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Solubility of Propylene in Aqueous Silver Nitrate

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The solubility of propylene in aqueous silver nitrate was measured by the pressure-drop method at temperatures from 278 to 308 K, at total gas pressures up to 0.64 MPa, and at silver nitrate concentrations from 1.0 to 6.0 M. From the temperature dependence of the solubility, values were determined for enthalpy and entropy changes. Solubility increased significantly with small decreases in temperature. The solubility of propylene increases with increases in pressure and silver nitrate concentration. 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 -23.5 kJ·mol^{-1} and the entropy was -68.2 J·mol^{-1}·K^{-1}; at 6.0 M $AgNO_3$ the enthalpy was -25.8 kJ·mol^{-1} and the entropy was -71.2 J·mol^{-1}·K^{-1}. The propylene 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 results with an average error of ±8%.

Introduction

The separation of propylene from mixtures with saturated hydrocarbons can be accomplished by absorption (*1*) and membrane processes (*2*). For the proper process design of membrane separation (*2, 3*) and pressure-swing adsorption process (*4*) systems, reliable solubility data of the olefinic gas in a compatible solvent are required. Enhanced separation of propylene from paraffinic gases can be 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 (*5, 6−13*). Aqueous solutions of silver nitrate have been used for purifying olefinic gases by selective formation of a liquid complex with silver nitrate (*1, 8, 9*).

Although studies have been published on the solubility of propylene in water (*14−16*), very little information has been reported on the solubility of propylene in aqueous silver nitrate and in other metal−salt solutions at elevated pressures over wide ranges of temperature and salt concentration. Some of the available investigations on the propylene solubility are discussed below (*1, 2*).

Francis (1) reported the solubility of propylene from a liquid mixture of (propylene + propane) with mole fractions of propylene in the mixture of (propylene + propane) up to 0.945—in aqueous silver nitrate at 298 K and 1.17 MPa. This work indicates that the solubility of liquid propylene at 298 K is 18.7 mass % in 71 mass % aqueous silver nitrate and 9.6 mass % in 39 mass % aqueous silver nitrate. Kawakami and co-workers (2) studied the selective permeation of propylene through Rh^{3+}−poly(ethylene glycol) (PEG) liquid membranes. In this work, propylene solubilities in metal ion−PEG systems were presented at 298 K and at low pressure (up to 0.02 MPa) using Ag^+, Fe^{2+}, Co^{2+}, Cu^+, Rh^{3+}, Pd^{2+}, Ir^{3+}, and Pt^{2+} metal ions. Propylene solubilities increased because of olefin−metal ion interaction in Rh^{3+}, Pd^{2+}, and Pt^{2+} mixtures.

There is a meager amount of propylene solubility data published. This has precluded an understanding of the effects of silver nitrate concentration (c), pressure (P), and temperature (T). This paper presents the first measurements of propylene solubility in aqueous silver nitrate as a function of $AgNO_3$ concentration, pressure, and temperature.

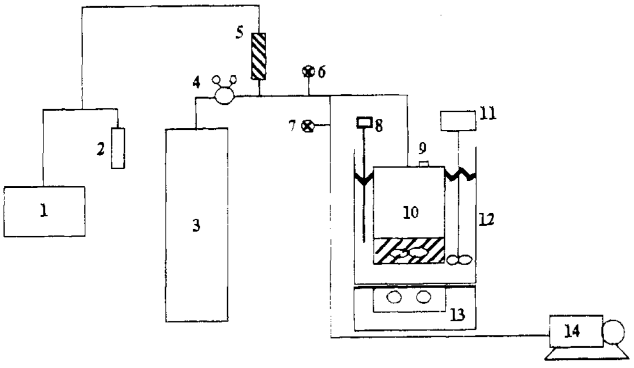

Figure 1. Experimental apparatus: (1) chart recorder, (2) power supply, (3) propylene gas cylinder, (4) gas regulator, (5) pressure transducer, (6, 7) gas line valves, (8) thermometer, (9) solvent inlet, (10) cell, (11) electric stirrer, (12) constant temperature bath, (13) magnetic stirring hot plate,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

Experimental Section

The solubility of propylene 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 a determining the pressure change in the cell until steady state conditions are reached.

