Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Influence of Intermolecular Interactions on the Complex Index of Refraction for Binary Liquid Mixtures in the Infrared

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Contents:

S1 Data Collection Parameters

Table S1. Data collection parameters for the NIR and MIR measurements with FTIR instruments.

Collection range - MIR	7800 – 400 cm^{-1}		Beamsplitter	KBr broadband
Collection range - NIR	10000 – 400 cm^{-1}		Detector type	RT-DLaTGS
Source	Glow bar for MIR, Tungsten lamp NIR		High pass filter	1 Hz
Data acquisition mode	Double-sided, forward-backward		Low pass filter	10 kHz
Number sample scans	128		Aperture setting	3.0 mm
Number background scans	256		Pre-amplifier gain	3x
Apodization function	Norton-Beer medium		Scanner velocity	10 kHz
Phase resolution	16 cm^{-1}		High-folding limit - MIR	15802 cm^{-1}
Phase correction mode	Mertz		High-folding limit - NIR	31602 cm^{-1}
Zerofilling factor	4x		Low folding limit	0 cm^{-1}
Resolution	2.0 cm^{-1}		Data point spacing	0.482 cm^{-1}

S2 Complex Index of Refraction for Neat Liquids

Complex index of refraction plots from 1 to 25 μm (10,000 to 400 cm^{-1}) are provided in Figure S1 and Figure S2 to compare the characteristics of TBP with n-dodecane and 1-butanol, respectively.

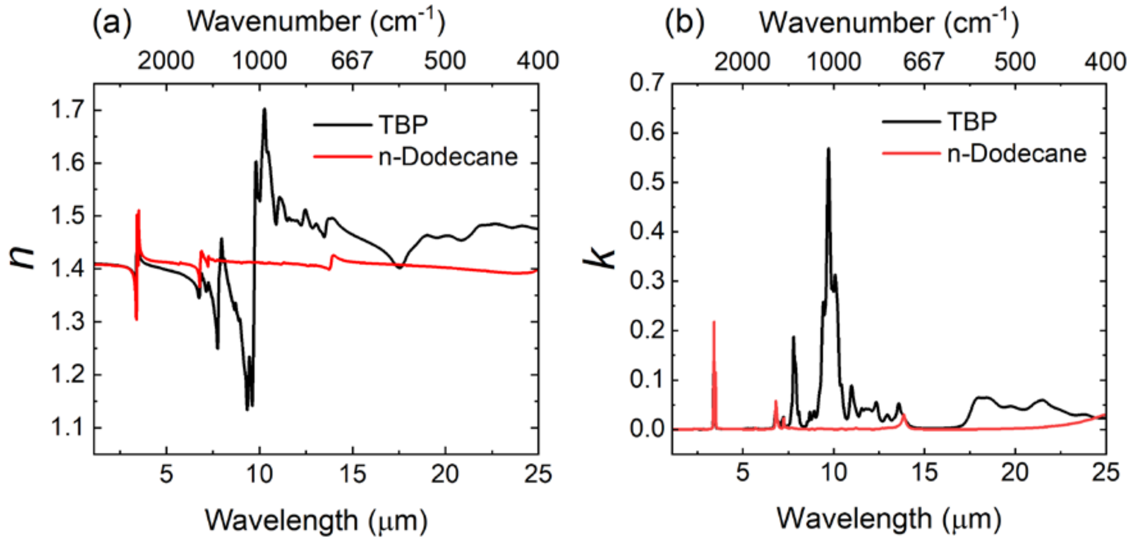


Figure S1. The (a) real (n) and (b) imaginary (k) parts of the complex index of refraction for neat TBP (black trace) and neat n-dodecane (red trace).

