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Solvent dependent frequency shift and Raman noncoincidence effect of S=O stretching mode of Dimethyl sulfoxide in liquid binary mixtures

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ABSTRACT

The isotropic and anisotropic Raman peak frequencies of S=O stretching mode of Dimethyl sulfoxide (DMSO) have been discussed in different chemical and isotopic solvent molecules using different mechanisms. The shifting of peak frequency in further dilution of DMSO with solvent molecule is observed for all solvents. Transition dipole – transition dipole interaction and hydrogen bonding may play a major role in shifting of peak frequencies. The non-coincidence effect (NCE) of DMSO was determined for all the solvents and compared with four theoretical models such as McHale's model, Mirone's modification of McHale's model, Logan's model and Onsager–Fröhlich dielectric continuum model respectively. Most of the theoretical models are largely consistent with our experimental data.

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Introduction

In binary liquid mixtures, the chemical dilution of the reference molecule produces three effects namely, breaking of the liquids structure in the dilution process, change of force law and concentration fluctuation modifying the local chemical composition. These effects lead to the spectral change of both the isotropic and anisotropic Raman components of the reference vibrational mode of solute molecule. The peak frequency shifts of both the isotropic and anisotropic Raman components with the change of solvent concentration provide useful information regarding the solute–solvent interaction and intermolecular forces [1–5]. The well-known phenomenon, Raman noncoincidence effect (NCE) observed in a molecular liquids is the difference in the peak frequencies of anisotropic (ν_{aniso}) and isotropic (ν_{iso}) components of the vibrational band profile of a Raman active vibrational mode i.e. $\nu_{\text{aniso}} - \nu_{\text{iso}} = \Delta\nu$ [6–9]. It arises due to the manifestation of vibrational energy transfer induced by transition dipole–transition dipole (td–td) interaction occurring in the presence of a short-range or long-range orientational order of molecular dipoles [9–15].

The NCE considered as an efficient probe of the structure and dynamics of polar liquids has been studied in a wide variety of molecular liquids [6–36]. In order to describe the dependence of the NCE on concentration in binary liquid mixtures, several

theoretical models [8,10,11,16–18] have been proposed. The models were developed assuming binary liquid mixtures as an ideal solution such that all the concentrations on a mole fraction scale can easily converted into volume fractions. Musso et al. [9] studied NCE in acetone–CCl₄ binary mixtures and found that the relative NCE of C=O mode in non-isotopic mixtures appeared largely consistent with Logan's theory. They observed negative NCE at low solute concentrations and concluded that the spectral asymmetries occurring in the reference mode may be one reason of this phenomenon. Wang and McHale [10] developed a general expression for a coupling Hamiltonian, they concluded that local short range order is not the basic mechanism for NCE, even though its existence can modify the frequency shift between isotropic and anisotropic positions. The NCE may be both positive and negative depending upon the orientation of the dipoles during their interactions [23]. Dipoles that are arranged in either antiparallel side-by-side or parallel head to tail give rise to a positive NCE, whereas if they are in either parallel side-by-side or antiparallel head to head give rise to negative NCE. Giorgini [12] observed that the NCE is large and positive in case of liquid structures dominated by dipolar forces, whereas NCE is negative for those liquids dominated by non-dipolar forces. Torii [13,14] studied the pressure dependence on NCE of liquid methanol with the combination of molecular dynamics simulation. He observed that the NCE decreases with increase in density of the liquid, with the reason that the hydrogen bonds become slightly shorter while other molecules belonging to different hydrogen-bond chain get closer to each other [13]. Giorgini et al. [15] investigated about the sign inversion of NCE

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of acetone in C_6H_6 and C_6D_6 molecules and found that the NCE is positive in the whole concentration range.

Recently, Musso and his coworkers [22,24] used simulation methods such as Monte Carlo (MC), and molecular dynamic (MD) simulations to study the NCE and bandwidth. Such study supports the experimental data while interpreting the interaction between binary liquid mixtures. Torii [25] focused his study on NCE of OH and CO stretching modes in neat methanol as well as in Methanol–LiCl solution using MD simulations. He observed that nature of hydrogen bonding is responsible for the origin of noncoincidence effect of OH and CO stretching vibrations—first case is due to vibrational interaction between hydrogen bonding and second case is due to the weakening of hydrogen bonding by other interacting molecules. Giorgini et al. [26] studied NCE of C=O stretching mode in acetone/DMSO and acetone/ CCl_4 binary liquid mixtures. They found that the NCE of the reference mode in both mixtures exhibits different concentration dependences—one in downward and other in upward pattern. The change in short-range orientational order of acetone in acetone/DMSO and in acetone/ CCl_4 binary liquid mixtures may exhibit different data pattern which was supported by MD simulations and by theoretical predictions.

