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Carbon monoxide solubility in ionic liquids: determination, prediction and relevance to hydroformylation†

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The solubility of carbon monoxide in 37 ionic liquids and in some organic solvents has been determined using high-pressure ^{13}C NMR spectroscopy; a method for predicting the CO solubility is demonstrated, and it was shown that the rate of the hydroformylation of 5-hexen-2-one does not correlate with the CO solubility, as expected from the determined relative solubility of CO compared to H_2.

Room temperature ionic liquids, defined as salts that melt at or below room-temperature, are candidates for solvents in biphasic catalysis, allowing good catalyst recyclability. They have been described as "designer" solvents, due to the ability to tune their properties to specific applications, notably in organic synthesis and catalysis.[1] Many of the catalytic reactions evaluated in ionic liquids employ gases as substrates and therefore it is important to know their solubility. While gas solubility data are available for all the important gases in ionic liquids,[2] there is one notable exception—CO. Carbon monoxide is used in numerous catalytic processes, notably hydroformylation and carbonylation (see below).

The solubility of CO was studied in several organic solvents (Table 1) using high-pressure ^{13}C NMR spectroscopy. The method is analogous to that used to determine the solubility of H_2 in ionic liquids.[3] The CO solubility determinations in organic solvents were used to validate the methodology and further details are given in ESI.†

Table 2 lists the ionic liquids‡ (see Fig. 1 for the cations), their densities and the CO solubility data at 1 bar partial pressure, as well as the corresponding Henry's constants. The solubility of CO was found to be similar to, or higher than, that of H_2 for the ionic liquids where H_2 solubility data are available,[3] and generally somewhat higher than in water (1.1 mM bar^{-1}).[4] The solubility of CO is more dependent upon the nature of the ionic liquid than H_2, presumably due to the presence of a dipole moment, and higher polarisability.[5]

For the 1-butyl-3-methylimidazolium cation (1, R = $-C_4H_9$) the solubility of CO increases according to the series $[BF_4]^-$ < $[PF_6]^-$ < $[SbF_6]^-$ < $[CF_3CO_2]^-$ < $[Tf_2N]^-$ (Tf_2N^- = bis(trifluoromethylsulfonyl)imide). This coincides with an increase in the size of the anion, and a decrease in π* interactions.[6] From the series of $[Tf_2N]^-$ ionic liquids additional trends are apparent; the solubility increases with the chain length of the alkyl substituent in the pyridinium and imidazolium liquids (the solubility also increases with chain length for 1-methyl-3-alkylimidazolium tetrafluoroborate salts). In addition, the solubility of CO decreases when the alkyl group is replaced by a benzyl group, which also corresponds to an increase in π* interactions,[7] which generally leads to a decrease in solubility.†

Table 1 Solubility of CO in molecular solvents at 295 K

Solvent	ρ/g cm^{-3}	K_H/bar[a]	[CO]/mM[b]
Methanol	0.791	2285	10.8 (9.4)
Toluene	0.867	1289	7.3 (7.4)
1-Hexene	0.673	471	17.0
1-Octene	0.714	578	11.0 (10.2)[c]
1-Decene	0.741	741	7.1

[a] Henry's constant, $K_H = P_{CO}/\chi_{CO}$. [b] Calculated for a partial pressure of 1 bar, assuming linear increase of solubility with pressure. Literature data in parentheses.[4] [c] At 323 K.

The solubility of CO decreases with increasing temperature, although the effect is rather small.† The corresponding enthalpies of absorption of CO in 1-butyl-3-methylimidazolium (**1**) and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide were estimated as −2.0 and −1.5 kJ mol^{-1}, respectively.†

We have also developed a method for using the NMR chemical shift data of sets of probes in ionic liquids that allows the prediction of the solubility of carbon monoxide and other solvent properties with good precision. By referencing the ^{13}C NMR chemical shifts of chloroform (Δ_b), 1,2-dichloroethane (Δ_c) and benzonitrile

