Journal of Atmospheric Chemistry **22:** 285–302, 1995.

Solubilities of Pyruvic Acid and the Lower (C_1–C_6) Carboxylic Acids. Experimental Determination of Equilibrium Vapour Pressures Above Pure Aqueous and Salt Solutions

I. KHAN[1], P. BRIMBLECOMBE[2] and S. L. CLEGG[2]
[1]*Department of Chemistry, University of Peshawar, Peshawar, Pakistan*
[2]*School of Environmental Sciences, University of East Anglia, Norwich NR4 7TJ, U.K.*

(Received: 25 April 1994; in final form: 4 October 1994)

Abstract. Henry's law constants K'_H (mol kg^{-1} atm^{-1}) have been determined at 298.15 K for the following organic acids: formic acid ($5.53 \pm 0.27 \times 10^3$); acetic acid ($5.50 \pm 0.29 \times 10^3$); propionic acid ($5.71 \pm 0.34 \times 10^3$); n-butyric acid ($4.73 \pm 0.18 \times 10^3$); isobutyric acid ($1.13 \pm 0.12 \times 10^3$); isovaleric acid ($1.20 \pm 0.11 \times 10^3$) and neovaleric acid ($0.353 \pm 0.04 \times 10^3$). They have also been determined from $T = 278.15$ K to $T = 308.15$ K for n-valeric acid ($\ln(K'_H) = -14.3371 + 6582.96/T$); n-caproic acid ($\ln(K'_H) = -13.9424 + 6303.73/T$) and pyruvic acid ($\ln(K'_H) = -4.41706 + 5087.92/T$). The influence of 9 salts on the solubility of pyruvic acid at 298.15 K has been measured. Pyruvic acid is soluble enough to partition strongly into aqueous atmospheric aerosols. Other acids require around 1 g of liquid water m^{-3} (typical of clouds) to partition significantly into the aqueous phase. The degree of partitioning is sensitive to temperature. Considering solubility and dissociation (to formate) alone, the ratio of formic acid to acetic acid in liquid water in the atmosphere (at equilibrium with the gas phase acids) is expected to increase with rising pH, but show little variation with temperature.

Key words: Henry's law, solubility, removal, salt effect, formic acid, acetic acid, propionic acid, n-butyric acid, isobutyric acid, n-valeric acid, isovaleric acid, neovaleric acid, n-caproic acid, pyruvic acid.

1. Introduction

Carboxylic acids are common organic constitutents of aerosols and rain drops (Graedel and Weschler, 1981), with formic and acetic acids contributing significantly to natural acidity in precipitation and cloud water (Keene and Galloway, 1988). Propionic and pyruvic acids are also widespread (Kawamura *et al.*, 1985; Talbot *et al.*, 1990). In addition, a wide variety of carboxylic acids with C ≥ 3 is found in urban aerosols (Schuetzle *et al.*, 1975; Cronn *et al.*, 1977; Grosjean *et al.*, 1978), in marine aerosols (Burger and Garrett, 1976; Kawamura and Gagosian, 1990) and in precipitation (Keene and Galloway, 1984; Lunde *et al.*, 1977; Levsen *et al.*, 1990).

Most of the carboxylic acids in the atmosphere are stable under ambient conditions. The acids are found in aerosols and rain water as well as in the gas phase, so a quantitative assessment of wet versus dry removal requires a description of carboxylic acid partitioning between liquid and gas phases. This in turn requires a knowledge of the Henry's law constants and dissociation constants of these weak acids. Here we determine Henry's law constants for (C_1–C_6) carboxylic acids, and the solubility of pyruvic acid in aqueous salt solutions, in order to predict their behaviour and fate in the atmosphere.

The organic acids studied here are: formic (IUPAC: methanoic acid, HCOOH), acetic (IUPAC: ethanoic acid, CH_3COOH), propionic (IUPAC: propanoic acid, C_2H_5COOH), n-butyric (IUPAC: butanoic acid, n-C_3H_7COOH), isobutyric (IUPAC: 2-methylpropanoic acid, $(CH_3)_2CHCOOH$), n-valeric (IUPAC: pentanoic acid, n-C_4H_9COOH), isovaleric (IUPAC: 3-methylbutanoic acid, $(CH_3)_2CHCH_2COOH$), neovaleric (IUPAC: 2,2-dimethylpropanoic acid, $(CH_3)_3CCOOH$), n-caproic (IUPAC: hexanoic acid, n-$C_5H_{11}COOH$) and pyruvic acid (IUPAC: 2-oxopropanoic acid, $CH_3C(O)COOH$). Measurements for all acids were made at 298.15 K, and in addition n-valeric, n-caproic and pyruvic acid Henry's law constants were determined at 278.15, 288.15 and 308.15 K. Equilibrium vapour pressures of pyruvic acid were measured above solutions containing 9 different salts at 298.15 K.

2. Theoretical Background

The equilibrium of a weak acid HA between aqueous and gas phases is represented by:

$$HA_{(g)} \rightleftharpoons HA_{(aq)} \tag{1}$$

$$K'_H = m\mathrm{HA}\gamma_{\mathrm{HA}}/f\mathrm{HA} \tag{2}$$

where K'_H (mol kg^{-1} atm^{-1}) is the thermodynamic Henry's law constant, mHA (mol kg^{-1}) the molality of the undissociated acid molecule, γ_{HA} the activity coefficient of HA, and fHA (atm [= 101325 Pa]) its fugacity in the gas phase (fugacity is here assumed to be equivalent to partial pressure pHA). The use of the 'prime' in Equation (2) distinguishes the Henry's law constant from that used for strong electrolytes, such as HCl or HNO_3, which are treated as fully dissociated in the aqueous phase (Clegg and Brimblecombe, 1986). Solutions of the pure acids studied here, with the exception of pyruvic acid, were dilute enough for the activity coefficient γ_{HA} to be assumed to be unity. However, this is not the case for solutions containing dissolved salts, where the salt effect is expressed through a change in γ_{HA}, and usually results in a decrease in solubility.

Henry's law constants of the acids were determined by measuring equilibrium partial pressures pHA for a series of known aqueous molalities (mHA), and applying Equation (2). Changes in the activity coefficients of neutral (undissociated) solutes – here pyruvic acid – brought about by dissolved salts have a relatively simple form. They are described using the Pitzer activity coefficient model (Pitzer, 1991; Clegg and Brimblecombe, 1990a), which ascribes interactions to individual ions and thus allows activity coefficients in salt mixtures to be estimated. The equations are given in Section 4.3.

3. Experimental Methods and Materials

Equilibrium partial pressures of carboxylic acids above their aqueous solutions were measured using the dynamic method developed by Scarano *et al.* (1971) and modified by Clegg and Brimblecombe (1985). Generally 6–10 experimental runs, at different molalities, were made for each organic acid. The application of the method to weak acids is described in our previous work on the Henry's law constants of pyruvic and methacrylic acids (Khan *et al.*, 1992). Briefly, the carboxylic acid is stripped from test solutions of known concentration with a nitrogen gas stream. The gas is passed into 10.0 ml of 1.0 M unbuffered KCl solution (previously purged of CO_2) and the resulting pH change recorded as a function of gas volume. The decrease in the concentration of the acid in the test solution over the course of the experiment is generally negligible, thus a constant partial pressure is maintained. Even for neovaleric acid, which is the most volatile of the acids studied here, a maximum possible depletion of only 9% was estimated for the lowest aqueous molality measured (0.0032 mol kg^{-1}). As this represents an extreme case, involving flushing with a large volume of nitrogen, no correction was applied. The amount of acid present in the gas stream is calculated using the results of separate calibration experiments, which relate changes in pH caused by the addition of each acid directly to the acid concentration in the KCl solution.