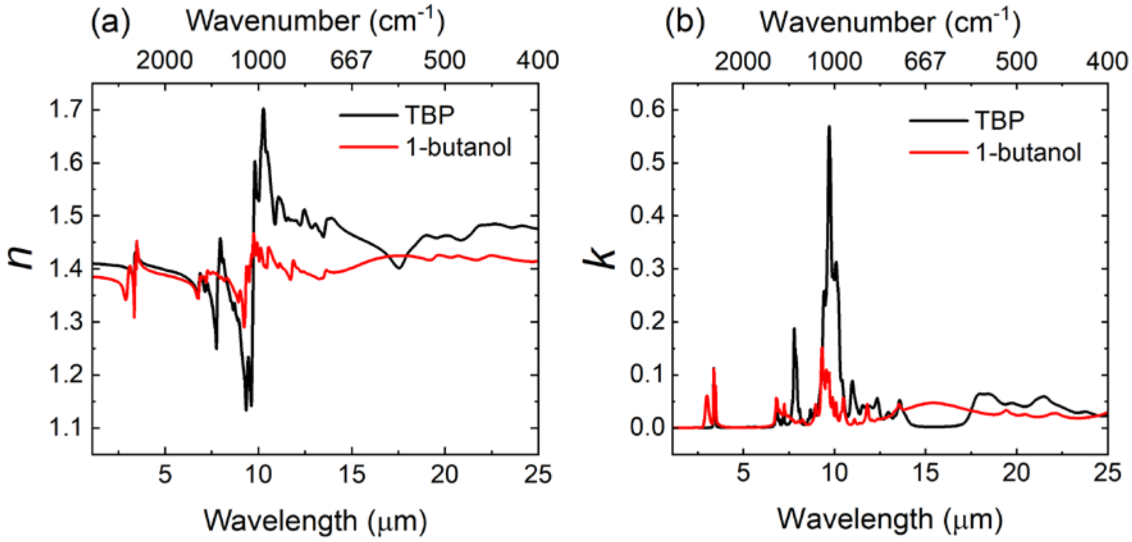


Figure S2. The (a) real (n) and (b) imaginary (k) parts of the complex index of refraction for TBP (black trace) and 1-butanol (red trace) are shown.

S3 Intermolecular Interactions

The energies of the various intermolecular interactions between the molecules in the mixtures, including London dispersion, dipole-induced-dipole, and dipole-dipole interactions, were quantified according to the treatment described by Fawcett.[1]

1) Dipole-Dipole (U_{dd}):

$$U_{dd} = \frac{-2\mu_a^2\mu_b^2}{3(4\pi\varepsilon_0)^2 k_B T(0.5[\sigma_a + \sigma_b])^6}$$

where μ_a and μ_b are the dipole moments of molecule a and b, respectively, ε_0 is the permittivity of free space, k_B is Boltzmann's constant, T is temperature, and σ_a and σ_b are the molecular diameters of molecule a and b, respectively.

2) Dipole-Induced Dipole (U_{id}):

$$U_{id} = \frac{\mu_a^2\alpha_b + \mu_b^2\alpha_a}{(4\pi\varepsilon_0)^2(0.5[\sigma_a + \sigma_b])^6}$$

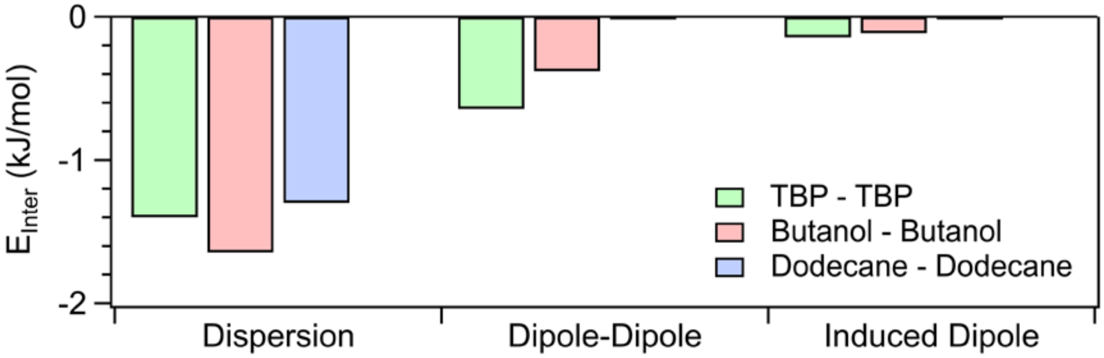
where α_a and α_b are the polarizabilities of molecule a and b, respectively.

3) Dispersion (U_{dis}):

$$U_{dis} = \frac{3I_aI_b\alpha_a\alpha_b}{2(I_a + I_b)(4\pi\varepsilon_0)^2(0.5[\sigma_a + \sigma_b])^6}$$

where I_a and I_b are the ionization potentials of molecule a and b, respectively. The various physical parameters for each molecule (i.e., dipole moment, polarizability, ionization potential, and molecular diameter) were deduced via *ab initio* calculations using the NWChem suite of programs.[2] With the exception of the ionization potentials, all parameters were deduced as a routine part of geometry optimization calculations run at the B3LYP/6-31G(d) level of theory. Complementary frequency calculations (B3LYP/6-31G(d)) were also used to ensure that the deduced geometry was neither a transition state nor a saddle point. Ionization potentials were deduced by also optimizing the geometries of the corresponding cations and taking the difference of the energies of the two species (i.e., $I = E_{ion} - E_{neutral}$).

