Chemical equilibria of aqueous ammonium-carboxylate systems in aqueous bulk, close to and at the water-air interface

Yina Salamanca Blanco,[a,†] Önder Topel,[a,‡] Éva G. Bajnóczi,[a] Josephina Werner,[a,b] Olle Björneholm[b] and Ingmar Persson[a,*]

[a] Department of Chemistry and Biotechnology, Swedish University of Agricultural Sciences, P.O. Box 7015, SE-750 07 Uppsala, Sweden,

[b] Department of Physics and Astronomy, Uppsala University, P.O. Box 516, SE-751 20 Uppsala, Sweden.

Electronic Supplementary Information

Table S1. Summary of acidic constants of the carboxylic acids, RCOOH, R=C_nH_{2n+1}, n=0-8, and the ammonium ion, NH_4^+, at zero, 0.2, 0.50 and 1.00 mol·dm^{-3} ionic strength and 298 K, the stability constant, K_x, of the reaction $RCOO^- + NH_4^+ \rightleftharpoons RCOOH + NH_3$ at *0.0*/0.20/0.50/1.00 mol·dm^{-3} ionic strength and 298 K, the percentage carboxylic acid in the aqueous phase calculated from the K_X, $RCOOH_{calc}$.

Common name	pK_a	pK_X	$RCOOH_{calc}$	
Formic acid		*3.75*[a]/3.53/3.50/3.46	*5.50*/5.78/5.85/5.97	*0.18*/0.13/0.12/0.10
Acetic acid	*4.75*[a]/4.56/4.55/4.53	*4.50*/4.75/4.80/4.91	*0.56*/0.42/0.40/0.35	
Propionic acid	*4.87*[a]/4.69/4.68/4.66	*4.38*/4.62/4.67/4.78	*0.65*/0.49/0.46/0.41	
Butyric acid	*4.81*[a]/4.74/4.71/4.64	*4.44*/4.57/4.64/4.80	*0.60*/0.52/0.48/0.40	
Valeric acid	*4.82*[a]/4.76/-/-	*4.43*/4.55/-/-	*0.61*/0.53/-	
Caproic acid	*4.88*[a]/-/-/-	*4.37*[b]/-/-/-	*0.65*[b]/-/-	
Enanthic acid	*4.89*[a]/-/-/-	*4.36*[b]/-/-/-	*0.66*[b]/-/-	
Caprylic acid	*4.89*[a]/-/-/-	*4.36*[b]/-/-/-	*0.66*[b]/-/-	
Pelargonic acid	*4.96*[a]/-/-/-	*4.29*[b]/-/-/-	*0.71*[b]/-/-	
Ammonium ion	*9.25*[a]/9.31/9.35/9.43			

[a] *CRC Handbook of Chemistry and Physics*, Lide, D. R., Ed., 96th edition 2015-2016, p. 5-93-102.

[b] As the pK_a value for the ammonium ion increases with increasing ionic strength, while the opposite is found for the carboxylic acids the pK_X values at zero ionic strength can be regarded as minimum values and the highest possible calculated RCOOH concentrations.

Table S2. Summary of the accumulated amount ammonia trapped in vessel 2 during 24 hours recalculated to percentage of complete reaction at 0.10/0.25/0.50 mol·dm^{-3} ammonium carboxylate concentration (Accum. NH_3 (%), 24 h), the observed amount carboxylic acid formed in the aqueous bulk determined by ^{1}H-NMR recalculated to percentage of complete reaction (NMR (%)), and the initial reaction rates in aqueous solution from the amount ammonia trapped in vessel 2 at 0.10/0.50 mol·dm^{-3} ammonium carboxylate concentration (init. reac. rate (mmol·dm^{-3}/h)).

Carboxylic acid	Theor. NH_3/RCOOH (%)*	Accum. NH_3 (%), 24 h	NMR (%)	Init. reac. rate (mM/h)	Reac. rate after24 h (mM/h)
Formic acid	*0.18*	0.53/-/0.57	0.68[a]	0.061/-/0.26	0.014/-/
Acetic acid	*0.56*	1.20/1.08/0.94	1.24[b]	0.094/0.23/0.42	0.034/0.075/0.205
Propionic acid	*0.65*	1.36/1.25/1.29	1.26[a]	0.13/0.22/0.52	0.031/0.068/0.185
Butyric acid	*0.60*	1.56/1.51/1.33	1.54[a]	0.15/0.33/0.68	0.025/0.065/0.165
Valeric acid	*0.61*	1.02/-/0.96	-	0.075/0.21/0.32	0.034/0.063/0.175
Caproic acid	*0.65*	1.48/1.49/1.59	1.52[a]	0.16/0.36/0.66	0.019/0.055/0.105
Enanthic acid	*0.66*	1.66/1.54/1.91	1.58[a]	0.12/0.29/0.66	0.019/0.055/0.080
Caprylic acid	*0.66*	0.95/3.20/6.14	6.20[c]	0.059/0.52/1.98	0.033/0.275/0.975
Pelargonic acid	*0.71*	3.55/-/13.31		0.19/-/4.80	0.162/-/1.99
Succinic acid	0.62	2.75/-/-	-	-	

