Summary
The thermodynamic parameters viz. excess molar volume $V^E$ and ultrasonic speed $u$, transport parameter viscosity $\eta$ and spectroscopic parameters viz. IR, $^1$H, $^{13}$C NMR have been determined for the liquid mixtures of isomeric butanediol and $\alpha, \omega$-alkanediols in non-aqueous medium viz. pyrrolidin-2-one and $N,N$-dimethylformamide in the absence and presence of $\beta$-cyclodextrin over the whole composition range. The partial molar quantities $Q^E$, excess isentropic compressibility $K^E$, deviation in isentropic compressibilities $\Delta\kappa_s$, deviation in ultrasonic speed $u^D$, viscosity deviation $\Delta\eta$, deviation in Gibbs energies of activation for viscous flow $g(x)$ and excess NMR chemical shift $\delta^E$ have also been estimated and analyzed.

**Excess molar volume**

The $V^E$ values are positive for all the mixtures of (BTD + PY) except for 1,4-BTD + PY for which it shows S-shaped behavior and follow the order 1,4-BTD < 1,2-BTD < 1,3-BTD < 2,3-BTD. Positive $V^E$ indicates that the dispersion forces are responsible for the breaking of self-association of diols and PY. The position of hydroxyl groups in BTD caused a noticeable effect on $V^E$. In the presence of $\beta$-CD, the magnitude of $V^E$ in BTD + PY mixtures is different. A comparative analysis of $V^E$ of BTD + ($\beta$-CD + PY) with its parent system i.e. BTD + PY reveals that particularly noticeable are the change with 1,4-BTD in ($\beta$-CD + PY) system. A large volume loss is observed on addition of $\beta$-CD. This has been explained on the basis of fitting of 1,4-BTD molecules in the hydrophobic cavity of $\beta$-CD. The possibility of fitting decreases from 1,4-BTD to 1,2-BTD, as suggested by the comparatively small volume loss at the lower diol mole fraction region. There is negligibly small change in $V^E$ values on addition of $\beta$-CD in the mixtures of 1,3-BTD + PY and 2,3-BTD + PY, indicating absence of complexation of 1,3-BTD and 2,3-BTD with $\beta$-CD.

For $\alpha, \omega$-alkanediols + PY systems, $V^E$ vary in order 1,4-BTD ~ 1,3-PPD < 1,5-PTD < 1,2-ED. The values are positive for 1,2-ED and 1,5-PTD and both negative and positive for 1,3-PPD and 1,4-BTD. The breaking of self-associated diols, particularly in the case of 1,2-ED and non-specific physical interactions of 1,5-PTD with PY (with longer-chain $\alpha, \omega$-alkanediols, attractive interactions between unlike species decrease) dominates, making the $V^E$ positive. Negative $V^E$ values at lower
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mole fraction regions of PY are indicative of the strong interactions between PY and 1,3-PPD and 1,4-BTD. Interaction is mainly because of strong hydrogen bonding between >C=O group of PY and -OH groups of diols. Presence of β-CD makes the $V^E$ positive for all the mixtures of α,ω-alkanediols in (β-CD + PY) except for 1,5-PTD + (β-CD + PY), for which S-shaped behavior is observed. This may be due to the fact that with increase in hydrophobicity, the possibility of fitting of diols in the hydrophobic cavity of β-CD increases. Volume loss for 1,5-PTD in (β-CD + PY), particularly at lower diol concentration region, infer that 1,5-PTD is fitting in the hydrophobic cavity of β-CD. Whereas, the dispersion forces are more prevalent for β-CD in 1,3-PPD + PY system.

