The Salting Out of Helium and Argon by Sodium Iodide in Methanol and in Water at 30° C.

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The solubility of both argon and helium has been measured at 30° C. and 1 atm. total pressure in mixtures varying from 0 to 4 molar NaI in methanol. Argon solubilities have been measured in mixtures varying from 0 to 7 molar NaI in water. The Setschenow salting out constants are Ar-NaI-H_2O, 0.153; Ar-NaI-CH_3OH, 0.126; He-NaI-CH_3OH, 0.254. The density of NaI-methanol solutions was measured and is reproduced by the equation d = 0.781 + 0.129 *M* where *M* is the NaI molarity.

THE SOLUBILITY of argon in water-sodium iodide mixtures, and the solubility of both argon and helium in methanol-sodium iodide mixtures was measured at a total pressure of 1 atm. at 30° C. The solubility of helium in water-sodium iodide mixtures was estimated from the data of Morrison and Johnstone (*9*).

Both gases are salted out by the sodium iodide. Argon is salted out more in water than in methanol; helium is salted out more in methanol than water. The reversal can be explained in part by a qualitative consideration of the van der Waals London dispersion energies between the rare gas atoms and the solvent-sodium iodide mixture.

EXPERIMENTAL

Materials. The methanol was Merck Anhydrous and the sodium iodide was Baker Analyzed Reagent Grade. Both were used as received. The helium and argon were Matheson regular grade stated to be 99.99 and 99.998% pure, respectively.

Procedure. The solvent was degassed by refluxing, then cooling under vacuum. The sodium iodide molarity was determined by the Volhard method on a solvent sample taken after the solubility determination. Solvent densities were determined at the same time by weighing 10 ml. of solution.

Apparatus. The solubility apparatus was modeled after that of Markham and Kobe (*7*). The only modification was the use of a length of true bore tubing of cross section 0.4643 sq. cm. as the gas buret. The volume of gas, presaturated with solvent, and at a total pressure of 1 atm. taken up by 103.1 sq. cm. of solution was measured. Height differences in the gas buret were determined with a cathetometer. Bunsen coefficients were calculated from the directly measured Ostwald coefficients.

The methanol-sodium iodide densitites were linear with molarity. The least square equation d = 0.781 + 0.129 *M* reproduced the experimental densities within 0.5%. The densities seem consistent with some reported at 25° C. by Ewart and Raikes (*3*).

The solubilities are given in Table I as S_0/S ratios where S_0 is the solubility in either pure water or pure methanol and S the solubility in the appropriate salt solution. The Bunsen coefficient of argon in water (S_0 = 0.0281) agreed within 0.4% of the value of Morrison and Johnstone (*8*). The Bunsen coefficients of argon (S_0 = 0.230) and helium (S_0 0.0338) in methanol agreed with Lannung's (*5*) values within 5 and 1.5%, respectively.

In solutions of low nonelectrolyte concentration the Setschenow equation relates the nonelectrolyte activity coefficient, *f*, the solubility ratio, S_0/S, and the salt concentration, *C*. [A more complete discussion is available (*6*)].

$$\log f = \log S_0/S = \mathrm{K}C$$

Table I. Solubility Ration S_0/S for Helium and Argon in Methanol-Sodium Iodide and Water-Sodium Iodide Mixtures at 30° C.

Solvent	Sodium Iodide, Moles/Liter	S_0/S Helium	S_0/S Argon
Methanol	0.0	1	1
	0.171	1.065	...
	0.227	...	1.130
	0.419	1.285	...
	0.762	...	1.230
	1.32	2.225	...
	1.91	...	1.750
	2.31	2.560	...
	2.47	...	2.135
	2.82	3.395	...
	3.40	...	2.490
	3.53	4.165	...
	3.84	...	3.155
Water	0.0	...	1
	0.782	...	1.350
	1.33	...	1.575
	2.23	...	1.950
	3.56	...	2.605
	5.25	...	3.615
	6.99	...	4.370

Table II. Setschenow Salting Out Constants and Some Related Properties of the Gases and the Solvents

Gas	Setschenow Constants: Water, Molar	Water, Molal	Methanol, Molar	Methanol, Molal	Polarizability[a] cc. x 10^{24}
Helium	. . .	0.10	0.254	0.198	0.204
Argon	0.153	0.145	0.126	0.088	1.626
Polarizability[a] cc. x 10^{24}	1.444		3.31		
Dipole Moment, D (*8*)	1.85		1.70		
Dielectric Constant 30° C. (*9*).	78.54		32.63		

[a] Calculated from optical properties (*10*).

