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Solubility of Ethylene in Aqueous Silver Nitrate

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The solubility of ethylene was measured at pressures up to 0.64 MPa, at silver nitrate concentrations from 1.0 to 6.0 M, and over a temperature range from 278 to 308 K. From the temperature dependence of the solubility, values were determined for enthalpy and entropy changes. The solubility of ethylene increased with increase in pressure, increase in silver nitrate concentration, and decrease in temperature. The results for the solubility of ethylene in 2.0, 4.0, and 6.0 M aqueous silver nitrate at 298 K are in good agreement with the earlier measurements of Hughes and co-workers. The enthalpy and entropy of solution were found to increase with silver nitrate concentrations from 1.0 to 6.0 M; at 1.0 M $AgNO_3$ the enthalpy was -21.9 $kJ{\cdot}mol^{-1}$ and the entropy was -62.5 $J{\cdot}mol^{-1}{\cdot}K^{-1}$; at 6.0 M $AgNO_3$ the enthalpy was -24.9 $kJ{\cdot}mol^{-1}$ and the entropy was -65.3 $J{\cdot}mol^{-1}{\cdot}K^{-1}$. The ethylene solubility in aqueous silver nitrate was empirically correlated as a function of system pressure (P), temperature (T), and silver nitrate concentration (c), and the correlation fits the data with an average error of ±8%.

Introduction

The basic equilibrium data (i.e., solubility) for gas−liquid systems are required to design industrial equipment, such as gas absorption columns and chemical reactors for gas−liquid heterogeneous systems. The proper process design of membrane separation (*1−4*) and for the pressure-swing adsorption (*5*) systems requires reliable solubility data of olefinic gas (i.e., ethylene) in a compatible solvent (*2−4, 6*). Enhanced separation of ethylene from paraffinic gases is obtained by use of aqueous silver nitrate, which functions as a selective carrier of olefins. This selectivity is based on the fact that olefins can react with Ag^+ and form a silver−olefin complex with 1:1 formation (*7−15*).

Although a number of studies have been presented on ethylene solubility in water (*16−18*), very little information has been reported on the solubility of ethylene in aqueous silver nitrate (*4*) and in different metal−salt solutions (*3*) at elevated pressures over wide ranges of temperature and silver nitrate concentration. Hughes and co-workers (*4*) measured the solubility of ethylene in aqueous silver nitrate at 298 K as a function of ethylene pressure and Ag^+ concentration. Ethylene pressures up to 2.83 MPa and Ag^+ concentrations of 2.0, 4.0, and 6.0 M were used to measure the solubility of ethylene. These measurements indicate how the ethylene pressure and Ag^+ concentration should affect the membrane performance on ethylene separation by facilitated transport membranes.

A review of the literature for ethylene solubility in aqueous silver nitrate indicates the significant lack of relevant solubility data at elevated pressures over wide ranges of temperature and silver nitrate concentration. This precludes an understanding of the effects of silver nitrate concentration (c), pressure (P), and temperature (T). Ethylene solubility in silver nitrate has not been correlated as a function of these three variables. This paper presents the first measurement of ethylene solubility in aqueous silver nitrate as a function of A_gNO_3 concentration, pressure, and temperature. The technique used in this study of ethylene solubility is essentially the same as that employed in earlier work on propylene (*19*).

Experimental Section

The solubility of ethylene in aqueous silver nitrate was measured by the pressure-drop method. This method measures the amount of gas absorbed by a given volume of solvent by determining the pressure change in the cell until steady state conditions are reached.

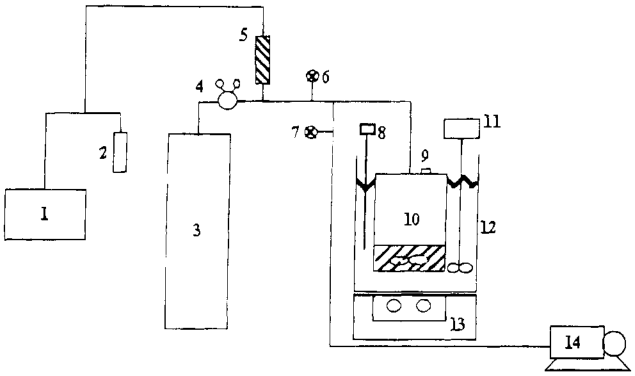

Figure 1. Experimental apparatus: (1) chart recorder, (2) power supply, (3) ethylene gas cylinder, (4) gas regulator, (5) pressure transducer, (6, 7) gas line valves, (8) thermometer, (9) solvent inlet, (10) cell, (11) electric stirrer, (12) constant temperature bath, (13) magnetic stirring hot plate, (14) vacuum pump.