Various researchers studied about Dimethyl sulfoxide (DMSO) molecule and acquired interesting information about the interacting systems [37–48]. Czeslik et al. [39] studied the effect of pressure and temperature in liquid DMSO. They found that NCE of S=O stretching mode increases with the increase in pressure, whereas the effect of temperature on NCE at constant pressure arises due to change in density. Czeslik et al. [40] also studied the NCE of DMSO confined to porous silica glasses. They found that NCE of DMSO increased with the decrease in pore radius of silica glass. They concluded that the formation of stable dipole–dipole configurations generated between neighbouring dimers may be responsible for this. Vaisman et al. [43] studied pure DMSO and water–DMSO mixtures using molecular dynamics simulations. They found that hydrogen bonding is playing an important role in the interacting systems and the local order in DMSO is determined by dipolar forces as well as molecular association. Sastry et al. [48] performed second derivative analysis of S=O stretching band in Raman spectra of DMSO in CCl_4 and water. DMSO– CCl_4 mixtures may have monomers, cyclic and linear dimers and polymers, whereas DMSO–water systems show the existence of hydrogen bonded complexes in addition to smaller concentrations of monomers, dimers and polymers. However, comparative Raman bandshape studies about this molecule in different chemical and isotopic solvent molecules have not been studied so far. DMSO is an important molecule having wide applications in industrial, medicinal and biological sciences due to its specific properties. DMSO has a great medicinal value as it can not only dissolve substances but also penetrates human skin and carries the dissolved substances along with it. Regarding its properties as carrier molecule and to get more insights of this molecule in interacting phenomena, detailed study of the molecule is needed. So, the present work is focused on the study of NCE of S=O stretching mode of DMSO molecule in chloroform (CLF), chloroform-d (CLFd), acetonitrile (ACN) and acetonitrile- d_3 (ACNd) solvents. An attempt has been made to test the following theoretical models, namely McHale's model, Mirone's modification of McHale's model, Logan's model and Onsager–Fröhlich dielectric continuum model, against our experimental data to probe screening factor effects in liquid binary mixtures.

Experimental

Raman spectra were recorded for S=O stretching band of DMSO at various solute concentration (volume fraction) ranging from 10%

to 100% in CLF, CLFd, ACN and ACNd solvents separately. The samples were of high purity and spectroscopic graded and they are used for analysis without further purification. To record the spectra, a Renishaw RM 1000 Micro-Raman spectroscopic setup equipped with grating of 2400 grooves/mm and a peltier cooled CCD has been used. The software GRAM-32 was used for data collection. The accumulation time for one spectrum was 60 s. The 514.5 nm line of argon ion laser was used as an excitation source. The laser power was maintained at 50 mw. The accuracy of the measurement is believed to be $\pm 0.5 \text{ cm}^{-1}$. The refractive index of liquid mixtures has been measured using Abbe Refractometer at room temperature (25°C). The refractive index of each liquid mixture was measured three times and the average was taken so as to minimize the error. The accuracy of the refractive index is ± 0.001 . The volume concentration of liquid mixtures was prepared using micropipette having accuracy of $\pm 0.005 \text{ ml}$.

Results and discussion

The polarized and depolarized Raman spectra of S=O stretching mode of DMSO were recorded in CLF, CLFd, ACN and ACNd solvents with solute concentration ranging from 10% to 100% separately. The isotropic and anisotropic components of Raman spectra were determined by using the relation [49]

$$I_{\text{iso}}(\nu) = I_{\text{VV}}(\nu) - \frac{4}{3}I_{\text{VH}}(\nu) \quad (1)$$

$$I_{\text{aniso}}(\nu) = I_{\text{VH}}(\nu) \quad (2)$$

where $I_{\text{VV}}(\nu)$ and $I_{\text{VH}}(\nu)$ are Raman intensities of the polarized and depolarized Raman components measured experimentally and ν is the wavenumber in cm^{-1} . The Raman spectrum of neat DMSO for S=O stretching mode is shown in Fig. 1. The isotropic and anisotropic peak frequencies were found to be 1040.3 cm^{-1} and 1046 cm^{-1} respectively. Fig. 2a–d show the variation of the Raman peak frequencies of isotropic (ν_{iso}) and anisotropic (ν_{aniso}) components of S=O stretching mode with solute concentrations ranging from 10% to 100% in CLF, CLFd, ACN and ACNd solvents respectively. The Raman peak frequencies of both components show a red shifting with the increase of solute concentrations in all the four solvents. In DMSO molecule, there may be chances of formation of self-association which may be cyclic and chain dimers [43–48]. However, the amount of self association observed depends upon the nature of the solvent chosen. As we are not getting exactly symmetric spectra of the neat

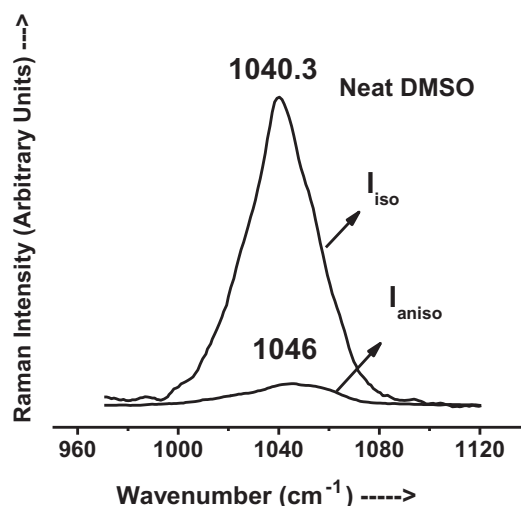


Fig. 1. Raman spectrum of neat DMSO.

