km$, where m is the salt molality, the temperature coefficient of the salting out parameter, K, can be used to calculate the enthalpy change and heat capacity change

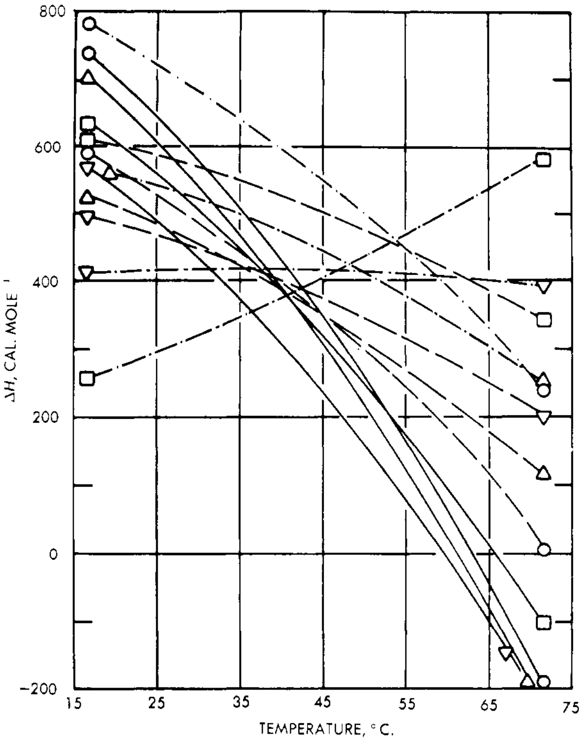

Figure 4. Enthalpy change on transfer of gas from water to 1 molal salt solution vs. temperature

———LiCl. ------NaCl. —·—·—KI

○ Methane. △ Ethane. ▽ Propane. □ Butane

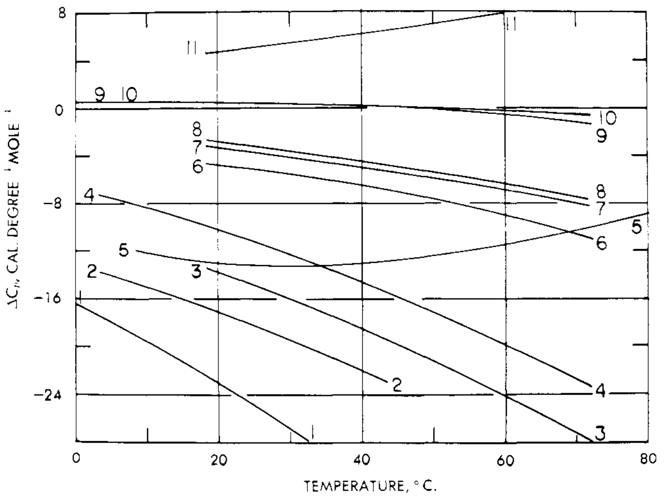

Figure 3. Heat capacity change on transfer of gas from water to 1 molal salt solution vs. temperature

1. Ar-NaCl. 2. Ar-LiCl. 3. N_2-NaCl. 4. Ar-NaI. 5. Methane-NaCl. 6. Ethane-NaCl. 7. Propane-NaCl. 8. Butane-NaCl. 9. CO_2-NaCl. 10. Ethylene-NaCl. 11. H_2-NaCl

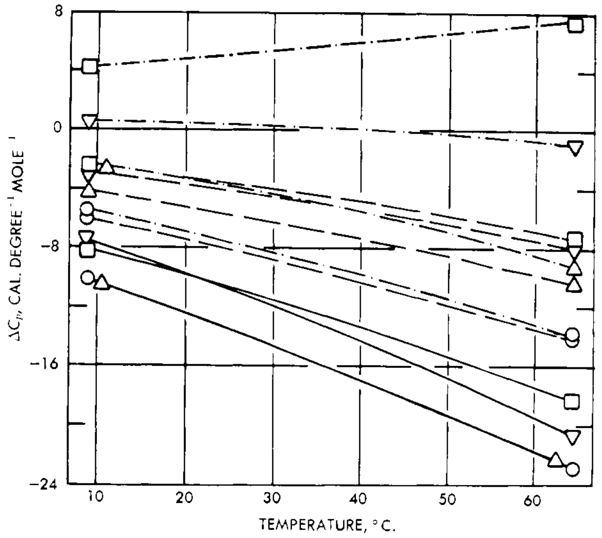

Figure 5. Heat capacity change on transfer of gas from water to 1 molal salt solution vs. temperature

