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Probing Solvent-Solvent and Solute-Solvent Interactions in Surfactant Binary Mixtures: Solvatochromic Parameters, Preferential Solvation, and Quantum Theory of Atoms in Molecules Analysis

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Abstract

Solvatochromic absorbance probes (4-Nitroaniline, 4-Nitroanisole, and Reichardt's dye) behavior within binary mixtures of polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether (Triton X-100 or TX-100)/organic solvents (2-Propanol, Hexanol, Butyl acetate, THF, Toluene, and p-Xylene) were extensively explored by using solvatochromism and quantum theory of atoms in molecules (QTAIM). To be more precise, the polarity parameters, E_T^N, and Kamlet–Taft parameters, such as the hydrogen bond donor ability (HBD) (α), hydrogen bond acceptor ability (HBA) (β), and dipolarity/polarizability (π^*), have been investigated in selected mixtures at 298 K. All binary mixtures exhibit complex behavior for chosen probes. The results indicate that 4-Nitroanisole and Reichardt's dye have stronger interactions with binary mixtures of alcohols/TX-100. The interaction energies decreased in the following order: Butyl acetate > Hexanol ~ 2-Propanol > THF > p-Xylene ~ Toluene. The preferential solvation model was applied to provide insight into the nature of solute-solvent and solvent-solvent interactions in these binary mixtures. Specific solute-solvent and solvent-solvent interactions are believed to be responsible for deviation from ideality.

Keywords: Triton X-100, Solvatochromic parameters, Quantum theory of atoms in molecules, Interaction energy, Preferential solvation.

1. Introduction

Surfactants are widely used as wetting agents, emulsifiers and detergents owing to their potential to reduce surface tension in their binary mixtures.[1,2] Surfactants classified by their chemical structures in to anionic, cationic, and non-ionic series.[3,4] Polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether (Triton X-100 or TX-100) is a non-ionic surfactant, which forms a hydrophilic polyethylene oxide chain and aromatic hydrocarbon hydrophobic group, with high purity, moderate foaming properties, and water solubility at 298 K.[5] Triton X-100 has cloud point (CP) ~340 K, critical micelle concentration (CMC) ~ 0.27 mM and aggregation number (N_{agg}) ~139 in its water mixture.[6-8] In the presence of additives, the surfactant-solvent interactions are significantly altered and consequently change the CMC values, surface activity, micelle size and phase behavior.[8-10] Triton X-100 is freely soluble in non-aqueous solvents and formed the micro emulsion.[11, 12]

It is well documented that a shift in absorption wavelength of probes in their binary mixtures provides more information about the details of solute-solvent interactions. This shift is termed as solvatochromism and depends on the electronic structures of solvent molecular and selected indicators.[13- 16] Moreover, both positive and negative deviation of binary mixtures from ideality can be monitored by using solvatochromism. Notably, the sign of their deviations depends on the difference in dipole moment between the ground and excited states of the chromophore.[17] Indeed, solvatochromism is an appropriate method for perusing solute-solvent interactions which can be used for investigating the specific and non-specific conforming interactions.[18, 20] Kamlet-Taft solvatochromic parameters are utilized to evaluate the solvent properties.[20, 21] These parameters including: the dipolarity/polarizability parameter (π^*), the hydrogen-bond acceptor basicity (β), and the hydrogen-bond donor acidity (α), provide information that can be used to measure the solvent effects in solvation and reaction processes and thus are widely used in choosing suitable solvents for chemical systems.

The investigation of the solute-solvent and solvent-solvent interactions in the binary mixtures of the Triton X-100 and organic solvents (2-Propanol, Hexanol, Tetrahydrofuran (THF), Butyl acetate, Toluene, and p-Xylene) by recovered solvatochromic parameters and quantum theory of atoms in molecules is the main objective of present work. Besides, preferential solvation model was applied for analyzing solvents interactions.

2. Methods

2.1. Computational method

A first insight into the organization patterns of molecular solvent around TX-100 were obtained by optimizing their mixtures at the B3LYP/6-311++G(d,p) level of theory using the Gaussian 03 package of programs.[22] The accuracy of optimized geometries were checked to be a true local minimum by frequency calculations. Counterpoise method [23] was implemented to eliminate the basis set superposition errors (BSSE).[24] Moreover, quantum theory of atoms in molecules (QTAIM) analysis[25] were carried out at the same theoretical level for achieving more details periphery formed hydrogen bonds of aforementioned mixtures by means of the MultiWFN 3.1 program.[26]

2.2. Experimental Section

Triton X-100, and all organic solvents including, 2-Propanol, Hexanol, Tetrahydrofuran (THF), Butyl acetate, Toluene and p-Xylene were supplied from Merck. Also, implemented dyes such as 4-Nitroanisole and 4-Nitroaniline were purchased from Merck (recrystallized from water/ethanol and water/acetone, respectively). Besides, 2,6-Diphenyl-4-(2,4,6-triphenylpyridinium-1-yl) phenolate (Reichardt's dye) was obtained from Aldrich (>99%).

The solution of probes were prepared in high purity ethanol and stored in dark glass at 4 ± 1 °C. The aforesaid binary mixtures in a specific mole fraction, were provided by weighing using an electrical balance, with accurate to ±0.1 mg. A suitable amount of indicator solution was transferred to quartz cell and was purged with dry N_2 to remove the ethanol. Then each solvatochromic probes dissolved in the chosen binary mixtures in different molar ratio. Spectrophotometric measurements were performed on a UV-vis Cintra 40 spectrophotometer, and 1 cm quartz cells at 298 K were applied in the whole study. In this study all of the measurements were recorded three times, and the average was reported.

3. Results and Discussion

3.1 Electrostatic potential map

Electrostatic potential map (ESP) of selected molecules were calculated at B3LYP/6-311++G(d,p) level of theory. According to Fig. S1, (in the Electronic supplementary information (ESI)) blue color is the domains with the lowest negative charge, and red color implies to the area with the concentration of negative charge.[27] It can be easily observed that the highest charge separation is attributed to the acetate and alcohol molecules, followed by THF, while Toluene and p-Xylene represent more neutral structures. Actually, negative charge of TX-100, Butyl acetate, alcohols, and THF are mainly resided on the O atoms, whereas it located on the top and below of benzene ring for Toluene and p-Xylene molecules.

