Evolution of Microscopic Heterogeneity and Dynamics in Choline Chloride-based Deep Eutectic Solvents

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**Table 1.** Peak widths in Hz at 333 K as a function of composition.

| Composition | a | b | c | d | e | f | g | h | i |
|-------------|---|---|---|---|---|---|---|---|---|
| Glycerol    | 15| 22| 24| 17| 14|    |    |    |   |
| 5 mol% ChCl | 30| 26| 13| 22| 24| 9  | 14 | 18 | 11|
| 10 mol% ChCl| 19| 21| 7 | 14| 21| 7  | 9  | 11 | 13|
| 20 mol% ChCl| 15| 17| 5 | 13| 14| 9  | 8  | 13 | 14|
| 33 mol% ChCl| 14| 15| 6 | 11| 12| 10 | 8  | 12 | 17|
Table 2. $^1$H chemical shifts in ppm at 333 K as a function of composition.

| Composition | a | b | c | d | e | f | g | h | i |
|-------------|---|---|---|---|---|---|---|---|---|
| Glycerol    | 4.63 | 3.31 | 3.39 | 3.49 | 4.75 |   |   |   |   |
| 5 mol% ChCl | 4.65 | 3.37 | 3.47 | 3.56 | 4.76 | 3.03 | 3.44 | 3.86 | 4.97 |
| 10 mol% ChCl| 4.62 | 3.39 | 3.49 | 3.58 | 4.73 | 3.07 | 3.47 | 3.88 | 4.96 |
| 20 mol% ChCl| 4.54 | 3.39 | 3.48 | 3.57 | 4.64 | 3.09 | 3.45 | 3.88 | 4.93 |
| 33 mol% ChCl| 4.46 | 3.34 | 3.42 | 3.52 | 4.51 | 3.11 | 3.39 | 3.84 | 4.91 |

Figure 1. $^1$H NMR spectra for 0 and 33mol% ChCl in ethylene glycol at 333 K.

Figure 2. Density as a function of mol% Choline Chloride in Glycerol at 300K for CMD and experimental methods.
Figure 3. Viscosity as a function of mol% Choline Chloride in Glycerol at 300K for CMD and experimental methods.

Figure 4. Partial RDFs for site–site interactions with chloride from CMD and AIMD simulations at 400K.
Figure 5. Comparison of CMD and AIMD simulated neutron scattering $S(q)$ versus $q$ for 33 mol% ChCl in Glycerol at 400K.

Figure 6. The structure factors associated with the ionic species obtained from neutron scattering for fully deuterated ChCl/glycerol mixtures.
Table 3. Full coordination numbers and standard deviation of coordination numbers derived from CMD simulations at 300K for 0, 5, 10, 20, and 33 mol% ChCl in Glycerol.