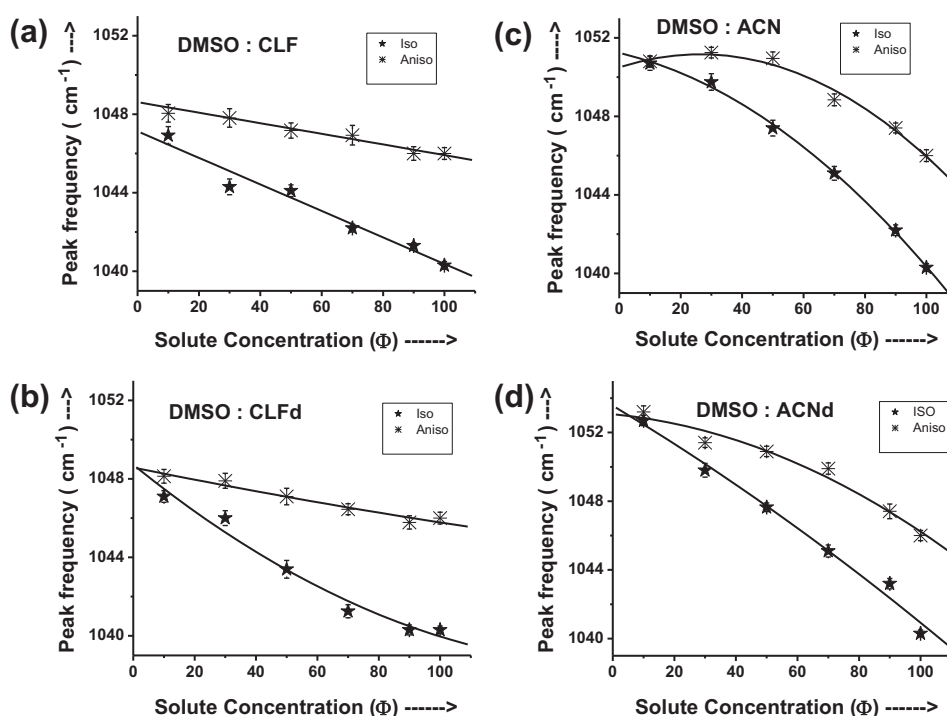


Fig. 2. Variation of isotropic and anisotropic Raman peak frequencies of S=O stretching mode of DMSO as a function of solute concentration at different solvents.

DMSO, there are possible chances of formation of self-association in the molecule. Hence on introducing solvent molecule, the molecules diffuse towards the solute molecules thereby weakening the bonds responsible for self-associated structure. In both CLF and ACN solvents, there is always chance of formation of hydrogen bond between the hydrogen atom present in the solvent and with the lone pair of oxygen or with the sulphur of the solute molecule DMSO. However, the hydrogen atom of CLF or ACN may not approach towards sulphur atom of DMSO due to the presence of steric hindrance offered by CH_3 molecule of the solute. Hence, the chance of hydrogen bond formation with the oxygen atom is more in comparison with the sulphur atom of DMSO. At high dilution the solvent molecules diffuse towards the reference molecule breaking its structure, thereby weakening the dipole–dipole interaction of the solute molecules. This has led to the formation of hydrogen bond $\text{S=O} \cdots \text{H-C}$ in binary mixtures. In CLFd and ACNd solvents, the interaction between solute and solvent may be of form $\text{S=O} \cdots \text{D-C}$ hydrogen bond. The formation of hydrogen bond between molecules leads to shifting of wavenumber to higher region with the increase in solvent concentration or red shifting with the increase in solute concentration [50,51]. In Fig. 2a–d the peak frequencies data do not differ very much in isotropic and chemical solvents. However, the peak frequencies of S=O stretching mode in deuterated solvents CLFd and ACNd are slightly higher than their respective chemical solvents CLF and ACN. This may be due to the difference in $\text{S=O} \cdots \text{H-C}$ and $\text{S=O} \cdots \text{D-C}$ hydrogen bond. The $\text{O} \cdots \text{D}$ distance is smaller than the distance $\text{O} \cdots \text{H}$, leading to shift of peak frequency to higher wavenumber at low solute concentration [52]. From Fig. 2a–d it was also found that the Raman peak frequencies of both the isotropic and anisotropic components of S=O stretching mode in ACN and ACNd solvents are comparatively larger than those in CLF and CLFd solvents. This may be due to high dielectric constant of ACN and ACNd in comparison to CLF and CLFd (Table 1). The higher value of dielectric constant of ACN or ACNd reduces the polarity of DMSO on further dilution of solute.

Variation of the NCE ($\Delta\nu$) of S=O stretching mode of DMSO with the change of solute concentration in all the four solvents is shown in Fig. 3a–d. In our study, the NCE of S=O stretching mode of DMSO is positive in all the four solvents which may be due to either

antiparallel side-by-side or parallel head to tail interaction of the interacting dipoles. The NCE increases on further increase of solute concentration in all the four solvents. The NCE value is proportional to the structure factor ξ which provides information about the local structure of a liquid [40]. The value of NCE increases for stable dipole–dipole configuration in which ξ is positive whereas its value decreases for unstable dipole pairs. This may be the reason that the value of NCE is very less which tends to zero at low solute concentration and high at high solute concentration. Furthermore, NCE arises due to the manifestation of vibrational energy transfer induced by transition dipole – transition dipole interaction occurring in the presence of a short-range and long-range orientational order of molecular dipoles [9–11]. There is a modification in the spatial distributions of the interacting dipoles and their relative alignment on further dilution of the solute. This results to weakening of the pair interaction formed due to cage effect where solvent molecules surround the solute molecule and leads to decrease in non-coincidence effect on further dilution of solute.

In Fig. 3a–d it was found that the NCE disappears faster in ACN and ACNd solvents than CLF and CLFd solvents. Dipole moment of solvents may be playing an important role for the data pattern. The dipole moment of ACN and ACNd solvents are comparatively larger than that of CLF and CLFd solvents (Table 1). As the amount of solute concentration decreases (or increase in solvent concentration), the dipole moment of ACN or ACNd solvent reduces the polarity of DMSO in faster way [26,53].

