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A New Approach to Explain Concentration-Dependent Changes of Isotropic Raman Line Width in the Associated Binary Mixtures

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We report on a new empirical relationship to explain the concentration-dependent isotropic Raman line width changes of a vibrational mode in uniform binary mixtures. The factors contributing to the intrinsic line width and several other broadening mechanisms are, in general, concentration-dependent. Concentration fluctuation in a microscopic volume and microviscosity are the two factors that are known to cause a concentration-dependent line width variation. These two factors combined in a specific manner successfully explain the variation of the line width with concentration strongly associated with binary systems. A readily usable empirical relationship for line width is suggested. It has been demonstrated that it can successfully explain the line width variation with concentration in a given class of hydrogen-bonded systems taking some representative binary mixtures.

1. Introduction

An added advantage of Raman spectroscopy to study vibrational dephasing processes in liquid mixture is primarily due to the fact that the contributions to the experimental Raman line width originating from vibrational dephasing and reorientational motion can be separated out by polarized Raman measurement[1,2] by using the following relationships

$$I_{\mathrm{iso}}(\omega) = I_{\|}(\omega) - (4/3)I_{\perp}(\omega)$$

and

$$I_{\mathrm{anis}}(\omega) = I_{\perp}(\omega) \tag{1}$$

where $I_{\|}$ and $I_{\perp}$ are the experimentally measured parallel and perpendicular components of the Raman scattered intensity, respectively. The $I_{\mathrm{iso}}(\omega)$ is the isotropic contribution, which is directly related to the vibrational dephasing, and $I_{\mathrm{anis}}(\omega)$ is the anisotropic contribution to the Raman line profile coming from the reorientational motion. This methodology has extensively been applied to study vibrational dephasing in many associated/nonassociated systems.[3−13] In recent years, this aspect of Raman spectroscopic technique has been employed to study the hydrogen-bonded systems, and attempts have been made to explain the experimental results using existing models.[1,13−15] In all these studies, mostly the crucial parameter to be analyzed was the line width. However, it was experienced during the course of these studies that the experimental results on both the concentration-dependent wavenumber shifts and the line width changes in all kinds of binary systems are not explained satisfactorily by any of the existing models, and this point was brought out rather clearly by Morresi et al.[1] The concentration fluctuation model suggested by Bondarev and Mardaeva[13] is successful in explaining the line width of ν(C−H) stretching vibration in noninteracting systems, but it fails badly in those systems where hydrogen bonds are formed between the solute and solvent molecules, in general, especially when the difference in the viscosities of the solute and the solvent is relatively large or, at least, appreciable. The vibrational dephasing in the hydrogen-bonded $C_5H_5N + CH_3OH$ system was explained[3] using the concentration fluctuation model proposed by Bondarev and Mardaeva,[13] which predicts essentially a linear concentration dependence of the wavenumber shift of the normal mode under study. The experimentally measured line width was considered to have two contributions, one due to intrinsic line width and the other one due to the concentration fluctuation, the two contributions being additive. The contribution due to concentration fluctuation is expected to have a maximum when the number of solvent and solute molecules are equal (mole fraction of the reference system, $C = 0.5$) according to this model.[13] This simple model, however, fails to explain the experimental results on wavenumber shifts and line width changes in many hydrogen-bonded systems.[7−8,11]

The problem of intermolecular vibrational relaxation in liquids was studied by Woerkom et al.[14] also, but they confined their studies to the experimental data obtained from isotopic dilution measurements and the interpretation of isotopic dilution effect, especially amplitudes of wavenumber shift ($\Delta\Omega$) and line width change ($\Delta\Gamma$) between neat liquid and infinite dilution, in terms of the transition dipole−transition dipole coupling. In this context, it is to be noted that the isolated binary collision (IBC) model of Fischer and Laubereau[15] was based on a semiclassical collision theory to describe the dephasing of vibrationally excited molecules in a liquid. In this work, the nonresonant contribution of the repulsive part of the interaction potential to the dephasing rate was estimated. In a recent work,[5] the IBC model was extended to include the resonant transfer of the vibrational quantum to the neighboring molecule, and it was quite successful. The work is being further extended[16] to include also the resonant contribution of the repulsive interaction and resonant as well as nonresonant part of the attractive interaction to the overall dephasing rate, which ultimately decides the line width. Schweizer and Chandler[17] developed another phenomenological theory where the repulsive and slowly varying attractive forces were taken into account and the induced wavenumber shifts were related to the line broadening and

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dephasing rate. This theory, however, is too complicated to apply in a practical problem so as to give some meaningful quantities, which could be compared directly to an experimentally measured quantity.

The simple model of Bondarev and Mardaeva[13] was further extended for the nonlinear concentration dependence for the isotropic line width of the vibrational mode, where Ω is simply replaced by the gradient of the shift, $d\Omega/dC$ at each mole fraction by Fujiyama et al.[18] Knapp and Fischer[19] extended this model by introducing a discrete binomial distribution function of the nearest neighbor molecules and by including two-particle exchange processes. This model, however, in our viewpoint, requires a lot of computational efforts and it is also cumbersome, but for no major gain. Other more general theories for the Raman line shapes in liquids were given by Bratos and coworkers.[20,21] In the approximation of the lattice gas model and for slow modulation, they also get a similar expression as Fujiyama et al.[18] for the isotropic part of the vibrational Raman band in case of isotopic mixtures. But for binary mixtures of different kinds, they were also able to give only some general trends and not an explicit expression, probably due to the complexity of the problem. We believe that the discrepancy is due to several other factors, such as viscosity, refractive index, and rate of diffusion of solvent into solute matrix, and these factors influence the wavenumber and line width of any vibrational mode of the solute molecule in binary mixtures to an appreciable extent, but they have not been addressed adequately in a single model so as to give a comprehensive picture.