The pH change which occurs on addition of weak organic acids to a KCl solution is a function of both the initial pH and the total amount of acid added. Thus the calibration experiments, as well as the partial pressure measurements, are sensitive to the starting pH. All experiments were therefore conducted with an initial pH of 5.4 ± 0.2 in the KCl absorbant. The error arising from the different starting pH values, within these limits, was found to be less than 7% in the calculated partial pressure. As in earlier experiments (Clegg and Brimblecombe, 1985), measured partial pressures over single test solutions were insensitive to the nitrogen flow rates adopted, confirming that equilibrium between aqueous and gas phases was attained. In addition, previous measurements of the partial pressure of HCl above pure aqueous HCl at 25 °C, over four orders of magnitude of partial pressure, agreed well with other data and with theoretical predictions (Clegg, 1986). Thus the gas-phase acids are absorbed by the KCl solution without loss.

The method adopted here can be subject to a systematic error due to transfer of test solution, as an aerosol, into the cell containing the KCl solution. The magnitude of this error is dependent upon the ratio of acid gas partial pressure to its molality in the aqueous (and therefore aerosol) phase. Comparisons with extensive test measurements for aqueous HCl (Clegg, 1986) suggest that, first, errors due to aerosol transfer can be neglected for the acids studied here. Second, the random component of experimental error is of the order 5–15%.

The aqueous solutions of carboxylic acids were prepared by weighing distilled water (about 35 g) into a beaker (100 ml) and then adding the required amount of acid with a pipette. Laboratory grade organic acids purchased from suppliers were used without any further treatment. Hydrochloric acid (at 0.05–0.1 mol kg^{-1}) was added to the aqueous organic acid solutions to suppress dissociation, and thus ensure that the molality of (undissociated) HA taking part in the Henry's law equilibrium was the same as that of the total acid. Such low concentrations of HCl have no significant vapour pressure over the aqueous solution ($< 3 \times 10^{-9}$ atm).

In experiments using n-valeric, isovaleric and n-caproic acids, an apparent trend of increasing K'_H with aqueous concentration was observed. The effect was traced to loss of acid during preparation of the test solutions, where small amounts of acid adhered to the glass walls of the vessel. Both (n- and iso-) valeric acids and n-caproic acid have low aqueous solubility and could sometimes be seen floating on the solution surface. Subsequent titration experiments showed that the loss of acid increased with the concentration of the test solutions, with maximum values of about 20% for n-valeric, 14% for isovaleric and 10% for n-caproic acid. The molalities of the test solutions for these acids have therefore been adjusted in order to correct for the error, assuming a linear relationship between acid loss and molality mHA. Neovaleric acid, being a solid, showed no evidence of loss to glass surfaces during solution preparation.

An Orion combination pH electrode No. 84449, connected to a microprocessor Ionalyser model 901, was used to measure the pH (to the third decimal place) of the KCl solution. This was recorded continuously during the experimental runs. Buffer solutions of pH 7 and pH 4 were used for electrode calibration prior to both the partial pressure determinations and the separate calibration experiments relating acid concentration to measured pH. The pH change over the course of a partial pressure measurement was about 0.5 units. The experimental apparatus was maintained at constant temperature (± 0.1 °C for $t \geq 25$ °C, ± 0.3 °C for $t < 25$ °C) by immersion in a water bath.

4. Results

4.1. HENRY'S LAW CONSTANTS

Measured partial pressures and calculated Henry's law constants for C_1–C_6 carboxylic acids are listed in Table I. Experimental results for the straight chain acids at 298.15 K are also plotted in Figure 1, as the ratio mHA/pHA against mHA. The lines on the graph indicate the calculated mean K'_H for each acid. Since the maximum acid molality is only 0.3 mol kg^{-1} for the results in Table I, we assume the activity coefficients (γ_{HA}) of all the acids to be unity: thus mHA/pHA is equivalent to K'_H. The validity of this assumption is borne out by the fact that there are no discernable trends in mHA/pHA with acid molality.

TABLE I. Measured partial pressures and calculated Henry's law constants of aqueous (C_1–C_6) carboxylic acids

Formic acid		Acetic acid		Propionic acid		*n*-Butyric acid[a]	
*m*HA	*p*HA	*m*HA	*p*HA	*m*HA	*p*HA	*m*HA	*p*HA
298.15 K		298.15 K		298.15 K		298.15 K	
0.005	9.63×10^{-7}	0.005	9.68×10^{-7}	0.013	2.12×10^{-6}	0.005	1.29×10^{-6}
0.009	1.62×10^{-6}	0.012	2.19×10^{-6}	0.054	9.43×10^{-6}	0.012	2.96×10^{-6}
0.050	9.62×10^{-6}	0.052	1.03×10^{-5}	0.100	1.61×10^{-5}	0.051	1.05×10^{-5}
0.106	1.80×10^{-5}	0.104	1.80×10^{-5}	0.150	2.81×10^{-5}	0.104	2.19×10^{-5}
0.130	2.24×10^{-5}	0.158	2.84×10^{-5}	0.200	3.74×10^{-5}	0.150	3.03×10^{-5}
0.202	3.61×10^{-5}	0.200	3.49×10^{-5}	0.250	4.43×10^{-5}	0.200	4.42×10^{-5}
0.279	5.08×10^{-5}	0.250	4.35×10^{-5}	0.300	5.34×10^{-5}	0.250	5.19×10^{-5}
						0.300	6.61×10^{-5}
$K'_H = 5530 \pm 265$		$K'_H = 5502 \pm 290$		$K'_H = 5713 \pm 340$		$K'_H = 4727 \pm 178$	
Isobutyric acid		*n*-Valeric acid		*n*-Valeric acid		*n*-Valeric acid	
*m*HA	*p*Ha	*m*HA	*p*HA	*m*HA	*p*HA	*m*HA	*p*HA
298.15 K		278.15 K		288.15 K		298.15 K	
0.0017	1.56×10^{-6}	0.015	1.30×10^{-6}	0.010	1.79×10^{-6}	0.008	3.61×10^{-6}
0.0032	2.74×10^{-6}	0.020	1.69×10^{-6}	0.020	3.52×10^{-6}	0.010	4.61×10^{-6}
0.0040	3.71×10^{-6}	0.025	2.10×10^{-6}	0.024	4.31×10^{-6}	0.030	1.27×10^{-5}
0.0076	6.08×10^{-6}	0.030	2.39×10^{-6}	0.030	5.11×10^{-6}	0.043	1.87×10^{-5}
0.0100	9.37×10^{-6}	0.035	2.72×10^{-6}	0.036	6.66×10^{-6}	0.056	2.58×10^{-5}
0.0259	2.56×10^{-5}	0.040	3.28×10^{-6}	0.043	8.26×10^{-6}	0.077	3.41×10^{-5}
0.0500	4.99×10^{-5}					0.094	4.36×10^{-5}
0.1000	7.47×10^{-5}						
$K'_H = 1127 \pm 118$		$K'_H = 12147 \pm 500$		$K'_H = 5544 \pm 229$		$K'_H = 2232 \pm 76$	
n-Valeric acid		Isovaleric acid		Neovaleric acid		*n*-Caproic acid	
*m*HA	*p*HA	*m*HA	*p*HA	*m*HA	*p*HA	*m*HA	*p*HA
308.15 K		298.15 K		298.15 K		278.15 K	
0.003	4.84×10^{-6}	0.005	4.54×10^{-6}	0.0032	1.06×10^{-5}	0.01	1.69×10^{-6}
0.006	9.51×10^{-6}	0.010	9.93×10^{-6}	0.005	1.46×10^{-5}	0.02	3.32×10^{-6}
0.009	1.07×10^{-5}	0.020	1.51×10^{-5}	0.008	1.95×10^{-5}	0.03	5.05×10^{-6}
0.011	1.37×10^{-5}	0.0274	2.10×10^{-5}	0.010	2.61×10^{-5}	0.04	6.56×10^{-6}
0.015	1.53×10^{-5}	0.032	2.71×10^{-5}	0.012	3.74×10^{-5}	0.05	8.27×10^{-6}
0.020	2.03×10^{-5}	0.042	3.38×10^{-5}	0.015	4.19×10^{-5}	0.06	9.94×10^{-6}
0.023	2.19×10^{-5}	0.045	3.72×10^{-5}				
$K'_H = 1141 \pm 69$		$K'_H = 1195 \pm 111$		$K'_H = 353 \pm 40$		$K'_H = 6006 \pm 74$	
n-Caproic acid		*n*-Caproic acid		*n*-Caproic acid			
*m*HA	*p*HA	*m*HA	*p*HA	*m*HA	*p*HA		
288.15 K		298.15 K		308.15 K			
0.008	3.05×10^{-6}	0.0047	3.51×10^{-6}	0.003	4.84×10^{-6}		
0.020	7.33×10^{-6}	0.010	7.02×10^{-6}	0.006	9.51×10^{-6}		
0.025	8.55×10^{-6}	0.013	9.63×10^{-6}	0.0075	1.07×10^{-5}		
0.028	9.64×10^{-6}	0.017	1.18×10^{-5}	0.0092	1.37×10^{-5}		
0.036	1.29×10^{-5}	0.022	1.65×10^{-5}	0.0096	1.53×10^{-5}		
0.050	1.84×10^{-5}	0.031	2.14×10^{-5}	0.0146	2.03×10^{-5}		
				0.023	2.19×10^{-5}		
$K'_H = 2785 \pm 111$		$K'_H = 1388 \pm 54$		$K'_H = 666 \pm 40$			