3.1.2. Interaction energies

Fig. S2 (in ESI) demonstrates the optimized conformers of organic solvents/TX-100 binary mixtures alongside their intermolecular interactions mixtures. The estimated interaction energies decreased in the following order: Butyl acetate > Hexanol ~ 2-Propanol > THF > p-Xylene ~ Toluene. In the most stable conformers, tremendous propensity of organic molecules to interact with –OH functional group of TX-100 and O atoms of Butyl acetate, Hexanol, 2-Propanol, and THF can be observed. Whilst for neutral solvents such as p-Xylene and Toluene weaker interaction constituted through delocalized π orbital of benzene ring. Moreover, O atoms in the side chain of TX-100 exhibit weak intermolecular interactions with H sites of solvents.

3.1.3. Quantum theory of atoms in molecules

Fig. S3 (in ESI) exhibits the optimized geometries of selected binary mixture accompanied with their bond critical points (BCPs) in orange color, cage critical points (CCPs) as well as ring critical point (RCP) in yellow color. QTAIM based on the topological analysis of electron density (ρ_b) and its Laplacian ($\nabla^2\rho_b$), kinetic-energy density (G_b), the potential-energy density (V_b), the total energy density ($H_b = G_b + V_b$), the ratio of the kinetic-energy and the potential-energy density ($-G_b/V_b$), electron location function (ELF), and localized orbital locator (LOL) at BCPs were calculated and summarized in Table 1. The indexes of BCPs in Table 1 correspond with numbers in Fig S3 (in ESI).

It should be noted that ρ_b indicates the bond strength, in that the greater interaction energies are associated with higher ρ_b. Totally, ρ_b is greater than 0.20 au in covalent bonding, while less than 0.10 au in a closed-shell interaction.[28,29] The strong O…H interactions between TX-100 and molecular solvents, such as Butyl acetate, alcohols, and THF can be discovered from ρ_b values in Table 1.

According to the fact, the negative $\nabla^2\rho_b$ indicate the shared (covalent) interaction, whilst positive values of matching property implies to the closed-shell bonding such as ionic, hydrogen bonding, and van der Waals interactions.[29, 30] To be more precise, normal H-bond possess $\nabla^2\rho_b$ values in the range of 0.02 to 0.139 au.[31] As a main result, H bonds are formed via acidic H atom of TX-100 and O atoms of selected solvents. In addition, the ratio of G_b and V_b at the critical point ($-G_b/V_b$) for all interactions are more than 1.0, proposing the non-covalent character. The positive values of H_b for all BCPs are another reliable evidence for this assertion.

Eventually, electron location function (ELF) [29,30] and localized orbital locator (LOL) [29,30] were analyzed through BCPs in Table 1 and visualized in Figs. 1 and 2. It should be emphasized that a large value of ELF and LOL show that electrons are significantly localized, which is a sign of the covalent bond constitution, whereas small value of corresponding functions verifying the closed-shell interaction. The ELF and LOL results are in good agreement with the aforementioned topological analysis.

Summing up, strong O…H interaction between TX-100 and Butyl acetate, alcohols, and THF molecules is as a main achieved result of interaction energy and QTAIM analysis.

3.2. Behavior of Reichardt's dye and E_T^N

The Reichardt's dye indicator has charge transfer spectra due to having a zwitterion form, which are highly sensitive to the hydrogen bond donating (HBD) ability of solvents.[32,33] Reichardt's dye has been applied to determine the polarity of the organic solvents, ionic liquids, and many different solvent mixtures. The molar electronic transition energy of this probe which is largely influenced by polarizability, dipole moment, and hydrogen bond, can be computed using Eq.1, as follows:

$$E_T(30)(kcal.mol^{-1}) = \frac{hcN_A}{\lambda_{max}\,(nm)} = \frac{28591.5}{\lambda_{max}(nm)} \qquad (1)$$

where h is the Planck's constant, c implies to the velocity of light and N_A is the Avogadro's number. This parameter normalized by using tetramethylsilane (TMS) and water with value 1 and 0, respectively (Eq. 2). [34]

$$E_T^N = \frac{E_T\,(Solvent) - E_T\,(TMS)}{E_T(Water)\; - E_T\,(TMS)} = \frac{E_T\,(Solvent) - 30.7}{32.4} \qquad (2)$$

The yielded findings of E_T^N values of investigated binary mixtures are given in Table 2. According to Table 2, neat TX-100 has higher normalized polarity than in comparison to mentioned solvents, with the exception of alcohols. Although, ESP results demonstrated that the lowest charge separation is attributed to TX-100, having many acceptor sites (O atoms) on its side chain high molecular volume is beloved to be responsible for observed trend. The highest values of E_T^N is ascribed to the alcoholic solvents, which is in excellent consistency with ESP findings. Ascending behavior with a negative deviation from ideality can be seen for E_T^N in 2-Propanol/TX-100 and Hexanol/TX-100 binary mixtures (Fig S4. A, B in ESI). While in the other mixtures a regular depletion is viewed with increasing $X_{solvent}$, thus no synergistic behavior can be observed (Fig S4. C- F in ESI).

3.3. Kamlet-Taft parameters

Empirical Kamlet-Taft parameters (dipolarity/polarizability (π^*), hydrogen-bond donating (HBD) ability (α), and hydrogen-bond accepting (HBA) basicity (β)) are measured from Eqs. 3-5. [35]

$$\pi^* = 0.427\,(34.12 - \nu_{ANS}) \qquad (3)$$

$$\alpha = 0.186\,(10.91 - \nu_B) - 0.72\,\pi^* \qquad (4)$$

$$\beta = \frac{31.10 - 3.14\pi^* - \nu_{ANI}}{2.79} \qquad (5)$$

where ν_{ANS} implies to the absorption behavior of 4-Nitroanisole, and ν_B and ν_{ANI} are related to the maximum wavelength of Reichardt's dye and 4-nitroaniline in selected binary mixtures, respectively.[36,37] The computed values of these parameters are collected in Table 2. As it can be seen, π^* values for 2-Propanol, Hexanol, Tetrahydrofuran (THF), Butyl acetate, Toluene and p-

Xylene are less than that for neat Triton X-100. All mixtures show the positive deviation from ideality behavior (Fig S5. A-F in ESI). In initial mole fraction of solvent in 2-Propanol/TX-100, Hexanol/TX-100, THF/TX-100, Toluene/TX-100 and p-Xylene/TX-100 mixtures, π^* does not remarkable change and by adding more solvent, matching parameter linearly decreases. This decline is more distinctive for Butyl acetate/TX-100 mixtures (Fig S5. D, in ESI), which is confirmed by the obtained results of interaction energy and QTAIM analysis.

