Subscripts

1 = tetrahydrofuran (THF)
2 = water
3 = dimethylformamide (DMF)
i = component

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Solubility of Ethylene in Aqueous Silver Nitrate and Potassium Nitrate Solutions

Silver Ion–Ethylene Association Constant

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The solubility of ethylene gas in aqueous silver nitrate and potassium nitrate solution was determined at 0.945-atm. ethylene partial pressure and 30° C. The enhanced solubility in silver nitrate solution was assumed due to a 1 to 1 $CH_2{=}CH_2{-}Ag^+$ association. The zero ionic strength association constant for the reaction $Ag^+(aq.) + CH_2{=}CH_2(aq.) \rightleftarrows CH_2{=}CH_2{-}Ag^+(aq.)$ is 76, and for $Ag^+(aq.) + CH_2{=}CH_2(CCl_4) \rightleftarrows CH_2{=}CH_2{-}Ag^+(aq.)$ is 2.36.

EQUILIBRIUM constants for the silver ion–alkene association are reported (*2, 3, 6, 7, 10, 11, 12*) for various alkenes, cycloalkenes, and methylenecycloalkanes for the reaction

$$Ag^+(aq.) + \text{alkene}\ (aq.) \rightleftarrows \text{alkene}\cdot Ag^+(aq.) \qquad K_1$$

or

$$Ag^+(aq.) + \text{alkene}\ (CCl_4) \rightleftarrows \text{alkene}\cdot Ag^+(aq.) \qquad K_0$$

The two association constants are related through the distribution constant of the alkene between carbon tetrachloride and water (or salt solution)

$$\text{Alkene}\ (aq.) \rightleftarrows \text{alkene}\ (CCl_4) \qquad K_D$$

by $K_1 = K_D K_0$. Reported here is the association constant of the reaction

$$CH_2{=}CH_2(aq.) + Ag^+(aq.) \rightleftarrows CH_2{=}CH_2\cdot Ag^+(aq.)$$

calculated from ethylene gas solubilities in dilute aqueous solutions of silver nitrate and potassium nitrate.

EXPERIMENTAL

Chemicals. Ethylene, Matheson C.P. grade, 99.5% minimum. Reagent grade silver nitrate and potassium nitrate were used without further purification.

Gas solubility apparatus was similar to that described by Markham and Kobe (*9*). Solubilities were measured at an ethylene partial pressure of 0.945 atm. at 30° C.

Aqueous solutions of silver nitrate and potassium nitrate were prepared, degassed by refluxing under vacuum, and transferred to the solubility apparatus without contact with atmospheric gases. The solubility of ethylene gas at a partial pressure of 0.945 atm. was measured by observing the volume of gas, saturated with water vapor from the solution, taken up by an 88.5-ml. sample of the degassed solution at 30° C. and a total pressure of 1 atm.

RESULTS AND DISCUSSION

Results are tabulated in Table I. The solubilities are reported as volume of ethylene, in milliliters, reduced to

Table I. Solubility of Ethylene in Aqueous Silver Nitrate and Potassium Nitrate Solutions at 30° C.

Solubility in Silver Nitrate		Solubility in Potassium Nitrate		
$AgNO_3$, m./l.	C_2H_4, ml. (STP)/ liter solution at 0.945 atm.	KNO_3, m./l.	C_2H_4, ml. (STP)/ liter solution at 1 atm.	$S°/S$
0.0	92.8 ± 0.5 (5)[a]	0.0	98.2 ± 0.5 (5)	1.000
0.0011	99.2 ± 0.2 (2)	0.0084	96.2 (1)	1.021
0.0028	104 ± 0.0 (2)	0.0173	92.7 ± 1.0 (2)	1.059
0.0056	119 ± 2.0 (2)	0.0280	89.6 ± 3.0 (2)	1.096
0.0113	149 ± 2.0 (2)	0.115	84.2 ± 2.5 (3)	1.166
0.0226	200 ± 2.0 (2)	0.525	73.0 ± 5.2 (4)	1.345
0.0338	242 (1)	1.08	71.0 ± 1.6 (3)	1.383

[a] Numbers in ( ) are number of determinations.

standard temperature and pressure, taken up by 1 liter of solution. Division by 22,414 converts the solubilities to units of moles per liter. The ethylene solubility in potassium nitrate solutions is corrected to 1-atm. ethylene partial pressure by assuming Henry's law. It is questionable that Henry's law applies to ethylene solubility in silver nitrate solutions, where a definite chemical reaction takes place, so this solubility is reported at the partial pressure of 0.945 atm. used in the measurement. The ethylene gas solubility in potassium nitrate solution is also reduced to a pressure of 0.945 atm. for calculation of the association constant.

