Supplementary Information

Probing Polarity Structure-Function Relationships in Amine-Water Mixtures

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Materials and Methods

Chemicals and Samples Preparation

99% dipropylamine (DPA), ≥99.5% diisopropylamine (DIPA), 99% *N*,*N*-dimethylcyclohexylamine (DMCHA), >99% *N*-ethylcyclohexylamine (ECHA), and ≥99% 4-nitroaniline (4-NAi) were acquired from MilliporeSigma (Burlington, MA, United States). 95% *N*,*N*-dimethyl-4-nitroaniline (NND4) was procured from AstaTech (Bristol, PA, United States). All solvents were dried with 3 Å molecular sieves for at least 12 h before further sample preparations. Solvent-water mixtures were prepared by combining appropriate amounts of solvent and deionized (DI) water from a Milli-Q system (Millipore, Billerica, MA, United States) and stirring for at least 30 min. The water contents of the desiccated solvents and solvent-water mixtures were characterized by Karl Fischer titration with the volumetric method (870 Titrino plus, Metrohm, Herisau, Switzerland).[1] The weight percents of water in the desiccated solvents were determined to be 0.13% (DPA), 0.09% (DIPA), 0.17% (DMCHA), and 0.16% (ECHA).

Relative Permittivity Determination

Relative permittivity was characterized using an Epsilon+ dielectricity sensor with an Omega thermostat (Flucon, Barbis, Germany). The temperature was controlled within ±0.01 °C between 25–60 °C in 5 °C increments using a ramp rate of 0.2 °C/min. 8.0 mL of solvent or solvent-water mixture was pipetted directly into the test cell for each measurement.

Kamlet-Taft Parameter Determination

Kamlet-Taft parameters were determined following the method outlined in our prior work.[2] Individual stock solutions of 4-NAi and NND4 probes were prepared in acetone. Probe-solvent solutions were produced by pipetting the acetone stock solutions into clean, dry glass vials and removing the acetone by gentle evaporation under ambient conditions. The dye was redissolved in 3.0 mL of the appropriate solvent or solvent-water solution and stirred for 30 min. 2.0 mL of this working solution was added to a capped 10 mm quartz cuvette. The dye concentrations were adjusted to maintain the maximum absorbance below 1 absorbance unit. Absorbance spectra for DIPA, DMCHA, and ECHA (and their solvent-water mixtures) were collected on a GENESYS 10S UV-visible spectrophotometer in conjunction with a Thermo Scientific air-cooled Peltier temperature controller; absorbance spectra for DPA were collected on a Cary 100 UV-visible spectrophotometer in conjunction with a Cary Temperature Controller. For both

spectrophotometers, the temperature was controlled within ±0.1 °C between 25–60 °C in 5 °C increments with an equilibration time at each temperature of at least 5 min. Spectral data were collected in 0.1 nm steps. The SciPy Python package was used to analyze the spectral data; wavelength-absorbance curves were first smoothed with a Savitzky-Golay filter, and the find_peaks function was used to find the wavelength corresponding to maximum absorbance. In cases where more than one absorbance peak was observed, the lowest energy (highest wavelength) peak was used per the definition of the Kamlet-Taft parameters.[3–5]

The Kamlet-Taft solvatochromic parameters, β and π^*, were determined as a function of temperature and water concentration from the frequency corresponding to the maximum absorbance for each probe according to the equations modified by Lagalante et al.[6] The frequencies of maximum absorption for the reference solvents for β and π^* were taken from Lagalante et al. and fixed at the 25 °C values, which is recommended to maintain a consistent normalized scale. The π^* parameter measures the combined dipolarity and polarizability of the solution. The solvatochromic shift of the NND4 probe used to calculate π^* depends on probe-solvent dipole-dipole and dipole-induced dipole interactions. π^* is calculated from the maximum absorbance frequency in the NND4-solvent mixture ($\nu_{\mathrm{NND4}}^{\mathrm{solvent}}$) relative to cyclohexane ($\nu_{\mathrm{NND4}}^{\mathrm{cyclohexane}}$) and dimethyl sulfoxide ($\nu_{\mathrm{NND4}}^{\mathrm{DMSO}}$):

$$\pi^* = \frac{\nu_{\mathrm{NND4}}^{\mathrm{solvent}} - \nu_{\mathrm{NND4}}^{\mathrm{cyclohexane}}}{\nu_{\mathrm{NND4}}^{\mathrm{DMSO}} - \nu_{\mathrm{NND4}}^{\mathrm{cyclohexane}}} = \frac{\nu_{\mathrm{NND4}}^{\mathrm{solvent}} - 28.18}{-3.52} \tag{S1}$$