Replacing PY with DMF, $V^E$ variation is different. The values are negative for 1,4-BTD, positive for 1,3-BTD and 2,3-BTD and both negative and positive for 1,2-BTD in the mixtures of BTD + DMF. It has been found that in the case of 1,4-BTD strong hydrogen bonding between >C=O group of DMF and -OH groups of 1,4-BTD (which are present on extreme ends of the molecule and are more available to form hydrogen bonding than the other isomers) dominates the breaking of self-associated diols resulting in overall negative $V^E$. As the hydroxyl groups shift from ends (i.e. 1,4-position), the interaction between >C=O group and -OH groups is expected to decrease in the order 1,4-BTD > 1,2-BTD > 1,3-BTD > 2,3-BTD. The breaking of self-associated diols, particularly in the case of 1,3-BTD and 2,3-BTD dominates, making the $V^E$ positive. In comparison, $V^E$ values are negative for the mixtures of 1,4-BTD and 1,2-BTD in β-CD + DMF. Negative $V^E$ values are indicative of strong intermolecular interactions between different components in 1,4-BTD and 1,2-BTD systems. However, $V^E$ values are positive for 1,3-BTD and 2,3-BTD, inferring that dispersion forces are prevalent in these mixtures. The values vary in the order 1,4-BTD < 1,2-BTD < 1,3-BTD < 2,3-BTD. This trend is similar as obtained for BTD + DMF mixtures, however, addition of β-CD in 1,4-BTD + DMF and 1,2-BTD + DMF, resulted in less overall volume, possibly due to occupation of β-CD cavity by 1,4-BTD and 1,2-BTD.

A comparative analysis of $V^E$ values of BTD in (β-CD + DMF) with BTD in (β-CD + PY) support the idea of fitting 1,4-BTD and 1,2-BTD (partially) in
hydrophobic cavity of $\beta$-CD, as the volume loss for these two diol systems is significant in both the solvents i.e. PY and DMF. However, the possibilities of occupation of $\beta$-CD cavity by 1,3-BTD and 2,3-BTD in PY and DMF are much less as indicated by positive $V^E$ values. It may be due to the shortest hydrophobic tail or chain length of 1,3-BTD and 2,3-BTD among all isomer of BTD.

Negative $V^E$ has been obtained for all the mixtures of $\alpha, \omega$-alkanediols and decreases in the order 1,5-PTD < 1,4-BTD < 1,3-PPD < 1,2-ED. Variation in $V^E$ with successive addition of $-\text{CH}_2$ group in these systems is related to an increase in hydrophobicity resulting from the extension of the hydroxyl groups. The results denote a strong dependence on both the diol chain length and the nature of the amide, as can be inferred from the noticeably different results reported for the binary mixtures of the same diols with PY. The $V^E$ is also negative for mixtures of $\alpha, \omega$-alkanediols in ($\beta$-CD + DMF) and decrease in the order 1,3-PPD > 1,2-ED > 1,5-PTD. Large negative $V^E$ values for 1,5-PTD in ($\beta$-CD + DMF) indicate that specific interactions between different components are maximum. The addition of $\beta$-CD in 1,2-ED + DMF and 1,3-PPD + DMF mixtures has negligible effect on $V^E$ value. However, the volumetric behavior of 1,5-PTD in ($\beta$-CD + DMF) system is significantly different from their parent system. Volume loss for 1,5-PTD in ($\beta$-CD + PY), infer that 1,5-PTD is fitting in the hydrophobic cavity of $\beta$-CD due to its largest hydrophobic chain among all the diols under consideration.