The hydroxyl group (OH) in 2-Propanol and Hexanol, and Triton X-100 contributes toward the HBD ability, which is in good agreement with the optimized geometries in Fig S2 (in ESI). The α value of Triton X-100 is found to be lower than that of alcohols. Furthermore, Butyl acetate shows slight HBD ability due to the weak acidity of H atoms in its alpha-carbon. The THF, Toluene and p-Xylene have no HBD sites and consequently have α values close to zero. By adding alcoholic solvents to TX-100, α parameters are enhanced with a negative deviation from ideal behavior (Fig S6. A, B, in ESI), whereas a descending trend can be found by adding of p-Xylene with a positive deviation from ideality. Interestingly, the variation of this parameter in Toluene/TX-100 binary mixtures is slightly constant (Fig S6. E, in ESI), the maximum change for corresponding mixture is occurred at $0.8 < X_{\mathrm{Toluene}} < 1$. This changing procedure for α parameter is in excellent agreement with the yielded finding of ESP and interaction energies.

In THF/TX-100, Butyl acetate/TX-100 ($X_{\mathrm{Butyl\ acetate}} > 0.3$), Toluene/TX-100 and p-Xylene/TX-100 binary mixtures a positive deviation is observed. It can be justified by the solvation of probe by the new species formed by the interaction of TX-100 with these organic solvents. However, the negative deviation of α in Butyl acetate/TX-100 ($X_{\mathrm{Butyl\ acetate}} < 0.3$) mixtures indicates that the probe solvated by Butyl acetate.

It is worthy to note that the E_T^N parameter is a blend of dipolarity/polarizability and HBD acidity of the media. The ascending trend of E_T^N and α parameters for alcohols/TX-100 binary mixtures can be related to the strong O…H hydrogen bonding interactions in their mixtures, which is previously confirmed by optimized structures and QTAIM analysis.

Alcoholic solvents have a higher β value than Triton X-100. The contributor to the HBA basicity of 2-Propanol and Hexanol is ascribed to the –OH functional group.

The lowest values of β parameter measured for Toluene and p-Xylene, owing to the lack of HBA sites. Actually, in 2-Propanol/TX-100 and Hexanol/TX-100 mixtures, by addition of molecular solvents, this parameter increases with negative deviation from ideality (Fig S7. A, B, in ESI). This result was earlier confirmed by the optimized conformers and also topological analysis.

Solvation of probe by the two compounds in Toluene/TX-100 and p-Xylene/TX-100 mixtures can be understood from the positive deviation of this parameter from ideal behavior (Fig S7. E, F, in ESI).

The β value in THF and TX-100 is similar to each other. A slight negative deviation from ideality was shown for this parameter in THF/TX-100 mixtures. Notably, Butyl acetate/TX-100 mixture has different behavior from the other ones. In initial mole fraction of Butyl acetate ($X_{\text{Butyl acetate}} < 0.4$) a negative deviation is observed, whilst the opposite trend can be found for $X_{\text{Butyl acetate}} > 0.4$. The main reason for this observation lies in the fact that the probe solvated by Butyl acetate and new structure which formed by both molecular solvent and Triton X-100.

In this study three solvatochromic dyes (4-Nitroanisole, 4-Nitroaniline and Reichardt's dye) exhibit unusual solvatochromism within binary mixtures of Triton X-100 and molecular solvents.

According to the results, it can be concluded that the probes in these mixtures are not equally solvated by the two compounds, and consequently preferential solvation of the probes is verified.

3.4. Preferential solvation

Additional details of solute-solvent and solvent-solvent interactions in binary mixtures can be achieved by investigation of the preferential solvation. It is well established that this model as powerful tool can be utilized in order to explain the solvation behavior of indicators and the structure-property relationship of the mixed solvent systems.[38-41] Preferential solvation model developed by Skwierczynsi et al.[42] and extended by Bosch and Roses [43], later other researcher used this model for illustrating the solvation phenomena in solvent mixtures.[44-46] According to this model, the solvent exchange can be given by Eqs. 6 and 7:

$$I(S1)_2 + IS2 \leftrightarrow I(S2)_2 + 2S1 \tag{6}$$

$$I(S1)_2 + S2 \leftrightarrow I(S12)_2 + S1 \tag{7}$$

Where *I*, (S1 and S2), and S12 refer to the probe, pure solvents and the mixed solvents, respectively. *I*(S1) implies the probe solvated by the S1 solvent, *I*(S2) by the S2 solvent, and *I*(S12) by the S12. The exchange of solvent S1 by S2 within the solvation microenvironment of the probe is indicated by Eq. 6, while Eq. 7 depicts the exchange of solvent S1 by the S12. Furthermore, $f_{2/1}$ and $f_{12/1}$ constants can be calculated by use of Eqs. 8 to 10:

$$f_{2/1} = \frac{x_2^s / x_1^s}{(x_2^\circ / x_1^\circ)^2} \tag{8}$$

$$f_{12/1} = \frac{x_{12}^s / x_1^s}{x_2^\circ / x_1^\circ} \tag{9}$$

$$f_{12/2} = \frac{f_{12/1}}{f_{2/1}} \tag{10}$$

Where x_i^s and x_i^0 represent the solvent mole fraction in solution sphere of the probe and in bulk, respectively. With the help of pure solvent trait (Y_1 and Y_2), the solvatochromic property of binary mixture (Y_{12}) can be computed by Eq. 11. The correction term (ΔY) can be expressed by the Eq. 12:

$$Y = \frac{Y_1(1-x_2^{\circ})^2 \ + \ Y_2 f_{2/1}(x_2^{\circ})^2 \ + \ Y_{12} f_{12/1}(1-x_2^{\circ})x_2^{\circ}}{(1-x_2^{\circ})^2 \ + \ f_{2/1}(x_2^{\circ})^2 \ + \ f_{12/1}\,(1-x_2^{\circ})x_2^{\circ}} \qquad (11)$$

$$\Delta Y = \frac{k f_{2/1}(x_2^{\circ})^2\,[(1-x_2^{\circ})^2 \ + \ f_{12/1}(1-x_2^{\circ})\,x_2^{\circ}/2]}{[(1-x_2^{\circ})^2 \ + \ f_{2/1}(x_2^{\circ})^2 \ + f_{12/1}(1-x_2^{\circ})x_2^{\circ})]^2} \qquad (12)$$

where k is proportionality constant. The wave numbers of the 4-Nitroanisole, 4-Nitroaniline, and Reichardt's dye at whole range have been fitted to the proposed Eq. 11 and the results are given in Table 3. Six binary mixtures represent a complex behavior for all three indicators.