Figure 1 shows the ethylene solubility at 0.945 atm. in dilute potassium nitrate and silver nitrate solutions. In the absence of a direct chemical interaction, salts normally decrease the dissolved nonelectrolyte solubility (increase the nonelectrolyte activity coefficient), as potassium nitrate decreases ethylene solubility. The enhanced solubility in the silver nitrate solutions is assumed to be due to the formation of a 1 to 1 ethylene–silver ion complex, since earlier work (*11*) indicated only that complex to be important. It is further assumed that the silver nitrate and potassium nitrate electrostatic properties result in an identical salting out of ethylene, since the silver and potassium ions are of a similar size. If the salting out correction is ignored, the K_1 value is about 8% lower than the value reported below.

The following procedure was used to calculate the association constant from the solubility data in salt solutions of a given molarity. The ethylene solubility in potassium nitrate solution is taken as the aqueous ethylene concentration. The difference in ethylene solubility between the potassium and silver nitrate solutions of the same concentration is the complex concentration. The difference in initial silver ion and complex concentrations is the equilibrium silver ion concentration. Values of the three equilibrium concentrations calculated from the smoothed curves of Figure 1 are given in Table II at four salt concentrations. The calculated association constant, K_1, at zero ionic strength is 76.

To calculate K_0, a value of K_D is required. This is obtained from the solubility ratio of ethylene gas at 1 atm. in CCl_4 (*4*) and in water (*1*, *8*), which is 32.2 at 30° and 31.0 at 25° C. This gives a K_0 value for $CH_2{=}CH_2{-}Ag^+$ of 2.36. This agrees well with the value of 2.44 reported (*11*) at 25° from a study of the distribution of ethylene between CCl_4 and aqueous solutions 1*M* in $(Ag^+, K^-)\ NO_3^-$. The reported K_1 value (*11*) differs because it refers to unit ionic strength and the present value refers to essentially zero ionic strength. The K_1 value also compares well with another earlier K_1 value of 77.2 (*2*) at 30° C. reported from work in solutions of 0.1*M* $AgNO_3$, 0.025*M* trifluoroacetic acid, and 0.875*M* sodium trifluoroacetate. When 0.1*M* $AgNO_3$ alone was used, an insoluble precipitate formed. The precipitate did not form in the presence of sodium trifluoroacetate. We did not observe a precipitate in our experiment, but a tendency toward a precipitate may be the reason why our ethylene solubility in 0.0334*M* $AgNO_3$ appears a little low (Figure 1).

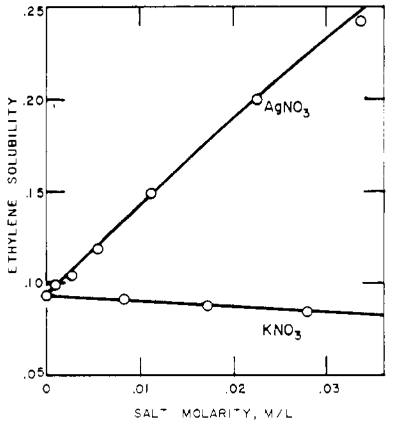

Figure 1. Solubility of ethylene in dilute aqueous solutions of potassium nitrate and silver nitrate

0.945 atm., 30° C.

Table II. Equilibrium Concentrations of Ethylene, Silver Ion, and Ethylene–Silver Ion Complex from Smoothed Solubility Data of Figure 1

Molar Concentrations × 10^3

Initial $AgNO_3$ Concn.	Equilibrium Concentration			Concentration Quotient	
	$AgNO_3$	C_2H_4	$C_2H_4\text{-}Ag^-$	K_1	K_0
5.00	3.82	4.08	1.18	76	
10.00	7.66	4.01	2.34	76	
					2.36
20.00	15.45	3.87	4.55	76	
30.00	23.33	3.76	6.67	76	

Other workers have preferred to use K_0 as a measure of the alkene complexing power with silver ion, because it eliminates in part salt effects on the alkene in aqueous solution. However, such a comparison assumes K_D values about the same for all alkenes. Values of K_D range (*12*) from 830 for isobutene (2-methylpropene) to 9050 for 1-hexene, with most values falling near 4000. Ethylene is definitely anomalous, with a K_D value of only 31. To find where ethylene complexing power with silver ion fits, it seems better to compare K_1 values. The K_1 values fall into three groups. Compounds with K_1 values less than 35 are trimethylethylene < *trans*-2-butene < dimethylbutadiene. Compounds with K_1 values between 60 and 120 are isobutene < *trans*-2-pentene < *cis*-2-butene < 2-methylpropene < ethylene < *cis*-2-pentene < 1-butene. Compounds with K_1 values between 850 and 2400 are 1-hexene < biallyl. There are K_0 values on 12 more olefins (*10*), but they cannot be compared with ethylene, since the corresponding K_D and K_1 values are not known. In view of differences in temperature and ionic strength, and a lack of complete knowledge of K_1, further comparison is not warranted.