Materials. Propylene and propane 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 this water were 10×10^6 Ω·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 propylene 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

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compressed air. After no leaks were found, the cell was filled with a predetermined amount (150 mL) of aqueous silver nitrate of known concentration. The 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 the propylene 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. Propylene solubility was determined from the observed pressure changes on the basis of the following assumptions:

(i) There is no evaporation of water. The 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 propylene 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 propylene solubility, s, 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 is determined from the measured pressure drop, α ($=V_l/V_g$) is the volume ratio of liquid to gas phase in the cell, and $\Delta P = (P_0 - P_s)$ is the pressure drop in the cell during dissolution of gas (P_0 is the initial pressure and P_s is the saturation pressure).

Experimental values of the enthalpy of solution are normally obtained in one of two ways: (1) from the temperature dependence of the free energy, derived from the pressure measurements at a series of temperatures; and (2) from the direct calorimetric measurements upon the dissolving process.

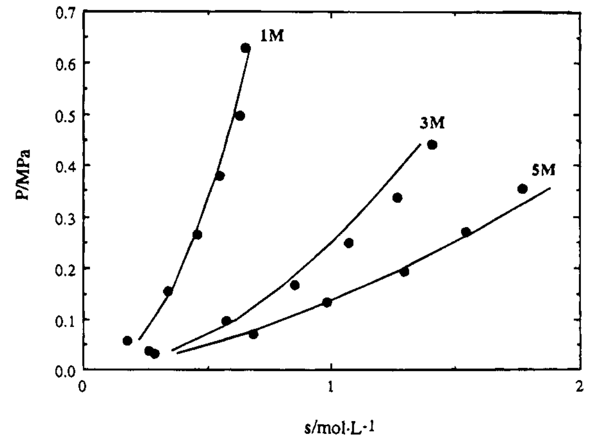

Figure 2. Propylene solubility s dependence on pressure P at different aqueous silver nitrate concentrations at 298 K: (●) experimental; (—) calculated from eq 7.

For the dissolution of propylene in this study, the enthalpy of solution ($\Delta_{sol}H$) and the entropy of solution ($\Delta_{sol}S$) are determined by the above method 1 as the following equations (*17–21*):

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

and

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

To apply eq 6 for the determination of thermodynamic quantities (ΔH and ΔS), 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 propylene in aqueous $AgNO_3$ at 298 K as a function of pressure and silver nitrate concentration. The saturation pressures were up to 0.633 MPa, and Ag^+ concentrations were 1.0, 3.0, and 5.0 M. These measurements indicate how gas pressure and silver nitrate concentration affect the solubility of propylene. The solubility of propylene increases with increases in pressure and silver nitrate concentration. In Figure 2 the calculated values are based on a nonlinear regression analysis for all of the solubility measurements.

The change in propylene to silver ion mole ratio as a function of aqueous silver nitrate concentration, at constant pressure, is illustrated in Figure 3. As the silver nitrate concentration increases, the mole ratio of propylene to Ag^+ decreases. That is, Ag^+ at higher concentrations becomes less efficient on a per-mole basis for complexing with olefinic gas. This effect could be caused by a reduced Ag^+ activity at higher concentrations.

The calculated isotherms for the solubility of propylene in 1.0, 3.0, and 5.0 M aqueous silver nitrate are smooth lines when plotted against saturation pressure (see Figures 4–6). Temperatures were 278, 288, 298, and 308 K. The experimental observations are consistent with the calcu-

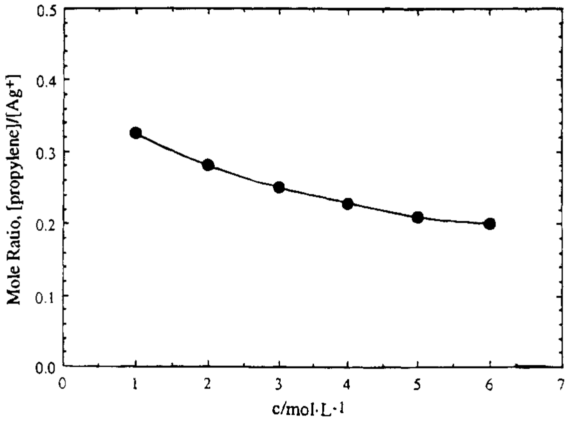

Figure 3. Plot of the mole ratio of [propylene]/[Ag$^+$] against the concentration of aqueous silver nitrate c at saturation pressure, 0.15 MPa, and T = 298 K.