The β value measures the hydrogen bond accepting capabilities of the solution. β value of a solution is proportional to the displacement of its solvatochromic shift from that of the reference solvent (hexamethylphosphoramide) for a given solvatochromic probe pair. NND4 and 4NAi were used as the probe pair, as recommended by Lagalante et al. for N-H donor solvents.[6]

$$\beta = \frac{0.9841\nu_{\mathrm{NND4}}^{\mathrm{solvent}} + 3.49 - \nu_{\mathrm{4NAi}}^{\mathrm{solvent}}}{2.759} \tag{S2}$$

Results and Discussion

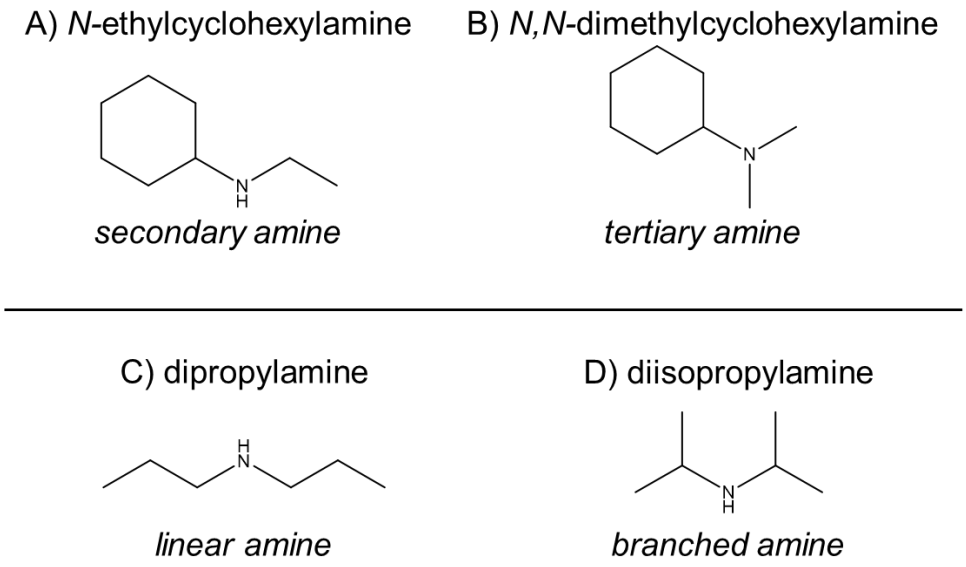

Figure S1. Chemical structures of the thermomorphic hydrophilicity amine solvents used in this study. The horizontal line separates the pairs of constitutional isomeric solvents. Throughout the study, A) *N*-ethylcyclohexylamine (ECHA), a secondary amine, is compared against B) *N,N*-dimethylcylohexylamine (DMCHA), a tertiary amine. C) Dipropylamine (DPA), a linear amine, is juxtaposed against D) diisopropylamine (DIPA), a branched amine. DMCHA and ECHA are constitutional isomers.

