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Estimates of internal energies of vaporisation of some room temperature ionic liquids

Konrad Swiderski,[a] Andrew McLean,*[a] Charles M. Gordon*[b] and D. Huw Vaughan[a]

[a] *Department of Chemistry & Chemical Engineering, University of Paisley, Paisley, Scotland, UK PA1 2BE. E-mail: mcle-ch0@paisley.ac.uk*

[b] *Institut für Technische Chemie und Makromolekulare Chemie, RWTH Aachen, Worringer Weg 1, 52074 Aachen, Germany. E-mail: gordon@itmc.rwth-aachen.de*

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Systematic variation in the bimolecular rate constant, k_q, for the reaction of singlet oxygen and 1,4-dimethylnaphthalene has led to estimates of the Hildebrand solubility parameter, cohesive pressures and internal energies of vaporisation of some room temperature ionic liquids.

Room temperature ionic liquids, RTILs[1] are attracting great interest as 'greener' alternatives to conventional organic solvents because of their wide thermal liquid range and negligibly low vapour pressures.[2] The latter factor means that direct experimental determination of the internal energy of vaporisation, ΔU_{vap}, is effectively impossible for these materials. However, in general it is possible to estimate ΔU_{vap} indirectly from the Hildebrand solubility parameter, δ, of a solvent which is given by $(\Delta U_{vap}/V_m)^{0.5}$, where V_m is the molar volume of the solvent.[3] The term inside the brackets gives the cohesive energy density or cohesive pressure, c, of the solvent.[3] δ is effectively a measure of the strength of molecular interactions between solvent molecules; the value of δ is lower for non-polar solvents such as cyclohexane and higher for more polar solvents such as acetonitrile or water.[3]

The solvent dependence of the bimolecular rate constant, k_q, for the Diels–Alder reaction between the first singlet excited state of molecular oxygen ($^1O_2$*) and 1,4-dimethylnaphthalene (DMN) has previously been investigated in 28 conventional solvents[4] and was fitted to the Kamlet–Taft equation (eqn. (1)) which attempts to quantify solvation effects on some observable physical parameter, X:[5]

$$\log X = \text{constant} + x\pi^* + y\delta + a\alpha + b\beta \qquad (1)$$

There are four terms in this equation: polarisability/dipolarity given by π^*, δ and Brønsted acidity/basicity terms given by α and β respectively. Considerable effort has been made to determine the values of these terms for RTILs, as this could enable systematic design of novel solvent systems and quantitative comparison with more conventional solvent media.[6] π^*, α and β values have been determined for several RTILs,[6b] but to date there have been no experimentally derived estimates of δ values. The solvent dependence of k_q in conventional solvents was found to be effectively fitted by eqn. (2):

$$\log k_q = 2.15 + 1.18\pi^* + 0.07\delta \ (r^2 = 0.95) \qquad (2)$$

where δ has units $(\text{MPa})^{0.5}$.[4] The solvent dependence of k_q for this reaction therefore depends only on π^* and δ. Given that π^* varies little with RTIL structure, this reaction should be a very useful probe for δ and thereby c and ΔU_{vap} values of RTILs.

We selected several RTILs based on combination of the 1-methyl-3-butylimidazolium cation, $[\text{bmim}]^+$, and its 2-methyl derivative, $[\text{bm}_2\text{im}]^+$, with the anions $[PF_6]^-$, $[SbF_6]^-$, $[BF_4]^-$, $[CF_3SO_3]^-$ and $[(CF_3SO_3)_2N]^-$.[7] The reaction of $^1O_2$* with DMN was monitored using established methods involving time resolved near IR detection of $^1O_2$* phosphorescence in solution (355 nm laser excitation, phenazine as photosensitiser, O_2 saturated conditions).[8] The lifetime of $^1O_2$*, τ_Δ, was obtained in the absence of DMN, and k_q was determined by monitoring the first order rate constant, k_{obs}, for the decay of $^1O_2$* as a function of DMN concentration (Fig. 1). All these results together with the calculated δ, c and ΔU_{vap} values derived from eqn. (2) are summarised in Table 1.