(a) Self-Interactions



(b) Cross-Interactions

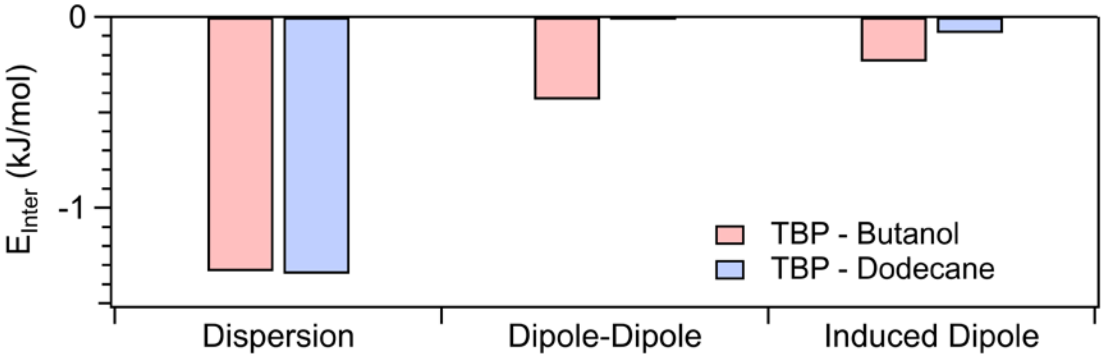


Figure S3. Calculated intermolecular interaction energies for TBP, 1-butanol, and n-dodecane, including London dispersion, dipole-dipole, and dipole-induced dipole. (a) Self-interactions for each of the molecules and (b) cross-interactions for 1-butanol and n-dodecane with TBP.

S4 Measured and Modeled Values for *n* at 1 µm

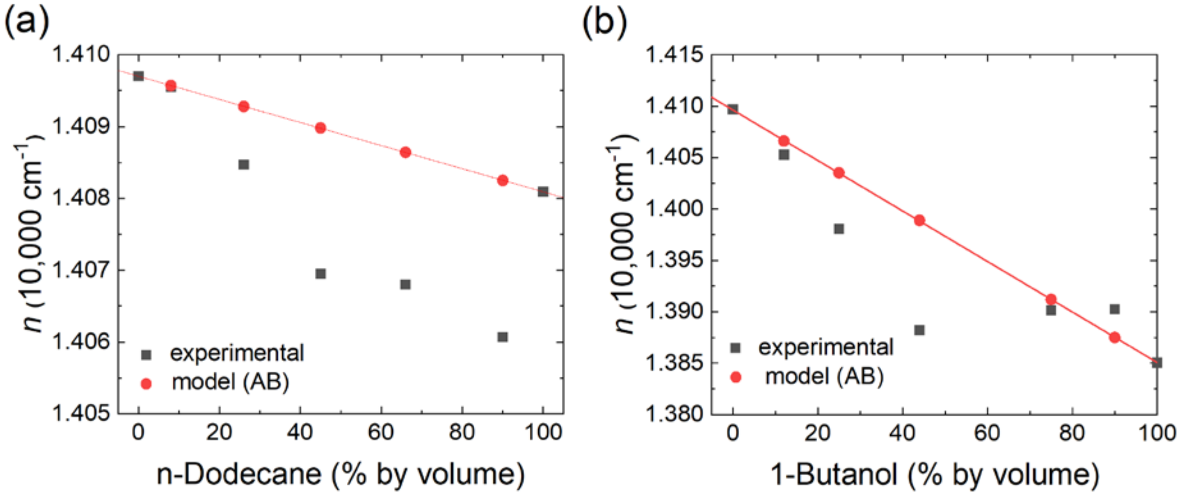


Figure S4. The (a) real parts of the complex index of refraction at 1 µm (10,000 cm^{-1}) for mixtures of TBP and (a) n-dodecane and (b) 1-butanol for both the values derived from experimental measurements (black squares) and theoretical calculations based on linear combinations of the neat liquids using the Arago-Biot (AB) model (red circles). The red line shows the linear fit for the modeled data.

