Solubilities of $CH_3C(O)O_2NO_2$ and HO_2NO_2 in Water and Aqueous H_2SO_4

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Abstract

Henry's law constants of **peroxyacetyl nitrate** ($CH_3C(O)O_2NO_2$, **PAN**) in water near room temperature, literature values of the associative enthalpy change of solvation, and solubilities of PAN and peroxynitrate (HO_2NO_2, PNA) in aqueous H_2SO_4 (46 to 74 wt%) at temperatures relevant to the stratosphere (T = 200-230 K) are analyzed and found to be thermodynamically consistent. The results are then used to determine the effective Henry's law constants (in units of mol kg^{-1} atm^{-1}): $\ln(H^*) = 1.07 - mH_2SO_4 \times (0.69 - 152/T) - 5810 \times (1/T_0 - 1/T)$ for PAN and $\ln(H^*) = 3.69 - mH_2SO_4 \times (-0.25 + 65/T) - 8400 \times (1/T_0 - 1/T)$ for PNA where mH_2SO_4 is the molality of **sulfuric acid**, T is the temperature of solutions, and $T_0 = 298.15$ K. To a first-order approximation, the activity coefficients of PAN and PNA in aqueous H_2SO_4 have a simple Setchenow-type dependence upon H_2SO_4 molality. In addition, the effective Henry's law constant and the associative enthalpy change of solvation of PNA in **water** are determined to be 39.95 mol kg^{-1} atm^{-1} and -69.84 kJ mol^{-1} at 298.15 K, respectively.

solubility

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Introduction

Peroxyacetyl nitrate (PAN), $CH_3C(O)O_2NO_2$, and peroxynitrate acid (PNA), HO_2NO_2, have been identified as two major forms of reservoir species for the reactive nitrogen-containing compounds (NOy). In the troposphere PAN is formed primarily from photochemical reactions of a wide variety of small nonmethane hydrocarbons by the reaction of peroxyacetyl radical with NO_2. PAN is relatively stable in the lower stratosphere, and its main sinks include thermal decomposition, ultraviolet photolysis, and reactions with atomic chlorine or hydroxyl radicals (OH). PAN can be re-distributed throughout the atmosphere by wind circulation, providing a source of nitrogen oxides (NO_x) in the free troposphere where they are critical to the formation of ozone and oxidation of hydrocarbons. Recent atmospheric measurements have revealed a significant concentration of PAN in the free atmosphere [Singh et al., 1996]. Similarly, PNA is formed in a termolecular reaction of NO_2 with HO_2 and is intricately linked to the nitrogen and hydrogen radicals. The major sinks for PNA include unimolecular decomposition as well as photodissociation and bimolecular reaction with OH. In addition, both PAN and PNA may interact with atmospheric particulate, which could affect their gas/particle partitioning.

In order to quantify the interaction of PAN with cloud, fog, seasalt droplets, and sulfate aerosols, a few laboratory studies have reported on the solubility of PAN in water near room temperature (Holdren et al., 1984; Lee, 1984; Kames et al., 1991; Kames and Schurath, 1995) and aqueous H_2SO_4 under stratospheric conditions (Zhang and Leu, 1997). Also, Zhang et al. (1997) have measured the uptake of PNA in liquid H_2SO_4 and have derived the effective Henry's law constant at stratospheric temperatures. To our knowledge, there is no report on the solubility of PNA in water.

Recently Huthwelker et al. (1995) have analyzed the thermodynamic data for hypochlorous acid (HOCl) in water and aqueous sulfuric acid. Since HOCl does not dissociate appreciably in the highly acidic H_2SO_4, it undergoes weaker interactions with the ions in the solution. They have concluded that the activity coefficient of HOCl in aqueous H_2SO_4 has a simple Setchenow-type dependence upon H_2SO_4 molality. A simple equation for the effective Henry's law constant has been used to express the solubility data,

$$\ln(H^*) = \ln[K_H(T_0)] - mH_2SO_4 \times (a + b/T) + (\Delta H^0/R) \times (1/T_0 - 1/T) \qquad (1)$$

where H* is the effective Henry's law constant of the solution, $K_H(T_0)$ is the Henry's law constant in water at T_0, mH_2SO_4 is the molality of sulfuric acid, a and b are Setchenow coefficients, ΔH^0 is the associative enthalpy change of solvation, and $T_0 = 298.15$ K.