The obtained results from preferential solvation model for Reichardt's dye in alcoholic solvents/TX-100, Butyl acetate/TX-100, Toluene/TX-100, and p-Xylene/TX-100 mixtures were depicted in Fig. 3. The Y_{12} value is higher than the Y_1 and Y_2 values in 2-Propanol/TX-100 mixture, which indicate a higher dipolarity/polarizability of the solvent/TX-100 complex, made up by solvent-solvent interactions of 2-Propanol molecules with Triton X-100. In the case of the Hexanol/TX-100 mixture, $f_{2/1}$ and $f_{12/1}$ values are higher than unity, reflecting the solvation of the Reichardt's dye by Hexanol and Hexanol/TX-100 complexes. In the other mixtures, including, THF/TX-100, Toluene/TX-100, and p-Xylene/TX-100 mixtures, the $f_{2/1} < 1$ and $f_{12/1} > 1$ indicate the solvation of this probe with Triton X-100 and mixed solvents in mentioned mixtures. The Butyl acetate/TX-100 mixture also demonstrates that $f_{2/1}$ and $f_{12/1}$ values are higher than unity, which clearly indicates the solvation of probe by Butyl acetate molecule and mixed compounds. The higher value of $f_{2/1}$ and $f_{12/1}$ parameters in Butyl acetate/TX-100 and Hexanol/TX-100 mixtures may be rationalized by the highest interaction energies between forenamed mixtures, which is previously verified by the *ab initio* calculations and QTAIM analysis.

Notably, 4-Nitroanisole shows an ascending behavior in all mixtures (Fig. 4). In Butyl acetate/TX-100 mixtures, $f_{2/1}$ and $f_{12/1}$ values (Table 3) are higher than unity, which indicate that the solvation of this probe by Butyl acetate and mixed solvents. Preferential solvation by the mixed solvents can be easily comprehended from the high values of $f_{12/1}$ and $f_{12/2}$ parameters in the other binary mixtures. The obtained consequence demonstrates that the wavenumber of maximum absorption of all mixed solvent S12 (Y_{12}) are lower than Y_1 and Y_2 values, with the exception of 2-Propanol/TX-100 and THF/TX-100 mixtures. This trend indicated stronger dipolarity/polarizability of the organic solvents/TX-100 complexes.

The spectral response of 4-Nitroaniline indicator depends upon the solvent HBA basicity. Fig. 5 exhibits the obtained results of preferential solvation of this probe in all binary mixtures. 4-Nitroaniline is preferentially solvated by the pure Hexanol and THF as well as their mixtures, while this indicator is preferentially surrounded by the mixed solvent/TX-100 for the other selected mixtures due to having higher values of $f_{12/1}$.

4. Summary and conclusions

Solute-solvent and solvent-solvent interactions in binary mixtures of Triton X-100 and molecular solvents such as 2-Propanol, Hexanol, Butyl acetate, THF, Toluene and p-Xylene, were investigated by solvatochromism combined with QTAIM analysis. An ascending behavior of E_T^N and α is observed in alcohols/TX-100 mixtures. It may be related to the O…H hydrogen bonding between TX-100 and alcohols solvents. This result is in great agreement with the QTAIM analysis and optimized structures of these mixtures. Notably, ideal and linear variation of E_T^N parameter can be found in alcohols/TX-

100 mixtures. Totally, the yielded consequences of solvatochromism, QTAIM analysis and optimized structures represent that the highest solvent/TX-100 intermolecular interactions is attributed to the Butyl acetate/TX-100 and 2-Propanol /TX-100 mixtures, which is followed by Hexanol /TX-100 and the lowest of the solvent/TX-100 association is ascribed to non-polar organic molecules. The obtained results from preferential solvation model confirmed solvent-solvent and solute-solvent interactions. Eventually, preferential solvation is in excellent consistency with solvatochromic, *ab initio*, and QTAIM findings.

† **Electronic supplementary information (ESI) available:** Electrostatic potential map (ESP) (Figure S1). The optimized geometries in binary mixtures accompanied with their interaction energies (Figure S2). BCPs, CCPs, and RCPs of optimized structures in selected binary mixtures (Figure S3). The variation of solvatochromic parameters (E_T^N, π^*, α, and β) in solvents/TX-100 binary mixtures (Figures S4-S7).

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Table 1. Topological properties for the intermolecular interactions at the BCPs of solvent/TX-100 binary mixtures calculated at the B3LYP/6-311++G(d,p) theoretical level. Indexes are shown in Fig S3 (in ESI).

Butyl acetate/TX-100	ρ_b	$\nabla^2\rho_b$	G_b	V_b	$-G_b/V_b$	H_b	ELF	LOL
1	0.02694	0.09844	0.02265	-0.02068	1.09526	0.00197	0.08599	0.23480
2	0.00575	0.02262	0.00468	-0.00371	1.26146	0.00097	0.01259	0.10169
3	0.00808	0.02371	0.00524	-0.00455	1.15165	0.00069	0.03072	0.15138
4	0.00566	0.01692	0.00367	-0.00311	1.18006	0.00056	0.01931	0.12335
Hexanol/TX-100	ρ_b	$\nabla^2\rho_b$	G_b	V_b	$-G_b/V_b$	H_b	ELF	LOL
1	0.02768	0.10049	0.02340	-0.02168	1.07934	0.00172	0.08799	0.23707
2	0.02254	0.08563	0.01904	-0.01667	1.14217	0.00237	0.06841	0.21329
3	0.00477	0.02113	0.00421	-0.00313	1.34505	0.00108	0.00841	0.08451
2-Propanol/TX-100	ρ_b	$\nabla^2\rho_b$	G_b	V_b	$-G_b/V_b$	H_b	ELF	LOL
1	0.02770	0.10063	0.02343	-0.02169	1.08022	0.00174	0.08807	0.23717
2	0.02358	0.08538	0.01934	-0.01733	1.11598	0.00201	0.07649	0.22357
3	0.00468	0.01751	0.00354	-0.00271	1.30627	0.00083	0.01109	0.09598
THF/TX-100	ρ_b	$\nabla^2\rho_b$	G_b	V_b	$-G_b/V_b$	H_b	ELF	LOL
1	0.02898	0.10608	0.02498	-0.02343	1.06615	0.00155	0.08986	0.23916
2	0.00851	0.02655	0.00584	-0.00503	1.16103	0.00081	0.02943	0.14852
3	0.00603	0.01805	0.00396	-0.00339	1.16814	0.00057	0.02053	0.12674
p-Xylene/TX-100	ρ_b	$\nabla^2\rho_b$	G_b	V_b	$-G_b/V_b$	H_b	ELF	LOL
1	0.00939	0.02664	0.00533	-0.00399	1.33584	0.00134	0.04823	0.18403
2	0.00582	0.01747	0.00382	-0.00326	1.17178	0.00056	0.01953	0.12397
Toluene/TX-100	ρ_b	$\nabla^2\rho_b$	G_b	V_b	$-G_b/V_b$	H_b	ELF	LOL
1	0.00868	0.02425	0.00483	-0.00359	1.34540	0.00124	0.04520	0.17901
2	0.00609	0.01878	0.00408	-0.00347	1.17579	0.00061	0.01994	0.12511