S5 NMR Characterization

Proton-NMR determines the electron density perturbations, i.e., the chemical shifts, for the various protons. Phosphorus-31 NMR probes the phosphorus in TBP and can determine if TBP and 1-butanol are interacting with each other. The ^{1}H (Figure S5) and ^{31}P NMR (Figure S6) experiments were recorded using a 500 MHz Varian/Agilent spectrometer with a liquids state HX OneNMR probe. The ^{1}H chemical shift was set using the $CDCl_3$ shift at 7.23 ppm from the butanol dissolved in $CDCl_3$ sample. All other ^{1}H samples and ^{31}P samples were run without solvent or deuterium lock. The ^{31}P chemical shift was set with an external reference of concentrated phosphoric acid set at 0 ppm.

Figure S4 shows that the biggest change for the ^{1}H NMR data is for the O-H proton, which is shifted upfield with increasing TBP concentration. An upfield chemical shift of 1 ppm is observed for the 75:25 mixture compared to neat 1-butanol, indicating increased shielding of the O-H proton with increasing TBP concentration.

In addition, Figure S6 shows a change in the shielding for ^{31}P in TBP. With the addition of 1-butanol, an up-field chemical shift for the ^{31}P is observed with increasing 1-butanol concentration (e.g., chemical shift is ca. 0.6 ppm for the 25:75 mixture compared to neat TBP). These NMR results support the notion that the O-H groups are beginning to interact with the P=O group as the O-H proton experiences a upfield shift while the P=O group experiences a downfield shift with increasing TBP concentration.

