Electronic Supplementary Information Origin of structural and dynamic heterogeneity in thymol and coumarin based hydrophobic deep eutectic solvents as revealed by molecular dynamics

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S1 Calculation Details

The total X-ray scattering structure function $(S(q))^{1-6}$ was computed using

$$S(q) = \frac{\rho_0 \sum_{i=1}^n \sum_{j=1}^n x_i x_j f_i(q) f_j(q) \int_0^{L/2} 4\pi r^2 [g_{ij}(r) - 1] \frac{\sin qr}{qr} \omega(r) dr}{[\sum_{i=1}^n x_i f_i(q)]^2},$$
(S1)

where ρ_0 denotes the total number density given by $N_{atom}/\langle V \rangle$. *n* is the number of different *i* and *j* type of atoms with mole fractions x_i and x_j , respectively. The X-ray atomic form factors for calculating S(q) for *i* and *j* atom types are represented by $f_i(q)$ and $f_j(q)$, respectively. $g_{ij}(r)$ denotes the radial distribution function (RDF) between *i* and *j* atom types considering both intermolecular and intramolecular atoms. The box-length is *L*. $\omega(r)$ is the Lorch window function, formulated as $\omega(r) = \sin(2\pi r/L)/(2\pi r/L)^{7,8}$, which reduces the impact of finite truncation of *r*.

The total neutron scattering structure function $(S^N(q))^9$ was computed using

$$S^{N}(q) = \frac{\rho_{0} \sum_{i=1}^{n} \sum_{j=1}^{n} x_{i} x_{j} b_{i} b_{j} \int_{0}^{L/2} 4\pi r^{2} [g_{ij}(r) - 1] \frac{\sin qr}{qr} \omega(r) dr}{\sum_{i=1}^{n} x_{i} b_{i}^{2}},$$
(S2)

where b_i and b_j are the neutron scattering lengths of different *i* and *j* type of atoms. RDF¹⁰ highlighting real space correlations between various atomic pairs, was computed as

$$g_{ij}(r) = \frac{\left\langle \sum_{i=1}^{N_i} \sum_{j=1, j \neq i}^{N_j} \delta(r - r_{ij}) \right\rangle}{\rho_j N_i}.$$
(S3)

Integration of $g_{ij}(r)$ over distance r' gives cumulative coordination number of j type species around i type species, given as

$$n_{ij}(r') = 4\pi\rho_j \int_0^{r'} g_{ij}(r)r^2 dr,$$
(S4)

where, the bulk number density of the species of type *j* is ρ_j . Radial angular distribution function $(g_{ij}(r, \theta))^{11,12}$ was computed using

$$g_{ij}(r,\theta) = \frac{\left\langle \sum_{i=1}^{N_D} \sum_{j \neq i}^{N_A} \delta(r - r_{ij}) \delta(\theta - \theta_{ij}) \right\rangle}{N_A \rho_D},$$
(S5)

where θ_{ij} is hydrogen-donor-acceptor angle (\angle HDA). The number of acceptor and donor molecules is represented by N_A and N_D , respectively. ρ_D is the bulk number density of the donor molecules.

Hydrogen-bond auto-correlation function $(C(t))^{13-15}$ was computed using

$$C(t) = \langle h(0)h(t) \rangle / \langle h(0)^2 \rangle, \tag{S6}$$

where the hydrogen-bond population is represented by the variable h(t), which has a value of 1 if the hydrogen bond was present at time t = 0 and is still present at time t; in other cases, it has a value of 0. We found that a combination of an exponential function and a stretched exponential function was required to obtain the best fit for the calculated C(t), which subsequently enabled us to correctly compute the average hydrogen-bond lifetime as

$$C(t) = ae^{-t/\tau_1} + (1-a)e^{-(t/\tau_2)^b},$$
(S7)

where, τ_1 and τ_2 represent the time constants having relaxation amplitudes of *a* and 1-a, respectively. The stretching exponent is represented by *b* whose value is $0 \le b \le 1$. More dynamic heterogeneity is indicated by a larger deviation in *b* from unity. ¹⁶ Integrating Eq. S7 yields the average lifetime, given as

$$\langle \tau \rangle = a\tau_1 + \frac{(1-a)\tau_2}{b}\Gamma(\frac{1}{b}),\tag{S8}$$

where Γ corresponds to the gamma function.