Ultrasonic Speeds

The estimated $K^E_s$, $u^D$ and $\Delta \kappa_s$ values from the combination of $u$ and $\rho$ have been analyzed in detail. In the mixtures of BTD + PY, the $K^E_s$ values decrease in the order: 1,3-BTD > 2,3-BTD > 1,4-BTD > 1,2-BTD. The $K^E_s$ values are large negative for 1,2-BTD + PY system. This may be due to the fitting of hydrophobic tail of 1,2-BTD in the cavity of self-associated PY dimer (1,2-BTD has largest hydrophobic tail among all isomers). The trend in $K^E_s$ is different than those of $V^E$, since different shapes of structural isomer affect $K^E_s$ and $V^E$ differently. Trends of $K^E_s$ and $u^D$ are exactly the opposite, as expected and increases in the order 1,3-BTD < 2,3-BTD < 1,4-BTD < 1,2-BTD. The $\Delta \kappa_s$ values are negative for the mixtures of BTD in ($\beta$-CD +
PY) over the entire composition range except for 1,3-BTD, which shows positive behavior and vary in the order 1,4-BTD < 1,2-BTD < 2,3-BTD < 1,3-BTD. The values are large negative for 1,4-BTD system indicating that 1,4-BTD form more compressible species in β-CD + PY than the other isomer of BTD.

The $K_s^E$ values are negative for mixtures of α,ω-alkanediols in PY except for 1,5-PTD in PY, for which it shows S-shaped behavior and vary in the order 1,3-PPD < 1,4-BTD < 1,2-ED < 1,5-PTD. The results show that 1,3-PPD and 1,4-BTD form more compressible species with PY than 1,2-ED and 1,5-PTD. However, on the addition of β-CD in α,ω-alkanediols + PY, positive $\Delta \kappa_S$ values are obtained for 1,2-ED system. Breaking of self-associated 1,2-ED molecules in the mixture may be responsible for this behavior. $\Delta \kappa_S$ values are negative for 1,3-PPD over the entire composition range, however, it shows both positive and negative behavior for 1,5-PTD system.

Using DMF instead of PY in mixtures of BTD, negative $K_s^E$ for 1,4-BTD and 1,2-BTD and positive $K_s^E$ for 1,3-BTD and 2,3-BTD are obtained. Trends of $K_s^E$ and $\nu^D$ are exactly the opposite, as expected. The $\Delta \kappa_S$ values of BTD in (β-CD + DMF) vary in the order 1,4-BTD < 1,2-BTD < 1,3-BTD < 2,3-BTD. A comparison of compressibility of BTD in (β-CD + DMF) with of BTD + DMF, reveals that the addition of β-CD has mainly affected 1,4-BTD and 1,2-BTD as indicated by large negative compressibility factor of 1,4-BTD and 1,2-BTD than without β-CD. This comparison favors the idea of the fitting of 1,4-BTD and 1,2-BTD in the cavity of β-CD. The $K_s^E$ values for mixtures of α,ω-alkanediols + DMF are also negative for all the mixtures that indicates that more compressible species are being formed than pure components. The magnitude of compressibilities follow the order 1,5-PTD < 1,4-BTD < 1,3-PPD < 1,2-ED. In the presence of β-CD, the $\Delta \kappa_S$ values are positive for 1,2-ED in (β-CD + DMF) system, mainly due to breaking of self-associated components in the mixture. $\Delta \kappa_S$ values are negative for 1,3-PPD and 1,5-PTD over the entire composition range. The addition of β-CD has affected 1,5-PTD as indicated by large negative compressibility factor in the presence of β-CD. This comparison again favors the idea of fitting of 1,5-PTD in the cavity of β-CD.
Partial molar quantities

In the dilute PY region, partial molar quantities, $V_i^E$ and $K_i^E$, for the mixtures of BTD + PY show a marked increase from a negative value for 1,4-BTD to a positive value of 2,3-BTD. The negative partial molar quantities are indicative of interaction by hydrogen bonding between >C=O group of PY and -OH groups of 1,4-BTD, which are present on extreme ends of the molecule and are more available to form hydrogen bonding than the other isomers. The breaking of self associated PY and 2,3-BTD > 1,3-BTD > 1,2-BTD > 1,4-BTD seems to be more significant and makes a positive contribution accordingly. A comparison of partial molar quantities for the mixtures of BTD in ($\beta$-CD + PY) with the BTD + PY system also infer that the addition of $\beta$-CD in BTD + PY has a significant effect in 1,4-BTD system. $V_i^{\Delta m}$ and $\Delta K_i^n$ values are highly negative for 1,4-BTD in ($\beta$-CD + PY) than 1,4-BTD in PY.