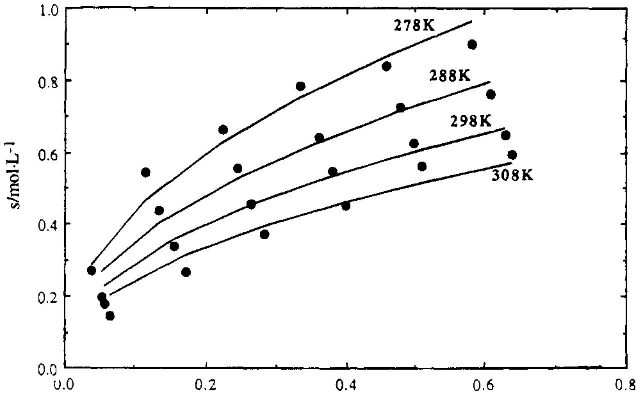

Figure 4. Solubility of propylene s in 1.0 M aqueous silver nitrate as a function of pressure P at various temperatures, 278–308 K: (●) experimental; (—) calculated from eq 7.

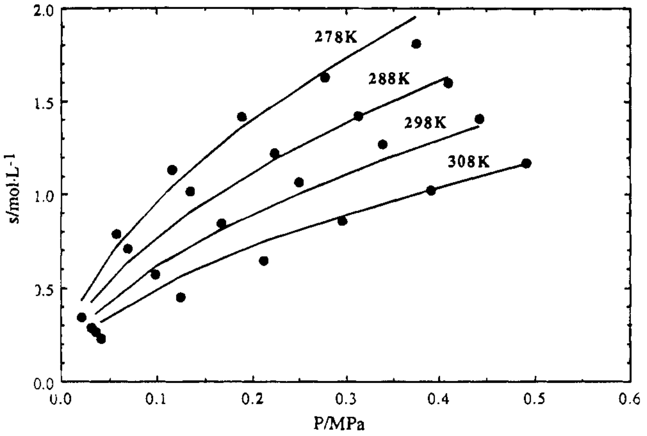

Figure 5. Solubility of propylene s in 3.0 M aqueous silver nitrate as a function of pressure P at various temperatures, 278–308 K: (●) experimental; (—) calculated from eq 7.

lated values; the average error is ±8.0%. As expected, propylene solubility increased with increasing pressure and decreasing temperature. All propylene solubility data points (144) as a function of aqueous silver nitrate concentration, pressure, and temperature are listed in Table 1.

In a complex compound of an olefin with Ag$^+$, the double bond of olefin is functioning in the Ag$^+$–olefin union, whereas the corresponding saturated compounds are completely incapable of similarly reacting (*6, 7*). For example, propane and propylene solubilities in aqueous silver nitrate exhibit significant differences because of the degree of unsaturation (*1, 7–9*). In this study the solubility of propane was measured to compare its solubility with that of propylene.

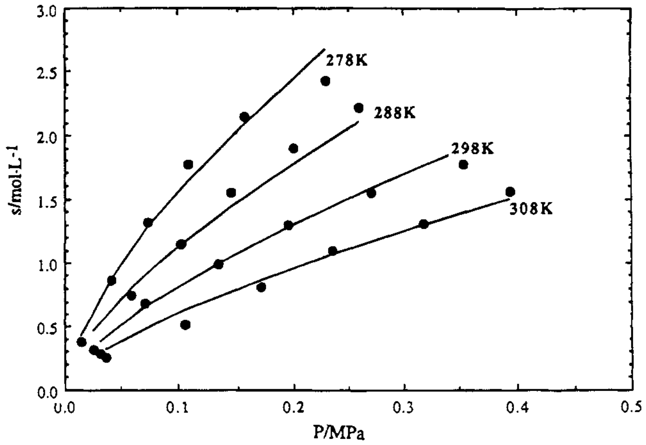

Figure 6. Solubility of propylene s in 5.0 M aqueous silver nitrate as a function of pressure P at various temperatures, 278–308 K: (●) experimental; (—) calculated from eq 7.