In Fig. 3a–d we observed convex curvature of NCE with solute concentrations in CLF, CLFd, ACN and ACNd solvents which is in good agreement with the results obtained by various researchers [9,26,53,54]. They observed convex curvature of NCE with respect to solute concentration in binary mixtures having $\epsilon_{\text{solute}} > \epsilon_{\text{solvent}}$, whereas concave curvature for the case of $\epsilon_{\text{solute}} < \epsilon_{\text{solvent}}$. In our study, dielectric constant of solute is larger than the solvent molecules.

To have a clear cut idea about the non-coincidence effect of the liquid mixtures under study, isotropic and anisotropic Raman spectra were examined in terms of peak frequencies and first moments.

Table 1
The molecular parameters of the solute–solvent system. [55,56].

Molecules	Dielectric constant (ϵ)	Dipole moments (μ)/D	Molar mass (M)/kg/mole $\times 10^{-3}$	Density (at 25 °C) (ρ)/kg/m ³ $\times 10^3$
DMSO	46.70	3.96	78.13	1.1004
CLF	4.81	1.04	119.38	1.4830
CLFd	4.81	1.10	120.39	1.5000
ACN	37.50	3.91	41.05	0.7810
ACNd	37.50	3.50	44.07	0.8390

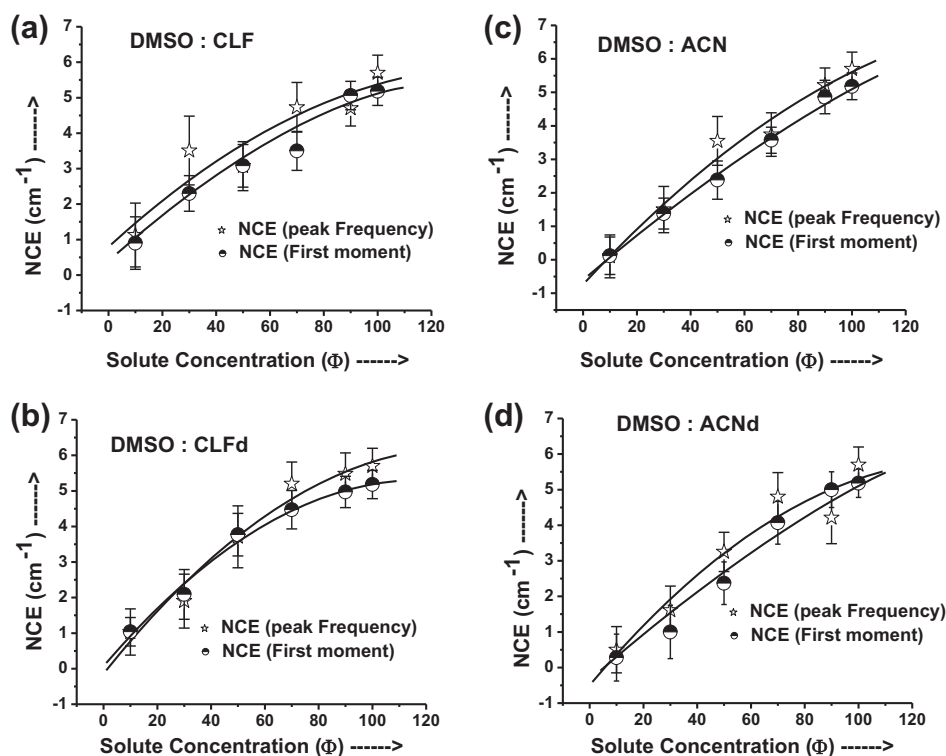


Fig. 3. Variation of NCE of S=O stretching mode of DMSO as a function of solute concentration at different solvents.

The NCE determined from the first moments $M_{aniso} - M_{iso} = \Delta M_{NCE}$ were plotted with solute concentration (Fig. 3). In Fig. 3a–d it was found that both $\Delta\nu$ and ΔM_{NCE} show similar data pattern in all the solvents under study [15].

Various models were developed to study the non-coincidence effect (NCE) phenomena in liquids and its dependency on concentration. Some of the models are examined with our experimental data [11,17,20,36]. We have chosen $\Delta\nu$ data to study various models developed for NCE.

The splitting term in the transition dipole coupling model is given by [11]

$$\Delta\nu = \frac{2\mu^2 \left(\frac{\partial\mu}{\partial Q} \right)^2}{25\pi^2 m\nu_0 kTd^3} \frac{N_0}{V_M} \frac{\phi}{\epsilon^2} \quad (3)$$

where μ is the dipole moment, ν_0 and Q are the vibrational frequency and the normal coordinates of the isolated molecule, V_M is the molar volume of the solute, d is the minimum intermolecular distance, N_0 is the Avogadro's number, kT is the thermal energy, ϕ is the volume fraction (concentration) of solute and $\Delta\nu$ is the peak frequency difference ($\nu_{aniso} - \nu_{iso}$) at different solute concentration.

The dielectric constant of the solution is given as

$$\epsilon = \epsilon_1(1 - \phi) + \epsilon_2\phi \quad (4)$$

where ϵ_1 and ϵ_2 are dielectric constants of solvent and solute respectively.