|                | 0 mol%  | 5 mol%   | 10 mol%  | 20 mol%  | 33 mol%  |
|----------------|---------|----------|----------|----------|----------|
|                | N_{coor} | stdev    | N_{coor} | stdev    | N_{coor} | stdev    | N_{coor} | stdev    | N_{coor} | stdev    |
| Gly-Gly        |          |          |          |          |          |          |          |          |          |          |
| Oc-Hc          | 0.30     | 0.0005   | 0.28     | 0.0002   | 0.26     | 0.0013   | 0.23     | 0.0027   | 0.31     | 0.0013   |
| Oc-Ht          | 0.53     | 0.0016   | 0.50     | 0.0002   | 0.46     | 0.0032   | 0.39     | 0.0022   | 0.08     | 0.0009   |
| Ot-Hc          | 0.32     | 0.0008   | 0.31     | 0.001    | 0.29     | 0.0012   | 0.25     | 0.0011   | 0.42     | 0.0023   |
| Ot-Ht          | 0.71     | 0.0008   | 0.65     | 0.001    | 0.61     | 0.0016   | 0.52     | 0.0023   | 0.10     | 0.0009   |
| Cl-Gly         |          |          |          |          |          |          |          |          |          |          |
| Cl-Hc          |          |          | 0.81     | 0.030    | 0.76     | 0.0103   | 0.67     | 0.0056   | 0.55     | 0.0086   |
| Cl-Ht          |          |          | 2.33     | 0.030    | 2.13     | 0.0199   | 1.82     | 0.0092   | 1.42     | 0.0111   |
| Cl-Ch          |          |          |          |          |          |          |          |          |          |          |
| Cl-Hy          |          |          | 0.11     | 0.011    | 0.21     | 0.0109   | 0.34     | 0.0059   | 0.50     | 0.0087   |
| Gly-Ch         |          |          |          |          |          |          |          |          |          |          |
| Oc-Hy          |          |          | 0.01     | 0.001    | 0.03     | 0.0011   | 0.05     | 0.0006   | 0.08     | 0.0009   |
| Ot-Hy          |          |          | 0.02     | 0.000    | 0.03     | 0.0004   | 0.06     | 0.0005   | 0.10     | 0.0009   |
| Ch-Gly         |          |          |          |          |          |          |          |          |          |          |
| Oy-Hc          |          |          | 0.09     | 0.008    | 0.09     | 0.0052   | 0.07     | 0.0051   | 0.05     | 0.0030   |
| Oy-Ht          |          |          | 0.11     | 0.014    | 0.10     | 0.0067   | 0.08     | 0.0007   | 0.05     | 0.0009   |
| Ch-Ch          |          |          |          |          |          |          |          |          |          |          |
| Oy-Hy          |          |          | 0.00     | 0.001    | 0.00     | 0.0008   | 0.01     | 0.0008   | 0.01     | 0.0002   |

Table 4. Coordination numbers and standard deviation of coordination numbers derived from three 6ns long CMD simulations at 340K for 33 mol% ChCl in Glycerol.

|                | 33% 340K |
|----------------|----------|
|                | N_{coor} | stdev   |
| Gly-Gly        |          |         |
| Oc-Hc          | 0.17     | 0.0007  |
| Oc-Ht          | 0.28     | 0.0018  |
| Ot-Hc          | 0.20     | 0.0006  |
| Ot-Ht          | 0.38     | 0.0011  |
| Cl-Gly         |          |         |
| Cl-Hc          | 0.59     | 0.0026  |
| Cl-Ht          | 1.47     | 0.0075  |
| Cl-Ch          |          |         |
| Cl-Hy          | 0.51     | 0.0054  |
| Gly-Ch         |          |         |
| Oc-Hy          | 0.08     | 0.0002  |
| Ot-Hy          | 0.10     | 0.0006  |
| Ch-Gly         |          |         |
| Oy-Hc          | 0.04     | 0.0142  |
| Oy-Ht          | 0.05     | 0.0049  |
| Ch-Ch          |          |         |
| Oy-Hy          | 0.01     | 0.0037  |

The real and imaginary parts of complex permittivity and complex conductivity are shown in Figures 7-11 for 0, 5, 10, 20, and 33 mol% ChCl in glycerol for one representative temperature. The fitting parameters for all temperatures are listed in Supplementary Tables 5-9. The derivative representation of the imaginary part of complex permittivity, described in the BDS methods, is also shown in the same plot as the imaginary part of complex permittivity. It is clear from this analysis that more information is obtained by using the derivative representation.

Figure 5a in the main text shows the structural relaxation rates from fs-TA, BDS, and DMS as a function of temperature with Vogel-Fulcher-Tammann (VFT) fits. The VFT equation is

$$\tau = \tau_0 \exp\left(\frac{A}{(T - T_0)}\right)$$

where $\tau_0$, $A$, and $T_0$ are fitting parameters.

The data for the real part of complex permittivity of 33 mol% ChCl in glycerol at 221 K from Faraone et al. is plotted in the top of Supplementary Figure 13. Data from this paper at 33 mol% ChCl at 220 K is plotted as well for reference. In the bottom, the derivative analysis was formed to show that if considered, a secondary, slower process (the sub-$\alpha$ relaxation) is present. The electrode polarization occurs at lower frequencies in our data, which could be due to a larger sample thickness used. This unveils even more information for the secondary relaxation.