The observed τ_Δ values in RTILs range from 3 to 40 μs. A full discussion of factors controlling these values will be reserved for a future publication, but these values are within the range anticipated

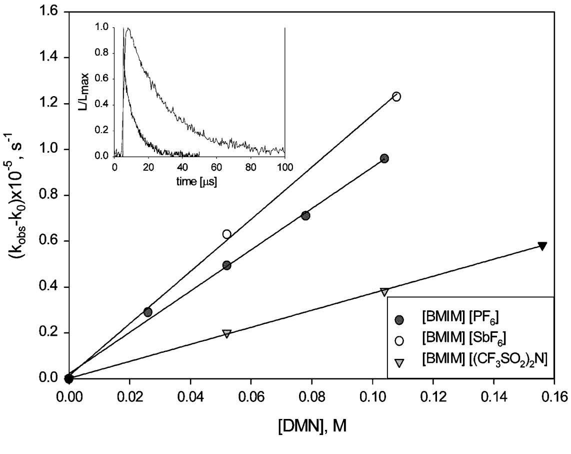

Fig. 1 Plot of k_{obs} as a function of [DMN] in various RTILs. The intercept on the k_{obs} axis has been offset by k_0 ($1/\tau_\Delta$) for clarity. Inset shows variation in $^1O_2$* decay profiles in [bmim][PF$_6$] with [DMN] = 0 and 0.1041 mol dm^{-3}.

Table 1 Parameters determined for RTILs used in this study at 298 K

Solvent	τ_Δ/μs	k_q/mol^{-1} dm^3 s^{-1}	π^{*a}	δ/(MPa)$^{0.5}$	c/J cm^{-3}	[RTIL]/mol dm^{-3}	ΔU_{vap}/kJ mol^{-1}
[bmim][BF$_4$]	11	1.17×10^6	1.047	31.6	998	4.96	201
[bmim][SbF$_6$]	21	1.13×10^6	1.039	31.5	992	4.45	223
[bmim][PF$_6$]	22	9.0×10^5	1.032	30.2	912	4.82	189
[bmim][(CF$_3$SO$_2$)$_2$N]	46	3.71×10^5	0.984	25.5	650	3.41	191
[bmim][CF$_3$SO$_3$]	3.5	3.6×10^{5b}	1.006	24.9	620	4.51	139
[bm$_2$im][(CF$_3$SO$_2$)$_2$N]	5.6	3.20×10^5	1.010	24.2	586	3.27	179

[a] From ref. 5b. [b] Lower limit of k_q, associated δ; c and ΔU_{vap} values should be regarded as lower limits.

based on structurally related conventional solvents.[4] The value of 3.5×10^5 mol^{-1} dm^3 s^{-1} for [bmim][CF_3SO_3] should be regarded as a lower limit because the τ_Δ values were approaching the instrumental response time (1 μs). This, in turn, leads to lower limits for the associated thermodynamic quantities. This liquid apart, we estimate that the k_q values are accurate to within $\pm 10\%$. All of the k_q values are at least one hundred times lower than diffusion control rate constants in these systems.[9] We are therefore confident that our reaction kinetics are 'pre-equilibrium' controlled[10] as was the case in the original study using conventional solvents. This ensures the probity of eqn. (2) when applied to the RTILs studied here.

As would be expected for solvents largely held together by electrostatic interactions, δ and c values are uniformally high for the RTILs studied. We estimate errors of ± 1.5 in δ values which, because of the squared dependence, results in large error limits for both c and ΔU_{vap} (± 100 J cm^{-3} and ± 20 kJ mol^{-1} respectively). Nevertheless, it is satisfying to note that our c values straddle that of 810 J cm^{-3} obtained for [bmim][PF_6] by other workers using computational techniques.[11] The latter result equates to a δ value of 28.5, in very good agreement with our experimental value of 30.2 given the error limits of our data and the assumptions made in the computational studies. The c values are comparable with those of acetonitrile and *N*-methyl formamide (580 and 1000 J cm^{-3} respectively) and significantly lower than that of water (2500 J cm^{-3}),[3c] even though the conventional solvents have much larger vapour pressures than RTILs at room temperature. However, the ΔU_{vap} values of RTILs (*ca.* 200 kJ mol^{-1}) are significantly greater than those of conventional solvents (20–30 kJ mol^{-1})[3c] reflecting the negligible vapour pressures of the former. A mean interaction energy of 30–40 kJ mol^{-1} between RTIL ions in solution can be estimated based on the ΔU_{vap} values in Table 1 if it is assumed that each RTIL molecule is surrounded by six others.[12]