Applying Eq. (4) in the above Eq. (3), McHale [11] formulated an expression for relative splitting $\left(\frac{\Delta\nu}{\Delta\nu_{neat}} \right)$ to study the dependence of NCE on the dielectric constant and solute concentration given by

$$\frac{\Delta\nu}{\Delta\nu_{neat}} = \frac{\epsilon_2^2\phi}{[\epsilon_1(1 - \phi) + \epsilon_2\phi]^2} \quad (5)$$

or,

$$\frac{\Delta\nu}{\Delta\nu_{neat}} = \frac{\phi}{[\phi(1 - x) + x]^2}, \quad (6)$$

where

$$x = \frac{\epsilon_1}{\epsilon_2} \quad (7)$$

$\frac{\Delta\nu}{\Delta\nu_{neat}}$ was calculated theoretically using the Eq. (6). Molecular parameters of solute and solvent molecules used to determine the relative splitting using Eq. (6) are given in Table 1. The experimental data obtained from Raman bandshape was used to find experimental $\frac{\Delta\nu}{\Delta\nu_{neat}}$. The relative splitting $\left(\frac{\Delta\nu}{\Delta\nu_{neat}} \right)$ value determined from experimental and theoretical data were plotted with the solute concentrations in all the four solvents (Fig. 4a–d). In CLF and CLFd solvents, the theoretical curve (shown in solid line) of McHale's model are found decreasing exponentially with the increase in solute concentration while the experimental data (shown in dotted line) increases with the increase in solute concentration

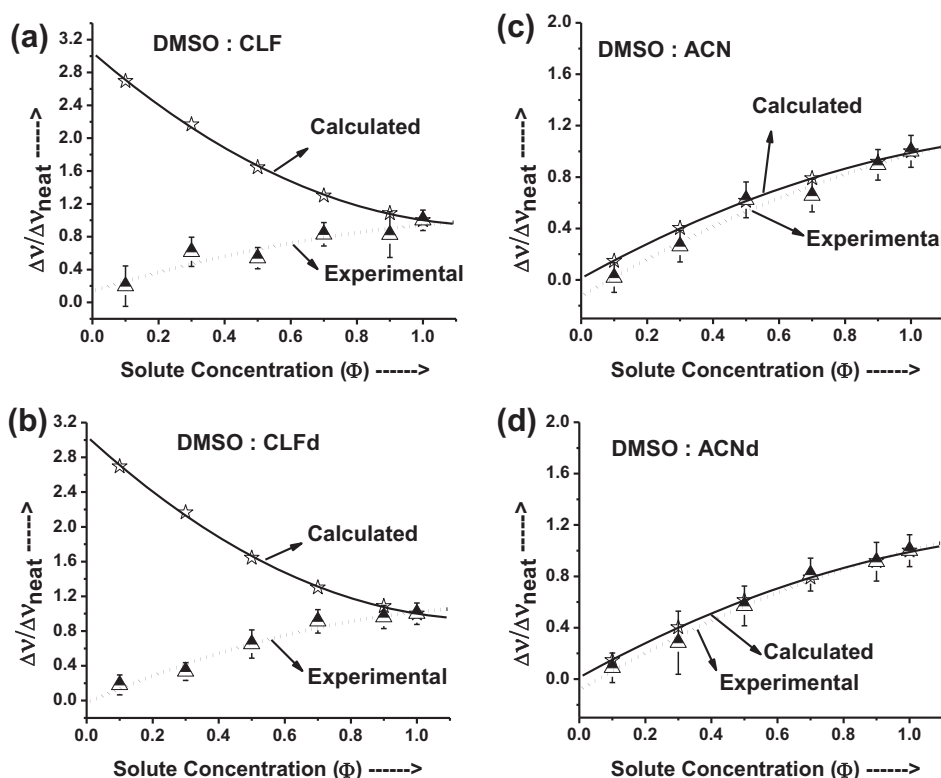


Fig. 4. Variation of relative splitting ($\frac{\Delta v}{\Delta v_{neat}}$) of both the experimental (dotted line) and calculated (solid line) values from McHale's model as a function of solute concentration.

(Fig. 4a–b). Hence, the model fails in predicting the relative NCE of our experimental data. This may be due to the fact that dielectric constant of solute ($\epsilon_2 = 46.7$) is about ten times greater than that of solvent ($\epsilon_1 = 4.81$) i.e. $\epsilon_1 \ll \epsilon_2$ or $x \ll 1$, which leads a large value of relative splitting at the region of low solute concentration. McHale's model [11] could justify the plots of Mirone and Fini for $x > 1$, $x = 1$ and $x < 1$ cases. However, his model did not discuss for the case $x \ll 1$ and it seems that the model might not obey the data patterns discussed above. This may be the reason of getting different calculated and experimental data pattern at $x \ll 1$. However, both the experimental and calculated values of $\frac{\Delta v}{\Delta v_{neat}}$ in ACN ($\epsilon_1 = 37.5$) and ACNd ($\epsilon_1 = 37.5$) solvents are found having similar data patterns which are increased exponentially with the increase in solute concentration. Theoretical data fall within the error bars of experimental data and thus the graphs in ACN and ACNd solvents are found in better agreement with McHale's model for $\epsilon_1 < \epsilon_2$ [11]. Negligence of other molecular parameters which play important role in interacting systems may lead to failure of this model.

Considering these shortcomings, Mirone [18,36] modified McHale's model and the modified equation is given as

$$\frac{\Delta v}{\Delta v_{neat}} = \left(\frac{2\epsilon_2 + n_2^2}{n_2^2 + 2} \right)^2 \left(\frac{n^2 + 2}{2\epsilon + n^2} \right)^2 \frac{\epsilon}{\epsilon_2} \phi \quad (8)$$

$$= P\phi, \quad \text{where } P = \left(\frac{2\epsilon_2 + n_2^2}{n_2^2 + 2} \right)^2 \left(\frac{n^2 + 2}{2\epsilon + n^2} \right)^2 \frac{\epsilon}{\epsilon_2}$$

where ϕ is the concentration of the solute, ϵ is the dielectric constant of the mixture, n is the refractive index of the solution, n_2 and ϵ_2 are the refractive index and the dielectric constant of solute respectively.