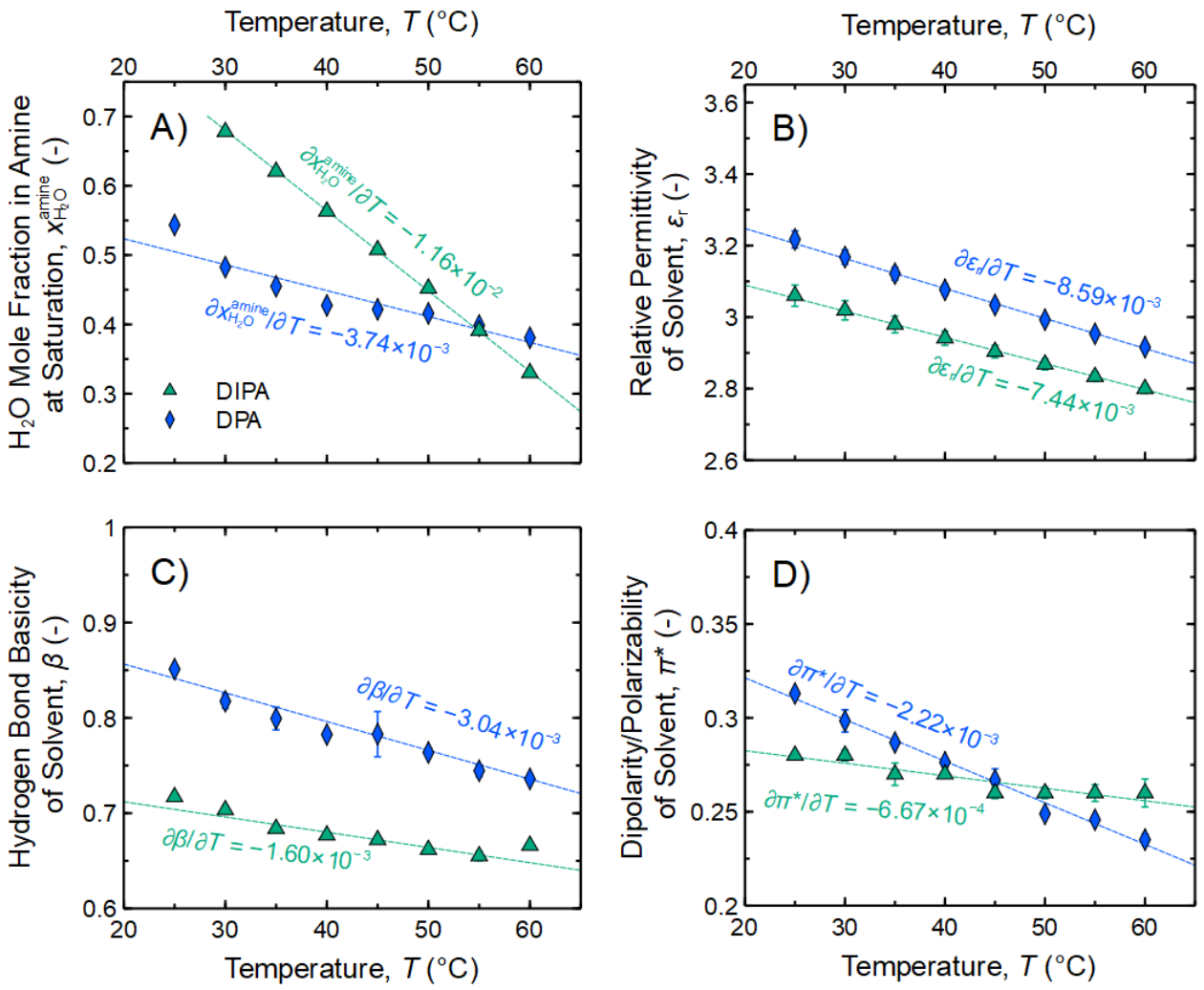

Figure S2. Temperature-dependent properties of dipropylamine, DPA, and diisopropylamine, DIPA (blue diamond and green triangle symbols, respectively): A) mole fraction solubility of water in amine ($x_{H_2O}^{amine}$), B) relative permittivity (ε_r), C) hydrogen bond basicity, i.e., hydrogen bond acceptor ability, (β), and D) dipolarity/polarizability (π^*). Note that the amines are desiccated in B–D. Data points and error bars in B–D are means and standard deviations, respectively, from duplicate samples. Dashed lines are ordinary least squares linear regressions, with slopes ($\partial/\partial T$) labeled.

Table S1. Compilation of polarity scale data: relative permittivity (ε_r).

Temperature (°C)	Water Content (volume fraction)				
	N,N-dimethylcyclohexylamine				
	0.0	**0.01**	**0.03**	**0.04**	**0.07**
25	2.82	3.23	4.09	4.31	5.21
30	2.81	3.20	4.05	4.28	5.14
35	2.79	3.17	4.00	4.28	5.10
40	2.77	3.14	3.99	4.30	5.08
45	2.75	3.11	3.99	4.37	5.13
50	2.74	3.08	4.00	4.50	5.38
55	2.72	3.05	4.03	separates into biphasic mixture	
60	2.71	3.03	4.00		
	N-ethylcyclohexylamine				
	0.0	**0.01**	**0.03**	**0.04**	**0.06**
25	3.36	3.81	4.66	5.50	6.25
30	3.32	3.76	4.62	5.41	6.15
35	3.27	3.70	4.57	5.31	6.05
40	3.23	3.65	4.53	5.23	5.95
45	3.19	3.60	4.48	5.14	5.87
50	3.16	3.55	4.44	5.06	5.80
55	3.12	3.50	4.39	4.98	5.74
60	3.09	3.45	4.34	4.91	5.70
	Diisopropylamine				
	0.0	**0.01**	**0.02**	**0.04**	**0.05**
25	3.06	3.43	4.18	4.80	5.54
30	3.02	3.38	4.11	4.72	5.44
35	2.98	3.33	4.04	4.64	5.38
40	2.94	3.28	3.97	4.57	5.34
45	2.90	3.23	3.91	4.51	5.33
50	2.87	3.18	3.84	4.48	5.34
55	2.83	3.13	3.78	4.46	5.42
60	2.80	3.09	3.72	4.44	5.58

	Dipropylamine				
	0.0	**0.01**	**0.03**	**0.04**	**0.06**
25	3.22	3.60	4.47	5.10	5.82
30	3.17	3.54	4.38	5.00	5.70
35	3.12	3.48	4.30	4.90	5.59
40	3.08	3.42	4.22	4.81	5.50
45	3.03	3.37	4.14	4.73	5.42
50	2.99	3.32	4.07	4.66	5.35
55	2.95	3.27	4.00	4.60	5.31
60	2.92	3.22	3.94	4.56	5.27

Table S2. Compilation of polarity scale data: hydrogen bond accepting ability or basicity (β).