[a] Data for lowest two molalities not used to calculate K'_H.

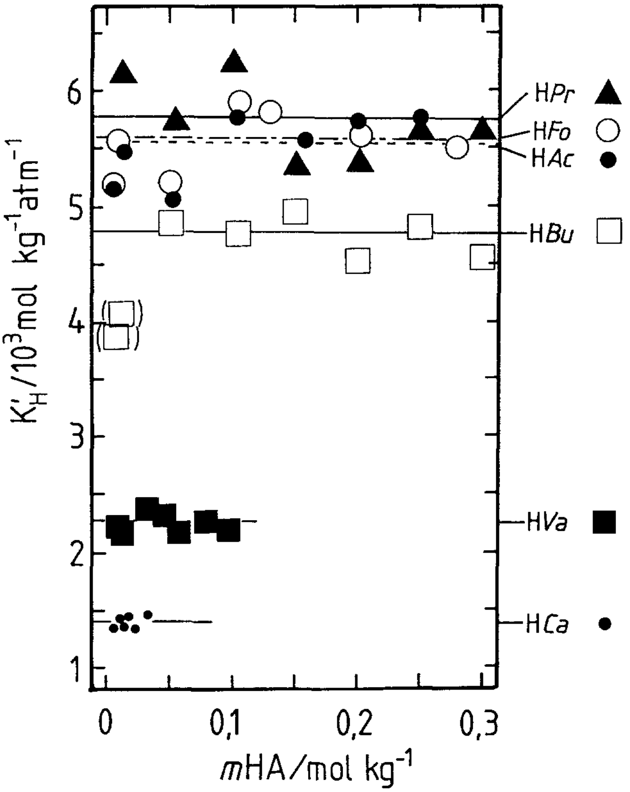

Fig. 1. Henry's law constants (K'_H, equivalent to mHA/pHA assuming unit activity coefficients) of C_1–C_6 straight chain carboxylic acids at 298.15 K, plotted against acid molality mHA. Horizontal lines indicate mean values. The acids, and corresponding symbols, are indicated to the right of the plot: H*Fo*, formic acid; H*Ac*, acetic acid; H*Pr*, propionic acid; H*Bu*, *n*-butyric acid; H*Va*, *n*-valeric acid; H*Ca*, *n*-caproic acid. The two measurements for *n*-butyric acid in parentheses were omitted from the calculation of the mean K'_H.

From Figure 1 it is clear that the K'_H of the C_1–C_3 acids are very similar at 298.15 K, but addition of further carbon atoms leads to decreases in the Henry's law constants (a lowering of solubility). The K'_H of formic and acetic acids determined in this study agree well with the values of 5.2×10^3 and 5.24×10^3 mol kg^{-1} atm^{-1} obtained by Clegg and Brimblecombe (1990b) from other literature data. More recently, Servant *et al.* (1991) have determined vapour pressures (at 296 K to 297 K) over aqueous formic, acetic, propionic and isobutyric acids using a bubble column technique. For their two lower aqueous phase concentrations (1 and 10 ppmv acid, directly comparable with our results), Servant *et al.* (1991) obtained the following Henry's law constants: formic acid, 10.3×10^3 and 13.4×10^3; acetic acid, 9.3×10^3 and 11.2×10^3; propionic acid, 6.2×10^3 and 6.7×10^3; isobutyric acid, 3.5×10^3 and 5.7×10^3 mol dm^{-3} atm^{-1}. While there is reasonable agreement with our K'_H for propionic acid, values for all the acids are higher than we obtained.

Khan *et al.* (1992) have previously measured the K'_H of pyruvic acid at 298.15 K, and here we extend this work over the range 278.15–308.15 K. Pyruvic acid is highly soluble in water, allowing partial pressures to be measured to molalities of 5 mol kg^{-1}. The results, including those for 298.15 K, are given in Table II as the ratio $m\mathrm{H}Py/p\mathrm{H}Py$. It is clear that this quantity increases with acid molality at each temperature, implying a corresponding reduction in the activity coefficient of pyruvic acid ($\gamma_{\mathrm{H}Py}$). This is taken into account in the calculation of K'_H as follows:

$$\ln(m\mathrm{H}Py/p\mathrm{H}Py) = \ln(K'_H) - \ln(\gamma_{\mathrm{H}Py}) \tag{3}$$

where:

$$\ln(\gamma_{\mathrm{H}Py}) = 2m\mathrm{H}Py\ \ \lambda_{\mathrm{H}Py,\mathrm{H}Py} \tag{4}$$

Equation (4) for the activity coefficient of pyruvic acid is based on the Pitzer formalism (Pitzer, 1991). The parameter $\lambda_{\mathrm{H}Py,\mathrm{H}Py}$ describes the self-interaction of pyruvic acid in aqueous solution, and has a value of –0.010 at 298.15 K (Khan *et al.*, 1992). Analysis of the results in Table II showed that $\lambda_{\mathrm{H}Py,\mathrm{H}Py}$ was invariant with temperature, within the experimental error of the measurements, hence the activity coefficients of pyruvic acid in pure aqueous solution from 278.15 to 308.15 K are given by $\gamma_{\mathrm{H}Py} = \exp(-0.02m\mathrm{H}Py)$. These activity coefficients are listed in the last column of Table II. Values of $m\mathrm{H}Py/p\mathrm{H}Py$ are plotted in Figure 2 for the data at all temperatures, together with the fitted $K'_H/\gamma_{\mathrm{H}Py}$. The Henry's law constants at each temperature are given by the intercepts of the fitted line (when $m\mathrm{H}Py = 0$, and $\gamma_{\mathrm{H}Py} = 1$), and are listed in Table II.