The values of refractive index (n) have been measured experimentally. The value of ϵ is determined using Eq. (4). The value of $\frac{\Delta v}{\Delta v_{neat}}$ is measured experimentally from Raman bandshape, while

the right hand side of Eq. (8) is calculated using the values of molecular parameters shown in Tables 1 and 2. The two parameters $\frac{\Delta v}{\Delta v_{neat}}$ and $P\phi$ are plotted as a function of solute concentration in all the four solvents shown in Fig. 5a–d. In these figures, data pattern of $\frac{\Delta v}{\Delta v_{neat}}$ and $P\phi$ are found to increase at higher concentrations of solute. However, the data patterns of two parameters are found slightly different in CLF and CLFd solvents. This may be due to the high dielectric constant of solute ($\epsilon_2 = 46.7$) compared

Table 2

Refractive index of neat liquid and liquid binary mixtures measured experimentally.

Mixture	Solute concentration (Φ)	Refractive index (n)
DMSO	1.0	1.476
DMSO-CLF1	0.9	1.474
DMSO-CLF3	0.7	1.465
DMSO-CLF5	0.5	1.460
DMSO-CLF7	0.3	1.458
DMSO-CLF9	0.1	1.454
DMSO-CLFd1	0.9	1.473
DMSO-CLFd3	0.7	1.465
DMSO-CLFd5	0.5	1.460
DMSO-CLFd7	0.3	1.456
DMSO-CLFd9	0.1	1.453
DMSO-ACN1	0.9	1.454
DMSO-ACN3	0.7	1.428
DMSO-ACN5	0.5	1.414
DMSO-ACN7	0.3	1.391
DMSO-ACN9	0.1	1.365
DMSO-ACNd1	0.9	1.460
DMSO-ACNd3	0.7	1.440
DMSO-ACNd5	0.5	1.418
DMSO-ACNd7	0.3	1.392
DMSO-ACNd9	0.1	1.365
CLF		1.449
CLFd		1.448
ACN		1.344
ACNd		1.341

to solvents CLF ($\epsilon_1 = 4.81$) and CLFd ($\epsilon_1 = 4.81$) respectively. According to Mirone [18] a much lower value of dielectric constant of solute should be taken to minimize discrepancy of data for $\frac{\Delta v}{\Delta v_{neat}}$. The theoretical and experimental curves are found almost coincide in ACN and ACNd solvents and minimum difference of dielectric constants of solute and solvent may lead to better consistency of the data. Hydrogen bonding may be responsible for the slight departure of the experimental results from the calculated value, as it may change the orientational alignment of transition dipole moment during the interaction [47].

To investigate the concentration dependence of the relative splitting of Raman NCE, Logan developed a theoretical model, which gives the following relation [17]

$$\frac{\Delta v}{\Delta v_{neat}} = \frac{[1 + 1.25Y_0(\phi)]}{[1 + 2.5Y_0(\phi)]^2} \frac{[1 + 2.5Y_0(1)]^2}{[1 + 1.25Y_0(1)]} \phi \quad (9)$$

$$Y_0(\phi) = \xi \left[\phi + \left(\frac{\mu_1}{\mu_2} \right)^2 \frac{1 - \phi}{R} \right] \quad (10)$$

$$\xi = \frac{\mu_2^2 \rho(1)}{72 \epsilon_0 k T} \quad (11)$$

where ϕ is the solute concentration (volume fraction), μ_1 and μ_2 are the dipole moments of solvent and solute respectively, R is the ratio of molar volumes of solvent and solute $\left(\frac{V_M^s}{V_M^l} \right)$, $\rho(1)$ is the number density of the neat solute, ϵ_0 is the permittivity of a vacuum, k is the Boltzmann's constant and T is the absolute temperature.

$\frac{\Delta v}{\Delta v_{neat}}$ was calculated theoretically using the Eq. (9) by using the following parameters: $\epsilon_0 = 8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$, $T = 298 \text{ K}$, $k = 1.3806 \times 10^{-23} \text{ J K}^{-1}$ and other parameters are given in the Table 1. The experimental $\frac{\Delta v}{\Delta v_{neat}}$ was determined from the experimentally measured Raman bandshape. Both the experimental and

calculated values were plotted as a function of solute concentration in all the four solvents shown in Fig. 6a–d. In these figures, theoretical and experimental data are found increasing with the increase of solute concentration. The experimental $\frac{\Delta v}{\Delta v_{neat}}$ data pattern shows a slight departure from the linearity over the whole range of solute concentration and most of the experimental data points are slightly deviated from the calculated data. In Fig. 6a–d it was found that the variation of the calculated $\frac{\Delta v}{\Delta v_{neat}}$ data as a function of solute concentration in CLF and CLFd solvents are exponential curves and give a positive deviation from the linearity, while in ACN and ACNd solvents the variation of calculated $\frac{\Delta v}{\Delta v_{neat}}$ data is a straight line. This may be due to the dependence of relative splitting on the relative dipole moments of solute and solvent molecules [17]. In CLF and CLFd solvents, the relative dipole moment $\left(\frac{\mu_1}{\mu_2} < 1 \right)$ is less than one; while in ACN and ACNd solvents, $\frac{\mu_1}{\mu_2} \approx 1$. This may lead to different data patterns in all the four solvents.