In this article we correlate the effective Henry's law constants of PAN and PNA in aqueous H_2SO_4 previously measured in our laboratory (Zhang and Leu, 1997; Zhang et al., 1997), and solubility data of PAN in pure water (Holdren et al., 1984; Lee, 1984; Kames et al., 1991; Kames and Schurath, 1995) using the approach discussed in the article by Huthwelker et al. (1995). Our analysis suggests that all of data are mutually consistent and the correlative results can be used to predict the solubilities of PAN and PNA in liquid H_2SO_4 over a wide range of temperatures and acid compositions. In addition, we also demonstrate that this approach can be used to predict the Henry's law constant of PNA in water which is not previously available in the literature.

Data Correlation

The first step of data analysis is to convert weight percentage to molality for H_2SO_4 composition as reported by Zhang and Leu (1997) and Zhang et al. (1997). This step is necessary for the fitting of data using Equation (1) because of molatity basis for all thermodynamic data. The results are shown in Tables 1 and 2. The ranges of molality are found to be between 8.69 and 29.04.

To derive the best fit of solubility data for PAN using Equation (1), we evaluate four sets of data in water and one set of data in liquid H_2SO_4. For the data in water, we have adopted the results reported by Schurath group (Kames et al., 1991; Kames and Schurath, 1995); however, these four sets of data are consistent within the quoted experimental errors. We fix the value for $K_H(T_0)$ as 2.9 mol kg^{-1} atm^{-1}. A linear regression program is used to obtain the following expression for the effective Henry's law constant for PAN,

$$\ln(H^*) = 1.07 - mH_2SO_4 \times (0.69 - 152/T) - 5810 \times (1/T_0 - 1/T) \qquad (2)$$

We also derive a value for the associative enthalpy change of solvation for PAN in water to be $\Delta H^0 = -48.3$ kJ mol^{-1} at 298.15 K, in excellent agreement with the data reported by Lee (1984) and Kames and Schurath (1995).

There is only one set of solubility data reported for PNA in liquid sulfuric acid (Zhang et al., 1997). Again, a linear regression program is used to calculate the slope and intercept from the plot of ln(H*) vs. 1/T reported by Zhang et al. (1997) The best fit of the data is given by

$$\ln(H^*) = 3.69 - mH_2SO_4 \times (-0.25 + 65/T) - 8400 \times (1/T_0 - 1/T) \qquad (3)$$

This implies that $K_H(T_0) = 39.95$ mol kg^{-1} atm^{-1} and $\Delta H^0 = -69.84$ kJ mol^{-1} for PNA in water at 298.15 K.

Discussion

Comparison of the measurements of the effective Henry's law constant for PAN in water and aqueous H_2SO_4 with those calculated on the basis of Eq. (2) is shown in Table 1. The calculated results are in excellent agreement with the observed data from Holdren et al. (1984), Lee (1984), Kames et al. (1991), Kames and Schurath (1995), and Zhang and Leu (1997) within the quoted error limits. Apparently the activity coefficients of PAN in aqueous H_2SO_4 have a simple Setchenow-type dependence upon H_2SO_4 molality.

Similarly, we also compare the measured and calculated values of the effective Henry's law constants of PNA in liquid H_2SO_4 as shown in Table 2. The calculated values are in excellent agreement with those measured in our laboratory by Zhang et al. (1997) On the basis of Equation (3) we obtain the Henry's law constant of PNA in water, 39.95 mol kg^{-1} atm^{-1}, and the associative enthalpy change of solvation, -69.84 kJ mol^{-1}, respectively at 298.15 K. To our knowledge there is no reported data for PNA in water. It has been noted that in aqueous solutions HO_2NO_2 may dissociate or undergo unimolecular decomposition producing HONO and O_2. (Kenley et al., 1981; Logager and Schested, 1993) The acid dissociation constant for PNA in water is about 1.4×10^{-6} M at room temperature (Logager and Schested, 1993). Park and Lee (1988) have determined the Henry's law constant of HONO in water to be 49 ± 3 mol kg^{-1} atm^{-1} and an acid dissociation constant of 5.3×10^{-4} M at 298 K. Apparently, PNA is a weaker acid than HONO and is expected to be slightly less soluble in water.