[a] 0.25 mol·dm^{-3} solution [b] 0.10 mol·dm^{-3} solution [c] 0.50 mol·dm^{-3} solution * extrapolated to zero ionic strength

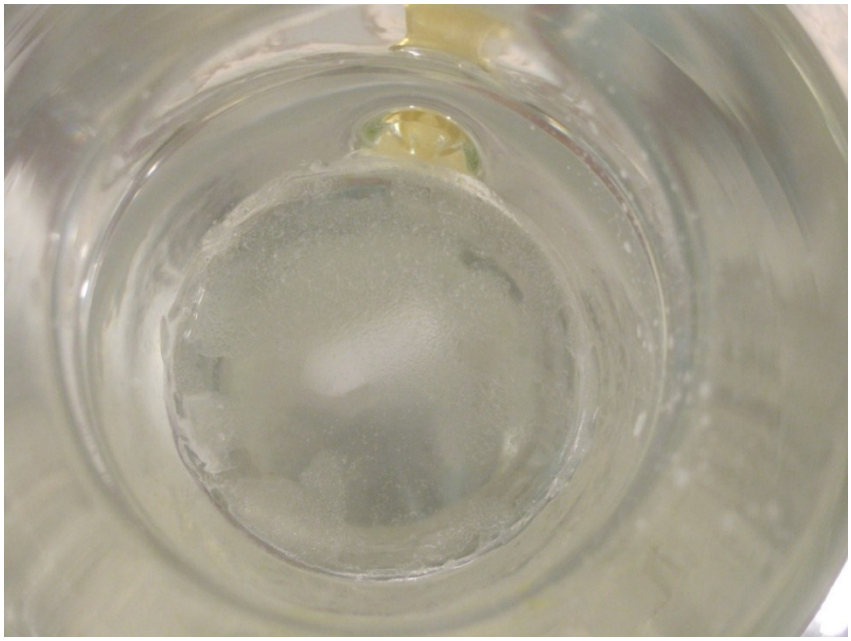

Figure S1a. Photo of the disc of solid n-octanoic acid from top. Note the white stirrer bar at bottom on the vessel.

Figure S1b. Photo of the disc of solid n-octanoic acid from side of the vessel.

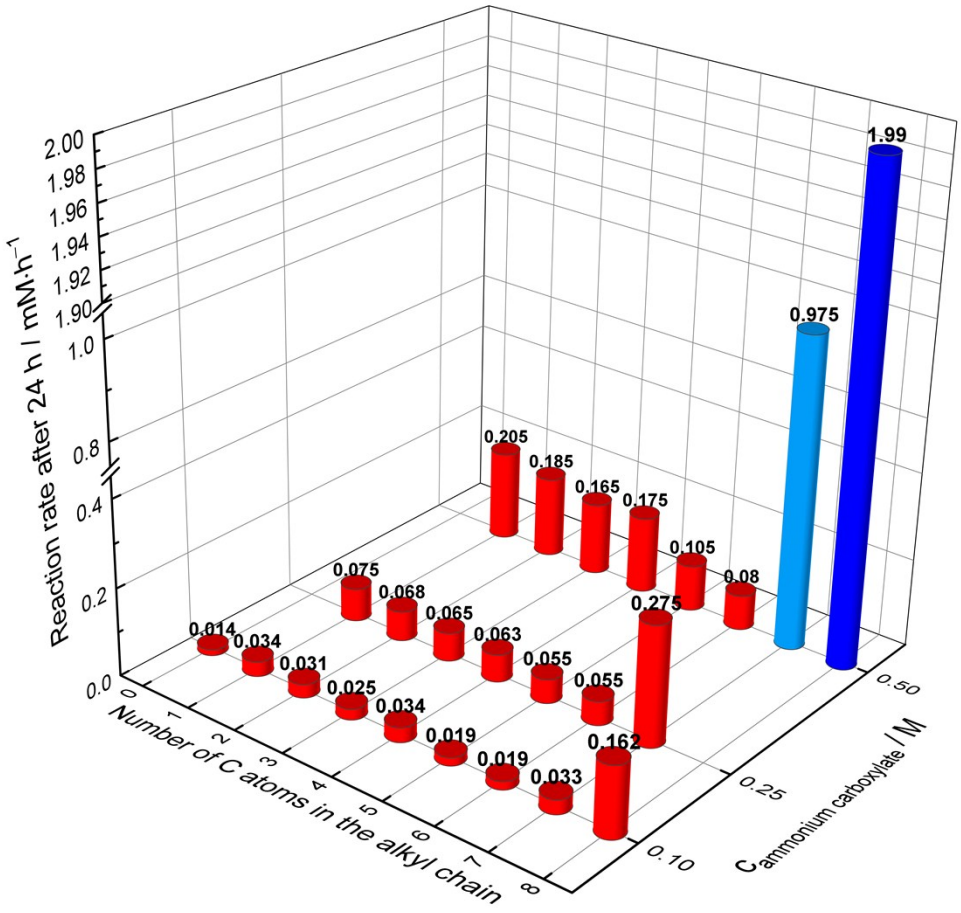

Figure S2. The reaction rate after 24 hours of the ammonia release as function of initial ammonium carboxylate and the number of carbon atoms in the alkyl chain at 298.15 K and at 4.0 mL·s^{-1} N_2 flow rate.