McHale's [11,20] theoretical expression for Δv is given by

$$\Delta v = \frac{2\mu^2 \left(\frac{\partial \mu}{\partial Q} \right)^2}{25\pi^2 c^2 v_0 k T d^3} \frac{N_0}{V_M} \phi S \quad (12)$$

where μ is the dipole moment, v_0 and Q are the vibrational frequency and the normal coordinates of the isolated molecule, V_M is the molar volume of the solute, d is the minimum intermolecular distance, N_0 is the Avogadro's number, kT is the thermal energy and S is the screening factors for the interaction energy of the two dipoles. S comprises two factors, S_p and S_t related respectively to the interaction of permanent and transition dipoles. According to the dielectric model of Onsager–Fröhlich, these two factors are given as

$$S_p = \left(\frac{n^2 + 2}{2\epsilon + n^2} \right)^2 \epsilon \quad (13)$$

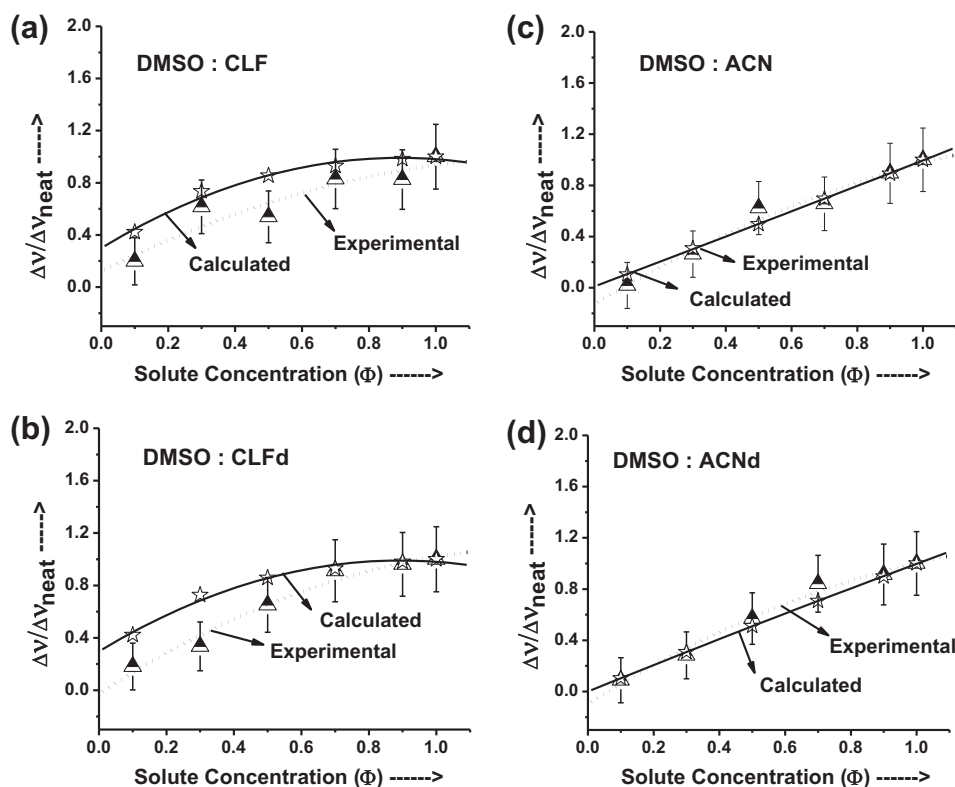


Fig. 5. Variation of relative splitting $\left(\frac{\Delta v}{\Delta v_{neat}} \right)$ of both the experimental (dotted line) and calculated (solid line) values from Mirone's modification of McHale's model as a function of solute concentration.