Table 2. E_T^N (Normalized polarity), π^*(polarizability/dipolarity), α (HBD ability), and β (HBA basicity) within Triton X-100 with molecular solvents (2-Propanol, Hexanol, Tetrahydrofuran (THF), Butyl acetate, Toluene and p-Xylene) binary mixtures.

Triton X-100												
	2-Propanol				Tetrahydrofuran (THF)				Toluene			
$X_{solvent}$	α	β	π^*	E_T^N	α	β	π^*	E_T^N	α	β	π^*	E_T^N
0	0.31	0.57	0.87	0.46	0.31	0.57	0.87	0.46	0.31	0.57	0.87	0.46
0.1	0.32	0.58	0.86	0.46	0.29	0.57	0.86	0.45	0.26	0.54	0.91	0.46
0.2	0.33	0.57	0.87	0.47	0.30	0.54	0.87	0.46	0.26	0.54	0.91	0.45
0.3	0.35	0.58	0.87	0.48	0.30	0.57	0.84	0.45	0.28	0.58	0.87	0.45
0.4	0.38	0.59	0.86	0.49	0.26	0.51	0.88	0.45	0.27	0.56	0.86	0.44
0.5	0.38	0.59	0.86	0.49	0.28	0.55	0.86	0.44	0.26	0.56	0.86	0.44
0.6	0.40	0.58	0.85	0.50	0.26	0.53	0.87	0.44	0.26	0.58	0.85	0.43
0.7	0.45	0.59	0.84	0.52	0.22	0.53	0.86	0.42	0.25	0.57	0.84	0.42
0.8	0.51	0.64	0.80	0.53	0.27	0.60	0.74	0.40	0.27	0.61	0.75	0.40
0.9	0.60	0.73	0.73	0.55	0.22	0.60	0.70	0.36	0.16	0.63	0.71	0.34
1	0.74	1.06	0.50	0.54	0.03	0.61	0.53	0.21	0.00	0.13	0.52	0.10
	Hexanol				Butyl acetate				p-Xylene			
$X_{solvent}$	α	β	π^*	E_T^N	α	β	π^*	E_T^N	α	β	π^*	E_T^N
0	0.31	0.57	0.87	0.46	0.31	0.57	0.87	0.46	0.31	0.57	0.87	0.46
0.1	0.29	0.51	0.90	0.47	0.25	0.54	0.87	0.44	0.26	0.52	0.89	0.45
0.2	0.26	0.52	0.89	0.45	0.27	0.53	0.88	0.45	0.26	0.55	0.88	0.44
0.3	0.28	0.52	0.89	0.46	0.27	0.54	0.87	0.44	0.26	0.51	0.88	0.44
0.4	0.33	0.53	0.88	0.48	0.28	0.54	0.86	0.45	0.24	0.52	0.86	0.43
0.5	0.38	0.56	0.85	0.49	0.28	0.54	0.84	0.44	0.22	0.50	0.89	0.43
0.6	0.35	0.50	0.89	0.49	0.31	0.57	0.80	0.44	0.19	0.48	0.89	0.41
0.7	0.45	0.54	0.83	0.52	0.30	0.56	0.76	0.42	0.17	0.48	0.85	0.39
0.8	0.54	0.63	0.75	0.53	0.27	0.54	0.75	0.40	0.16	0.54	0.77	0.36
0.9	0.60	0.65	0.71	0.55	0.27	0.55	0.66	0.37	0.10	0.55	0.70	0.30
1	0.81	0.93	0.50	0.57	0.09	0.49	0.48	0.23	0.00	0.11	0.46	0.08

Table 3. Parameters and standard deviation obtained by application of the preferential solvation model.

Indicator	Solvents	Y_1	Y_2	Y_{12}	$f_{2/1}$	$f_{12/1}$	$f_{12/2}$	N	R^2	k	σ
4-Nitroanisole	2-Propanol/TX-100	32.07	32.94	32.15	0.55	2.99	5.43	11	0.99	-1.86	0.00008
	Hexanol/TX-100	32.06	32.94	31.96	0.50	3.62	7.24	11	0.98	-0.029	0.00306
	THF/TX-100	32.06	32.86	32.48	0.60	1.23	2.05	11	0.97	-2.79	0.00405
	Butyl acetate/TX-100	32.07	32.99	32.04	1.12	7.56	6.75	11	0.99	0.02	0.00180
	Toluene/TX-100	32.05	32.89	31.99	0.67	6.46	9.64	11	0.98	0.48	0.00229
	p-Xylene/TX-100	32.06	33.03	32.03	0.44	1.78	4.04	11	0.99	-1.72	0.00118
4-Nitroaniline	2-Propanol/TX-100	26.77	26.55	26.74	0.43	4.68	10.88	11	0.91	0.068	0.00084
	Hexanol/TX-100	26.78	26.92	26.84	1.35	17.95	13.29	11	0.93	1.44	0.00079
	THF/TX-100	26.76	27.73	26.94	1.32	5.35	4.053	11	0.99	-2.06	0.00180
	Butyl acetate/TX-100	26.78	28.23	26.84	0.71	6.22	8.76	11	0.99	-0.29	0.00104
	Toluene/TX-100	26.75	29.11	26.77	0.15	9.94	66.26	11	0.99	1.69	0.00315
	p-Xylene/TX-100	26.76	29.34	27.00	0.06	2.11	35.16	11	0.99	-1.07	0.00192
Reichardt's dye	2-Propanol/TX-100	15.99	16.95	17.42	0.26	0.32	1.23	11	0.97	-0.75	0.00589
	Hexanol/TX-100	16.02	17.20	15.73	5.12	5.44	1.06	11	0.98	-1.43	0.00867
	THF/TX-100	15.97	13.16	15.84	0.27	3.79	14.03	11	0.99	0.32	0.00453
	Butyl acetate/TX-100	15.94	13.30	15.73	1.75	12.70	7.26	11	0.99	4.34	0.00977
	Toluene/TX-100	16.00	11.90	15.56	0.30	2.33	7.76	11	0.99	7.05	0.00128
	p-Xylene/TX-100	15.96	11.65	15.67	0.32	4.09	12.78	11	0.99	0.72	0.00421

