IUPAC Subcommittee on Gas Kinetic Data Evaluation – Data Sheet V.A1.19

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$CH_3C(O)OH$ + ice

Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
Partition coefficients: K_{linC}			
$1.9 \times 10^{-11} \exp(6800/T)$	220-245	Sokolov and Abbatt, 2002	CWFT-MS (a)
320	193	Picaud et al., 2005	CWFT-MS (b)
258	203		
153	213		
73	223		
$2.3 \times 10^{-10} \exp(6530/T)$	197-227	von Hessberg et al., 2007	CWFT-MS (c)
$1.9 \times 10^{-12} \exp(7400/T)$	213-243	Kerbrat et al., 2010	PBFT-CIMS (d)
$5.5 \times 10^{-9} \exp(5703/T)$	218 -238	Symington et al, 2010	CWFT-MS (e)

Comments

(a) Ice film made by freezing distilled water. Uptake was found to be reversible and equilibrium surface coverages were calculated using the geometric ice surface area. Equilibrium uptake of $CH_3C(O)OH$ to ice at various temperatures was analysed using the Langmuir isotherm. The values for K_{linC} at individual temperatures given in the Table uses the reported values of $K_{LangP}(T)$ and $N_{max}(T)$. No errors were reported. The temperature dependent expression of K_{linC} was derived by fitting to these five data points. A value of $\Delta H_{ads} = -73 \pm 12$ kJ mol^{-1} was reported. $CH_3C(O)OH$ concentration varied between $\approx 4 \times 10^{10}$ and 2×10^{13} molecule cm^{-3}. with between 2 and 20 % present as dimers.

(b) Ice film, 30-80 µm thick was made by freezing distilled water. Uptake was found to be reversible and equilibrium surface coverages were calculated using the geometric ice surface area. Equilibrium uptake of $CH_3C(O)OH$ to ice at various temperatures was analysed using the BET isotherm to derive a value of $\Delta H_{ads} = -33.5 \pm 4.2$ kJmol^{-1}. The parameterised BET isotherms were used to calculate values of K_{linC} at the four temperatures where reversible uptake was observed. The authors suggest that most of the acetic acid was in the form of dimers in their experiments.

(c) Ice film made by freezing distilled water. Uptake was found to be reversible and equilibrium surface coverages were calculated using the geometric ice surface area. Values of $N_{max} = 2.4 \times 10^{14}$ molecule cm^{-2} (independent of temperature) and $\Delta H_{ads} = -55 \pm 9$ kJ mol^{-1} were reported. $CH_3C(O)OH$ concentration varied between 3×10^{9} and 2×10^{11} molecule cm^{-3} and the fraction of dimers present was calculated to be less than 15 % for all temperatures and concentrations except for 197 K and [HC(O)OH] > 2×10^{10} molecule cm^{-3}.

(d) Packed ice bed flow tube at atmospheric pressure. Partition coefficients derived from analysis of breakthrough curves and using the geometric ice surface area.

(e) Ice film made by freezing distilled water. $CH_3C(O)OH$ concentration varied between ≈ 3 × 10^{10} and 2.6 × 10^{13} molecule cm^{-3}. Uptake was found to be reversible and equilibrium surface coverages were calculated using the geometric ice surface area. Equilibrium uptake of $CH_3C(O)OH$ to ice at various temperatures was analysed using the Langmuir isotherm and N_{max} was found to be 2.4×10^{14} molecule cm^{-2}. Linear least squares fit of selected data for concentrations <2.5 x10^{12} molecule cm^{-3} was used to determine the optimum values of K_{linC}. A value of ΔH_{ads} = -49 (± 8) kJ mol^{-1}, was reported.

Preferred Values

Parameter	Value	T/K
K_{linC} / cm	$1.5 \times 10^{-14} \exp(8500/T)$	195 - 240
N_{max} / molecule cm^{-2}	2.5×10^{14}	
Reliability		
$\Delta(E/R)$ / K	± 1000	195 - 240
$\Delta \log N_{max}$	0.1	

Comments on Preferred Values

There are five experimental studies of the reversible uptake of $CH_3C(O)OH$ to pure ice surfaces, the results differing somewhat, possibly due to the presence of varying amounts of the acetic acid dimer. Sokolov et al. (2002), von Hessberg et al.(2007), Kerbrat et al. (2010) and Symington et al. (2010) suggest that the fraction of dimers present in their samples was of the order of percent, whereas Picaud et al. (2005) calculated that almost 100 % of their sample was dimerised. It is not clear if this assumption was partially responsible for the much lower partitioning coefficients found by Picaud et al. The published data of Sokolov et al. (2002), von Hessberg et al. (2007), Kerbrat et al., (2010) and Symington et al., (2010) are in good agreement and were used to derive the preferred expression, which indicates an enthalpy of adsorption of 70 (± 10) kJ mol^{-1}. The values of N_{max} returned by the various studies is variable, probably due to extrapolations from low coverages and also due to lateral interactions at high coverages, which make this parameter generally difficult to access experimentally (Jedlovszky et al., 2006).

Theoretical investigations (Compoint et al. 2002; Picaud et al. 2005) have shown that the hydroxyl and carbonyl groups of acetic acid are bound to two surface water molecules, with the CH_3 group directed away from the ice surface. This would tend to suggest that acetic acid dimers, for which OH and CO bonds are no longer available, would undergo significantly weaker interaction with the ice surface.

References

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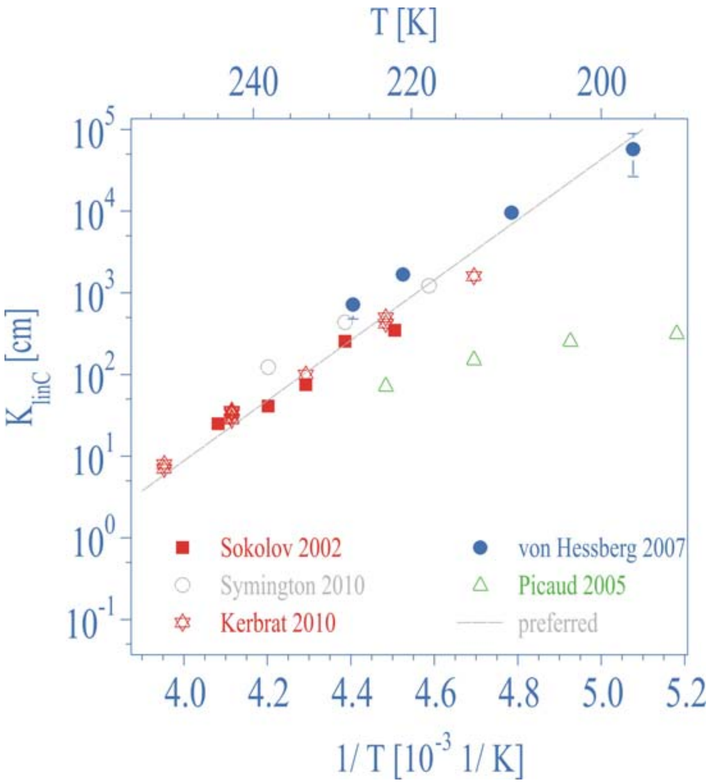

Partitioning coefficients (K_{linC}) for acetic acid uptake to ice.