Materials. Ethylene and ethane gases had minimum purities of 99.5 and 99.0% (Matheson Co.), respectively. Aqueous silver nitrate solutions were prepared using silver nitrate of 99.5% purity (Fisher Scientific Co.) and freshly distilled and deionized water. The resistivity (specific resistance) and the pH of pure water were 10×10^6 $\Omega{\cdot}m$ and 6.5, respectively, at 298 K.

Apparatus and Procedure. A schematic diagram of the apparatus is shown in Figure 1. The apparatus consists of a closed cell where ethylene gas dissolves in aqueous silver nitrate. This cell is made of chrome-coated stainless steel, type 316. It has a volume of 1.65 L. The cell is immersed in a constant temperature water bath with a capacity of 6.0 L. Temperature is monitored with a digital thermometer, 0−50 ± 0.1 °C.

The experimental procedure is as follows. Before an experimental run was started, the cell was rinsed with distilled water and dried under vacuum. For every run, system leakage was checked by a soap−water solution and compressed air in every run. After no leaks were found, the cell was filled with a predetermined amount (150 mL) of aqueous silver nitrate of known concentration. The

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constant temperature water bath was set to the desired temperature. Air was removed from the cell by a vacuum pump (Duo-Seal). Then, gas from a high-pressure cylinder was fed into the cell to a desired pressure, which was the initial pressure, P_0. The cell was closed, and the aqueous silver nitrate was stirred with a magnetic stirrer. During the stirring the pressure change was monitored with a pressure transducer (Omega, Model PX300-200GV) and a chart recorder. The stirring process was continued until no further change in pressure was observed. This measured pressure change was used to determine ethylene solubility. At the end of an experimental run, the stirrer was turned off and gas was discharged from the whole system using the vacuum pump. This procedure was repeated for each experiment, varying silver nitrate concentration, temperature, and pressure. With regard to safety precautions, standard laboratory procedures and attention were employed; vent gases were ducted directly into a hood. The estimated maximum percentage error of solubility is ±5.9%.

Determination of Solubility, Enthalpy, and Entropy of Solution. Ethylene solubility was determined from the observed pressure changes on the basis of the following assumptions:

(i) There is no evaporation of water. Gas in contact with liquid is assumed to consist solely of the gas under test, neglecting the presence of solvent vapor. This is justified because the maximum water vapor pressure at the highest temperature of all the measurements is less than 6% of the total pressure; at the lowest temperature the maximum percentage is less than 1%.

(ii) No volume change of the liquid is seen during the dissolution of gas.

(iii) Ideal gas behavior is observed. The compressibility factor of ethylene under experimental conditions of this study ranged from 0.98 to 0.99. The errors due to this assumption are small (less than 2%).

The ethylene solubility, s/mol·L^{-1}, is defined as the dissolved gas in the liquid as follows. Since the experiments were carried out in a closed system, the total number of moles (the initial moles, n_0) of the gas in the vessel was not changed during an experiment. Thus

$$n_0 = n_l + n_g \tag{1}$$

where n_l is the number of moles of gas dissolved into the liquid phase and n_g is the number of moles of gas in the vapor phase.

At equilibrium

$$P_s V_g = (n_0 - n_l)RT \tag{2}$$

$$s = n_l/V_l = (n_0 - n_g)/V_l = [(P_0 - P_s)/RT](V_g/V_l) \tag{3}$$

or

$$s = (\Delta P/RT)(1/\alpha) \tag{4}$$

where s is the amount of dissolved gas in the liquid and determined from the measured pressure drop, α ($=V_l/V_g$) is the volume ratio of liquid to gas phase in the cell, and ΔP = (P_0 − P_s) is the pressure drop in the cell during dissolution of gas (P_0 is the initial pressure and P_s is the saturation pressure).