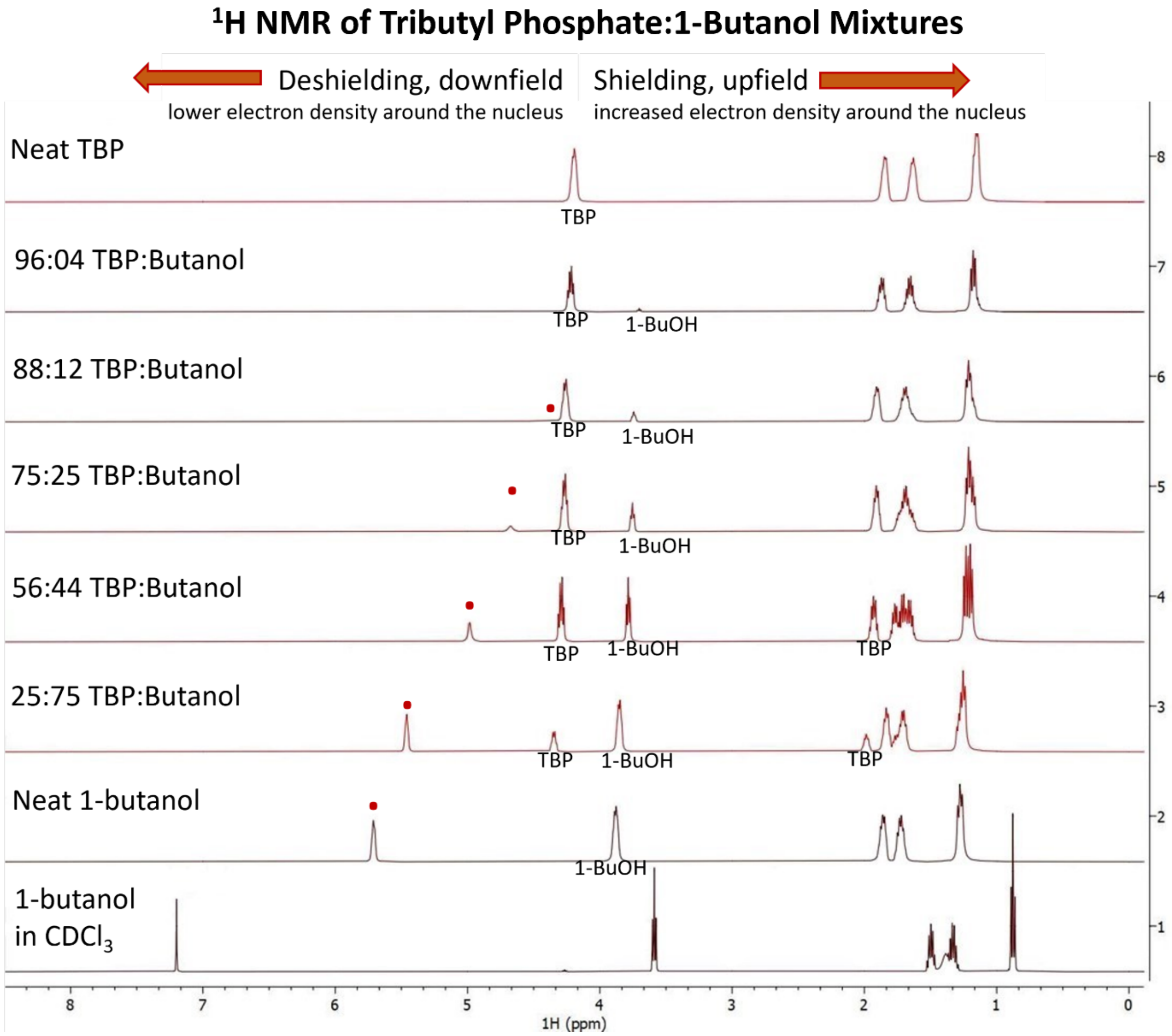


Figure S5. ^{1}H NMR spectra of tributyl phosphate:1-butanol mixtures, showing the upfield chemical shift for the OH proton (indicated by red circle) with increasing tributyl phosphate fraction.

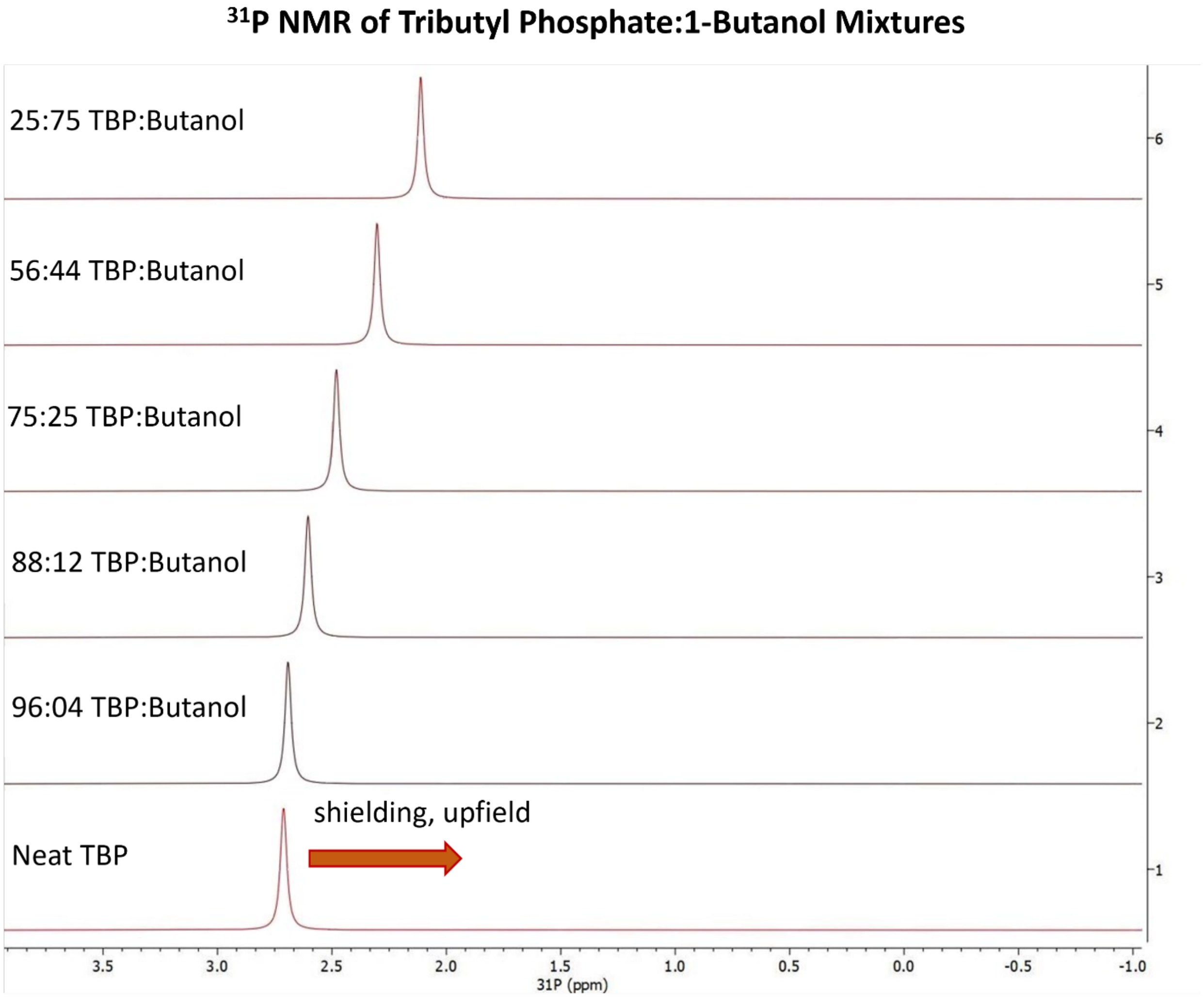
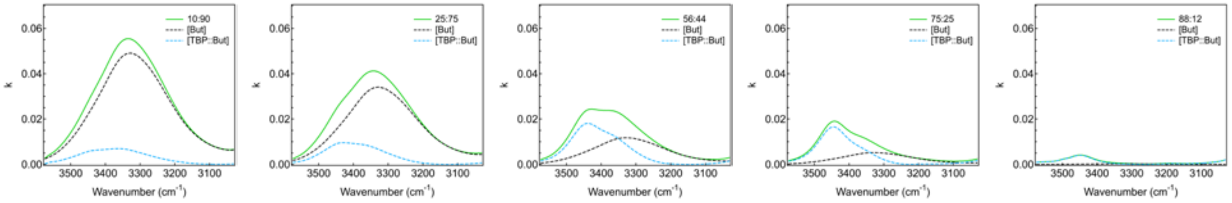