Finally, to predict the solubilities of PAN and PNA in liquid H_2SO_4 for conditions characteristic of upper troposphere and lower stratosphere, we use Equations (2) and (3) to calculate the effective Henry's law constants in the temperature range 185-250 K and acid composition 30-80 wt%. The results for PAN and PNA are shown in Figures 1 and 2, respectively. However, caution must be made to extrapolate Equations (2) and (3) outside of this temperature and acid composition ranges. In summary we have presented in this paper a simple method for estimation of the effective Henry's law constants of PAN and PNA. The Setchenow equation (1) appears to be very useful for expressing the solubility data of some trace gas species in aqueous H_2SO_4at stratospheric temperatures. [Huthwelker et al., 1995; Robinson et al. 1997]

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Table 1. Solubility data for PAN in water and aqueous H_2SO_4

T(K)	mH_2SO_4	ln(H*) (measured)	ln(H*)(calculated)	Reference
283.15	0	1.61	2.10	Holdren et al. (1984)
295.15	0	1.30	1.27	Lee (1984)
293.15	0	1.41	1.41	Kames et al. (1991)
293.15	0	1.41	1.41	Kames and Schurath (1995)
199.1	8.69	11.08	11.40	Zhang and Leu (1997)
199.1	8.69	11.11	11.40	
202.3	8.69	10.64	10.84	
207.2	8.69	10.03	10.00	
211.2	8.69	9.39	9.35	
216.5	8.69	8.62	8.52	
207.8	11.98	9.90	10.04	
208.2	11.98	9.85	9.97	
213.8	11.98	9.26	9.01	
214.9	11.98	9.09	8.83	
216.5	11.98	8.36	8.56	
216.8	11.98	8.41	8.52	
219.4	11.98	7.75	8.10	
226.0	11.98	6.77	7.08	
207.8	14.68	10.09	10.15	
208.9	14.68	10.03	9.95	
209.6	14.68	9.94	9.82	
211.5	14.68	9.73	9.47	
212.8	14.68	9.43	9.24	
214.7	14.68	9.01	8.91	
216.6	14.68	8.30	8.58	
207.8	26.24	10.93	10.63	
208.0	26.24	10.85	10.59	
208.1	26.24	10.86	10.56	
211.7	26.24	10.42	9.76	
212.6	26.24	10.27	9.57	
213.4	26.24	9.92	9.39	
214.8	26.24	9.55	9.09	
217.0	26.24	9.13	8.63	
219.2	26.24	8.66	8.18	
221.6	26.24	8.05	7.69	

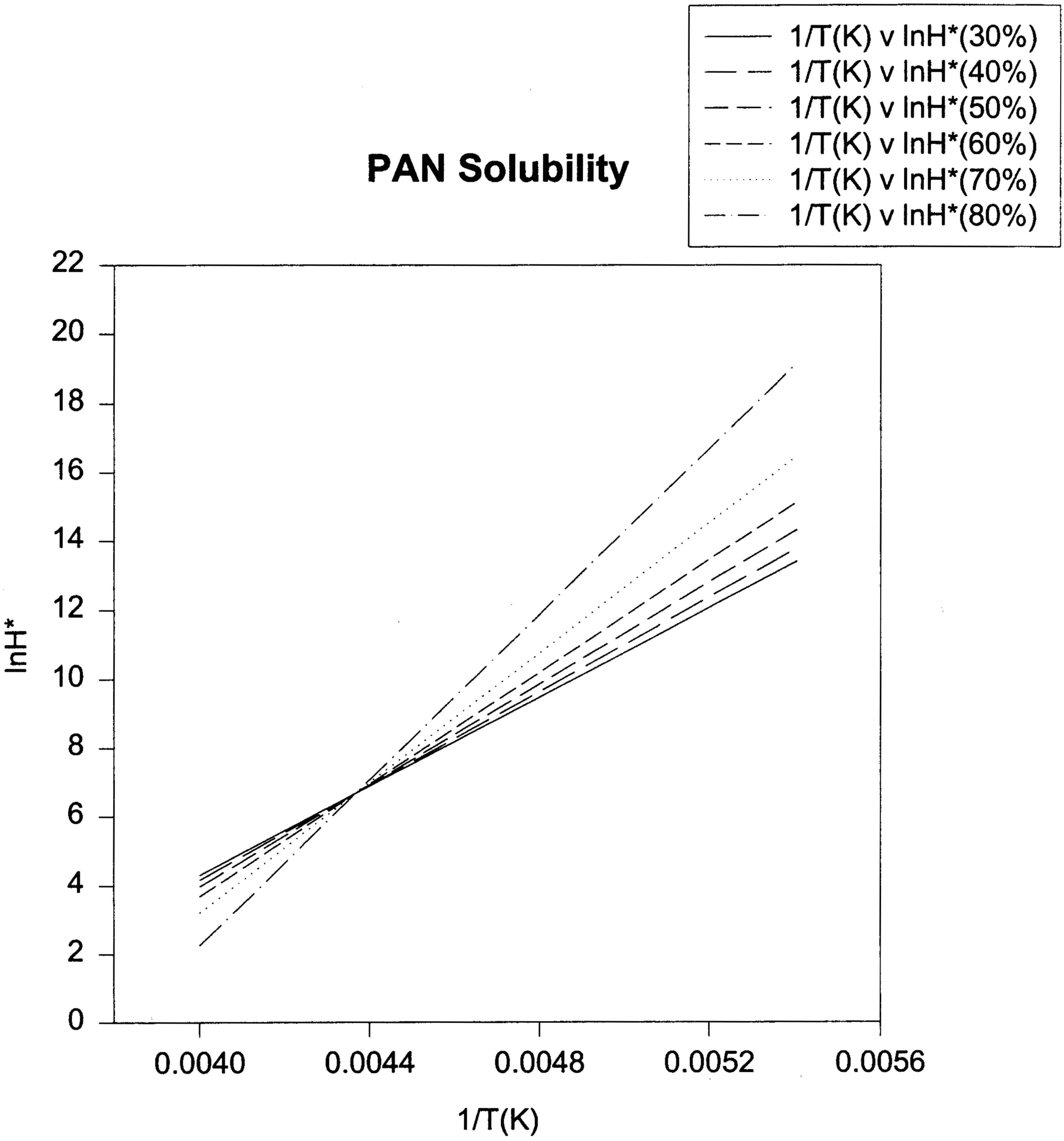
Table 2. Solubility data for PNA in water and aqueous H_2SO_4