The solubilities of propane and propylene in $AgNO_3$(aq) at 298 K and 0.65 MPa are presented in Table 2. From these results it is evident that propane solubility in $AgNO_3$(aq) does not change significantly with a factor of 6 change in $AgNO_3$ concentration. In addition, the solubilities of propane and propylene in pure water (*16–18*) are the same order of magnitude. An exact comparison between these values cannot be made here because the experimental conditions are different. With regard to propylene solubility in $AgNO_3$(aq), it increases by a factor of 2.3 with a 6-fold increase in salt concentration. The propylene solubility is more than 50 times the solubility of propane at 1 M $AgNO_3$(aq). Apparently, the solubility of propylene is dominated by the formation of a silver–olefin complex.

To develop an empirical expression for the propylene–Ag$^+$ system involving the solubility of propylene 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 a regression analysis using Nonlinear Regression Analysis (by Phillip H. Sherrod, Nashville, TN). Correlation results for the 144 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 = 0.6004, a_2 = 6750, a_3 = 210.4, a_4 = 0.8425, and a_5 = −13.41.

Figures 2 and 4–6 present the experimental and calculated solubility values of propylene from 278 to 308 K in aqueous silver nitrate. The validity of eq 7 was verified by graphically evaluating the residuals between the experimental and the calculated values of solubility (*22*). The dependence of the propylene solubility in aqueous silver nitrate was satisfactorily correlated by eq 7.

The enthalpy and the entropy of solution for propylene were determined from the slope and intercept of the plot in Figure 7. The slope is equal to $-\Delta_{\mathrm{sol}}H/R$, and the intercept is equal to $\Delta_{\mathrm{sol}}S/R$. Linear least-squares fits give correlation coefficients better than 0.99.

Table 1. Solubilities of Propylene *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}
$T = 278$ K											
0.039	0.269	0.036	0.282	0.022	0.342	0.017	0.364	0.014	0.377	0.012	0.386
0.114	0.542	0.089	0.650	0.057	0.789	0.044	0.845	0.041	0.858	0.039	0.867
0.224	0.663	0.150	0.984	0.115	1.135	0.089	1.248	0.074	1.313	0.071	1.326
0.334	0.784	0.261	1.101	0.189	1.413	0.134	1.651	0.108	1.764	0.102	1.790
0.459	0.841	0.373	1.213	0.277	1.630	0.203	1.950	0.157	2.150	0.139	2.228
0.583	0.901	0.491	1.300	0.375	1.803	0.269	2.262	0.229	2.436	0.215	2.496
$T = 288$ K											
0.054	0.197	0.052	0.205	0.032	0.289	0.030	0.297	0.026	0.314	0.023	0.326
0.134	0.439	0.122	0.489	0.069	0.711	0.063	0.736	0.060	0.749	0.058	0.757
0.244	0.556	0.188	0.791	0.134	1.017	0.113	1.104	0.102	1.150	0.098	1.167
0.361	0.644	0.274	1.008	0.223	1.222	0.162	1.477	0.144	1.552	0.138	1.577
0.479	0.728	0.378	1.150	0.313	1.422	0.228	1.778	0.200	1.895	0.193	1.924
0.609	0.761	0.498	1.226	0.409	1.598	0.301	2.050	0.260	2.221	0.249	2.267
$T = 298$ K											
0.057	0.178	0.055	0.186	0.036	0.263	0.034	0.271	0.031	0.283	0.029	0.291
0.155	0.340	0.127	0.453	0.098	0.570	0.081	0.639	0.071	0.679	0.069	0.687
0.264	0.457	0.202	0.708	0.167	0.849	0.147	0.930	0.133	0.986	0.119	1.043
0.380	0.546	0.283	0.938	0.250	1.071	0.222	1.185	0.195	1.294	0.174	1.379
0.498	0.627	0.397	1.035	0.339	1.270	0.298	1.435	0.271	1.544	0.243	1.658
0.630	0.651	0.519	1.100	0.443	1.407	0.388	1.629	0.353	1.771	0.312	1.937
$T = 308$ K											
0.064	0.145	0.061	0.156	0.042	0.231	0.039	0.243	0.037	0.250	0.034	0.262
0.171	0.266	0.149	0.352	0.124	0.450	0.109	0.509	0.106	0.520	0.104	0.528
0.282	0.372	0.238	0.544	0.212	0.645	0.179	0.775	0.171	0.806	0.166	0.825
0.399	0.454	0.334	0.708	0.296	0.857	0.250	1.037	0.236	1.091	0.233	1.103
0.509	0.563	0.444	0.818	0.391	1.025	0.335	1.244	0.318	1.310	0.314	1.326
0.639	0.595	0.564	0.888	0.492	1.170	0.409	1.494	0.394	1.553	0.391	1.565

Table 2. Solubilities of Propane and Propylene in Aqueous Silver Nitrate[a]

$c(AgNO_3)$/mol·L^{-1}	$s_{C_3H_8}$/mol·L^{-1}	$s_{C_3H_6}$/mol·L^{-1}	$s_{C_3H_6}/s_{C_3H_8}$
1.0	0.012	0.61	51
6.0	0.014	1.66	119

[a] Temperature = 298 K; pressure = 0.65 MPa.

