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Keto–Enol Tautomerism as a Polarity Indicator in Ionic Liquids

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The keto–enol tautomeric equilibrium for pentane-2,4-dione has been explored in several ionic liquids and these data have been used to give an indication of their polarities in the ground state. The results suggest higher apparent polarities than have been previously indicated by the use of solvatochromatic dyes.

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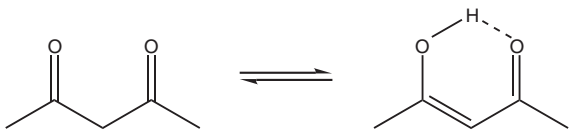
Ionic liquid polarity has been determined by several independent research groups over the past three years using probe molecules and dyes,[1–9] and the consensus is that the determined values place the apparent polarities of ionic liquids between those of methanol and ethanenitrile. However, these methods all investigated polarity via an excited state. By using tautomeric equilibria, we are here investigating polarity in the ground state.

The keto–enol tautomeric equilibrium of pentane-2,4-dione (see Scheme 1) in conventional solvents has been researched for decades.[10–23] It is well understood that the equilibrium depends upon the polarity of the solvent environment. Building upon this understanding, the polarity of ionic liquids was investigated.

The four ionic liquids investigated all contained the 1-butyl-3-methylimidazolium cation ([bmIm], Diagram 1). The four anions used in this study were tetrafluoroborate [BF_4], hexafluorophosphate [PF_6], trifluoromethanesulfonate [OTf], and bistrifluoromethanesulfonamide [NTf_2]. The ionic liquids were all prepared in the QUILL laboratory using proven methods.[24–27]

Solutions of four different concentrations of pentane-2,4-dione in each of these four ionic liquids were prepared, and studied by variable temperature ^{1}H NMR spectroscopy. The areas of the peaks were integrated and from that the enol/keto ratios were determined. The peaks used for the enol lie between δ 5.5 and 5.7 while the peaks for the keto lie between δ 3.5 and 3.7. Typical data are presented in Fig. 1 and Table 1.

Once these data were obtained, the next step was to compare the results with conventional solvents.[28,29] Thirty common solvents were chosen and many of their properties, along with the percentage of enol in pentane-2,4-dione in them,



Scheme 1. Tautomeric equilibrium of pentane-2,4-dione.

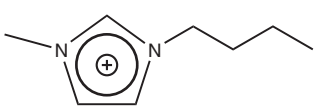


Diagram 1.

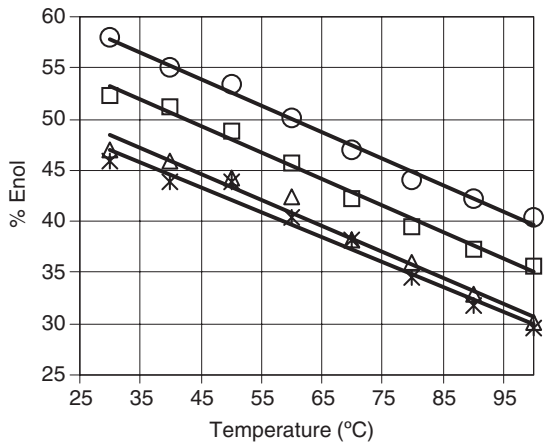


Fig. 1. Percentage enol versus temperature for pentane-2,4-dione in [bmIm][PF_6]. The lines from top to bottom represent: 70% pentane-2,4-dione in [bmIm][PF_6] by concentration (○), 40% (□), 10% (△), and 5% (✳). The correlation R^2 values lie between 0.993 and 0.974.

Table 1. Percentage of enol tautomer of pentane-2,4-dione versus temperature and [bmIm][PF_6] concentrations

T [°C]	Pentane-2,4-dione concentration [mol-%]			
	5	10	40	70
30	45.8	47.0	52.2	57.9
40	43.8	45.9	51.3	55.0
50	43.8	44.3	48.9	53.3
60	40.3	42.4	45.6	50.1
70	38.2	38.1	42.3	46.9
80	34.6	36.0	39.6	44.1
90	31.7	32.8	37.2	42.2
100	29.7	30.1	35.5	40.4

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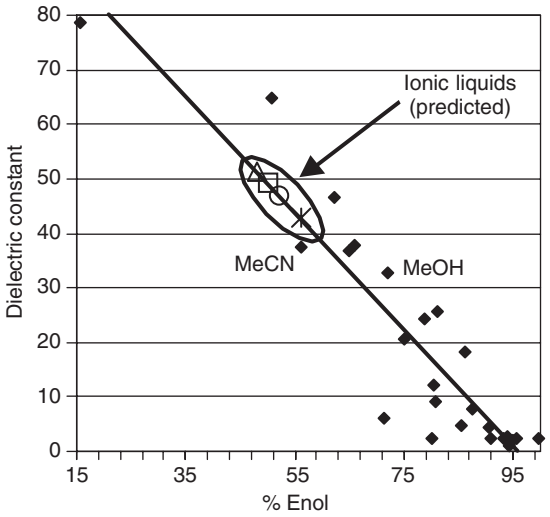

Fig. 2. Correlation of dielectric constants with percent enol for pentane-2,4-dione projected at 25°C. The black oval marks the predictions for the four ionic liquids. [bmIm][PF_6] is represented by (△), [bmIm][NTf_2] by (□), [bmIm][BF_4] by (○), and [bmIm][OTf] by (✳). The concentrations of the pentane-2,4-dione in the ionic liquids is 5 mol-%.

were compared. A correlation with three of these parameters properties stood out: reorganization energy (correlation R^2 0.64), Snyder polarity index (R^2 0.80), and dielectric constant (R^2 0.86). Given these significant, but by no means perfect, correlations, these properties of ionic liquids should be to some extent predictable. This is shown in Fig. 2 for the strongest correlation, dielectric constant. This interpolation thus suggests that the apparent dielectric constants of ionic liquids will fall between 40 and 55, and also that these ionic liquids are more polar than both methanol and ethanenitrile.

We emphasize that this work is preliminary in nature, and is being extended to more dilute solutions (requiring critical control of water content). Future work will also include a wider range of ionic liquids, other keto–enol tautomeric probe molecules (including 2-hydroxypyridine), and the effect of concentration on the tautomeric equilibrium. However, we would be very surprised if this contradicts the overall conclusion, that the apparent polarity of an ionic liquid is a function of the method used to measure it.

Acknowledgment

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