Figure Caption

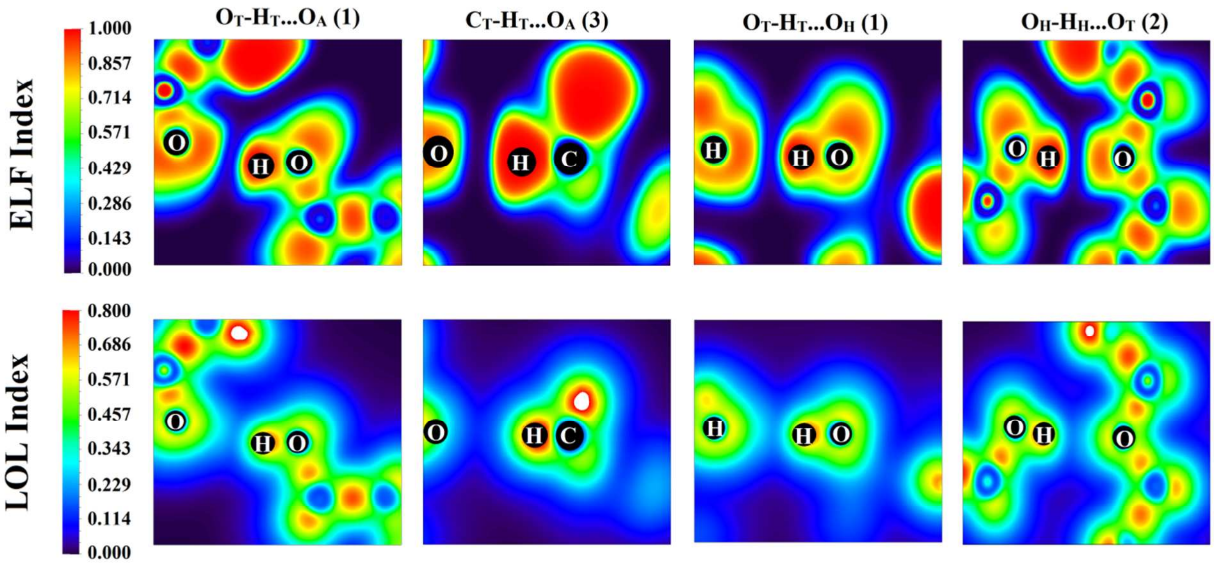
Figure 1. The electron location function (ELF) and localized orbital locator (LOL) of Butyl acetate/TX-100, Hexanol/TX-100 binary mixtures through O…H bond critical points. A, H, and T are referred to Butyl acetate, Hexanol, and Triton X-100, respectively.

Figure 2. The electron location function (ELF) and localized orbital locator (LOL) of Hexanol/TX-100, 2-Propanol/TX-100, and THF/TX-100 binary mixtures through O…H bond critical points. P and T are referred to 2-Propanol and Triton X-100, respectively.

Figure 3. Maximum wave number of Reichardt's dye absorbance in molecular solvents/TX-100 mixtures.

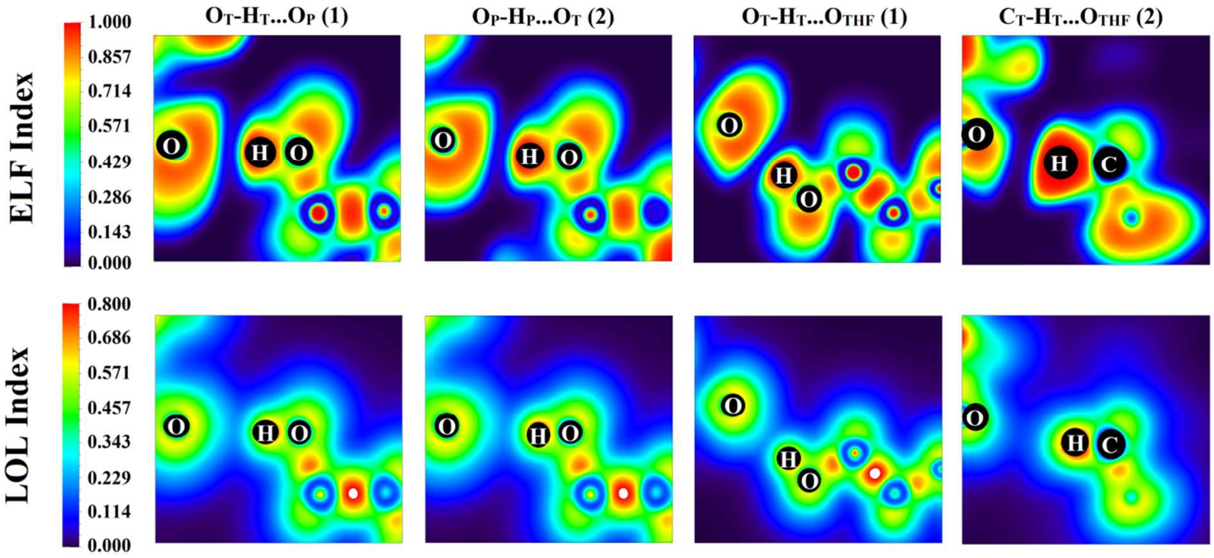
Figure 4. Maximum wave number of 4-Nitroanisole absorbance in molecular solvents/TX-100 mixtures.

Figure 5. Maximum wave number of 4-Nitroaniline absorbance in molecular solvents/TX-100 mixtures.