The measured Henry's law constants for all acids are summarised in Table III, which also presents equations for the K'_H of pyruvic, n-valeric and n-caproic acids as functions of temperature, and $\mathrm{p}K_\mathrm{a}$ values obtained from the literature. Enthalpy changes for the dissolution reaction ($\Delta_r H°$/J mol^{-1}), also given in Table III, were calculated from:

$$\partial \ln(K'_H)/\partial T = \Delta_r H°/(RT^2) \tag{5}$$

where R (8.3144 J mol^{-1} K^{-1}) is the gas constant and T (K) is temperature. The range of $\Delta_r H°$ (–42.3 to –54.7 kJ mol^{-1}) implies decreases in K'_H by factors of between 1.8 and 2 per 10° rise in temperature. Values for formic and acetic acids (–46.86 kJ mol^{-1} and –53.51 kJ mol^{-1}, respectively) are within the same range (Wagman *et al.*, 1982). This suggests that, where the temperature variation of K'_H for a carboxylic or similar acid is unknown, a round value of $\Delta_r H°$ of –50 kJ mol^{-1} is probably a reasonable estimate.

TABLE II. Measured values of $m\text{H}Py/p\text{H}Py$ (equivalent to $K'_H/\gamma_{\text{H}Py}$) and activity coefficient ($\gamma_{\text{H}Py}$) of pure aqueous pyruvic acid, $278.15 \leqslant T \leqslant 308.15$ K

	$m\text{H}Py/p\text{H}Py$ (10^5 mol kg^{-1} atm^{-1})				
$m\text{H}Py$	278.15	288.15	298.15	308.15	$\gamma_{\text{H}Py}$
0.10				1.76	0.998
0.20			(3.02)		0.996
0.30			3.12		0.994
0.40			3.13		0.992
0.50			3.13	1.78	0.990
0.60			3.14		0.988
0.80			3.16		0.984
1.00	11.54	5.30	3.21		0.980
1.50	12.17	5.25	3.24	1.81	0.970
2.00	11.32	5.59	3.23	1.86	0.961
2.50	12.05	5.09	3.23	1.96	0.951
3.00	12.25	5.51	3.29	1.99	0.942
3.50	11.68	5.38	3.36		0.932
4.00	12.54	5.89			0.923
4.50		6.20			0.914
5.00		6.23			0.905

Mean values of the Henry's law constants (K'_H) are as follows: 278.15 K, $11.48 \pm 0.3 \times 10^5$; 288.15 K, $5.27 \pm 0.3 \times 10^5$; 298.15 K, $3.11 \pm 0.02 \times 10^5$; 308.15 K, $1.79 \pm 0.05 \times 10^5$ mol kg^{-1} atm^{-1}.

The activity coefficient $\gamma_{\text{H}Py}$ is the same at all temperatures.

4.1.1. *Influence of Dissolved Salts on Gas Solubility*

Pyruvic acid is the only acid of those considered here that is sufficiently soluble to partition into the very small amounts of liquid water associated with atmospheric aerosols (10–100 μg m^{-3}; Seinfeld, 1986). Such aerosols are likely to contain dissolved salts at high enough concentration to significantly affect gas solubility. We have therefore measured equilibrium partial pressures of pyruvic acid at 298.15 K over aqueous solutions containing 1.5 mol kg^{-1} pyruvic acid and 9 different salts at various molalities, see Table IV. In these experiments we inadvertently omitted to add the small amount of HCl to the test solutions required to suppress pyruvic acid dissociation. A subsequent calculation to estimate this in aqueous NaCl suggested that dissociation would be of the order of 2–6% (thus reducing the partial pressure by the same amount), which is less than the uncertainty of the measurements. Consequently, we have not attempted to correct the data to account for this. The results are plotted in Figure 3 as $\ln(\gamma_{\text{H}Py})$ against salt molality. Note that the intercept is equal to the logarithm of the activity coefficient in 1.5 mol kg^{-1} of the pure aqueous acid ($\gamma_{\text{H}Py} = 0.97$). In all cases the presence of the salt leads to an

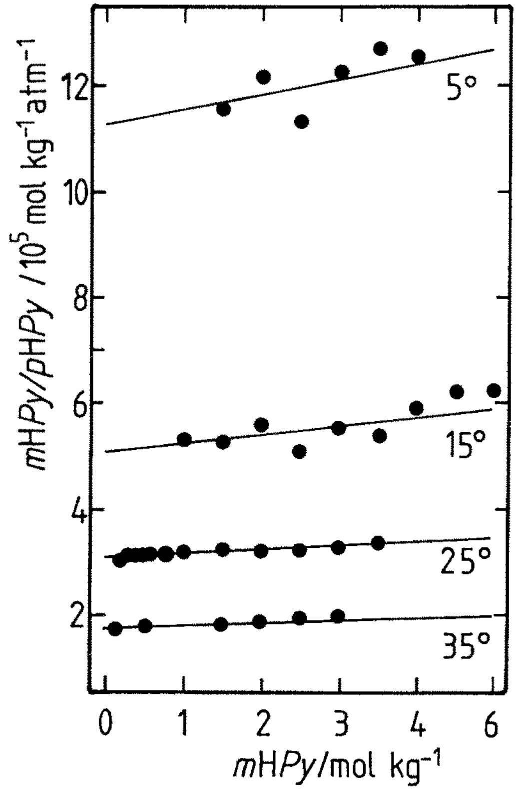

Fig. 2. The quantity $m\mathrm{H}Py/p\mathrm{H}Py$ (equivalent to $K'_H/\gamma_{\mathrm{H}Py}$), plotted against molality for four different centigrade temperatures. Mean values of K'_H (Table II), divided by the pyruvic acid activity coefficient, are shown as lines. Data for 25 °C from Khan *et al.* (1992).

increase in the activity coefficient, hence the acid is less soluble than in pure water for a given gas-phase partial pressure.

In Table IV we have listed, in addition to the partial pressures, values of the logarithm of the activity coefficient of pyruvic acid in the solutions. This has been corrected for the 'self-interaction' of the acid using the parameter $\lambda_{\mathrm{H}Py,\mathrm{H}Py}$ given in Equation (4), and enables the influence of individual ions on the activity coefficient of pyruvic acid to be estimated using the Pitzer formalism. The model equation for the activity coefficient of a neutral species (here, the undissociated pyruvic acid) in a solution containing a single salt $\mathrm{M}_{\nu_+}\mathrm{X}_{\nu_-}$ is (Pitzer, 1991):

$$\ln(\gamma_{\mathrm{H}Py}) = 2m\mathrm{H}Py\lambda_{\mathrm{H}Py,\mathrm{H}Py} + 2m\mathrm{MX}(\nu_+\lambda_{\mathrm{H}Py,\mathrm{M}} + \nu_-\lambda_{\mathrm{H}Py,\mathrm{X}}) \qquad (6)$$

hence:

$$\ln(\gamma_{\mathrm{H}Py} - 2m\mathrm{H}Py\lambda_{\mathrm{H}Py,\mathrm{H}Py}) = 2m\mathrm{MX}(\nu_+\lambda_{\mathrm{H}Py,\mathrm{M}} + \nu_-\lambda_{\mathrm{H}Py,\mathrm{X}}) \qquad (7)$$

where $m\mathrm{MX}$ is the salt molality, ν_+ and ν_- are the numbers of cations and anions in the formula of the salt, and $\lambda_{\mathrm{H}Py,\mathrm{M}}$ and $\lambda_{\mathrm{H}Py,\mathrm{X}}$ are parameters for the interaction

TABLE III. Henry's law constants (K'_H/mol kg^{-1} atm^{-1}) of pyruvic acid and the C_1–C_6 carboxylic acids