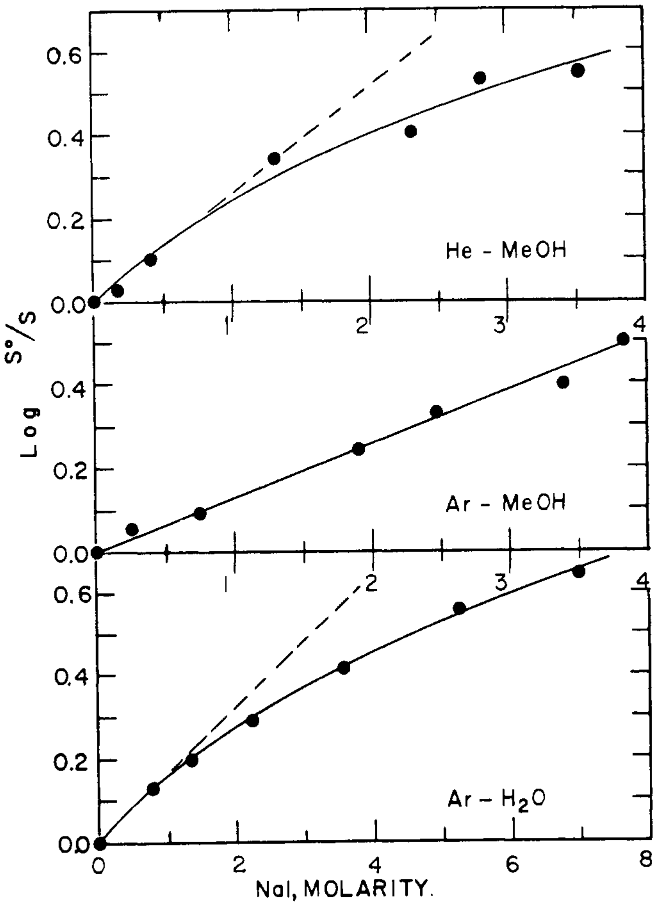

Figure 1. Plots of log S_0/S against molarity of sodium iodide

Plots of log S_0/S against molarity of sodium iodide are shown in Figure 1. The Setschenow constants, which are the limiting slopes of Figure 1, are in Table II. Included are values from plots of log S_0/S against molality. The values for helium in water-sodium iodide were estimated from the data of Morrison and Johnston (*9*), who have determined Setschenow constants for hellium in aqueous solutions of five alkali halides. Their values at 25° C. of LiCl, 0.050; NaCl, 0.081; NaBr, 0.087; KCl, 0.068; and KI, 0.083 suggest that a value of K of 0.10 for helium in NaI is a logical upper limit. Our confidence in this estimate is reinforced by our own experience with argon in the same series of alkali halides plus sodium iodide (*4*) and by the observed fact that the Setschenow constant usually decreases as temperature increases (*6*).

The theory of Debye and McAulay (*2*) relates salt effects to the influence of the nonelectrolyte on the dielectric constant of the solvent. If a nonelectrolyte brought about the same fractional change in the dielectric constant of two solvents, say methanol and water, then at the same concentration of a salt and the same concentration of nonelectrolyte the Debye-McAulay theory would predict a salting out ratio of

$$\frac{k_{\text{MeOH}}}{k_{\text{H}_2\text{O}}} = \frac{D^2_{\text{H}_2\text{O}}}{D^2_{\text{MeOH}}} = 5.8$$

where *D* is the solvent dielectric constant. As predicted helium is salted out more in methanol than water, but the observed ration is only 2.0.

Bockris, Bowler-Reed, and Kitchener (*1*) have taken into account van der Waals interactions between nonelectrolyte and salt ions, which if of sufficient magnitude can cause salting in. Their theory takes into account the polarizability of nonelectrolyte, electrolyte, and solvent, as well as dielectric constant of the solvent. Efforts to use their equation to predict salting out ratios between methanol and water for both helium and argon were not as successful as hoped. The equation accounted for only a few per cent of the observed change in salting out ratio.

The small polarizability of helium indicates van der Waals interaction energies are small in the helium systems. The Debye-McAulay approach explains much of the observed behavior. Argon is eight times more polarizable than helium and methanol is twice as polarizable as water. The interaction energies between argon and solvent oppose the Debye-McAulay salting out and not only result in less salting out of argon than might otherwise be expected but also result in the salting out of argon by the same salt being less in methanol than in water.

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