Using MSD, ¹⁰ we computed the self-diffusion coefficients (D_j^s) of the thymol (THY) and coumarin (COU) molecules present in the HDESs, given as

$$D_{j}^{s} = \frac{1}{6} \lim_{t \to \infty} \frac{d\langle |\vec{r}_{j}(t) - \vec{r}_{j}(0)|^{2} \rangle}{dt},$$
(S9)

where the coordinates of j^{th} type molecule in vector form at time *t* is given by $\vec{r}_j(t)$. To confirm that the MSD reaches a diffusive regime, we computed the $\beta(t)$ function as

$$\beta(t) = \frac{\mathrm{dlog}\langle |\vec{r}_j(t) - \vec{r}_j(0)|^2 \rangle}{\mathrm{dlog}\,t} \tag{S10}$$

The function $\beta(t)$ approaches unity when MSD reaches the diffusive region.

The normalized velocity auto-correlation function (VACF)¹⁰ for molecule of type *i* was computed using

$$VACF = \langle v_i(0)v_i(t) \rangle_{i,t_0} / \langle v_i(0)^2 \rangle_{i,t_0},$$
(S11)

where v_i is the center-of-mass velocity of the molecule of type *i* and $\langle \rangle_{i,t_0}$ depicts the ensemble average over the total number of molecule of type *i* and different time origins t_0 .

The non-Gaussian parameter $(\alpha_2(t))^{17,18}$ gives the deviation of displacements of of thymol and coumarin molecules from Gaussian behavior described as

$$\alpha_{2}(t) = \frac{3\langle \sum_{j=1}^{N} [\vec{r}_{j}(t) - \vec{r}_{j}(0)]^{4} \rangle}{5\langle \sum_{j=1}^{N} [\vec{r}_{j}(t) - \vec{r}_{j}(0)]^{2} \rangle^{2}} - 1.$$
(S12)

In cases where $\alpha_2(t)$ is more than 0, we found evidence of dynamic heterogeneity in the displacement of the thymol and coumarin molecules present in the HDESs.^{19,20}

The self van Hove correlation function $(G_s(r,t))^{21}$ for thymol and coumarin molecules present in the HDESs is given as

$$G_{s}(r,t) = \frac{1}{N} \langle \sum_{j=1}^{N} \delta(r - (|\vec{r}_{j}(t) - \vec{r}_{j}(0)|)) \rangle,$$
(S13)

where the Dirac-delta function is denoted by δ . If at time t = 0 the particle is at the origin, then $G_s(r,t)$ describes the probability of locating that particle at distance r at a later time t. If the particle's displacement is entirely diffusive, then $G_s(r,t)$ is equivalent to ideal Gaussian distribution $(G_s^{ideal}(r,t))$, ^{20,22} stated as

$$G_s^{ideal}(\mathbf{r},t) = \left[\frac{3}{2\pi\langle\Delta r^2(t)\rangle}\right]^{3/2} e^{-3r^2/2\langle\Delta r^2(t)\rangle},\tag{S14}$$

where,
$$\langle \Delta r^2(t) \rangle = \frac{1}{N} \langle \sum_{j=1}^N |\vec{r}_j(t) - \vec{r}_j(0)|^2 \rangle.$$

Table S1 Self-diffusion coefficients (D^{s} (10^{-7} cm^{2} s^{-1})) (defined by Eq. S9) calculated from center-of-mass MSD for thymol and coumarin in HDES systems.

HDES	thymol	coumarin
thymol:coumarin (1:1)	4.24 ± 0.0001	4.51 ± 0.0002
thymol:coumarin (2:1)	6.18 ± 0.0001	6.00 ± 0.0002



Figure S1 Equilibrated simulation boxes of thymol-coumarin based HDESs at molar ratios (a) 1:1 and (b) 2:1 of thymol and coumarin components. The red and yellow colors depict the thymol and coumarin components of the HDESs, respectively.



Figure S2 Computed total neutron scattering structure function, $S^N(q)s$ of thymol:coumarin HDES at 1:1 and 2:1 molar ratios, depicted in (a) wide and (b) small q regions. The $S^N(q)s$ are shifted vertically for clarity.



Figure S3 Simulated species-wise partial X-ray scattering structure functions, S(q)s, of thymol-coumarin HDES at two mole ratios of the components.



Figure S4 Probability of the number of hydrogen bonds (per thymol donor molecules) corresponding to (a) $O1_{COU}$ -HO_{THY} and (b) OH_{THY}-HO_{THY} hydrogen bonding interactions present in thymol:coumarin HDESs at molar ratios 1:1 and 2:1. Here, the carbonyl oxygen of coumarin is represented by $O1_{COU}$. OH_{THY} and HO_{THY} correspond to hydroxyl oxygen and hydroxyl hydrogen of thymol, respectively.



Figure S5 MSDs of (a) thymol and (b) coumarin molecules in thymol:coumarin HDESs at molar ratios 1:1 and 2:1. $\beta(t)$ denotes the first derivative of MSD for (c) thymol and (d) coumarin.

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