For the dissolution of ethylene gas in this system, the enthalpy ($\Delta_{sol}H$) and the entropy ($\Delta_{sol}S$) of solution are determined by the following equations (*20–24*):

$$k = A\exp(-\Delta_{sol}H/RT) \tag{5}$$

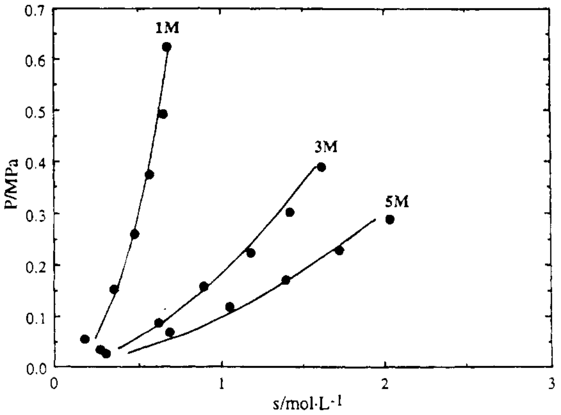

Figure 2. Ethylene solubility s dependence on pressure P at different aqueous silver nitrate concentrations at T = 298 K; (●) experimental; (—) calculated from eq 7.

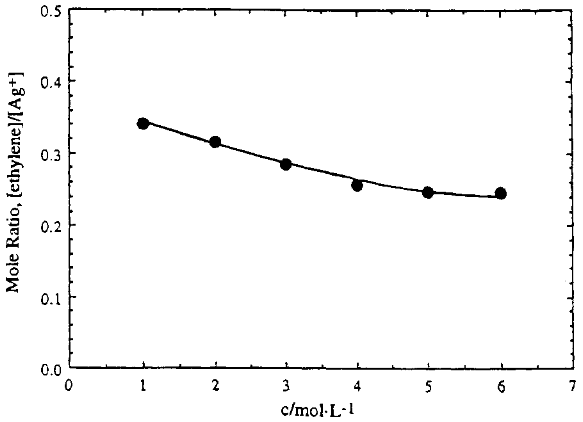

Figure 3. Plot of the mole ratio of [ethylene]/[Ag$^+$] against the concentration of aqueous silver nitrate c at saturation pressure, 0.15 MPa, and T = 298 K.

and

$$\ln(k) = A + B/T \tag{6}$$

To apply eq 6 for the determination of thermodynamic quantities ($\Delta_{sol}H$ and $\Delta_{sol}S$), it is necessary to define the solubility coefficient of dissolved gas in the liquid, k. The solubility coefficient, k, is defined by $k = s/P_s$, where P_s is the saturation pressure. In eq 6, the solubility coefficient is expressed as a two-constant equation for correlating solubility data as a function of temperature. A plot of ln(k) vs 1/T gives a straight line whose slope and intercept provide values of $\Delta_{sol}H$ ($=-RB$) and $\Delta_{sol}S$ ($=RA$), where R is the ideal gas constant.

Results and Discussion

Figure 2 presents the solubility of ethylene in aqueous $AgNO_3$ at 298 K as a function of pressure and silver nitrate concentration. Saturation pressures were up to 0.637 MPa, and Ag$^+$ concentrations were 1.0, 3.0, and 6.0 M. These measurements indicate how gas pressure and silver nitrate concentration affect the solubility of ethylene. The solubility of ethylene increases with increases in pressure and silver nitrate concentration. In Figure 2 the calculated values are based on nonlinear regression analysis for all solubility measurements.