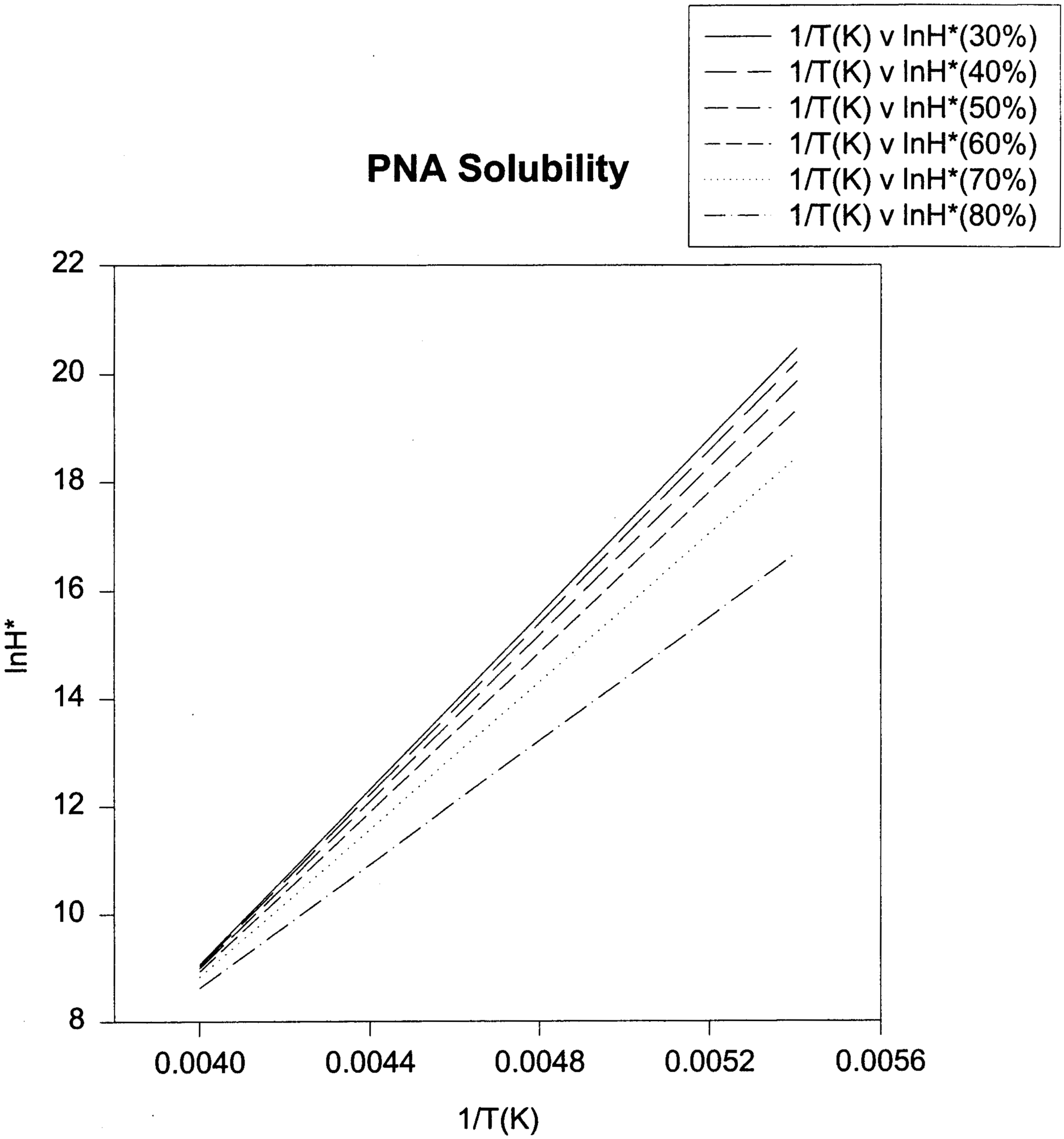
T(K)	mH_2SO_4	ln(H*)(measured)	ln(H*)(calculated)	Reference
298.15	0		3.69	this work
208.9	11.46	15.18	15.00	Zhang et al. (1997)
208.9	11.46	15.20	15.00	
214.4	11.46	14.29	14.06	
224.1	11.46	12.68	12.52	
229.1	11.46	12.04	11.77	
207.9	14.27	14.88	15.00	
207.9	14.27	14.88	15.00	
213.5	14.27	14.15	14.06	
218.9	14.27	13.22	13.19	
223.5	14.27	12.43	12.49	
226.8	14.27	11.92	12.00	
201.4	20.17	15.42	15.72	
202.6	20.17	15.32	15.51	
205.4	20.17	14.73	15.03	
210.4	20.17	14.00	14.21	
215.1	20.17	13.30	13.47	
215.1	20.17	13.29	13.47	
204.1	28.74	14.77	14.64	
204.2	28.74	14.73	14.63	
208.0	28.74	14.08	14.04	
213.6	28.74	13.35	13.22	
219.0	28.74	12.43	12.47	
223.6	28.74	11.98	11.85	
223.6	28.74	11.98	11.85	
223.6	28.74	11.92	11.85	
210.9	14.74	14.46	14.46	
215.6	14.74	13.58	13.69	
217.4	14.74	13.25	13.40	
222.0	14.74	12.61	12.69	
204.9	29.04	14.56	14.50	
215.1	29.04	13.02	12.99	
221.2	29.04	12.21	12.16	