The $V_i^E$ for mixtures of ($\alpha, \omega$-alkanediols + PY), vary as 1,3-PPD < 1,4-BTD < 1,5-PTD < 1,2-ED. The $V_i^E$ are negative for 1,3-PPD and 1,4-BTD and positive for 1,2-ED and 1,5-PTD. The negative value of partial molar volumes may be taken as a sign of strong interaction between 1,3-PPD and 1,4-BTD and PY through C=O--H-O hydrogen bonding. Whereas dispersion forces and non-specific physical interaction of 1,2-ED and 1,5-PTD with PY are dominating. Negative $K_i^n$ values for all the mixtures except for (1,5-PTD + PY) infer that hydroxyl groups in diols facilitate hydrogen bonding with carbonyl group of PY and these compression effects are maximum for 1,3-PPD. Their magnitude decrease as 1,3-PPD > 1,4-BTD > 1,5-PTD ~ 1,2-ED. In the dilute solvent region, for $\beta$-CD in $\alpha, \omega$-alkanediols + PY, both $V_i^E$ and $\Delta K_i^n$ show a significant increase from a negative value for 1,5-PTD to a positive value of 1,2-ED. Negative values in the case of 1,5-PTD may be taken as a sign of fitting of 1,5-PTD molecule in the hydrophobic cavity of $\beta$-CD (as the 1,5-PTD has longest methylene chain among all measured diols). In DMF mixtures, the $V_i^E$ varies as 1,4-BTD < 1,2-BTD < 1,3-BTD < 2,3-BTD. This trend is similar to as obtained for BTD + PY mixtures. Negative $K_i^n$ values for 1,2-BTD and 1,4-BTD infer that more compressible species are being formed than in 2,3-BTD and 1,3-BTD mixtures, which show positive values. In the presence of $\beta$-CD in (BTD + DMF), the trend of partial
molar quantities is same, however, $V_i^{E,co}$ and $\Delta \kappa_{S,j}^{E}$ values for 1,4-BTD and 1,2-BTD are large negative in comparison to their parent system i.e. BTD + DMF.

The $V_i^{E}$ values are negative for mixtures of $\alpha,\omega$-alkanediols in DMF and vary as 1,2-ED < 1,3-PPD < 1,4-BTD < 1,5-PTD. Negative $K_{S,j}^{E}$ values for all the mixtures imply that hydroxyl groups in diols facilitate hydrogen bonding with the carbonyl group of DMF. For the mixtures of $\alpha,\omega$-alkanediols in ($\beta$-CD + DMF), $V_i^{E}$ are negative for all the mixtures and increase in the order 1,5-PTD < 1,3-PPD < 1,2-ED. Whereas, $\Delta \kappa_{S,j}$ shows a significant increase from a negative value for 1,5-PTD to a positive value of 1,2-ED. Large negative values of partial quantities in the case of 1,5-PTD may be taken as a sign of fitting of 1,5-PTD molecule in the hydrophobic cavity of $\beta$-CD.