———LiCl. ------NaCl. —·—·—KI

○ Methane. △ Ethane. ▽ Propane. □ Butane

Table III^a. Constants for Equation $K = A + BT + CT^2 + DT^3$

System	A	$B \times 10^3$	$C \times 10^5$	$D \times 10^8$	Temp. Range, ° K.
Ar-LiCl	2.28731	14.3827	2.36092	. . .	278.15–313.15
Ar-NaCl	11.6079	–105.271	32.2075	–32.8955	273.15–348.15
Ar-NaI	1.27008	–5.37465	. . .	1.78880	278.15–313.15
CH_4-NaCl	4.50716	–35.0139	9.20713	–7.99611	278.15–423.15
CO_2-NaCl	0.257555	1.57492	–0.253024	0.438362	273.15–623.15

[a] Sufficient figures were kept to ensure a well-behaved second derivative for calculation of heat capacity change.

of transferring the nonelectrolyte gas from pure solvent to salt solution.

Gas (1 atm.) = gas-saturated water (S_2°, γ_2°)
Gas (1 atm.) = gas-saturated salt solution (S_2, γ_2)

For the transfer of one mole of gas from water solution to the salt solution the nonideal free energy of transfer is

$$\Delta G^\circ = 2.303\ RT \log \gamma_2/\gamma_2^\circ = 2.303\ RT\ K\ m$$

From the standard thermodynamic relation

$$\frac{\partial(\Delta G^\circ/T)}{\partial T} = -\ \Delta H^\circ/T^2 = 2.303R\frac{\partial \log\ (\gamma_2/\gamma_2^\circ)}{\partial T} = 2.303\ Rm\ \frac{\partial K}{\partial T} \qquad (5)$$

It follows that

$$\Delta H^\circ = -2.303\ RT^2\ m\ (\partial K/\partial T) \qquad (6)$$

and

$$\Delta C_p^\circ = \partial(\Delta H^\circ)/\partial T = -\ \frac{\partial}{\partial T}\ [2.303\ RT^2\ m\ (\partial K/\partial T)] \qquad (7)$$

If the salting out parameters are fit to a power series in temperature of the form

$$K = A + BT + CT^2 + DT^3 \qquad (8)$$

for the transfer of gas from water to 1 molal salt solution, Equations 6 and 7 become

$$\Delta H^\circ = -2.303\ R[BT^2 + 2CT^3 + 3DT^4] \qquad (9)$$

and

$$\Delta C_p^\circ = -(2)\ (2.303)\ R\ [BT + 3CT^2 + 6CT^3] \qquad (10)$$

The constants for Equation 8 for data shown in Figures 1 and 2 and for the Ar-NaI system are given in Table III. The calculated ΔC_p° values are shown in Figure 3 with ΔC_p° values for other systems from the literature (*18*) as calculated by the present authors from Equations 6 through 10. Values of ΔH° for the same systems are listed in Table IV for temperatures between 10° and 40° C. The heat capacity change is positive over the entire temperature range only for hydrogen; it is positive for carbon dioxide and ethylene below 40° C. For transfer of gas from water to 1 molal sodium chloride solutions at 30° C. ΔC_p° decreases in the order $H_2 > C_2H_4 > CO_2 > C_4H_{10} > C_3H_8 > C_2H_6 > CH_4 > N_2 > Ar$.

Figures 4 and 5 show enthalpy changes and heat capacity changes for the transfer of the simple hydrocarbon gases methane, ethane, propane, and butane from water to 1 molal LiCl, NaCl, and KI solutions. Literature (*18*) salting out parameters were fitted to Equation 8 and ΔH° and ΔC_p° calculated as outlined above. The considerable systemization that results in going from the enthalpy changes (Figure 4) to the heat capacity changes (Figure 5) is expected (*10*), and the ΔC_p°'s are of the proper magnitude (*2, 18*). For each gas the heat capacity of transfer decreases in the order KI>NaCl>LiCl. This order also holds for hydrogen, nitrogen, and ethylene in the three salt solutions (data not shown). The ΔC_p° values for methane-NaCl from the second temperature derivative of the salting out parameter from (*18*) and from the combined data (*7, 16, 17*) differ by 3 to 6 cal. deg.$^{-1}$ mole^{-1}, which is a measure of the uncertainty of ΔC_p° values by this method.

Table IV. Enthalpies of Transfer of Nonelectrolyte Gas from Water to 1 Molal Salt Solution

(Units, cal./mole)

System	Temperature, ° C.			
	10	20	30	40
Methane-NaCl	773	648	520	392
Ethane-NaCl	549	506	454	391
Propane-NaCl	512	483	445	399
Butane-NaCl	623	599	566	525
Ethylene-NaCl	397	336	263	179
Hydrogen-NaCl	70	114	165	224
Nitrogen-NaCl	850	725	576	402
Carbon dioxide–NaCl	197	201	203	203
Argon-NaCl	752	538	288	147
Argon-LiCl	371	213	29	–181
Argon-NaI	393	300	186	50

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