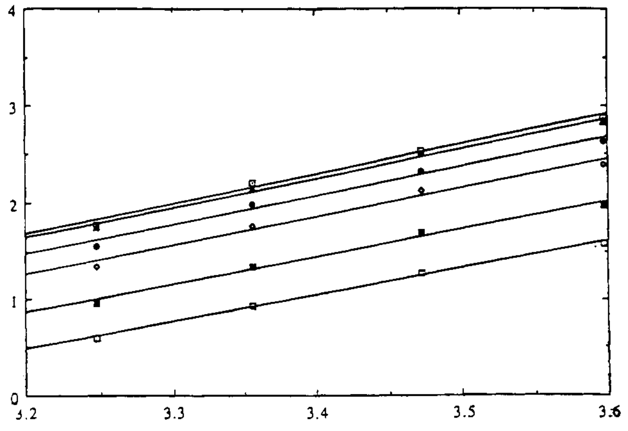

Figure 7. Temperature dependence of propylene solubility at constant silver nitrate concentration *c* at $P_s = 0.10$ MPa: (dotted square) 6.0 M; (▲) 5.0 M; (●) 4.0 M; (◇) 3.0 M; (■) 2.0 M; (□) 1.0 M.

The results of the thermodynamic quantities ($\Delta_{sol}H$ and $\Delta_{sol}S$) calculated from slopes and intercepts of Figure 7 by linear regression are listed in Table 3. The absorption of propylene 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 8, $\Delta_{sol}H$ vs *c* for propylene, are well-fitted by using a least-squares parabola; $\Delta_{sol}H = -22.4 - 1.14c + 0.098c^2$.

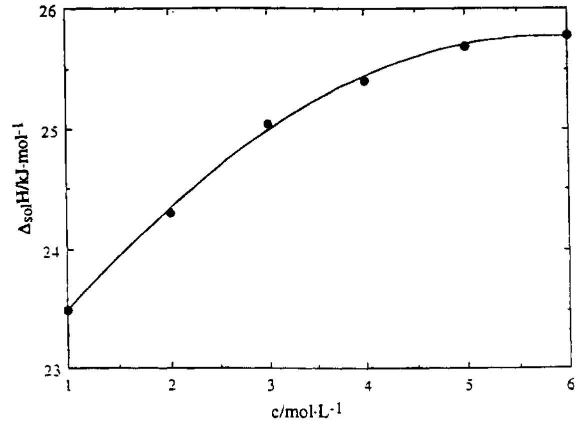

Figure 8. Enthalpy of solution for propylene as a function of aqueous silver nitrate concentrations *c*: (●) experimental.

Table 3. Enthalpy and Entropy of Solution for Propylene 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	−23.49	−68.20
2	−24.30	−68.27
3	−25.05	−69.18
4	−25.41	−69.78
5	−25.68	−70.68
6	−25.78	−71.20

Conclusions

The pressure-drop method was used to measure the solubility of propylene in aqueous silver nitrate solutions as a function of silver nitrate concentration, pressure, and temperature. The solubility measurements were made at pressures up to 0.65 MPa, silver nitrate concentrations from 1.0 to 6.0 M, and over a temperature range from 278 to 308 K. New values were determined for enthalpies and entropies of solution and heats of condensation and mixing for propylene in 1.0–6.0 M aqueous silver nitrate; at 1.0 M A_gNO_3 the enthalpy was -23.5 kJ·mol^{-1} and the entropy was -68.2 J·mol^{-1}·K^{-1}; at 6.0 M $AgNO_3$ the enthalpy was -25.8 kJ·mol^{-1} and the entropy was -71.2 J·mol^{-1}·K^{-1}. The experimental results of propylene solubilities were satisfactorily correlated by eq 7 within ±8%.

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