IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A1.21 HI21

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C_2H_5OH + ice

Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
Partitioning coefficients: K_{linC}			
$K_{linC} = 8.36$	228	Sokolov and Abbatt, 2002	CWFT-MS (a)
$K_{linC} = (7.5 \pm 3.0) \times 10^{-14} \exp\{(7445 \pm 200)/T\}$	218-233		
$K_{linC} = 197$	203	Peybernès et al., 2004	CWFT-MS (b)
$K_{linC} = 85$	213		
$K_{linC} = 23$	223		
$K_{linC} = 106 \pm 21$	213	Kerbrat et al., 2007	CWFT-MS (c)
$K_{linC} = 26.1 \pm 10$	223		
$K_{linC} = 2.94 \pm 0.23$	233		
$K_{linC} = 1.11 \pm 0.09$	243		

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 $C2H_5OH$ to ice at various temperatures was analysed using the Langmuir isotherm. The value for K_{linC} at 228 K given in the Table uses the reported values of $K_{LangP} = 1.22 \times 10^3$ Torr^{-1} and $N_{max} = 2.9 \times 10^{14}$ molecule cm^{-2}. (no error limits were reported). The temperature dependent expression was derived from their quoted values of $\Delta H_{ads} = (-61.9 \pm 1.7)$ kJmol^{-1}, $\Delta S_{ads} = (-113 \pm 4)$ Jmol^{-1}K^{-1}, so that $K_P^0 = \exp\{-(T * 113 - 61900) / 8.314*T\}$, and $V/A = 6.0 \times 10^{-8}$ cm (also quoted by the authors). The error in the pre-exponential factor stems from the error in ΔS_{ads}.

(b) Ice film (30 –100 μm thick) made by freezing distilled water at 253 K. Uptake of ethanol was found to be reversible for T between 203 and 223 K, equilibrium surface coverages were calculated using the geometric ice surface area. Values of $\Delta H_{ads} = (-57 \pm 8)$ kJmol^{-1}, $N_{max} = (2.8 \pm 0.8) \times 10^{14}$ cm^{-2} obtained using BET analysis of adsorption isotherms. The parameterised BET isotherms were used to calculate values of K_{linC} at the three temperatures where reversible uptake was observed.

(c) Method as described in note (b). Values of K_{linC} at 213 and 223 K were converted from values of N_{max} of (2.37 ± 0.27) at 213 K and (2.58 ± 0.62) at 223 K and values of K_{LangC} of (4.48 ± 0.72) x 10^{-13} and (1.01 ± 0.32) x10^{-13} cm^3 molecule^{-1} at 213 and 223 K, respectively. Values of K_{linC} at 233 and 243 K were obtained from linear relationship between N (surface coverage in molecule cm^{-2} of ice) and [C_2H_5OH] (units of molecule cm^{-3}). Enthalpy of adsorption derived as $\Delta H_{ads} = (-68 \pm 15)$ kJ mol^{-1}.

Preferred Values

K_{linC} = 5.0 x 10^{-14} exp(7500/T) cm over the range 210 K to 250 K.
N_{max} = 2.8 × 10^{14} molecules cm^{-2}, independent of temperature.

Reliability

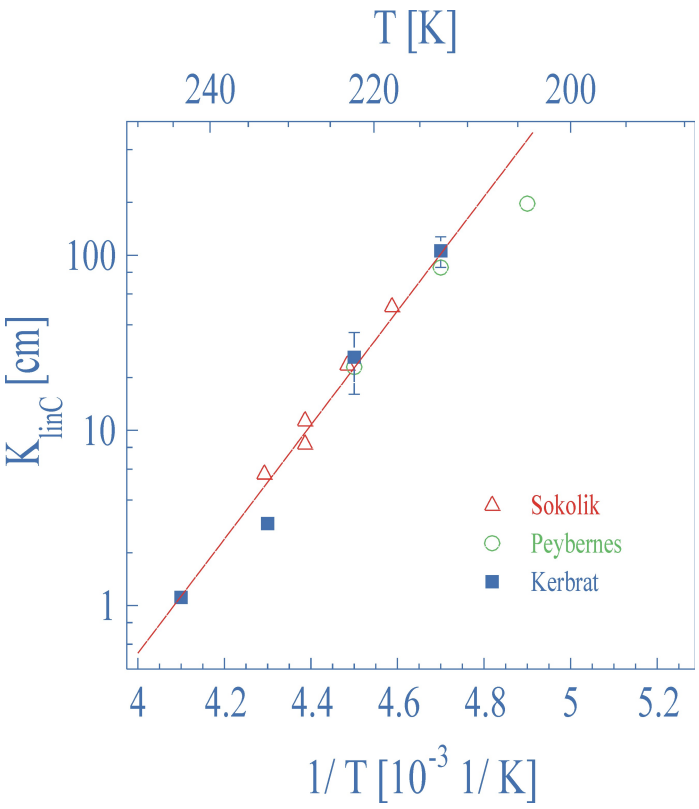
$\Delta(E/R)$ = ± 200 K.
$\Delta \log N_{max}$ = 0.15

Comments on Preferred Values

The three experimental investigations (all using the same method) of the reversible uptake of C_2H_5OH to pure ice surfaces at T > 200 K are in good agreement and the preferred value of K_{linC} is derived from a non weighted fit to all data sets. Good agreement is also obtained for the values of N_{max} derived from Langmuir or BET isotherm analyses.
Kerbrat et al. (2007) have observed that by generating ice from 0.63 or 2.49 wt% solutions of HNO_3, the uptake of C_2H_5OH is increased drastically (up to a factor of 60), but remains reversible. This phenomenon is attributed to the presence of supercooled liquid on the ice surface.
Molecular dynamics simulations of the C_2H_5OH – ice interaction (Peybernès et al., 2004) predict values of N_{max} and the adsorption energy which are in accord with the experimental data. C_2H_5OH is predicted to hydrogen bond to the ice surface with the alkyl group directed away from the ice surface.

References

Kerbrat, M., Le Calvé, S. and Mirabel, P.: J. Phys. Chem. A 111, 925-931, 2007.
Peybernès, N., Le Calve, S., Mirabel, P., Picaud, S. and Hoang, P. N. M.: J. Phys. Chem. B 108, 17425-17432, 2004.
Sokolov, O. and Abbatt, J. P. D.: J. Phys. Chem. 106, 775-782, 2002.



Experimental values of K_{linC} for interaction of C_2H_5OH with pure ice surfaces. The prefered value, $K_{linC} = 5.0 \times 10^{-14} \exp(7500/T)$ is given by the solid line.