Temperature (°C)	Water Content (volume fraction)				
	N,N-dimethylcyclohexylamine				
	0.0	**0.01**	**0.03**	**0.04**	
25	0.801	0.991	0.960	0.892	
30	0.757	0.972	0.942	0.905	
35	0.731	0.942	0.949	0.904	
40	0.713	0.929	0.939	0.898	
45	0.701	0.911	0.919	0.897	
50	0.692	0.880	0.918	0.892	
55	0.671	0.838	0.898	0.887	
60	0.668	0.793	0.888	0.880	
	N-ethylcyclohexylamine				
	0.0	**0.01**	**0.03**	**0.04**	**0.06**
25	0.887	0.939	1.06	1.05	0.959
30	0.885	0.956	1.03	0.995	0.931
35	0.880	0.947	1.03	0.981	0.919
40	0.881	0.917	1.02	0.912	0.935
45	0.878	0.907	1.03	0.921	0.918
50	0.879	0.913	1.04	0.922	0.917
55	0.884	0.915	1.03	0.914	0.945
60	0.888	0.925	1.02	0.911	0.959
	Diisopropylamine				
	0.0	**0.01**	**0.03**	**0.05**	
25	0.717	0.922	0.993	0.894	
30	0.703	0.889	0.975	0.910	
35	0.684	0.813	0.962	0.911	
40	0.677	0.760	0.942	0.900	
45	0.672	0.724	0.929	0.888	
50	0.662	0.690	0.907	0.885	
55	0.655	0.666	0.875	0.870	
60	0.666	0.649	0.855	0.844	

	Dipropylamine				
	0.0	**0.01**	**0.03**	**0.04**	**0.05**
25	0.879	0.987	0.960	0.890	0.827
30	0.836	0.96	0.991	0.885	0.816
35	0.812	0.950	0.985	0.894	0.809
40	0.788	0.886	0.978	0.903	0.826
45	0.779	0.856	0.971	0.913	0.841
50	0.746	0.785	0.948	0.918	0.874
55	0.744	0.802	0.908	0.878	0.818
60	0.736	0.787	0.891	0.904	0.852

Table S3. Compilation of polarity scale data: dipolarity/polarizability (π^*).

Temperature (°C)	Water Content (volume fraction)				
	N,N-dimethylcyclohexylamine				
	0.0	**0.01**	**0.03**	**0.04**	
25	0.296	0.359	0.441	0.523	
30	0.290	0.349	0.433	0.493	
35	0.282	0.341	0.414	0.478	
40	0.279	0.330	0.404	0.463	
45	0.271	0.323	0.393	0.447	
50	0.261	0.314	0.380	0.435	
55	0.254	0.305	0.369	0.418	
60	0.248	0.296	0.355	0.397	
	N-ethylcyclohexylamine				
	0.0	**0.01**	**0.03**	**0.04**	**0.06**
25	0.354	0.428	0.490	0.468	0.651
30	0.347	0.410	0.466	0.443	0.651
35	0.342	0.399	0.457	0.442	0.634
40	0.336	0.394	0.436	0.437	0.609
45	0.332	0.383	0.416	0.427	0.590
50	0.325	0.373	0.408	0.424	0.578
55	0.319	0.353	0.396	0.425	0.553
60	0.314	0.354	0.388	0.425	0.539
	Diisopropylamine				
	0.0	**0.01**	**0.03**	**0.05**	
25	0.284	0.331	0.418	0.551	
30	0.277	0.317	0.406	0.534	
35	0.271	0.314	0.389	0.509	
40	0.270	0.304	0.384	0.486	
45	0.261	0.292	0.372	0.466	
50	0.261	0.278	0.355	0.452	
55	0.260	0.272	0.346	0.430	
60	0.264	0.256	0.330	0.402	

	Dipropylamine				
	0.0	**0.01**	**0.03**	**0.04**	**0.05**
25	0.291	0.325	0.403	0.505	0.545
30	0.284	0.318	0.372	0.481	0.530
35	0.276	0.319	0.362	0.463	0.526
40	0.272	0.316	0.340	0.442	0.503
45	0.270	0.314	0.320	0.424	0.483
50	0.263	0.306	0.313	0.411	0.445
55	0.246	0.270	0.306	0.402	0.460
60	0.235	0.268	0.293	0.362	0.415

References

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