O_T-H_T...O_A (1)
C_T-H_T...O_A (3)
O_T-H_T...O_H (1)
O_H-H_H...O_T (2)
ELF Index
1.000
0.857
0.714
0.571
0.429
0.286
0.143
0.000
LOL Index
0.800
0.686
0.571
0.457
0.343
0.229
0.114
0.000
O
H
C

Figure 1.



O_T-H_T...O_P (1)
O_P-H_P...O_T (2)
O_T-H_T...O_THF (1)
C_T-H_T...O_THF (2)
ELF Index
1.000
0.857
0.714
0.571
0.429
0.286
0.143
0.000
LOL Index
0.800
0.686
0.571
0.457
0.343
0.229
0.114
0.000
O
H
C

Figure 2.

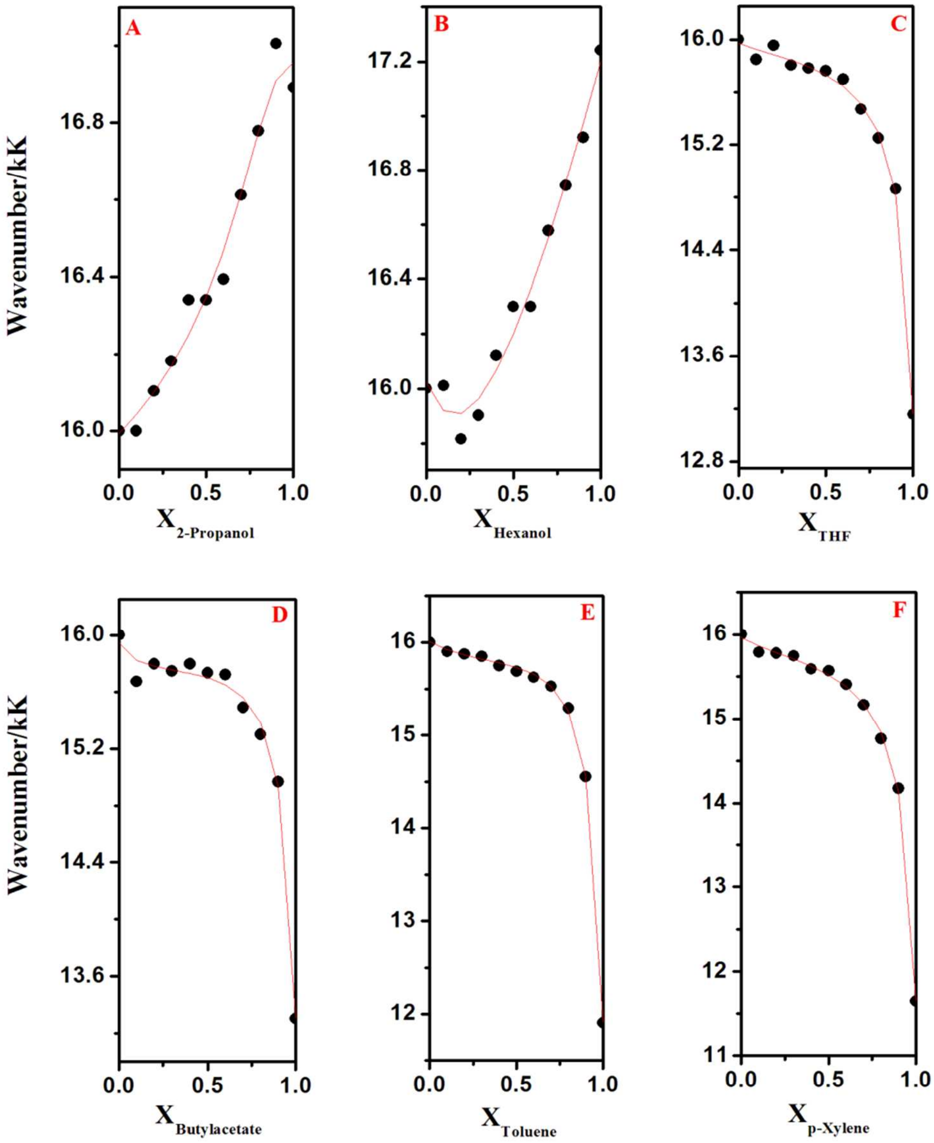

A
B
C
Wavenumber/kK
16.0
16.4
16.8
17.2
15.2
14.4
13.6
12.8
0.0
0.5
1.0
X2-Propanol
XHexanol
XTHF
D
E
F
Wavenumber/kK
16
15
14
13
12
11
XButylacetate
XToluene
Xp-Xylene

Figure 3.