The fs-TA data for 33 mol% ChCl in glycerol are shown in Supplementary Figure 14.
Figure 7. Real and imaginary parts of the complex dielectric function and complex conductivity function for glycerol at 215 K. The derivative representation of the dielectric loss is plotted in red. Solid lines are fits, which is a single Havriliak-Negami function.

Table 5. Fitting parameters for dielectric data of glycerol using a Havriliak-Negami function.

| Temp. [K] | $\varepsilon_\infty$ | $\Delta\varepsilon$  | $\tau_\alpha$ [s] | $\beta$ | $\gamma$ |
|-----------|----------------------|-----------------------|-------------------|--------|---------|
| 200       | 3.99                 | 61.3                  | 3.88E-01          | 0.90   | 0.67    |
| 205       | 3.89                 | 57.7                  | 4.19E-02          | 0.94   | 0.63    |
| 210       | 3.39                 | 56.1                  | 6.84E-03          | 0.96   | 0.61    |
| 215       | 3.50                 | 54.2                  | 1.28E-03          | 0.97   | 0.61    |
| 220       | 3.60                 | 52.4                  | 2.84E-04          | 0.97   | 0.62    |
| 225       | 3.60                 | 50.7                  | 7.44E-05          | 0.97   | 0.63    |
| 230       | 3.60                 | 49.2                  | 2.19E-05          | 0.97   | 0.64    |
| 235       | 3.70                 | 47.5                  | 7.19E-06          | 0.97   | 0.65    |
| 240       | 3.70                 | 46.1                  | 2.62E-06          | 0.97   | 0.66    |
| 245       | 3.70                 | 44.6                  | 1.05E-06          | 0.98   | 0.66    |
| 250       | 3.70                 | 43.3                  | 4.55E-07          | 0.98   | 0.66    |
| 255       | 3.69                 | 41.9                  | 2.04E-07          | 0.98   | 0.67    |
| 260       | 3.20                 | 41.2                  | 1.03E-07          | 0.98   | 0.66    |
| 265       | 3.30                 | 39.8                  | 5.15E-08          | 0.98   | 0.67    |
| 270       | 3.20                 | 38.8                  | 2.81E-08          | 0.98   | 0.68    |
Figure 8. Real and imaginary parts of the complex dielectric function and complex conductivity function for 5mol% ChCl in glycerol at 215 K. The derivative representation of the dielectric loss is plotted in red. Solid lines are fits, which is are a combination of a Debye function, Havriliak-Negami, and a Random Barrier Model.

Table 6. Fitting parameters for dielectric data of 5mol% ChCl in glycerol using a Debye, Havriliak-Negami function, and Random Barrier Model.

| Temp. [K] | $\varepsilon_\infty$ | $\Delta \varepsilon_{slow}$ | $\tau_{slow}$ [s] | $\Delta \varepsilon_{\alpha}$ | $\tau_{\alpha}$ [s] | $\beta$ | $\gamma$ | $\sigma_0$ [S cm$^{-1}$] | $\tau_{ion}$ [s] |
|-----------|------------------|-----------------|-----------------|-----------------|-----------------|--------|--------|----------------------|-----------------|
| 205       | 1.96             | 6.31            | 1.92E-01        | 43.8            | 1.09E-02        | 0.84   | 0.79   | 2.11E-11             | 8.20E-02        |
| 210       | 2.00             | 6.12            | 3.66E-02        | 42.1            | 1.94E-03        | 0.85   | 0.77   | 1.06E-10             | 1.56E-02        |
| 215       | 1.92             | 5.82            | 8.53E-03        | 40.3            | 4.18E-04        | 0.87   | 0.77   | 4.42E-10             | 3.82E-03        |
| 220       | 2.00             | 5.63            | 2.18E-03        | 39.1            | 1.08E-04        | 0.88   | 0.76   | 1.61E-09             | 9.88E-04        |
| 225       | 2.05             | 5.44            | 6.21E-04        | 37.8            | 3.17E-05        | 0.90   | 0.75   | 5.25E-09             | 2.86E-04        |
| 230       | 1.95             | 5.09            | 2.11E-04        | 36.3            | 1.00E-05        | 0.90   | 0.75   | 1.58E-08             | 9.84E-05        |
| 235       | 2.30             | 5.10            | 6.59E-05        | 35.9            | 3.60E-06        | 0.91   | 0.75   | 4.38E-08             | 2.82E-05        |
| 240       | 1.93             | 4.71            | 2.65E-05        | 33.7            | 1.39E-06        | 0.93   | 0.74   | 1.11E-07             | 1.35E-05        |
| 245       | 2.00             | 4.71            | 1.09E-05        | 32.8            | 6.03E-07        | 0.94   | 0.72   | 2.62E-07             | 5.22E-06        |
| 250       | 2.00             | 4.62            | 4.59E-06        | 33.2            | 2.84E-07        | 0.94   | 0.70   | 5.84E-07             | 1.82E-06        |
Figure 9. Real and imaginary parts of the complex dielectric function and complex conductivity function for 10mol% ChCl in glycerol at 215 K. The derivative representation of the dielectric loss is plotted in red. Solid lines are fits, which is are a combination of a Debye function, Havriliak-Negami, and a Random Barrier Model.

