Supplementary Information

Unveiling Molecular Interactions in Glycerol-based Deep Eutectic Solvents

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ENTHALPY OF DISSOLUTION



Figure S1. Temperature profiles of the solution calorimeter during the dissolution of an ampoule containing 109.5 mg of $[N_{4444}]Cl$ (dark green curve on the left) or 96.8 mg of $[N_{4444}]Br$ (wine curve on the right) in glycerol at 318 K. In both cases, the profiles include calibrations performed before and after breaking the ampoule.

This experiment measures the temperature variation while dissolving the salt in glycerol. The calorimeter used and its components are shown in Figure S2.



Figure S2. Precision solution calorimeter and its components housed in a TAM III thermostat. Adapted figure.^{1,2,3}

The temperature variation must be converted to the heat of dissolution to obtain the enthalpy of dissolution. The heat balance of the semi-adiabatic calorimeter is given by

$$-\frac{dQ}{dt} - \frac{dQ_F}{dt} = C_p \frac{dT}{dt} + \frac{C_p}{\tau_c} (T - T_S)$$
(1)

where dQ/dt is the heat of dissolution, dQ_F/dt is the dissipated heat, Cp is the heat capacity of the calorimeter, $C_p dT/dt$ is the heat accumulated in the system, $(C_p/\tau_c)(T-T_S)$ is related to the rate of heat exchanged with the surroundings, T is the temperature measured by the calorimeter thermistor, T_S is the temperature of the surroundings, and τ_c is the thermal relaxation time of the calorimeter

The baseline sections of the experiment are needed to determine some system parameters. When considering a baseline condition, and that is when no reaction is taking place, there will be no variation in temperature, and dQ/dt and dT/dt will be equal to zero. Equation (1) becomes:

$$\frac{dQ_F}{dt} = \frac{C_p}{\tau_c} (T_{\infty} - T_S)$$
(2)

where T_{∞} is the baseline temperature of the calorimeter. Equation (2) describes the steady state condition and can be substitute into equation (1), the heat balance equation becomes:

$$-\frac{dQ}{dt} = C_p \frac{dT}{dt} + \frac{C_p}{\tau_c} (T_\infty - T_S)$$
(3)

Both the heat capacity and the thermal relaxation time of the calorimeter can be determined with the calibration step and baseline sections. This process determines the amount of heat needed to cause a certain temperature change in the calorimeter. The enthalpy of dissolution is obtained by dividing the heat of dissolution to the amount of sample.

To calculate the enthalpy of dissolution, we assumed a first-order dissolution process for the salt (n).

$$\frac{dn(t)}{dt} = -\frac{1}{\tau_d} n(t) \Rightarrow n(t) = n_0 e^{\frac{t}{\tau_d}}$$
(4)

Based on this assumption, the dissolution curve was modeled using an exponential function to determine τ_d , the characteristic time associated with the dissolution process.

In parallel, heat loss to the surrounding thermostat was accounted for, as the calorimeter operates in a quasi-adiabatic mode. This heat loss was modeled by fitting an additional exponential function to the calibration curves, yielding τ_c , the characteristic time for thermal equilibration during the dissolution process. The fitted curves for τ_d and τ_c for both salts are presented in Figure S3. The difference between these parameters allows for the determination of the heat associated with the dissolution process and, consequently, the enthalpy of dissolution. For the dissolution of [N₄₄₄₄]Cl in glycerol, a sharp thermal peak was observed immediately after the breaking of the ampoule. This artefact, likely caused by thermal perturbations from the ampoule or parts of the sample contacting the thermostat, was excluded from the fitting as it does not originate from the dissolution process itself.



Figure S3. Temperature profile fitting for $[N_{4444}]Cl$ (left) and $[N_{4444}]Br$ (right) dissolution in glycerol, to determine τ_d and τ_c .