Table 2 Solubility of CO in ionic liquids at 295 K

Entry	Cation	–R	Anion	ρ/ g cm^{-3}	K_H/ kbar[a]	[CO] /mM[b]
1	1	$-CH_3$	$[Tf_2N]^-$[d]	1.580	1.34	3.13
2	1	$-C_2H_5$	$[Tf_2N]^-$	1.542	1.18	3.30
3	1	$-C_4H_9$	$[Tf_2N]^-$	1.433	0.95	3.60
4	1	$-C_6H_{13}$	$[Tf_2N]^-$	1.378	0.76	3.92
5	1	$-C_8H_{17}$	$[Tf_2N]^-$	1.337	0.67	4.20
6	1	$-C_7H_7$[c]	$[Tf_2N]^-$	1.493	1.41	2.33
7	2	$-C_2H_5$	$[Tf_2N]^-$	1.513	1.36	2.75
8	2	$-C_4H_9$	$[Tf_2N]^-$	1.421	1.04	3.14
9	3	$-C_2H_5$	$[Tf_2N]^-$	1.551	1.55	2.58
10	3	$-C_4H_9$	$[Tf_2N]^-$	1.449	1.14	3.05
11	3	$-C_6H_{13}$	$[Tf_2N]^-$	1.430	0.94	3.41
12	3	$-C_8H_{17}$	$[Tf_2N]^-$	1.364	0.82	3.52
13	3	$-C_7H_7$	$[Tf_2N]^-$	1.516	1.38	2.40
14	4	$-C_2H_5$	$[Tf_2N]^-$	1.521	1.62	2.34
15	4	$-C_4H_9$	$[Tf_2N]^-$	1.440	0.93	3.58
16	4	$-C_7H_7$	$[Tf_2N]^-$	1.474	2.02	1.57
17	5	$-C_4H_9$	$[Tf_2N]^-$	1.472	0.88	3.90
18	5	$-C_8H_{17}$	$[Tf_2N]^-$	1.317	0.90	3.03
19	6	$-C_2H_5$	$[Tf_2N]^-$	1.520	1.26	3.00
20	6	$-C_4H_9$	$[Tf_2N]^-$	1.408	0.92	3.55
21	6	$-C_8H_{17}$	$[Tf_2N]^-$	1.376	1.03	2.74
22	6	$-C_7H_7$	$[Tf_2N]^-$	1.505	1.30	2.49
23	8	$-C_4H_9$	$[Tf_2N]^-$	1.440	1.24	2.72
24	8	$-C_8H_{17}$	$[Tf_2N]^-$	1.306	0.94	2.87
25	9	$-C_2H_5$	$[Tf_2N]^-$	1.484	1.48	2.44
26	7	$-C_4H_9$	$[Tf_2N]^-$	1.387	3.26	3.06
27	7	$-C_7H_7$	$[Tf_2N]^-$	1.441	2.79	1.13
28	1	$-CH_3$	$[BF_4]^-$	1.373	8.05	0.93
29	1	$-C_2H_5$	$[BF_4]^-$	1.418	6.67	1.07
30	1	$-C_4H_9$	$[BF_4]^-$	1.213	3.37	1.59
31	1	$-C_6H_{13}$	$[BF_4]^-$	1.177	2.88	1.61
32	5	$-C_8H_{17}$	$[BF_4]^-$	1.133	1.91	2.02
33	1	$-C_4H_9$	$[PF_6]^-$	1.363	3.27	1.47
34	1	$-C_4H_9$	$[SbF_6]^-$	1.699	2.01	2.25
35	1	$-C_4H_9$	$[CF_3CO_2]^-$	1.198	1.91	2.49
36	7	$-C_4H_9$	$[CF_3CO_2]^-$	1.195	6.48	0.66
37	5	$-C_4H_9$	$[N(CN)_2]^-$	1.062	3.99	1.23

[a] Henry's constant, $K_H = P_{CO}/\chi_{CO}$. [b] Calculated for a partial pressure of 1 bar. [c] $-C_7H_7 = -CH_2C_6H_5$. [d] Tf_2N^- = bis(trifluoromethylsulfonyl)imide.

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† Electronic supplementary information (ESI) available: further experimental details. See http://www.rsc.org/suppdata/cc/b4/b401537a/

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(N^{13}**C**) (Δ_d) against cyclohexane, and the ^{19}F NMR chemical shift of 2-fluoropyridine against fluorobenzene (Δ_a), dissolved in the ionic liquid, and fitting the observed solubility to these data for eight ionic liquids, an equation with $R^2 = 0.993$ and $\sigma = 0.13$ mM (Fig. 2) was obtained. Hence it is possible to use this method to estimate CO solubilities in ionic liquids indirectly.

As mentioned above, CO solubilities in ionic liquids is relevant to hydroformylation[8] and carbonylation[9] reactions. Reports are, however, difficult to compare due to mass-transfer issues,[8b] although task-specific RTILs have been developed which address this problem and other issues, such as catalyst retention.[8c]

In order to establish the effect of the CO solubility on the rate of hydroformylation reactions, the RhH(CO)(PPh$_3$)$_3$ catalysed hydroformylation of 5-hexen-2-one was evaluated in the ionic liquids for which both CO and H$_2$ solubility data are available (see Table 3). All systems were homogeneous at 80 °C, and the absence of a mass-transfer barrier was checked by the addition of extra catalyst. The turnover frequency (TOF) does not appear to correlate to either the CO solubility or the viscosity, but experimental data, though limited, suggest that low solvent polarity is of particular importance. When increasing the partial pressure of H$_2$ relative to CO, from 10 : 10 bar (entry 8) to 16 : 4 bar (entry 9), the TOF increases. Given the absence of mass-transfer problems, this is presumably due to mass-action on the rate-limiting step, the oxidative insertion of hydrogen. Increasing the CO ratio leads to a decrease in TOF (entry 10), possibly due to the formation of stable carbonyl species.