Table 7. Fitting parameters for dielectric data of 10mol% ChCl in glycerol using a Debye, Havriliak-Negami function, and Random Barrier Model.

| Temp. [K] | $\varepsilon_\infty$ | $\Delta\varepsilon_{\text{slow}}$ | $\tau_{\text{slow}}$ [s] | $\Delta\varepsilon_\alpha$ | $\tau_\alpha$ [s] | $\beta$ | $\gamma$ | $\sigma_0$ [S cm$^{-1}$] | $\tau_{\text{ion}}$ [s] |
|-----------|------------------|-----------------|------------------|------------------|------------------|-------|-------|------------------|------------------|
| 200       | 2.13             | 5.88            | 2.44E-01         | 37.7             | 2.64E-02         | 0.75  | 0.87  | 1.85E-11         | 7.81E-02         |
| 205       | 2.00             | 5.45            | 4.55E-02         | 35.9             | 4.02E-03         | 0.75  | 0.89  | 9.93E-11         | 1.55E-02         |
| 210       | 2.00             | 5.54            | 9.49E-03         | 34.2             | 7.96E-04         | 0.78  | 0.86  | 4.53E-10         | 3.30E-03         |
| 215       | 2.00             | 5.58            | 2.26E-03         | 32.6             | 1.88E-04         | 0.80  | 0.84  | 1.76E-09         | 8.27E-04         |
| 220       | 2.00             | 5.46            | 6.36E-04         | 31.2             | 5.23E-05         | 0.82  | 0.83  | 6.00E-09         | 2.37E-04         |
| 225       | 2.00             | 5.03            | 2.04E-04         | 30.3             | 1.60E-05         | 0.82  | 0.84  | 1.86E-08         | 7.52E-05         |
| 230       | 2.00             | 4.99            | 6.56E-05         | 28.9             | 5.45E-06         | 0.84  | 0.82  | 5.30E-08         | 2.58E-05         |
| 235       | 2.00             | 4.76            | 2.58E-05         | 27.8             | 2.11E-06         | 0.84  | 0.83  | 1.33E-07         | 1.03E-05         |
| 240       | 2.00             | 4.68            | 9.55E-06         | 26.7             | 8.23E-07         | 0.87  | 0.80  | 3.44E-07         | 3.80E-06         |
| 245       | 2.94             | 4.09            | 4.24E-06         | 29.5             | 4.07E-07         | 0.86  | 0.77  | 7.85E-07         | 6.77E-07         |
| 250       | 2.00             | 3.78            | 1.90E-06         | 26.8             | 1.77E-07         | 0.85  | 0.80  | 1.67E-06         | 6.09E-07         |
Figure 10. Real and imaginary parts of the complex dielectric function and complex conductivity function for 20mol% ChCl in glycerol at 205 K. The derivative representation of the dielectric loss is plotted in red. Solid lines are fits, which is are a combination of a Debye function, Havriliak-Negami, and a Random Barrier Model.