The partial molar enthalpy of mixing of $[N_{4444}]Cl({}^{H_N{}^{E,\infty}_{4444}Cl})$ was derived from our dissolution data

through
$$H_{N_{4444}Cl}^{E,\infty} = H_{N_{4444}Cl}^{E,sol} - \sum \Delta_{trs} H_{N_{4444}Cl} = Q_{sol}/n_{N_{4444}Cl} - \sum \Delta_{trs} H_{N_{4444}Cl}$$
. López-Porfiri et al.⁹
measured the total enthalpy of dissolution ($\Delta_{sol}H$) by mixing solid [N₄₄₄₄]Cl with liquid glycerol at
a mole fraction of $x_{salt} \approx 0.2$ and $x_{salt} \approx 0.25$ at 323.15 K, effectively preparing the DES in their
calorimeter. They referred to the $\Delta_{sol}H$ data as H^E (Table 4 in ref 9), although it is not an excess
property. The total excess enthalpy can be derived from $\Delta_{sol}H$ by accounting for all first-order
transitions above 323 K: $H^E = \Delta_{sol}H - x_{N_{4444}Cl}\sum \Delta_{trs}H_{N_{4444}Cl}$, i.e. all transitions listed in Table 2 of
the manuscript as no $\Delta_{trs}H_{N_{4444}Cl}$ data were reported in ref 9. After normalizing with RT , we show
that $H_{N_{4444}Cl}/RT$ and H^E/RT are consistent when modelling the excess enthalpies with a simple zero-
order Redlich-Kister polynomial (Figure S4).



Figure S4. Comparison of the normalized partial molar enthalpy of mixing of $[N_{4444}]$ Cl at infinite dilution $({}^{H_{N_{4444}}El}Cl)$ measured in this work and the total excess enthalpy of mixing ${}^{H^{E}/RT}$ derived

from the data in ref 9. The lines represent a zero-order Redlich–Kister polynomial with fitting parameter p_0 fixed on $p_0 = H_{N_{4444}^{E,\infty}Cl}/RT = -8.00}$, as measured in this work.

DIFFERENTIAL SCANNING CALORIMETRY

Glycerol DSC measurements were obtained using the DSC600 temperature controller from Linkam. The DSC600 sample chamber is maintained at a N₂(g) flow to prevent water absorption during the measurements. The Linkam LNP95 pump is used for liquid nitrogen cooling. DSC data were collected at a rate of 5°C·min⁻¹ along cooling and heating cycles in the range 223 < T < 393K.



Figure S5. Cooling and heating DSC curves of glycerol obtained with the DSC600 from Linkam. Exothermic peaks are up.

Table S1. Different melting properties of [N4444]Cl published in literature.5-8

T_{onset}	$T_{\rm peak}$	$\Delta_{\rm trs} H$	Reference
Κ	Κ	kJ mol ⁻¹	
345.4	352.3	18.22	This work
	352.55	14.5	5
	313	14.6	6
	314	20.5	7
	344.0	14.69	8



Figure S6. Ideal phase diagram for the mixture $N_{4444}Cl + Gly$, calculated from the different T_m and $\Delta_m H$ of $N_{4444}Cl$ reported in the literature.⁵⁻⁸





Figure S7. X-ray diffractograms of $[N_{4444}]$ Br and $[N_{4444}]$ Br + Gly $x_{salt} = 0.70$ acquired at 303 K.



Figure S8. X-ray diffractograms of $[N_{4444}]Br$ (right) and $[N_{4444}]Br + Gly x_{salt} = 0.70$ (left) acquired at 303 K and after the first solid-solid transition.

DENSITY FUNCTIONAL THEORY



Figure S9. DFT optimized structures of the three glycerol molecules cluster, and the ionic pairs of $[N_{4444}]Cl$ and $[N_{4444}]Br$.

MOLECULAR SIMULATIONS



Figure S10. Collective time correlation function of center of mass velocities, $C_{\alpha\beta}(t)$, calculated by MD simulations of $[N_{4444}]Cl + Gly$ (green) and $[N_{4444}]Br + Gly$ (red), at $x_{salt} = 0.25$. Top panel: Gly-anion; Bottom panel: $[N_{4444}]^+$ -anion. The $C_{\alpha\beta}(t)$ has been normalized by its initial value $C_{\alpha\beta}(0)$.

MID-INFRARED REGION



Figure S11. MID-Infrared spectra of pure glycerol and the mixtures $N_{4444}Cl + Glycerol$ (green line) and $N_{4444}Br + Glycerol$ (red line) ($x_{salt} = 0.25$).

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