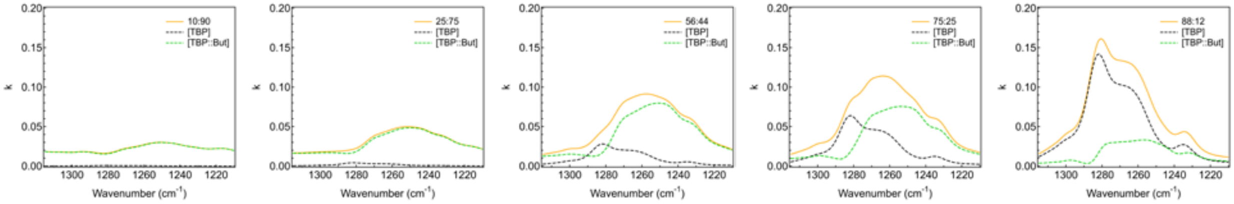
Figure S6. ^{31}P NMR spectra of tributyl phosphate:1-butanol mixtures, showing the upfield chemical shift of the ^{31}P with increasing TBP fraction.

S5 Spectral Deconvolution

(a) TBP-Butanol (O-H str.)



(b) TBP-Butanol (P=O str.)



(c) TBP-Dodecane (P=O str.)

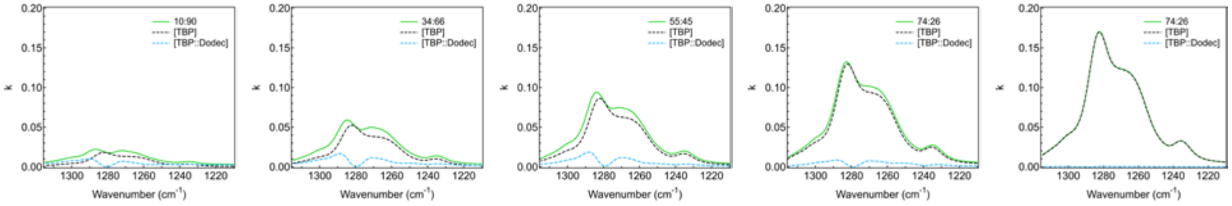


Figure S6. Spectral deconvolution of measured *k*-spectra into separate populations assignable to ether isolated or interacting liquids for (a) the P=O stretch of TBP in a TBP:1-butanol mixture, (b) the O-H stretch of 1-butanol in a TBP:1-butanol mixture, and (c) the P=O stretch of TBP in a TBP:n-dodecane mixture.

References

(1) Fawcett, W. R. *Liquids, Solutions, and Interfaces: From Classical Macroscopic Descriptions to Modern Microscopic Details*; Oxford University Press, 2004.
DOI: 10.1093/oso/9780195094329.001.0001.

(2) Aprà, E.; Bylaska, E. J.; de Jong, W. A.; Govind, N.; Kowalski, K.; Straatsma, T. P.; Valiev, M.; van Dam, H. J. J.; Alexeev, Y.; Anchell, J.; et al. NWChem: Past, present, and future. *The Journal of Chemical Physics* **2020**, *152* (18), 184102. DOI: 10.1063/5.0004997.