The change in ethylene to silver ion mole ratio as a function of aqueous silver nitrate concentration, at constant pressure, is illustrated in Figure 3. As silver nitrate concentration increases, the mole ratio of ethylene to Ag$^+$ decreases. That is, Ag$^+$ at higher concentrations becomes

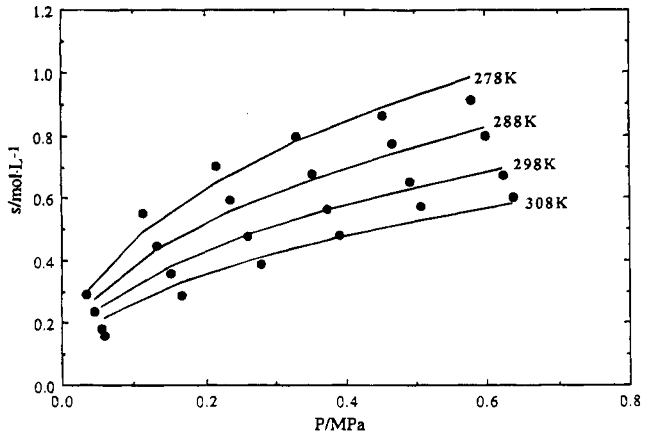

Figure 4. Solubility of ethylene *s* in 1.0 M aqueous silver nitrate as a function of pressure *P* at various temperatures, 278–308 K: (●) experimental; (—) calculated from eq 7.

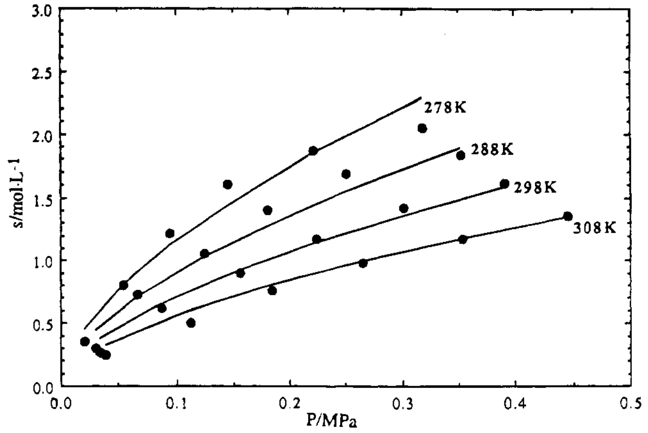

Figure 5. Solubility of ethylene *s* in 3.0 M aqueous silver nitrate as a function of pressure *P* at various temperatures, 278–308 K: (●) experimental; (—) calculated from eq 7.

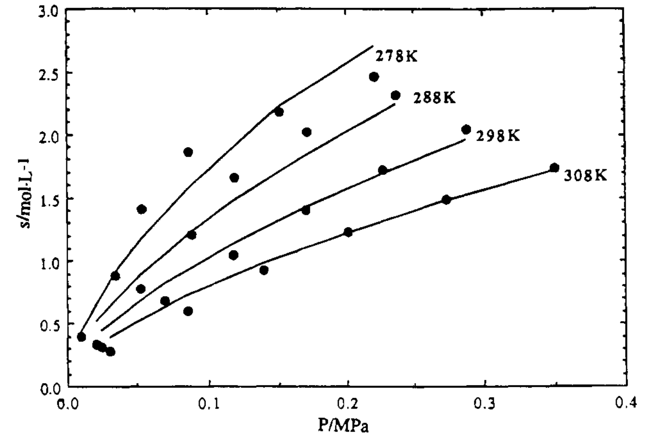

Figure 6. Solubility of ethylene *s* in 5.0 M aqueous silver nitrate as a function of pressure *P* at various temperatures, 278–308 K: (●) experimental; (—) calculated from eq 7.

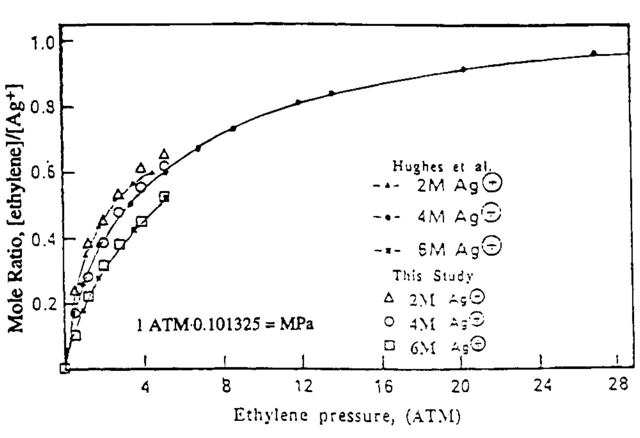

Figure 7. Comparisons with the relevant literature by Hughes et al. Plot of the [ethylene]/[Ag⁺] ratio vs ethylene pressure for silver nitrate concentrations of 2.0, 4.0, and 6.0 M at $T = 298$ K.

less efficient on a per-mole basis of complexing with olefinic gas. This effect could be caused by reduced Ag^+ activity at higher concentrations of solution.