Acid		Formula	T/K	K'_H
Formic	(methanoic)	HCOOH	298.15	5530 ± 265
Acetic	(ethanoic)	CH_3COOH	298.15	5502 ± 290
Propionic	(propanoic)	C_2H_5COOH	298.15	5713 ± 340
n-Butyric	(butanoic)	n-C_3H_7COOH	298.15	4727 ± 178
n-Valeric	(pentanoic)	n-C_4H_9COOH	278.15	12147 ± 500
n-Valeric	(pentanoic)	n-C_4H_9COOH	288.15	5544 ± 229
n-Valeric	(pentanoic)	n-C_4H_9COOH	298.15	2232 ± 76
n-Valeric	(pentanoic)	n-C_4H_9COOH	308.15	1141 ± 69
n-Caproic	(hexanoic)	n-$C_5H_{11}COOH$	278.15	6006 ± 74
n-Caproic	(hexanoic)	n-$C_5H_{11}COOH$	288.15	2785 ± 111
n-Caproic	(hexanoic)	n-$C_5H_{11}COOH$	298.15	1388 ± 54
n-Caproic	(hexanoic)	n-$C_5H_{11}COOH$	308.15	666 ± 40
Isobutyric	(2-methyl propanoic)	$(CH_3)_2CHCOOH$	298.15	1127 ± 118
Isovaleric	(3-methyl butanoic)	$(CH_3)_2CHCH_2COOH$	298.15	1195 ± 111
Neovaleric	(2,2-dimethyl propanoic)	$(CH_3)_3CCOOH$	298.15	353 ± 40
Pyruvic	2-oxo-propanoic)	$CH_3C(O)COOH$	278.15	$11.48 \pm 0.3 \times 10^5$
Pyruvic	2-oxo-propanoic)	$CH_3C(O)COOH$	288.15	$5.27 \pm 0.3 \times 10^5$
Pyruvic	2-oxo-propanoic)	$CH_3C(O)COOH$	298.15	$3.11 \pm 0.02 \times 10^5$
Pyruvic	2-oxo-propanoic)	$CH_3C(O)COOH$	308.15	$1.79 \pm 0.05 \times 10^5$

The following equations give K'_H as functions of temperature (T/K) over the measured range:

Pyruvic acid: $\ln(K'_H) = -4.41706 + 5087.92/T$
n-Valeric acid: $\ln(K'_H) = -14.3371 + 6582.96/T$
n-Caproic acid: $\ln(K'_H) = -13.9424 + 6303.73/T$

The enthalpy changes ($\Delta_r H°$) for the dissolution reaction implied by the above equations are: -42.3 ± 1 kJ mol^{-1} (pyruvic acid), -54.7 ± 3 kJ mol^{-1} (n-valeric acid) and -52.4 ± 1 kJ mol^{-1} (n-caproic acid).

The following values of the pK_a of the acids were obtained from the literature: formic acid, 3.751 (298.15 K) (Harned and Embree, 1934); acetic acid, 4.756 (298.15 K) (Harned and Ehlers, 1933a); propionic acid, 4.874 (298.15 K) (Harned and Ehlers, 1933b); n-butyric acid, 4.81 (293.15 K) (CRC Handbook, 1984); isobutyric acid, 4.84 (291.15 K) (CRC Handbook, 1984); n-valeric acid, 4.82 (291.15 K) (CRC Handbook, 1984); isovaleric acid, 4.77 (298.15 K) (CRC Handbook, 1984); neovaleric acid, *not found* (assumed value of 4.8 used in calculations); n-caproic acid, 4.83 (291.15 K) (CRC Handbook, 1984); pyruvic acid, 2.47 (298.15 K) (Fisher and Warneck, 1991).

of the acid with cation M and anion X respectively. Equation (6) can be shown to be equivalent to the empirical Setchenow equation for gas solubility (e.g., Long and McDevit, 1952). By convention, $\lambda_{\mathrm{H}Py,\mathrm{Cl}}$ is set equal to zero (since only sums and differences of the parameters can be determined from data). Using Equation (7), we have determined interaction parameters for the ions Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+ and SO_4^{2-} by simultaneous fitting (see Table IV). The lines plotted on Figure 3 were calculated using these parameters, and represent the data well. Since the influence of the ions on $\ln(\gamma_{\mathrm{H}Py})$ is additive, the activity coefficient can be calculated for

TABLE IV. Partial pressures of pyruvic acid ($p\mathrm{H}Py$/atm) above aqueous salt solutions, and values of $\ln(\gamma - 2m\mathrm{H}Py\lambda_{\mathrm{H}Py,\mathrm{H}Py})$ as a function of salt molality m (mol kg^{-1}) at 298.15 K and 1.5 mol kg^{-1} HPy

m	$10^6 p\mathrm{H}Py$	$\ln(\gamma - 2m\mathrm{H}Py\lambda_{\mathrm{H}Py,\mathrm{H}Py})$	m	$10^6 p\mathrm{H}Py$	$\ln(\gamma - 2m\mathrm{H}Py\lambda_{\mathrm{H}Py,\mathrm{H}Py})$
NaCl			$CaCl_2$		
0.94	6.006	0.240	0.20	5.544	0.162
1.70	7.368	0.441	0.32	6.105	0.256
2.72	8.868	0.622	0.50	7.443	0.450
3.80	11.98	0.919	0.70	8.778	0.612
4.83	15.32	1.162	0.89	10.61	0.799
KCl			NH_4Cl		
0.50	5.590	0.170	0.50	6.012	0.241
1.00	6.452	0.310	1.00	7.913	0.510
2.00	8.680	0.601	2.00	13.66	1.004
2.77	1.105	0.839	3.00	20.48	1.450
3.59	1.410	1.080			
$MgCl_2$			Na_2SO_4		
0.10	5.310	0.120	0.40	7.466	0.453
0.49	7.682	0.481	0.51	8.584	0.590
0.90	10.73	0.810	0.59	9.511	0.691
1.20	14.10	1.080	0.78	1.188	0.910
1.50	19.13	1.382	1.00	1.544	1.170
K_2SO_4			$MgSO_4$		
0.20	6.257	0.280	0.05	5.013	0.064
0.40	7.832	0.500	0.10	5.596	0.171
0.50	9.217	0.660	0.15	6.206	0.272
0.79	13.01	1.000	0.22	7.081	0.401
$(NH_4)_2SO_4$					
0.10	5.338	0.125			
0.30	7.375	0.441			
0.51	10.67	0.804			
0.69	13.57	1.042			
1.01	23.03	1.560			

Best fit values of the HPy-ion interaction parameters ($\lambda_{\mathrm{H}Py,i}$) are as follows: Na^+, 0.122; K^+, 0.152; NH_4^+, 0.240; Mg^{2+}, 0.459; Ca^{2+}, 0.442; Cl^-, 0.0 (defined); SO_4^{2-}, 0.323.

more complex, and realistic, mixtures by using the generalised form of Equation (6) (Pitzer, 1991). Clegg and Brimblecombe (1990a) have demonstrated the success of this general approach when applied to describing the solubility of oxygen in seawater and brines. For pyruvic acid this takes the form:

$$\ln(\gamma_{\mathrm{H}Py}) = 2m\mathrm{H}Py\lambda_{\mathrm{H}Py,\,\mathrm{H}Py} + 2\sum_{\mathrm{c}} m_{\mathrm{c}}\lambda_{\mathrm{H}Py,\,\mathrm{c}} + 2\sum_{\mathrm{a}} m_{\mathrm{a}}\lambda_{\mathrm{H}Py,\,\mathrm{a}} \tag{8}$$