The δ values in Table 1 do not correlate with either α or β values of the RTILs.[6b] The former values are more dependent upon cation acidity ([bmim]$^+$ > [bm$_2$im]$^+$) and the latter on anion basicity ([CF_3SO]$^-$ > [BF_4]$^-$ > [$(CF_3SO_2)_2N$]$^-$ > [PF_6]$^-$ > [SbF_6]$^-$).[6b] This suggests that the strength of H-bonding interactions between anions and cations comprising the RTIL do not influence the overall cohesive energy of the liquid as suggested by other workers.[13] However, there is a correlation between c values and the molar concentration of the ionic liquid, [RTIL]. Such a correlation is logical if one assumes that a higher concentration of ions would give rise to greater electrostatic stabilisation for a given volume of solution. This explanation is further supported by recent calculations which suggest that electrostatic interactions contribute considerably more to the total cohesive energy of [bmim][PF_6] than dispersion-type interactions.[11] We therefore conclude that variation in ion bulk and the concomitant electrostatic stabilisation energy per unit volume is the dominating factor in controlling c values for the RTILs listed in Table 1. Despite the narrow range of structural variation studied, the results in Table 1 suggest that relative c values of different RTILs may be estimated by comparison of molar concentrations, at least within the [bmim]$^+$ based series employed here.

It is known that π^* is effectively constant for the RTILs studied here.[6b] It is therefore natural to ask from where the k_q/δ correlation arises. Variation of Gibbs free energy with pressure at constant temperature gives a volume $(\partial \Delta G/\partial \Delta P)_T = \Delta V$. Based on this relationship, a plot of $\Delta G^\ddagger$ against c for these solvents[14] gives a slope corresponding to $\Delta V^\ddagger_{solv} = -8.0$ cm^3 mol^{-1}. A further -3.0 cm^3 mol^{-1} should be included because two bonds are formed in the activated complex,[15] giving a final value of $\Delta V^\ddagger_{tot} = -11$ cm^3. This result is in fair agreement with $\Delta V^\ddagger_{tot} = -16$ cm^3 obtained by variation of external pressure on similar reactions involving $^1O_2$* in conventional solvents.[15] The negative and constant value of $\Delta V^\ddagger_{solv}$ indicates that the product-forming transition state has a lower solvation volume than the reactants and that the structure of the product-forming transition state is independent of the nature of the solvent. This in turn suggests that activation entropies are independent of solvent within the solvents studied here. Variation in k_q within the RTIL series therefore arises due to lower activation enthalpies associated with decreased cavitation volumes for the transition state with respect to solvated reactants. It is this that leads to an increase in k_q with increasing c. The relative importance of cohesive ratios of Diels–Alder reactions in RTIL solvents has been much debated.[13] In cases where there are two competing product-forming transition states, that with the most negative $\Delta V^\ddagger_{solv}$ should be increasingly favoured as c is increased if cohesive pressure is the dominant controlling factor. There is little data on how c varies with ion concentration in conventional solvents, and no existing data for c values of RTILs. It is therefore unclear whether solvent effects on endo : exo ratios attributed to cation acidity, as measured by solvent α values, are more significant than those arising from variation of solvent c values in RTIL systems.

With this work we have shown that c and therefore δ varies independently of the other Kamlet–Taft parameters (α,β and π^*) for [bmim]$^+$ based RTIL systems. The lack of interdependency of these parameters considerably enhances the prospects of eqn. (1) to effectively describe the influence of RTILs on chemical processes. As a result, it may now prove possible to establish which parameter (or combination of) most influences any given reaction including endo : exo ratios of Diels–Alder reactions in [bmim]$^+$ based RTILs.

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