Figure Captions

Figure 1. Predicted values of the effective Henry's law constant (H^*/mol kg^{-1} atm^{-1}) of PAN for 30 to 80 wt% H_2SO_4 in the temperature range 185-250 K. The solutions at lower temperatures may be supercooled.

Figure 2. Predicted values of the effective Henry's law constant (H^*/mol kg^{-1} atm^{-1}) of PNA for 30 to 80 wt% H_2SO_4 in the temperature range 185-250 K. The solutions at lower temperatures may be supercooled.


PAN Solubility
1/T(K) v lnH*(30%)
1/T(K) v lnH*(40%)
1/T(K) v lnH*(50%)
1/T(K) v lnH*(60%)
1/T(K) v lnH*(70%)
1/T(K) v lnH*(80%)
22
20
18
16
14
12
10
8
6
4
2
0
lnH*
0.0040
0.0044
0.0048
0.0052
0.0056
1/T(K)


PNA Solubility
1/T(K) v lnH*(30%)
1/T(K) v lnH*(40%)
1/T(K) v lnH*(50%)
1/T(K) v lnH*(60%)
1/T(K) v lnH*(70%)
1/T(K) v lnH*(80%)
22
20
18
16
14
12
10
8
lnH*
0.0040
0.0044
0.0048
0.0052
0.0056
1/T(K)