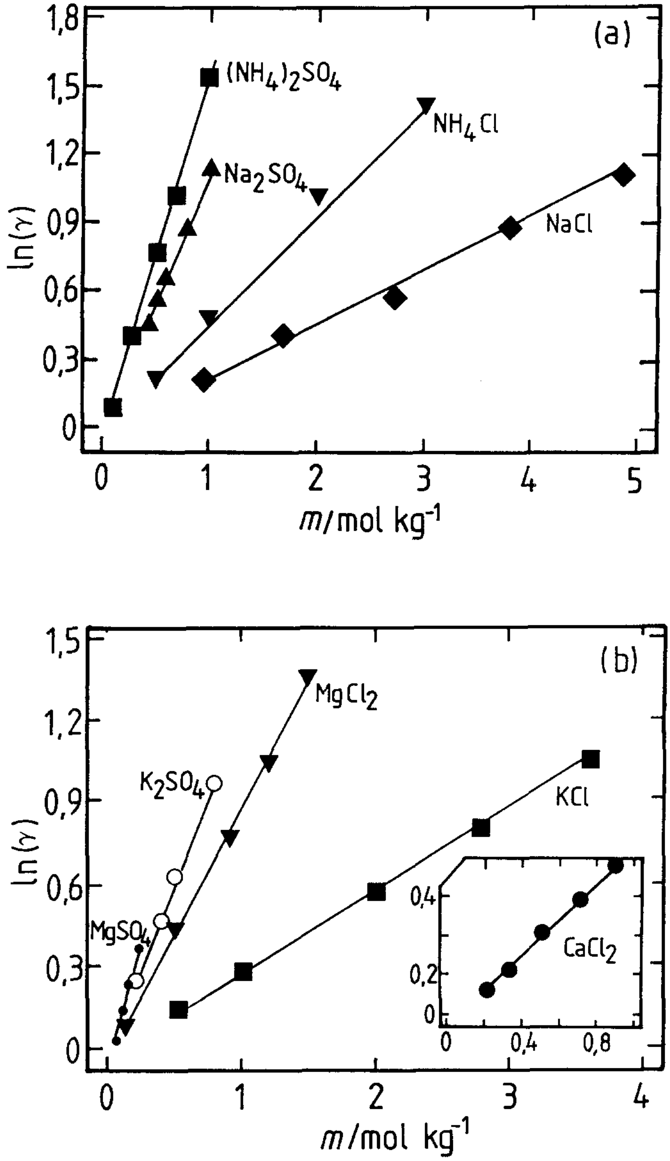

Fig. 3. Natural logarithm of the activity coefficient of 1.5 mol kg^{-1} pyruvic acid [ln(γ)] in aqueous salt solutions of molality m, at 298.15 K. Data are from Table IV. Lines are fitted values, calculated from Equation (7) and using the HPy-ion interaction parameters ($\lambda_{HPy,i}$) listed in the notes to Table IV.

where m_c and m_a are the molalities of the various cations (c) and anions (a) present in the solution, and the summations are over all cations and anions present. Activity coefficients, and therefore the parameters λ, vary with temperature. However, this variation is generally small – far less than that of the Henry's law constant – and will not significantly affect solubility calculations.

5. Partitioning of Organic Acids in the Atmosphere

The removal mechanism of the acids from the atmosphere (wet or dry deposition) is determined by the degree to which they partition into liquid water (e.g., cloud droplets or aerosols). The total molality of organic acid HA ($m\mathrm{HA_T}$) present in an aqueous solution is equal to ($m\mathrm{HA} + m\mathrm{A}^-$), and the dissociation constant K_a (mol kg^{-1}) for the equilibrium $\mathrm{HA_{(aq)}} \rightleftharpoons \mathrm{H^+_{(aq)}} + \mathrm{A^-_{(aq)}}$ is given by:

$$K_\mathrm{a} = m\mathrm{H}^+ m\mathrm{A}^- / m\mathrm{HA} \cdot \Gamma_\mathrm{a} \tag{9}$$

where Γ_a is the activity coefficient quotient ($\gamma_\mathrm{H}\gamma_\mathrm{A}/\gamma_\mathrm{HA}$), which can be assumed to be unity for very dilute solutions. The total molality $m\mathrm{HA_T}$ is therefore:

$$m\mathrm{HA_T} = m\mathrm{HA}(1 + K_\mathrm{a}/m\mathrm{H}^+) \tag{10}$$

The liquid water content of clouds is typically 0.1–1 g m^{-3}. We first calculate the partitioning of the organic acids considered in this study in an atmosphere containing 1 g of liquid water per m^3. Figure 4 is a plot of pK_a against $\log_{10}(K'_H)$, with contours indicating the cloudwater pH required to achieve equal partitioning between the two phases. Values for individual acids are plotted for 298.15–273.15 K. Typical cloud water pH is ~5.5 for equilibrium with atmospheric $\mathrm{CO_2}$, though the presence of other acids and bases can alter this value. Acids lying to the right of the contour giving the actual cloudwater pH (higher K'_H and/or smaller pK_a) will partition mainly into the aqueous phase, while those to the left will remain in the gas phase. It is clear that although formic and acetic acids have very similar Henry's law constants, formic acid has a much higher overall solubility due to greater dissociation.

Figure 4 also illustrates the strong dependence of partitioning on temperature. While the dissociation constants change little from 298.15–273.15 K ($< 8\%$ for formic, acetic and propionic acids), the Henry's law constants increase by a factor of about 5. Thus, while acetic acid is equally distributed between gas and liquid phases at 298.15 K and pH 5.5, 90% is expected be present in the liquid water at 273.15 K for normal cloud water pH. There are similar large shifts with temperature for other acids, see Table V. In Table V we also show calculated acid gas partitioning into 0.2 g of cloud water per m^3, for pH 5.6. At 298.15 K, the amount of formic acid in the liquid phase is reduced to 65% (compared to 90% for the 1 g m^{-3} case). Furthermore, if cloud water pH is reduced to 5.0 then only 35% will partition into the liquid phase due to decreased dissociation. These comparisons show that, except for pyruvic acid which will always be found in the liquid phase within clouds, the partitioning of the acids is dependent on temperature, and the amount of water present and its pH. This implies that both wet and dry deposition will contribute to their removal from the atmosphere, consistent with the conclusions of Grosjean (1989).

The ratio of formic to acetic acid in precipitation and cloud water has been reviewed by Keene and Galloway (1988). The average ratio in precipitation at six

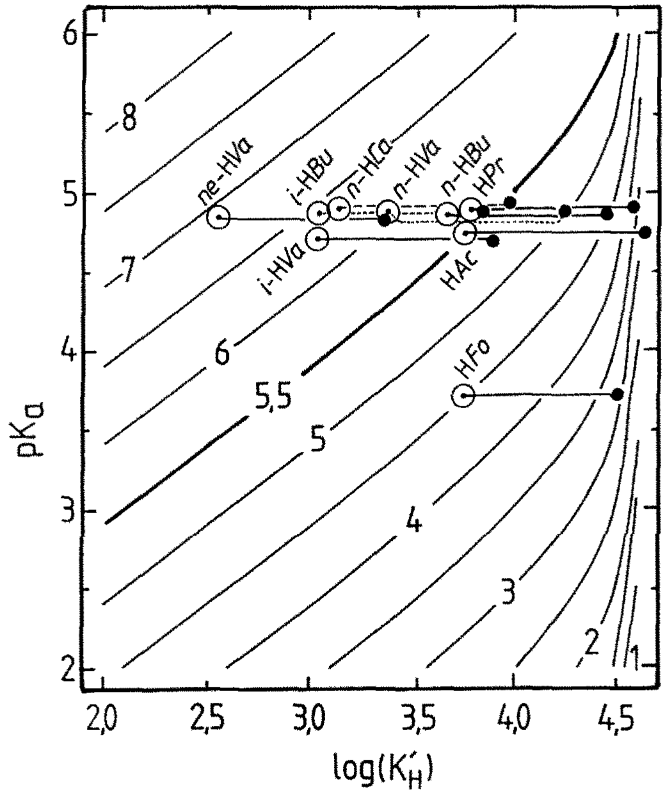

Fig. 4. Cloud water pH (contours) required for an acid gas to partition equally between liquid and gas phases for 1 g of water m^{-3} of atmosphere, as a function of Henry's law constant (K'_H) and dissociation constant (K_a). Values for individual acids are plotted for 298.15 K (open circles) and 273.15 K (dots): H*Fo*, formic acid; H*Ac*, acetic acid; H*Pr*, propionic acid; *n*-H*Bu*, *n*-butyric acid; *i*-H*Bu*, isobutyric acid; *n*-H*Va*, *n*-valeric acid; *i*-H*Va*, isovaleric acid; *ne*-H*Va*, neovaleric acid; *n*-H*Ca*, *n*-caproic acid. In these calculations the temperature variation of the pK_a of the acids has been ignored, as it is likely to be small compared to the change in Henry's law constants.