A Setchenow plot of log $S°/S$ against C, where $S°$ is the ethylene solubility in water and S the ethylene solubility in potassium nitrate solution of concentration, C, is shown in Figure 2. In dilute solution the salting out parameter has the high value of 1.4, compared to a more normal

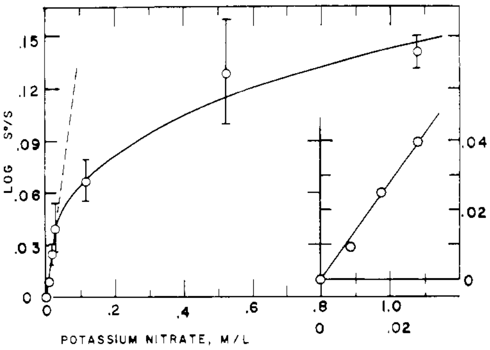

Figure 2. Setchenow plot of salting out of ethylene by potassium nitrate, 30° C.

Dilute solution range magnified in inset value (*5*) of about 0.14 one would obtain if the $1M$ solubility alone were used to establish the slope. We can find no studies that report on the salting in and salting out of gases in the salt concentration range of 0 to $0.03M$. Whether the high salting out constant of ethylene in this salt concentration range is due to some interaction of water, salt, and ethylene pi bonding system or the normal behavior of all gases in the limit of low salt concentration will require further study.

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Limiting Activity Coefficients of C_5 Hydrocarbons in Various Amides

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Gas-liquid chromatographic retention volumes and solute activity coefficients at infinite dilution have been determined for eight C_5 hydrocarbons in nine substituted amides. Temperature was varied so that partial heats of solution were obtained for the binary pairs involving solvents with relatively low vapor pressures at the indicated temperatures. Variation of activity coefficient with solvent structure is obvious.

ACTIVITY COEFFICIENTS determined by gas-liquid chromatography have appeared frequently in the literature recently and the experimental method is well known (*5*). The data produced in this manner are reproducible and are of interest from both a practical and a thermodynamic standpoint. In particular, one can get an idea of the relative nonideality of various binary pairs by this technique. Relative volatilities, obtainable from these data, are invaluable in solvent selection for extractive distillation precesses.

The following expression (*4*) relates the activity coefficient of the solute at infinite dilution in the liquid phase to the measured specific retention volume at 0° C.

$$\gamma_2^{\infty} = \frac{1.704 \times 10^7}{M p_2^\circ V_g^\circ} \qquad (1)$$

where

γ_2^{∞} = solute activity coefficient at infinite dilution
M = molecular weight of solvent
p_2° = vapor pressure of pure solute, mm. of Hg
V_g° = specific retention volume of solute, cc. of carrier gas per gram of solvent

Equation 1 assumes ideality of both the vapor phase above the solution and the pure solute vapor. The pure solute is chosen as the standard state; $\gamma_2 \rightarrow 1$ as $x_2 \rightarrow 1$ where x_2 is the solute mole fraction. The units of the constant in the numerator of Equation 1 are (cc.)(mm. of Hg).

For this work, a Beckman GC-2 chromatograph equipped with a thermal conductivity detector was used. A column packing was prepared, consisting of approximately 20% by weight of the liquid phase and 80% by weight of 60-mesh Johns-Manville Chromosorb W. The columns were 8-foot lengths of ¼-inch o.d. flexible copper tubing which could be easily coiled to fit the column chamber of the chromatograph. The carrier gas was helium and the flow was measured with a soap-film meter. The column outlet pressure was at all times atmospheric, and a mercury manometer to measure the inlet pressure was attached to a point immediately preceding the column inlet. Liquid hydrocarbon samples were injected with a 1.0-μl. Hamilton syringe. The solutes were obtained in pure form from the Phillips Petroleum Co. and blended before injection into the chromatograph. The solvents were used as received from the manufacturer. A reproducibility of values within 1% was realized for the activity coefficients.

To obtain the specific retention volumes, the following expression, developed by Littlewood (*3*), was employed:

$$V_g^\circ = \frac{(D)\ (F)}{(Z)\ (W)} \cdot \frac{273.2}{T_f} \cdot \frac{P_o - P_w}{P_o} \cdot {}^3\!/_2 \cdot \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \qquad (2)$$

where