**Viscosity**

The estimated $\Delta \eta$ values from $\eta$ for the mixtures of BTD + PY increase in the order 2,3-BTD < 1,3-BTD < 1,2-BTD < 1,4-BTD. The order is reflected in the relative position of hydroxyl groups on each isomer and their ability to form hydrogen bonds with PY. In the mixtures of BTD in ($\beta$-CD + PY), except the lower mole fraction of diol, $\Delta \eta$ values are negative for all the mixtures and increase in the order 2,3-BTD < 1,3-BTD < 1,2-BTD < 1,4-BTD. Large negative values for 2,3-BTD and 1,3-BTD systems show that dispersion forces are predominant in two mixtures. The values for the mixtures of BTD in ($\beta$-CD + PY) in comparison to its parent system are less negative. This may be taken as a sign of modification in intermolecular interactions on addition of $\beta$-CD in the BTD + PY. The $g(x)$ values are negative for all the mixtures except for (PY + 1,4-BTD) for which it shows S-shaped behavior and increase in the order 1,4-BTD < 1,2-BTD < 1,3-BTD < 2,3-BTD. In the presence of $\beta$-CD, $g(x)$ values are positive in the dilute diol concentration region inferring that specific interactions are dominating. At higher diol mole fraction, $g(x)$ values are large negative for all the mixtures, indicating that the dispersion forces are dominating. Negative values of $g(x)$ at higher diol mole fraction region for different BTD in ($\beta$-CD + PY) mixtures increase in order 1,4-BTD < 1,2-BTD < 1,3-BTD < 2,3-BTD. These features also infer that the dispersion forces have more effect in the case of 2,3-BTD and 1,3-BTD mixtures.
For \( \alpha, \omega \)-alkanediols + PY, \( \Delta \eta \) follow the order 1,5-PTD < 1,2-ED < 1,3-PPD. The \( \Delta \eta \) values are large and negative for (1,5-PTD + PY) and positive for 1,3-PPD. In the presence of \( \beta \)-CD, it has been found that with the successive addition of methylene group, an increase in \( \Delta \eta \) values is observed in the order 1,2-ED < 1,3-PPD < 1,5-PTD. The values are positive for the mixtures of 1,5-PTD and 1,3-PPD with \( \beta \)-CD + PY over the entire composition range. The values are negative throughout the composition range for 1,2-ED in (\( \beta \)-CD + PY). A comparative analysis of values of \( \alpha, \omega \)-alkanediols in (\( \beta \)-CD + PY) with its parent system i.e. \( \alpha, \omega \)-alkanediols + PY shows that viscosity behavior is significantly different for 1,5-PTD, which on addition of \( \beta \)-CD shows a transition in \( \Delta \eta \) values from large negative values to large positive values. The \( g(x) \) values decrease from (1,3-PPD + PY) to 1,5-PTD. The values of \( g(x) \) decrease as the strength of intermolecular interactions decreases, which support our assumption of strong interactions between (1,3-PPD + PY) than (1,5-PTD + PY). In the presence of \( \beta \)-CD, the \( g(x) \) decreases from 1,3-PPD + PY to 1,5-PTD. The values are negative for 1,2-ED, positive for 1,3-PTD and both negative and positive for 1,5-PTD. By comparing \( g(x) \) values of \( \alpha, \omega \)-alkanediols in (\( \beta \)-CD + PY) with \( \alpha, \omega \)-alkanediols + PY, it has been found that the addition of \( \beta \)-CD in 1,5-PTD + PY, particularly at lower diol concentration region, show increase in \( g(x) \) values from large negative values to large positive values.

Binary mixtures of DMF with BTD follow the order: 1,3-BTD \( \approx \) 2,3-BTD < 1,4-BTD < 1,2-BTD. The results show that dispersion forces are responsible for dissociation of self-associated diol molecules and the magnitude of dispersion forces are more for 2,3-BTD and 1,3-BTD than 1,4-BTD and 1,2-BTD. In the mixtures of BTD in (\( \beta \)-CD + DMF), \( \Delta \eta \) values are negative for all the mixtures and follow the order 2,3-BTD < 1,3-BTD < 1,2-BTD < 1,4-BTD. The values are less negative in comparison to its parent system i.e. BTD + DMF, which indicate that the addition of \( \beta \)-CD in the BTD + DMF, increases the specific interactions. The negative values of \( g(x) \) for BTD + DMF mixtures, suggest that dispersion forces are responsible for the breaking of self-association of diols that increase as 1,4-BTD < 1,2-BTD \( \approx \) 1,3-BTD < 2,3-BTD. In the mixtures of BTD in (\( \beta \)-CD + DMF), the values are also negative.
for all the mixtures. The magnitude of these forces increase in order 1,4-BTD < 1,3-BTD < 1,2-BTD < 2,3-BTD.