The calculated isotherms for the solubility in 1.0, 3.0, and 5.0 M aqueous silver nitrate are smooth lines when plotted against saturation pressure (see Figures 4, 5 and 6). System temperatures were at 278, 288, 298, and 308 K. The experimental observations are consistent with the calculated values; the average error is ±8.0%, which indicates reasonable experimental precision. As expected, ethylene solubility increased with increasing pressure and decreasing temperature. All ethylene solubility data points (144) as a function of aqueous silver nitrate concentration, pressure, and temperature are listed in Table 1.

Figure 7 illustrates the comparison of this study of ethylene solubility with the results of Hughes and co-workers (*4*). The experimental values for ethylene solubility in 2.0, 4.0, and 6.0 M aqueous silver nitrate at 298 K are fitted consistently along with the plot given by Hughes and co-workers. However, solubility data for ethylene at elevated pressures over wide ranges in temperature and silver nitrate concentration are not available in the literature.

Ethane and ethylene solubilities in aqueous silver nitrate exhibit significant differences because of the degree of unsaturation (*7–10*). In this study the solubility of ethane was experimentally determined to compare its solubility with that of ethylene. The solubilities of ethane and ethylene in $AgNO_3$(aq) at 298 K and 0.79 MPa are compared in Table 2. From these results it is evident that ethane solubility in $AgNO_3$(aq) does not change significantly with a factor of 6 change in $AgNO_3$ concentration. In addition, the solubilities of ethane and ethylene in pure water (*16–18*) are the same order of magnitude as the results tabulated. An exact comparison between these data cannot be made here because the system conditions are different. With regard to ethylene solubility in $AgNO_3$(aq), it increases by a factor of 2.7 with a 6-fold increase in salt concentration. The ethylene solubility is more than 40 times the solubility of ethane at 1 M $AgNO_3$(aq). Apparently, the solubility of ethylene is dominated by the formation of a silver–olefin complex.

To develop an empirical expression for the ethylene–Ag^+ system involving the solubility of ethylene as a function of $AgNO_3$ concentration, pressure, and temperature, the following equation satisfactorily correlates the experimental data with an average error of ±8%

$$\ln(s/\mathrm{mol{\cdot}L^{-1}}) = a_1 \ln(P/\mathrm{MPa}) + a_2/(T/\mathrm{K} + a_3) + a_4 \ln(c/\mathrm{mol{\cdot}L^{-1}}) + a_5 \quad (7)$$

where c is the silver nitrate concentration, P is the absolute pressure, and T is the temperature. The solubility results were fitted to the above equation by regression analyses using Nonlinear Regression Analysis (by Phillip H. Sherrod, Nashville, TN). Correlation results for the 144 ethylene solubility values at pressures up to 0.64 MPa, silver nitrate concentrations from 1 to 6 M, and temperatures from 278 to 308 K are $a_1 = 0.5780$, $a_2 = 9660$, $a_3 = 349.9$, $a_4 = 0.8602$, and $a_5 = -14.93$.

Table 1. Solubilities of Ethylene *s* in Aqueous Silver Nitrate at Concentrations of 1.0–6.0 M