Table 8. Fitting parameters for dielectric data of 20mol% ChCl in glycerol using a Debye, Havriliak-Negami function, and Random Barrier Model.

| Temp. [K] | $\varepsilon_\infty$ | $\Delta \varepsilon_{slow}$ | $\tau_{slow}$ [s] | $\Delta \varepsilon_\alpha$ | $\tau_\alpha$ [s] | $\beta$ | $\gamma$ | $\sigma_0$ [S cm$^{-1}$] | $\tau_{ion}$ [s] |
|-----------|-----------------------|---------------------------|-------------------|---------------------------|-------------------|-------|--------|----------------------------|------------------|
| 200       | 2.13                  | 5.88                      | 2.44E-01          | 37.7                      | 2.64E-02          | 0.75  | 0.87   | 1.85E-11                    | 7.81E-02 |
| 205       | 2.00                  | 5.45                      | 4.55E-02          | 35.9                      | 4.02E-03          | 0.75  | 0.89   | 9.93E-11                    | 1.55E-02 |
| 210       | 2.00                  | 5.54                      | 9.49E-03          | 34.2                      | 7.96E-04          | 0.78  | 0.86   | 4.53E-10                    | 3.30E-03 |
| 215       | 2.00                  | 5.58                      | 2.26E-03          | 32.6                      | 1.88E-04          | 0.80  | 0.84   | 1.76E-09                    | 8.27E-04 |
| 220       | 2.00                  | 5.46                      | 6.36E-04          | 31.2                      | 5.23E-05          | 0.82  | 0.83   | 6.00E-09                    | 2.37E-04 |
| 225       | 2.00                  | 5.03                      | 2.04E-04          | 30.3                      | 1.60E-05          | 0.82  | 0.84   | 1.86E-08                    | 7.52E-05 |
| 230       | 2.00                  | 4.99                      | 6.56E-05          | 28.9                      | 5.45E-06          | 0.84  | 0.82   | 5.30E-08                    | 2.58E-05 |
| 235       | 2.00                  | 4.76                      | 2.58E-05          | 27.8                      | 2.11E-06          | 0.84  | 0.83   | 1.33E-07                    | 1.03E-05 |
| 240       | 2.00                  | 4.68                      | 9.55E-06          | 26.7                      | 8.23E-07          | 0.87  | 0.80   | 3.44E-07                    | 3.80E-06 |
| 245       | 2.94                  | 4.09                      | 4.24E-06          | 29.5                      | 4.07E-07          | 0.86  | 0.77   | 7.85E-07                    | 6.77E-07 |
| 250       | 2.00                  | 3.78                      | 1.90E-06          | 26.8                      | 1.77E-07          | 0.85  | 0.80   | 1.67E-06                    | 6.09E-07 |

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Figure 11. Real and imaginary parts of the complex dielectric function and complex conductivity function for 33mol% ChCl in glycerol at 200 K. The derivative representation of the dielectric loss is plotted in red. Solid lines are fits, which is a combination of a Debye function, Havriliak-Negami, and a Random Barrier Model.

Table 9. Fitting parameters for dielectric data of 33mol% ChCl in glycerol using a Debye, Havriliak-Negami function, and Random Barrier Model.