different locations was 2.25 (on a molar basis). What factors related to solubility might affect this ratio? In Figure 5 we plot the ratio of liquid phase formic to acetic acid concentration against temperature and pH, for a system at equilibrium with equal gas-phase partial pressures of both acids. (In cases where these differ, the contour values in Figure 5 should be multiplied by the gas-phase concentration ratio of the two acids.) The ratio in the liquid phase depends most strongly on pH, since the variation of K'_H with temperature for both acids is rather similar. At a cloud water pH of ~ 5.5, 7–9 times more formic acid than acetic acid is present in the liquid phase, reflecting the much greater degree of dissociation of formic acid. However, at lower pH around 3.5, which may be attained in polluted conditions in the atmosphere, the ratio is close to unity. Here the dissociation of both acids is suppressed, and their overall solubility is determined by their Henry's

TABLE V. Calculated partitioning of organic acids into cloud water at pH 5.6

273.15 K (1 g water m^{-3})		298.15 K (1 g water m^{-3})		
Acid	% in liquid phase	Acid	% in liquid phase	α^a
Formic	100	Formic	90	0.99
Acetic	90	Acetic	50	0.87
Propionic	85	Propionic	50	0.84
n-Butyric	80	*n*-Butyric	45	0.86
Isobutyric	55	Isobutyric	15	0.85
n-Valeric	75	*n*-Valeric	30	0.86
Isovaleric	60	Isovaleric	20	0.87
Neovaleric	30	Neovaleric	5	(0.86)
n-Caproic	60	*n*-Caproic	15	0.85
Pyruvic	100	Pyruvic	100	0.999
273.15 K (0.2 g water m^{-3})		298.15 K (0.2 g water m^{-3})		
Acid	% in liquid phase	Acid	% in liquid phase	
Formic	90	Formic	65	
Acetic	60	Acetic	20	
Propionic	55	Propionic	15	
n-Butyric	50	*n*-Butyric	15	
Isobutyric	20	Isobutyric	5	
n-Valeric	40	*n*-Valeric	10	
Isovaleric	20	Isovaleric	5	
Neovaleric	10	Neovaleric	1	
n-Caproic	20	*n*-Caproic	5	
Pyruvic	100	Pyruvic	100	

In these calculations the dissociation constants of each of the acids (see notes to Table III) were assumed to be invariant with temperature, since those of formic, acetic and propionic acids all change by less than 8% from 273.15 K to 298.15 K.

[a] α is the degree of dissociation of the acid $[mA^-/(mHA + mA^-)]$, calculated for pH 5.6, and using the pK_a listed in Table III. The parenthesis around the value for neovaleric acid indicates that the pK_a used is an assumed value. Because the dissociation constants are treated as invariant with temperature (see above), α is the same for all four cases.

law constants which are similar. Keene and Galloway (1988) have plotted formic to acetic acid ratios in cloud water, collected over a three-week period, against hydrogen ion concentration, and find a decreasing trend with pH – the opposite of that suggested by Figure 5. They invoke a pH-dependent source of formic acid, first proposed by Chameides and Davis (1983), to explain their findings. Certainly such a relationship is not expected from partitioning considerations alone.

Pyruvic acid is the most soluble of those studied. We calculate that 50% partitioning into liquid water requires only 10^{-4} g of water per m^3 at 298.15 K, and 2×10^{-5} g m^{-3} at 273.15 K – amounts typical of those found in atmospheric aerosols (Seinfeld, 1986). Aerosols contain significant concentrations of dissolved

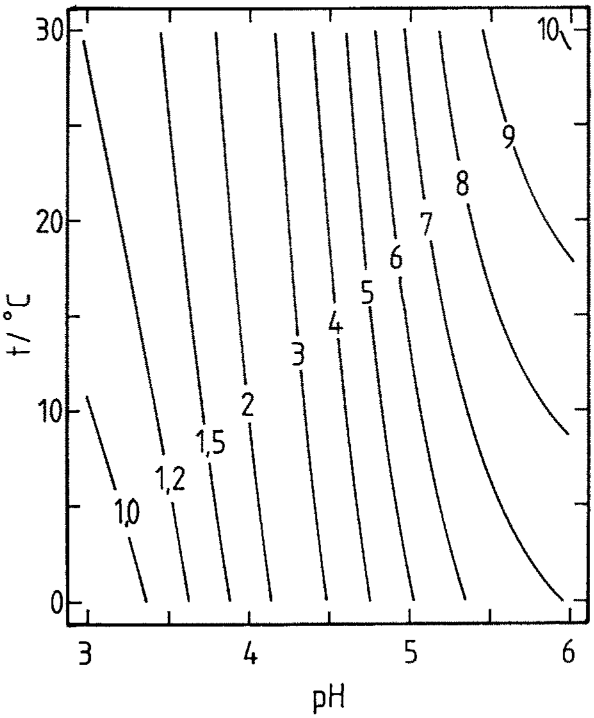

Fig. 5. The molar ratio of total formic acid to acetic acid (contours) in a liquid phase at equilibrium with equal partial pressures of the two acids, as a function of pH and centigrade temperature (*t*/°C).

material, such as sea salt, and their liquid water content is controlled by the ambient relative humidity. The pK_a of pyruvic acid (2.47 at 298.15 K; Fisher and Warneck, 1991) is sufficiently low that dissociation will only be suppressed in highly acidic aerosols. However, as we have shown in Section 4.3, dissolved salts reduce the solubility of molecular HPy. For a seasalt-based aerosol (assumed to be aqueous NaCl), this reduction would be a about factor of 4 at 75% relative humidity. Hence, an accurate assessment of pyruvic acid partitioning into aerosols will require a knowledge of their composition and the ambient relative humidity in addition to the amount of aerosol present. The fact that a large proportion of atmospheric pyruvic acid is likely to exist in aqueous form also implies that its destruction by gas-phase photolysis, which occurs in about 1 h in sunlight (Grosjean, 1983), may not always be an important removal mechanism especially when clouds are present.

Andreae *et al.* (1987) have measured formic and pyruvic acid concentrations in both gas and particulate (aerosol) phases, at locations in the U.S.A. and over the North Atlantic Ocean. The proportion of pyruvic acid in the aerosol phase ranged from 2% to 41%, whereas almost all the formic acid remained in the gaseous form.

This differential partitioning is consistent with the high solubility of pyruvic acid determined by Khan *et al.* (1992), and discussed above, and may also occur in clouds containing relatively small amounts of liquid water, at low pH (Table V). Thus the close correlation often found between formic and pyruvic acids in both gas and liquid phases at a variety of locations (Andreae *et al.*, 1987; Talbot *et al.*, 1990), which is thought to be due to similar biogenic sources for the acids, may not occur under all conditions.