The low solubilities exhibited by H$_2$ and CO underline the importance of vigorous convection when carrying out reactions involving these gases.

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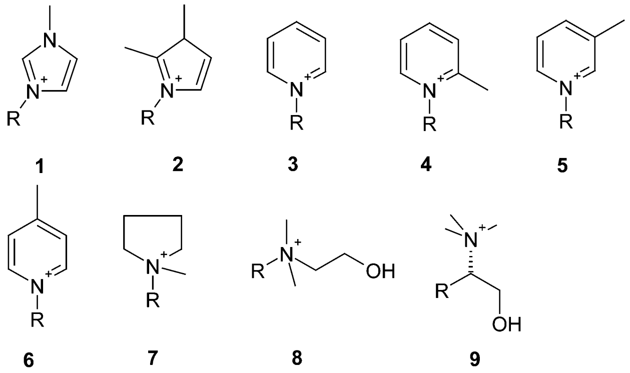

1 2 3 4 5

6 7 8 9

Fig. 1 Generic cation structures referred in Table 2.

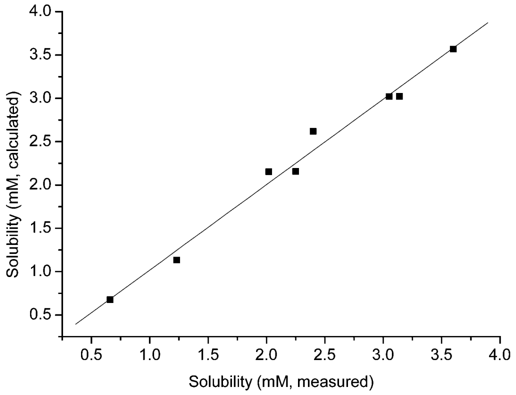

Fig. 2 Predicted *vs.* observed CO solubilities, entries (Table 2) according to the increasing measured solubilities: 36, 37, 32, 34, 13, 10, 8 and 3. [CO] (mM) = $k_a\Delta_a + k_b\Delta_b + k_c\Delta_c + k_d\Delta_d + m$ ($k_a = 0.51$, $k_b = 0.20$, $k_c = -5.08$, $k_d = -1.4$ and $m = 196.49$).†

Table 3 Hydroformylation of 5-hexen-2-one in cation **1** ionic liquids at 80 °C (300 μl substrate per 10 mg RhH(CO)(PPh$_3$)$_3$ and 1.0 ml ionic liquid)

Entry	–R	Anion	$P_{CO} : P_{H2}$/ bar	TOF[a]/ min^{-1}	Yield (%)	n/i[b]
1[c,d]	—	—	10 : 10	10.5	20[d]	2.0
2[e]	–C$_4$H$_9$	[BF$_4$]$^-$	10 : 10	0.9	12	2.1
3[e]	–C$_6$H$_{13}$	[BF$_4$]$^-$	10 : 10	3.1	40	2.4
4[e]	–C$_6$H$_{13}$	[BF$_4$]$^-$	10 : 10	3.3[f]	96	4.9
5[e]	–C$_4$H$_9$	[PF$_6$]$^-$	10 : 10	>7.9	100	3.3
6[c]	–C$_4$H$_9$	[PF$_6$]$^-$	10 : 10	>15.7	100	2.7
7[e]	–C$_4$H$_9$	[Tf$_2$N]$^-$	10 : 10	>7.9	100	3.0
8[c]	–C$_4$H$_9$	[Tf$_2$N]$^-$	10 : 10	7.7	49	4.3
9[c]	–C$_4$H$_9$	[Tf$_2$N]$^-$	4 : 16	>15.7	100	3.3
10[c]	–C$_4$H$_9$	[Tf$_2$N]$^-$	16 : 4	2.2	14	1.9

[a] Average TOF; moles of substrate converted per mole catalyst and minute. [b] Ratio of n- to iso-aldehyde. [c] After 15 min. [d] Neat in 0.5 ml 5-hexen-2-one [e] After 30 min. [f] Catalyst loading 23 mg per 300 μl substrate and 1.0 ml ionic liquid.

Notes and references

‡ Ionic liquids were synthesised according to published procedures or variations thereof.[10] Measurements were done on a Bruker DRX 400 MHz NMR spectrometer. Carbon monoxide (>99.97%) was supplied by Carbagas and used as received. ^{13}C-labelled CO (99% ^{13}C) was obtained from Cambridge Isotope Laboratories, Inc. Measurements were typically carried out under pressures between 1 and 100 bar using a 10 mm sapphire NMR tube.[11] Spectra were fitted using NMRICMA 2.8 (non-linear least-squares iterative fitting application for MatLab). Samples for the determination of Δ_b, Δ_c, and Δ_d were prepared by the addition of 50 μl of a 1 : 1 solution of cyclohexane and chloroform, 1,2-dichloroethane or benzonitrile and toluene respectively to 1.1 ml of ionic liquid. The same protocol applied to Δ_a. Data were fitted using MicroMath Scientist.

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