| Temp. [K] | $\varepsilon_\infty$ | $\Delta \varepsilon_{\text{slow}}$ | $\tau_{\text{slow}}$ [s] | $\Delta \varepsilon_{\alpha}$ | $\tau_{\alpha}$ [s] | $\beta$ | $\gamma$ | $\sigma_0$ [S cm$^{-1}$] | $\tau_{\text{ion}}$ [s] |
|-----------|-------------------|--------------------------------|--------------------------|--------------------------|----------------|-------|--------|----------------|------------------|
| 190       | 2.33              | 2.57                           | 1.85E-01                 | 19.0                     | 5.82E-02       | 0.74   | 0.76   | 1.72E-11       | 7.73E-02         |
| 195       | 2.33              | 2.81                           | 2.76E-02                 | 19.1                     | 8.00E-03       | 0.76   | 0.73   | 1.23E-10       | 1.05E-02         |
| 200       | 2.25              | 2.31                           | 5.68E-03                 | 18.0                     | 1.43E-03       | 0.74   | 0.79   | 5.58E-10       | 2.33E-03         |
| 205       | 2.26              | 2.49                           | 1.27E-03                 | 17.9                     | 3.02E-04       | 0.76   | 0.76   | 2.37E-09       | 5.41E-04         |
| 210       | 2.25              | 2.08                           | 3.65E-04                 | 17.0                     | 7.95E-05       | 0.76   | 0.79   | 7.99E-09       | 1.54E-04         |
| 215       | 2.45              | 2.39                           | 1.04E-04                 | 17.4                     | 2.47E-05       | 0.80   | 0.72   | 2.77E-08       | 3.75E-05         |
| 220       | 2.25              | 2.02                           | 3.64E-05                 | 15.7                     | 7.85E-06       | 0.78   | 0.79   | 7.38E-08       | 1.58E-05         |
| 225       | 2.24              | 2.32                           | 1.29E-05                 | 15.3                     | 2.81E-06       | 0.81   | 0.76   | 2.10E-07       | 5.60E-06         |
| 230       | 2.25              | 1.14                           | 5.85E-06                 | 15.8                     | 1.28E-06       | 0.78   | 0.79   | 4.90E-07       | 2.18E-06         |
| 235       | 2.24              | 1.67                           | 2.24E-06                 | 15.3                     | 5.68E-07       | 0.84   | 0.70   | 1.22E-06       | 8.39E-07         |
| 300       | 2.24              | 1.60                           | 2.87E-09                 | 14.5                     | 6.59E-10       | 0.79   | 0.78   | 7.99E-04       | 1.84E-09         |
Figure 12. The derivative representation of the dielectric loss for 33mol% ChCl in glycerol at room temperature plotted as a function of radial frequency.

| ChCl Content  | \( \tau_0 \) [s] | \( T_0 \) [K] | \( A \) |
|--------------|------------------|--------------|-------|
| glycerol     | 1.33E-15         | 127          | 2384  |
| 5mol% ChCl   | 1.93E-16         | 117          | 2755  |
| 10mol% ChCl  | 1.17E-16         | 114          | 2821  |
| 20mol% ChCl  | 5.04E-16         | 113          | 2592  |
| 33mol% ChCl  | 5.27E-16         | 109          | 2564  |

Table 10. Vogel-Fulcher-Tammann fit parameters for the structural relaxation rates for 0, 5, 10, 20, and 33mol% ChCl in glycerol.

The parameters for the VFT fits from Figure 5a are in Supplementary Table 10.
Figure 13. Top: Real part of complex permittivity for 33mol% ChCl in glycerol obtained for this paper and from Faraone et al. and 220 and 221 K respectively. Bottom: The derivative representation of the dielectric loss at 220 and 221 K from this paper and Faraone et al. respectively.
Figure 14. (a) Top panel: Steady-state UV-visible absorption of betaine-30, bottom panel: femtosecond transient absorption spectra at indicated delay times. (b) fs-TA kinetics of betaine-30 in glycerol at a probe wavelength of 566 nm. (c) Top panel: Steady-state UV-visible absorption of betaine-30, bottom panel: femtosecond transient absorption spectra at indicated delay times. (d) fs-TA kinetics of betaine-30 in 10 mol% Glycine at a probe wavelength of 590 nm.

Data presented in Supplementary Table 12 is done with a force field tuned to simulate ethylene glycol and choline chloride mixtures and is undergoing further refinement to better capture fine, concentration dependent dynamics trends.
Table 11. Coefficients (time in ns) fitted to Equation 5 for the dipole moment rotational dynamics based on CMD simulations at 298 K.