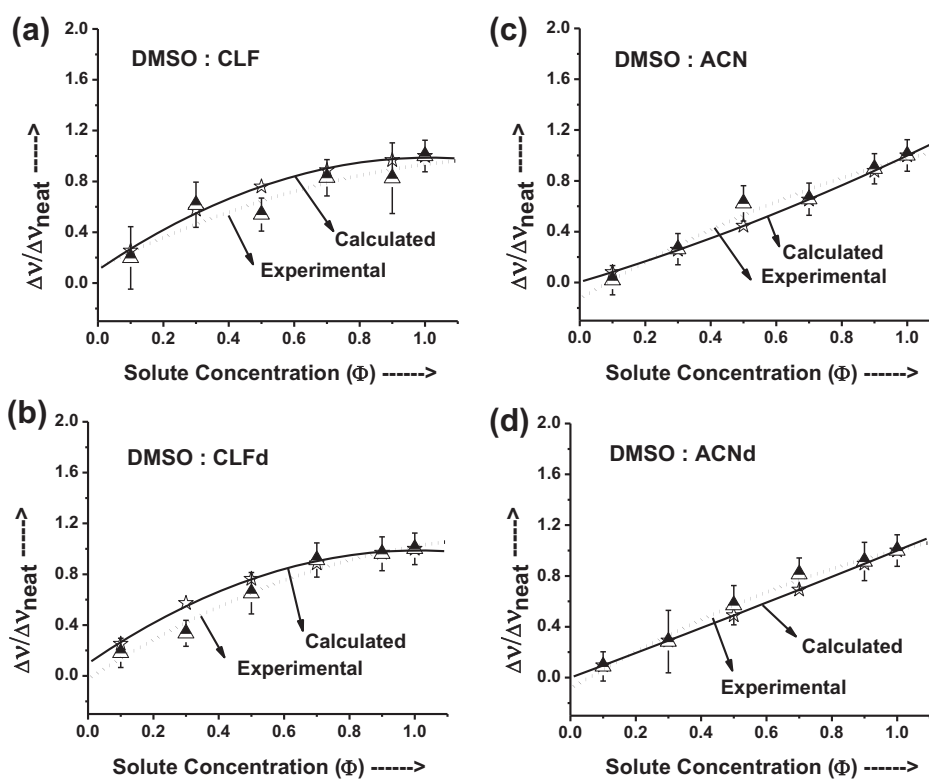


Fig. 6. Variation of relative splitting ($\frac{\Delta v}{\Delta v_{neat}}$) of both the experimental (dotted line) and calculated (solid line) values from Logan's model as a function of solute concentration.

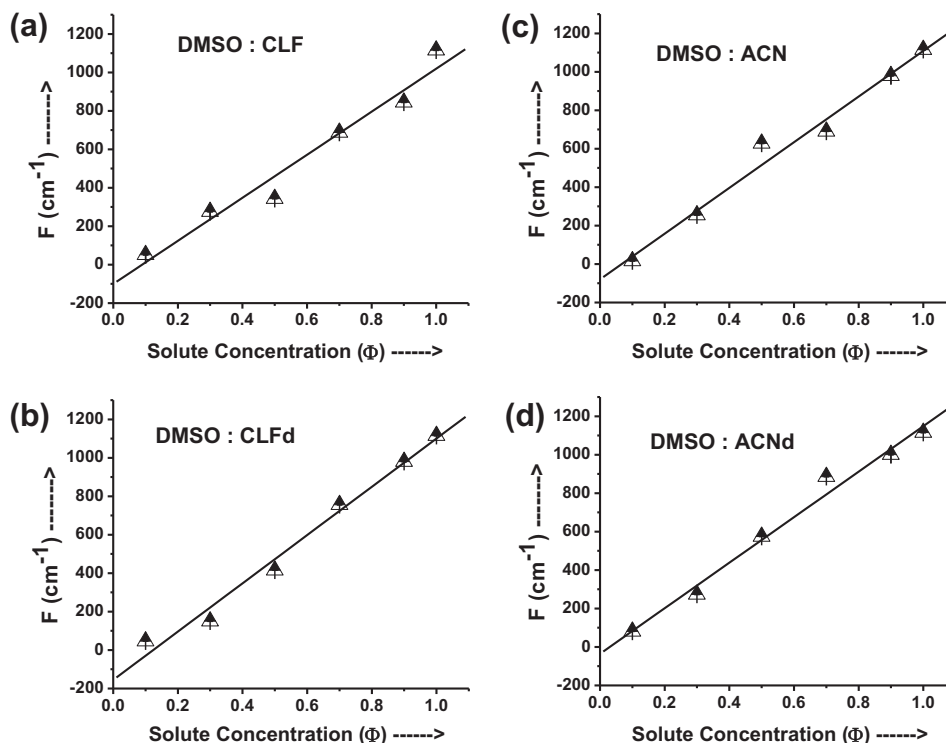


Fig. 7. Variation of $F = \Delta v(2\epsilon + n^2)^{\frac{1}{2}}$ as a function of solute concentration in CLF, CLFd, ACN and ACNd solvents.

and

$$S_t = \left(\frac{n^2 + 2}{2\epsilon_\infty + n^2} \right)^2 \epsilon_\infty \quad (14)$$

where ϵ is the static dielectric constant of the medium, ϵ_∞ is the dielectric constant at infinite frequency and n is the refractive index of the solute. The screening factor S_t does not vary much with the variation of the solvent, hence the term S_t can be considered as a

constant. Therefore, considering only S_p term, Eq. (12) takes the form

$$\Delta\nu(2\varepsilon + n^2)^2 \frac{1}{\varepsilon} = \frac{2\mu^2 \left(\frac{\partial\mu}{\partial Q}\right)^2 (n^2 + 2)^2}{25\pi^2 c^2 \nu_0 k T d^3} \frac{N_0}{V_M} \phi \quad (15)$$

To examine the Onsager–Fröhlich dielectric continuum model in our binary liquid system, the values of the parameter $F = \Delta\nu(2\varepsilon + n^2)^2 \frac{1}{\varepsilon}$ were determined using experimentally determined values of $\Delta\nu$, n and calculated values of ε using Eq. (4). The parameter (F) values are plotted as a function of solute concentration in all the four solvents shown in Fig. 7a–d. In these figures, the data points of F are found increasing linearly with the increase of solute concentration in all the four solvents. The linear dependence of the data point of F with solute concentration indicates that Onsager–Fröhlich dielectric continuum model holds good in all the four binary mixture systems chosen under study.

Conclusion

The solvent dependence of isotropic and anisotropic Raman peak frequencies of S=O stretching mode of DMSO was studied in CLF, CLFd, ACN and ACNd solvents. Peak frequency shifting was discussed using different mechanism. The peak frequency shifting is slightly higher in isotopic solvents than in their respective chemical solvents. Peak frequency shifting strongly depends on the concentration of the solvents. Hydrogen bonding may be playing an important role in shifting of peak frequencies. Variation of NCE as a function of solute concentration was discussed. Four theoretical models on NCE, namely McHale's model, Mirone's modification of McHale's model, Logan's model and Onsager–Fröhlich dielectric continuum model have been tested. Most of the theoretical models are in good agreement with our experimental data.

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