1.0 M		2.0 M		3.0 M		4.0 M		5.0 M		6.0 M	
P/MPa	s/mol·L^{-1}	*P*/MPa	s/mol·L^{-1}	*P*/MPa	s/mol·L^{-1}	*P*/MPa	s/mol·L^{-1}	*P*/MPa	s/mol·L^{-1}	*P*/MPa	s/mol·L^{-1}
T = 298 K											
0.034	0.290	0.031	0.303	0.020	0.351	0.014	0.377	0.010	0.394	0.008	0.403
0.112	0.550	0.082	0.680	0.054	0.802	0.039	0.867	0.035	0.884	0.028	0.914
0.215	0.702	0.152	0.975	0.095	1.222	0.072	1.322	0.053	1.404	0.045	1.439
0.331	0.797	0.256	1.122	0.145	1.604	0.109	1.760	0.086	1.859	0.083	1.872
0.454	0.862	0.364	1.252	0.222	1.868	0.177	2.063	0.151	2.176	0.137	2.236
0.580	0.914	0.475	1.370	0.318	2.050	0.255	2.323	0.221	2.470	0.212	2.509
T = 288 K											
0.045	0.234	0.033	0.284	0.030	0.297	0.024	0.322	0.021	0.335	0.018	0.347
0.132	0.448	0.099	0.586	0.066	0.724	0.059	0.753	0.052	0.782	0.047	0.803
0.235	0.594	0.176	0.841	0.125	1.054	0.101	1.155	0.088	1.209	0.082	1.234
0.353	0.678	0.267	1.037	0.180	1.401	0.142	1.560	0.119	1.657	0.112	1.686
0.468	0.774	0.365	1.205	0.251	1.682	0.213	1.841	0.171	2.016	0.157	2.075
0.600	0.799	0.475	1.322	0.352	1.837	0.291	2.092	0.237	2.318	0.220	2.389
T = 298 K											
0.056	0.182	0.037	0.259	0.034	0.271	0.029	0.291	0.025	0.307	0.023	0.315
0.151	0.356	0.107	0.534	0.087	0.615	0.078	0.651	0.069	0.687	0.066	0.699
0.259	0.477	0.186	0.772	0.156	0.894	0.138	0.966	0.118	1.047	0.108	1.088
0.375	0.566	0.277	0.962	0.224	1.177	0.196	1.290	0.170	1.395	0.147	1.488
0.492	0.651	0.374	1.128	0.302	1.419	0.265	1.569	0.227	1.722	0.196	1.848
0.624	0.660	0.488	1.225	0.391	1.617	0.339	1.827	0.288	2.034	0.259	2.132
T = 308 K											
0.060	0.160	0.043	0.227	0.039	0.243	0.036	0.254	0.031	0.274	0.028	0.286
0.166	0.286	0.132	0.419	0.112	0.497	0.095	0.563	0.085	0.602	0.081	0.618
0.278	0.387	0.218	0.622	0.184	0.755	0.161	0.845	0.140	0.927	0.136	0.943
0.392	0.481	0.316	0.778	0.265	0.978	0.230	1.115	0.201	1.228	0.196	1.248
0.507	0.571	0.422	0.904	0.353	1.174	0.307	1.353	0.273	1.486	0.256	1.553
0.637	0.602	0.537	0.994	0.445	1.353	0.391	1.565	0.350	1.725	0.322	1.835

Table 2. Solubility of Ethane and Ethylene in Aqueous Silver Nitrate[a]

$c(AgNO_3)$/mol·L^{-1}	$s_{C_2H_6}$/mol·L^{-1}	$s_{C_2H_4}$/mol·L^{-1}	$s_{C_2H_4}/s_{C_2H_6}$
1.0	0.016	0.66	41
6.0	0.019	2.13	112

[a] Temperature = 298 K; pressure = 0.79 MPa.

Table 3. Enthalpy and Entropy of Solution for Ethylene in Aqueous Solutions of Silver Nitrate, *T* = 278–308 K

$c(AgNO_3)$/mol·L^{-1}	$\Delta_{sol}H$/kJ·mol^{-1}	$\Delta_{sol}S$/J·mol^{-1}·K^{-1}
1	−21.92	−62.54
2	−22.39	−62.56
3	−23.30	−63.33
4	−24.02	−63.76
5	−24.56	−64.41
6	−24.93	−65.31

Figures 2 and 4–6 present portions of the experimental and calculated solubility values of ethylene at 278–308 K in aqueous silver nitrate. The validity of eq 7 was verified by graphically evaluating the residuals between the experimental and calculated values of solubility (*25*). The $c-P-T$ dependence of the ethylene solubility in aqueous silver nitrate was satisfactorily correlated by eq 7.