6. Conclusions

The Henry's law constants of pyruvic acid and 9 lower carboxylic acids have been measured, together with the salt effect on the solubility of pyruvic acid. The Henry's law constants show similar dependencies on temperature, and increase by about a factor of 2 for every 10° decrease. The carboxylic acids have pK_a in the range 4.7–4.9 (except formic acid, pK_a=3.75), and are all likely to dissociate in cloud water. The variation of the dissociation constants with temperature is small compared to that of the Henry's law constants.

Pyruvic acid is highly soluble, and will partition completely into cloud water, and even into atmospheric aerosols (water content per m^3 of air about $10^4 \times$ less). Formic acid should partition strongly into the aqueous phase in clouds with a high liquid water content (~ 1 g m^{-3}). However, this may not be true where both pH and the liquid water content of the clouds are significantly lower. The partitioning of the other carboxylic acids (50% in the liqud phase for acetic and propionic acids to 5% for neovaleric acid at 298.15 K, pH 5.6 and 1 g of water per m^3) is more dependent upon ambient temperature and the mass of liquid water present. In conditions where the amount of water is much less than 1 g m^{-3}, they are likely to occur mostly in the gas phase.

References

Andreae, M. O., Talbot, R. W., and Li, S.-M., 1987, Atmospheric measurements of pyruvic and formic acid, *J. Geophys. Res.* **92**, 6635–6641.

Burger, W. R. and Garrett, W. D., 1976, Surface active organic materials in air over the Mediterranean and over the eastern equatorial Pacific, *J. Geophys. Res.* **81**, 3151–3157.

Chameides, W. L. and Davis, D. D., 1983, Aqueous phase source for formic acid in clouds, *Nature* **304**, 427–429.

Clegg, S. L., 1986, Ph.D. Thesis, University of East Anglia, Norwich.

Clegg, S. L. and Brimblecombe, P., 1985, The solubility of methanesulphonic acid and its implications for atmospheric chemistry, *Environ. Technol. Lett.* **6**, 269–278.

Clegg, S. L. and Brimblecombe, P., 1986, The dissociation constant and Henry's law constant of HCl in aqueous solution, *Atmos. Environ.* **20**, 2483–2485.

Clegg, S. L. and Brimblecombe, P., 1990a, The solubility and activity coefficient of oxygen in salt solutions and brines, *Geochim. Cosmochim. Acta* **54**, 3315–3328.

Clegg, S. L. and Brimblecombe, P., 1990b, The solubility of volatile electrolytes, in D. C. Melchior and R. L. Bassett (eds.), *Chemical Modeling of Aqueous Systems II*, American Chemical Society, Washington, pp. 58–73.

CRC Handbook of Chemistry and Physics, 1984, Weast, R. C. (ed.), 64th edn., CRC Press, Boca Raton, FL.

Cronn, D. R., Charlson, R. J., Knights, R. L., Crittenden, A. L., and Appel, B. R., 1977, A survey of the molecular nature of primary and secondary components of particles in urban air by high-resolution mass spectroscopy, *Atmos. Environ.* **11**, 929–937.

Fisher, M. and Warneck, P., 1991, The dissociation constant of pyruvic acid: determination by spectrophotometric measurements, *Ber. Bunsenges. Phys. Chem.* **95**, 523–527.

Graedel, T. E. and Weschler, C. J., 1981, Chemistry within aqueous atmospheric aerosols and rain drops, *Rev. Geophys. Space Phys.* **19**, 505–539.

Grosjean, D., 1983, Atmospheric reactions of pyruvic acid, *Atmos. Environ.* **17**, 2379–2382.

Grosjean, D., 1989, Organic acids in southern California air: ambient concentrations, mobile source emissions, in situ formation and removal processes, *Environ. Sci. Technol.* **23**, 1506–1514.

Grosjean, D., Cauwenberghe, K. V., Schmid, J. P., Kelley, P. E., and Pitts Jr., J. N., 1978, Identification of C_3–C_{10} aliphatic dicarboxylic acids in airborne particulate matter, *Environ. Sci. Technol.* **12**, 313–317.

Harned, H. S. and Embree, N. D., 1934, The dissociation constant of formic acid from 0 to 60°, *J. Am. Chem. Soc.* **56**, 1042–1044.

Harned, H. S. and Ehlers, R. W., 1933a, The dissociation constant of acetic acid from 0 to 60° centigrade, *J. Am. Chem. Soc.* **55**, 652–656.

Harned, H. S. and Ehlers, R. W., 1933b, The dissociation constant of propionic acid from 0 to 60°, *J. Am. Chem. Soc.* **55**, 2379–2383.

Kawamura, K. and Gagosian, R. B., 1990, Mid-chain ketocarboxylic acids in the remote marine atmosphere: distribution patterns and possible formation mechanisms, *J. Atmos. Chem.* **11**, 107–122.

Kawamura, K., Ng, L.-L., and Kaplan, R. I., 1985, Determination of organic acids (C_1–C_{10}) in the atmosphere, motor exhausts, and engine oils, *Environ. Sci. Technol.* **19**, 1082–1086.

Keene, W. C. and Galloway, J. N., 1984, Organic acidity in precipitation of north America, *Atmos. Environ.* **18**, 2491–2497.

Keene, W. C. and Galloway, J. N., 1988, The biogeochemical cycling of formic and acetic acids through the troposphere: an overview of current understanding, *Tellus* **40B**, 322–334.

Khan, I., Brimblecombe, P., and Clegg, S. L., 1992, The Henry's law constants of pyruvic and methacrylic acids, *Environ. Technol.* **13**, 587–593.

Levsen, K., Behnert, S., Prieb, B., Svoboda, M., Winkeler, H. D., and Zietlow, J., 1990, Organic compounds in precipitation, *Chemosphere* **21**, 1037–1061.

Long, F. A. and McDevit, W. F., 1952, Activity coefficients of nonelectrolyte solutes in aqueous salt solutions, *Chem. Rev.* **51**, 119–169.

Lunde, G., Gether, J., Gjos, N., and Stobet Lande, M. B., 1977, Organic micropollutants in precipitation in Norway, *Atmos. Environ.* **11**, 1007–1014.

Pitzer, K. S., 1991, Ion interaction approach: theory and data correlation, in K. S. Pitzer (ed.), *Activity Coefficients in Electrolyte Solutions*, CRC Press, Boca Raton, FL, Chap. 3.

Scarano, E., Gay, G., and Forina, M., 1971, Hydrogen chloride partial pressure of dilute hydrogen chloride-concentrated lithium chloride aqueous solutions, *Anal. Chem.* **43**, 206–211.

Schuetzle, D., Cronn, D., and Crittenden, A. L., 1975, Molecular composition of secondary aerosol and its possible origin, *Environ. Sci. Technol.* **9**, 838–845.

Seinfeld, J. H., 1986, *Atmospheric Chemistry and Physics of Air Pollution*, Wiley, New York.

Servant, J., Kouadio, G., Cros, B., and Delmas, R., 1991, Carboxylic monoacids in the air of Mayombe Forest (Congo): role of the forest as a source or sink, *J. Atmos. Chem.* **12**, 367–380.

Talbot, R. W., Andreae, M. O., Berresheim, H., Jacob, D. J., and Beecher, K. M., 1990, Sources and sinks of formic, acetic, and pyruvic acids over central Amazonia, 2. Wet season, *J. Geophys. Res.* **95**, 16799–16811.

Wagman, D. D., Evans, W. H., Parker, V. B., Schumm, I. H., Bailey, S. M., Churney, K. L., and Nuttall, R. L., 1982, The NBS tables of chemical thermodynamic properties, *J. Phys. Chem. Ref. Data* **11**, Suppl. 2, 392 pp.