| Choline | $b_1$ | $\alpha_1$ | $b_2$ | $\alpha_2$ | $\tau_1$ | $\tau_2$ | $R^2$ |
|---------|-------|-------------|-------|-------------|---------|---------|-------|
| 0 mol% | -     | -           | -     | -           | -       | -       | -     |
| 5 mol% | 0.4695| 0.9690      | 0.5305| 0.6212      | 0.4277  | 0.0993  | 0.9970|
| 10 mol%| 0.4308| 0.9860      | 0.5692| 0.6892      | 0.3739  | 0.0558  | 0.9984|
| 20 mol%| 0.4555| 0.9659      | 0.5445| 0.6846      | 0.2503  | 0.0092  | 0.9988|
| 33 mol%| 0.4607| 0.9816      | 0.4258| 0.7546      | 0.1681  | 0.0069  | 0.9977|

| Glycerol | $b_1$ | $\alpha_1$ | $b_2$ | $\alpha_2$ | $\tau_1$ | $\tau_2$ | $R^2$ |
|---------|-------|-------------|-------|-------------|---------|---------|-------|
| 0 mol% | 0.4748| 0.9391      | 0.5252| 0.6923      | 0.1403  | 0.0082  | 0.9963|
| 5 mol% | 0.4916| 0.9142      | 0.5084| 0.6394      | 0.1330  | 0.0081  | 0.9970|
| 10 mol%| 0.4881| 0.9161      | 0.5119| 0.6806      | 0.1286  | 0.0069  | 0.9971|
| 20 mol%| 0.4908| 0.9150      | 0.5092| 0.6919      | 0.1109  | 0.0061  | 0.9964|
| 33 mol%| 0.4599| 0.9370      | 0.5143| 0.7111      | 0.0924  | 0.0029  | 0.9959|

Table 12. The average slow ($\tau_1$) and fast ($\tau_2$) characteristic time coefficients of dipole relaxation obtained from CMD simulations for choline and ethylene glycol at various ChCl concentrations in ethylene glycol.

| ChCl Concentration | $\tau_1$(ps) | $\tau_2$(ps) |
|--------------------|-------------|-------------|
| 0% ChCl | 3.3 | 0.3 |
| 5% ChCl | 25.0 | 2.2 |
| 10% ChCl | 46.0 | 5.6 |
| 16.7% ChCl | 84.1 | 9.3 |
| 20% ChCl | 149.1 | 15.8 |
| 25% ChCl | 210.1 | 17.8 |
| 33% ChCl | 486.4 | 30.7 |

The Stokes-Einstein relation can be written as

$$D = \frac{k_b T}{6\pi\eta r} \tag{2}$$

where $D$ is the self-diffusion coefficient, $k_b$ is the Boltzmann constant, $T$ is temperature, $\eta$ is viscosity, and $r$ is radius of the particle. Using Supplementary Equation 2, if we calculate $D\eta/T$, we obtain what should be $k_b/(6\pi r)$, which should be constant if the relation holds. As seen in Supplementary Figure 15, these mixtures do not abide by the Stokes-Einstein relation.
Table 13. Standard deviation of hydrogen bond dynamics time constants (ps) derived from CMD simulations at 300K for 0, 5, 10, 20, and 33 mol% ChCl in Glycerol.

| Site-site | 0 mol% | 5 mol% | 10 mol% | 20 mol% | 33 mol% |
|-----------|--------|--------|---------|---------|---------|
|           | \(\tau_f\) | \(\tau_b\) | \(\tau_f\) | \(\tau_b\) | \(\tau_f\) | \(\tau_b\) |
| Gly-Gly   | Oc-Hc  | 4.8    | 11.4    | 5.2     | 15.3    | 4.9     | 11.3    | 6.7     | 24.2    | 5.8     | 13.6    |
|           | Oc-Ht  | 4.8    | 11.0    | 2.6     | 10.5    | 7.4     | 15.9    | 4.0     | 12.7    | 4.9     | 8.9     |
|           | Ot-Hc  | 4.3    | 10.7    | 2.9     | 7.3     | 6.0     | 13.4    | 5.8     | 8.6     | 4.9     | 14.3    |
|           | Ot-Ht  | 4.8    | 11.4    | 3.7     | 6.3     | 6.8     | 9.5     | 7.2     | 13.7    | 4.8     | 8.3     |
| Cl-Gly    | Cl-Hc  | -      | -       | 12.5    | 12.2    | 7.8     | 7.6     | 5.6     | 7.0     | 5.1     | 6.1     |
|           | Cl-Ht  | -      | -       | 11.2    | 7.4     | 9.7     | 6.6     | 9.9     | 6.3     | 8.7     | 5.2     |
| Cl-Ch     | Cl-Hy  | -      | -       | 23.3    | 24.0    | 22.2    | 24.9    | 5.9     | 7.5     | 4.8     | 4.3     |
| Gly-Ch    | Oc-Hy  | -      | -       | 6.6     | 20.5    | 3.3     | 12.9    | 4.4     | 9.5     | 1.9     | 4.3     |
|           | Ot-Hy  | -      | -       | 1.1     | 2.0     | 4.3     | 12.5    | 5.8     | 9.1     | 3.4     | 5.8     |
| Ch-Gly    | Oy-Hc  | -      | -       | 8.5     | 63.1    | 5.2     | 23.3    | 4.1     | 48.2    | 3.1     | 32.0    |
|           | Oy-Ht  | -      | -       | 5.6     | 99.5    | 1.7     | 77.7    | 3.7     | 51.8    | 2.4     | 45.1    |
| Ch-Ch     | Oy-Hy  | -      | -       | 3.3     | 16.6    | 5.5     | 18.7    | 3.0     | 18.3    | 2.0     | 11.8    |