In the mixtures of $\alpha,\omega$-alkanediols + DMF, the $\Delta\eta$ values are negative and vary as 1,2-ED < 1,3-PPD < 1,4-BTD < 1,5-PTD. The results show that the magnitude of dispersion forces is more for 1,5-PTD than 1,2-ED, probably due to the longer alkyl chain length rendering the molecule more flexible. In the presence of $\beta$-CD, with successive addition of methylene group, show increase in $\Delta\eta$ values in the order as 1,2-ED < 1,3-PPD < 1,5-PTD. Positive values are seen for the mixtures of 1,5-PTD with $\beta$-CD + PY except at higher diol composition range. The negative $g(x)$ for the mixtures of $\alpha,\omega$-alkanediols + DMF also suggest that dispersion forces are responsible for the breaking of self-association of diols that increases as 1,5-PTD < 1,2-ED < 1,3-PPD < 1,4-BTD. In the mixtures of $\alpha,\omega$-alkanediols in ($\beta$-CD + DMF), the $g(x)$ values are negative for 1,2-ED and 1,3-PPD, however $g(x)$ values are positive for 1,5-PTD, indicating that specific interactions are prevalent in 1,5-PTD + ($\beta$-CD + DMF), whereas dispersion forces are predominating in the other two mixtures.

Spectroscopic analysis

IR measurements for the mixtures of BTD + PY over the entire composition range show that shift in wave number $\nu$ appears only for hydroxyl groups of BTD, indicating that interactions are taking place through these hydroxyl groups. The change in $\nu$ for $>\text{CO}$ of PY is very small and does not show the regular pattern i.e. non-specific in nature. However, for all other binary and ternary mixtures, it has been found that the shift in wave number $\nu$ appears for hydroxyl groups of diols and $>\text{CO}$ group of amides, indicating that the interactions are taking place through both $-\text{OH}$ and $>\text{CO}$ groups. The $^1\text{H}$ and $^{13}\text{C}$ NMR chemical shifts $\delta$ in these mixtures reveal that there is an appreciable change in $\delta$ values for $-\text{OH}$ protons of diols as a function of mole fraction of diol. However, not much change in $\delta$ values is seen for $-\text{NH}$ proton of PY, $>\text{CO}$ carbon of PY and $-\text{CH}_n$ proton and carbon of PY and diols. Whereas, for the binary mixtures of ($\alpha,\omega$-alkanediols + PY) and ternary mixtures of BTD in ($\beta$-CD + PY) and $\alpha,\omega$-alkanediols in ($\beta$-CD + PY), there is an appreciable change in $\delta$ values for $-\text{OH}$ protons of diols, $-\text{NH}$ proton of PY and $>\text{CO}$ carbon of PY as a function of mole fraction of diol.
In diols + DMF mixtures, the $^1$H and $^{13}$C NMR chemical shifts $\delta$ in the absence and presence of $\beta$-CD, show an appreciable change in $\delta$ values for -OH protons of diols, -HCO proton of DMF and >CO carbon of DMF as a function of mole fraction of diol. However, not much change in $\delta$ values is seen for -CH$_n$ proton and carbon of DMF and diols.

From spectroscopic measurements, it may be concluded that hydroxyl groups of isomeric butanediol are the active sites of interactions in PY + BTD mixtures. However, for all other binary and ternary mixtures, interactions are taking place through both hydroxyl groups of diols and >CO group of amides. In summary, the results show an excellent agreement among thermodynamic, viscosity and spectroscopic parameters. The maximum/minimum values of $^1$H and $^{13}$C NMR excess chemical shift $\delta^E$ and excess molar volume $V^E$ are positioned at about same mole fraction for all the mixtures.