The enthalpy and entropy of solution for ethylene were determined from the slope and intercept of the plot in Figure 8. The slope is equal to $-\Delta_{sol}H/R$, and the intercept is equal to $\Delta_{sol}S/R$. Linear least-squares fits give correlation coefficients better than 0.99.

The results of the thermodynamic quantities ($\Delta_{sol}H$ and $\Delta_{sol}S$) calculated from slopes and intercepts of Figure 8 by linear regression are listed in Table 3. The absorption of ethylene is an exothermic process, consistent with the observation of a decrease in solubility with increasing temperature. The magnitudes of enthalpies and entropies of solution increase with silver nitrate concentrations. The reason can be interpreted in the mixing effects (the effects of complex formation) due to the presence of the silver nitrate. The data in Figure 9, $\Delta_{sol}H$ vs c for ethylene, are well-fitted by a least-squares parabola: $\Delta_{sol}H = -21.0 - 0.894c + 0.040c^2$.

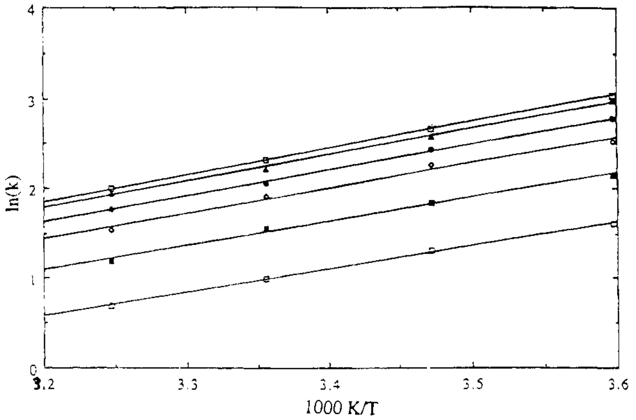

Figure 8. Temperature dependence of ethylene solubility [as ln(k)] at constant silver nitrate concentration c at P_s = 0.10 MPa: (dotted square) 6.0 M; (▲) 5.0 M; (●) 4.0 M; (◇) 3.0 M; (■) 2.0 M; (□) 1.0 M.

Conclusions

Ethylene solubility measurements were made at pressures up to 0.79 MPa, at silver nitrate concentrations from 1.0 to 6.0 M, and over a temperature range from 278 to 308 K. These solubilities, which cover a wide range of various experimental conditions, augment the literature of solubility data for ethylene. There is good agreement between results shown in the literature and those of this study for ethylene solubility in 2.0, 4.0, and 6.0 M aqueous silver nitrate at 298 K. New values were determined for enthalpies and entropies of solution and heats of condensation and mixing for ethylene in 1.0–6.0 M aqueous silver nitrate; at 1.0 M A_gNO_3 the enthalpy was −21.9 kJ·mol^{-1} and the entropy was −62.5 J·mol^{-1}·K^{-1}; at 6.0 M A_gNO_3

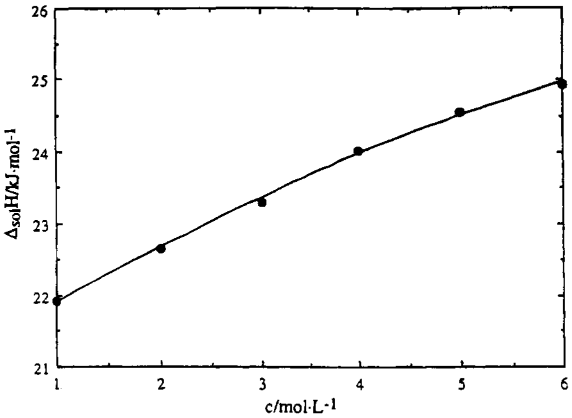

Figure 9. Enthalpy of solution for ethylene $\Delta_{sol}H$ as a function of aqueous silver nitrate concentration c: (●) experimental.

the enthalpy was −24.9 kJ·mol^{-1} and the entropy was −65.3 J·mol^{-1}·K^{-1}. The experimental results of ethylene solubilities were satisfactorily correlated by eq 7 within ±8%.

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