Figure 15. The self diffusion coefficient of choline and glycerol respectively multiplied by viscosity divided by temperature at 298 K plotted versus mol% ChCl to test the Stokes-Einstein relation.
Figure 16. Normalized dipole moment rotational correlation function of glycerol and choline in Glyceline (solid) and pure glycerol (dashed) at 300K.

The dielectric data of glycerol, only exhibiting the structural, $\alpha$-relaxation can be described by a single Havriliak-Negami (HN) function, shown in Supplementary Equation 3:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{(\Delta\varepsilon)_\alpha}{1 + (i\omega\tau_\alpha)^\gamma}$$

where $\varepsilon_\infty$ is the high frequency plateau, $\Delta\varepsilon$ is the dielectric strength, $\tau$ is the mean relaxation time, $\sigma_0$ is the dc conductivity, and $\gamma$ and $\beta$ are shape parameters. The HN function is a modified Debye function. A Debye function describes a system of non-interacting systems, and the HN version has added shape parameters to account for broadening in the distribution of relaxation times. Above 5mol% ChCl, the mixtures can be well described by a combination of a Debye function for the slow process, a HN function for the $\alpha$-relaxation, and a Random Barrier Model (RBM) for the ion dynamics. The RBM describes an ion hopping motion where the ions overcome a potential energy barrier to jump to the next spot. The full equation is:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{(\Delta\varepsilon)_{\text{Debye}}}{1 + (i\omega\tau_{\text{Debye}})} + \frac{\sigma_0\tau_{\text{ion}}}{\varepsilon_0(\ln(1 + i\omega\tau_{\text{ion}}))} + \frac{(\Delta\varepsilon)_\alpha}{1 + (i\omega\tau_\alpha)^\gamma}$$

where $\sigma_0$ is the dc ionic conductivity and $\tau_{\text{ion}}$ is the ion hopping time. The subscripts Debye, ion, and $\alpha$ denote the relaxation parameter is associated with.

The mechanical spectroscopy data were fit with two Cole-Davidson (CD) modified Maxwell models for the structural relaxation and the slow relaxation associated with hydrogen bonding structures as described in Supplementary Equation 5:

$$\eta^*(\omega) = \frac{G_{\infty, \text{slow}}}{\omega} \left[ 1 - \frac{1}{(1 + i\omega\tau_{\text{slow}})^2} \right] + \frac{G_{\infty, \alpha}}{\omega} \left[ 1 - \frac{1}{1 + (i\omega\tau_{\alpha})^2} \right]$$

where $G_\infty$ is the high frequency plateau in $G'$, $\tau$ is the relaxation time, $\gamma$ is the shape parameter, and the subscripts slow and $\alpha$ denote the distinct slow and $\alpha$ relaxations observed in the spectra. A Maxwell model describes a viscoelastic material, and the CD version adds the shape parameter exponent, $\gamma$, to account for broadening of the curves.