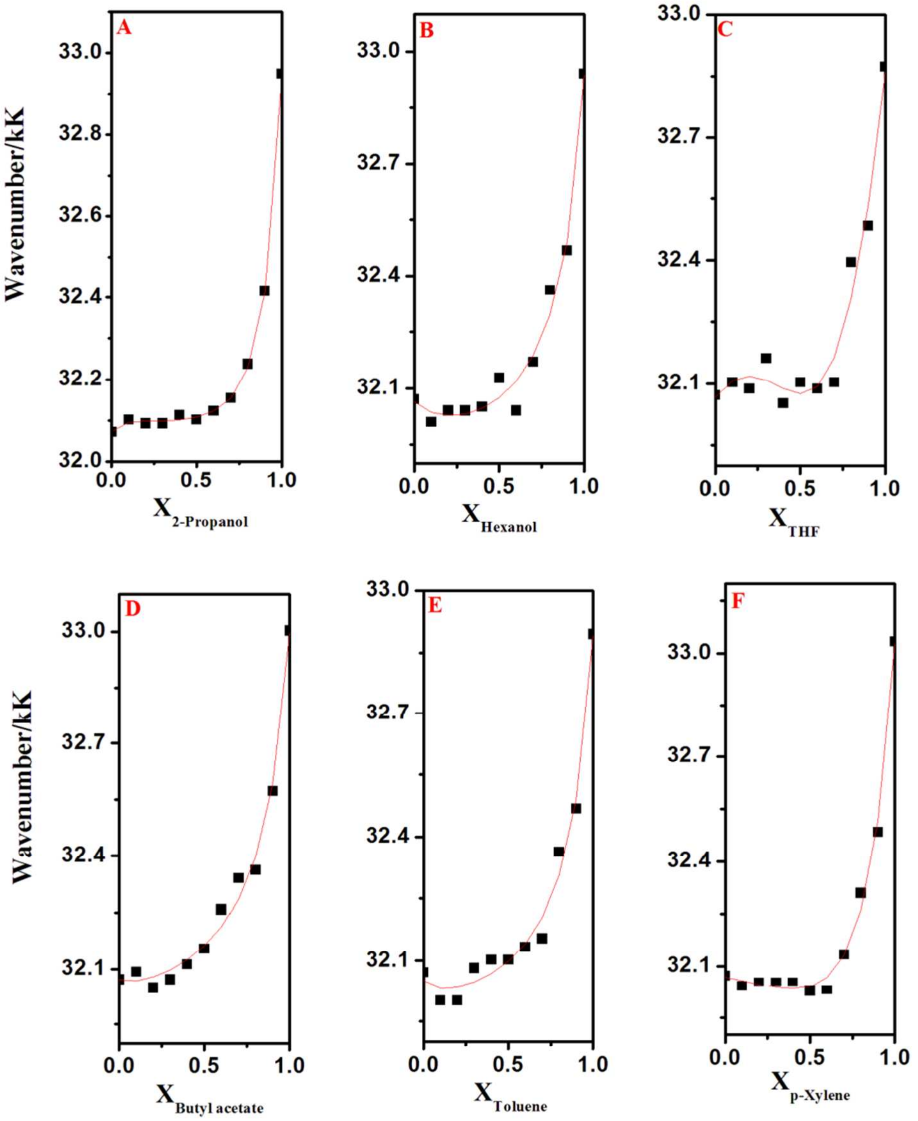

A
B
C
D
E
F
Wavenumber/kK
Wavenumber/kK
33.0
32.8
32.6
32.4
32.2
32.0
32.7
32.1
0.0
0.5
1.0
$X_{2\text{-Propanol}}$
$X_{Hexanol}$
X_{THF}
$X_{Butyl\ acetate}$
$X_{Toluene}$
$X_{p\text{-Xylene}}$

Figure 4.

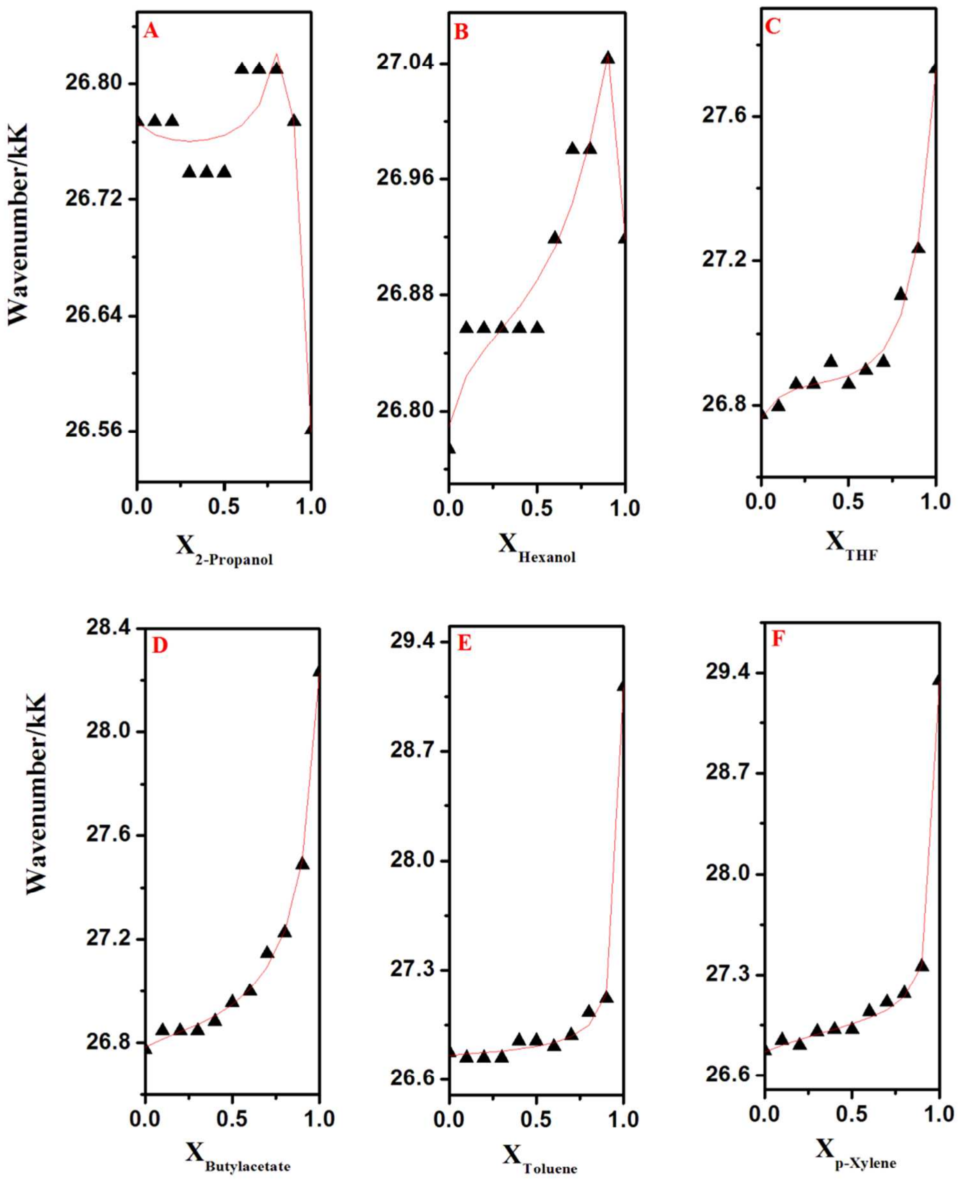

A
Wavenumber/kK
26.80
26.72
26.64
26.56
0.0
0.5
1.0
X2-Propanol
B
27.04
26.96
26.88
26.80
0.0
0.5
1.0
XHexanol
C
27.6
27.2
26.8
0.0
0.5
1.0
XTHF
D
Wavenumber/kK
28.4
28.0
27.6
27.2
26.8
0.0
0.5
1.0
XButylacetate
E
29.4
28.7
28.0
27.3
26.6
0.0
0.5
1.0
XToluene
F
29.4
28.7
28.0
27.3
26.6
0.0
0.5
1.0
Xp-Xylene

Figure 5.

TOC Graphics