The basic motivation for this study comes from the fact that the vibrational motion of the molecule is well affected by the surrounding medium, which includes the factor whether the surrounding medium is less or more viscous than the reference system. If the surrounding medium is less viscous, then the vibrational motion of the reference molecule is relatively more free than in the case when the surrounding medium is more viscous, and consequently, the vibrational motion of the reference molecule is somewhat damped. This essentially means that in both cases the lifetime of the vibrational mode of the reference molecule is affected by the surrounding. We have, therefore, attempted in the present study to include the effect of microviscosity to the line width change caused due to the change of microviscocity at different relative concentrations of the solute and the solvent as well as the effect of concentration fluctuation at the microlevel. Assuming these two contributions to be additive, a relationship has been suggested on the basis of an empirical model. This relationship has been applied successfully to explain the line width changes with concentration in different strongly associated systems, where concentration fluctuation alone was not adequate to explain the experimental results.

2. Emprical Relationship

Bondarev and Mardaeva[13] suggested a linear relationship between the wavenumber of the vibrational mode in question and the concentration of the reference molecule in mole fraction, C, as

$$\nu(C) = \nu_0 + C\Delta\Omega \tag{2}$$

where $\Delta\Omega$ is the amplitude of the wavenumber shift between the neat liquid and infinite dilution. A linear relationship as given in eq 2 explains the experimentally measured wavenumber shift with concentration in binary mixtures in a large number of cases. There are, however, such cases also where a significant deviation from the linear relationship is observed,[2,8,12,22] which poses limitation on the applicability of this model.[13] On changing the concentration, the different parameters change depending upon the relative concentration of the solute and the solvent in the binary system. The change in refractive index is one of such parameters, which is usually quite small, differing only at the third/fourth place of decimal. However, the line width changes considerably with another parameter, viscosity, as pointed out by Morresi et al.,[1] and we thought that viscosity might be one of the major factors to account for the discrepancies between the experimental results and the results expected if the concentration fluctuation model of Bondarev and Mardaeva[13] were to work. According to this model,[13] the random motion of the reference and the solvent molecules in the mixture causes the concentrations in the different microvolumes to fluctuate around a mean value. The two effects, namely wavenumber shift and concentration fluctuation result into a Gaussian-type line width variation peaking at $C = 0.5$, which is expressed by the following relationship

$$\Gamma_c = 2(2\ln 2)^{1/2}\Delta\Omega\left[\frac{C(1-C)}{n}\right]^{1/2} \tag{3}$$

where n is the number of the neighboring molecules influencing the reference mode. Considering the above contribution, Γ_c, to the line width and the intrinsic line width, Γ_i, to be additive, the total line width at concentration C, $\Gamma(C)$ can be expressed as

$$\Gamma(C) = \Gamma_c + \Gamma_i \tag{4}$$

It is to be noted that eqs 2 and 3 are interrelated through $\Delta\Omega$ and result in a maximum at $C = 0.5$ in the line width vs concentration plot for an ideal case where molecules of the solute and solvent are almost noninteracting. It is obvious that if $\Delta\Omega$ would be large, the variation of line width about its mean value at $C = 0.5$ would also be large. There are, however, practical cases where the line width change with concentration is large despite $\Delta\Omega$ being small. In such cases, the maximum shifts on either side of $C = 0.5$ cannot be explained using the Bondarev and Mardaeva[13] model. These authors[13] have themselves pointed out that eq 3 holds good only for ideal or noninteracting systems. If the solute−solvent system consists of interacting molecules, the maximum may shift toward higher concentration. In such a case, the concentration in mole fraction, C, has to be replaced by activity, γC, where $\gamma < 1$. It is to be noted that Rothschild[24] pointed out very clearly in his explanation for the line broadening by concentration fluctuation at $C = 0.5$ that in an nonideal situation, which essentially refers to the shift of maximum on either side of $C = 0.5$ in the $\Gamma(C)$ vs C plot, the mole fraction should be replaced by the activity $a = \gamma C$. Taking into account the activity in place of concentration, it is possible to explain the shift of maximum toward the higher concentration or a consistent decrease in line width upon dilution, but the shift of the maximum toward lower concentration or an increase in line width upon dilution cannot be explained on the basis of concentration fluctuation model,[13] even after replacing C by the activity, a. In a recent experimental study made by Oehme et al.,[25] the concept of a negative cross term between different dephasing mechanisms leading to a broadening of the isotropic Raman line upon isotopic dilution and wavenumber shift with concentration in isotopic mixtures of nitrogen as well as oxygen at near to boiling temperature of nitrogen has been discussed in a lucid manner. Thus it becomes obvious that in order to explain the line width variation with concentration in the interacting systems, such as hydrogen bonded systems, some additional factors need to be considered. It is well-known that, in pure liquids, the viscosity influences the line width.[1] Hence, viscosity may be one of the crucial factors to be accounted for rather carefully. To see the effect at the molecular level, however, instead of dynamic viscosity, the concept of microviscosity[23] has been used to study the solute–solvent interaction. The dynamic viscosity of the mixture would vary significantly with molar ratio of the solute and the solvent and, consequently, also the microviscosity, when the difference between the viscosities of the reference (solute) and the solvent is appreciable. The microviscosity, η_m, may be calculated using the relationship[26]

$$\eta_m = \mu\eta = \eta[0.16 + 0.4(r_1/r_2)] \tag{5}$$

where μ is the microfriction parameter, η is the dynamic viscosity, and the parameters r_1 and r_2 are the radii of the solute and the solvent molecules, respectively. We have calculated the microfriction parameter for the neat liquid as well as the mixtures, which are represented by μ_1 and μ_2, respectively. For the neat liquid, obviously r_1 and r_2 are equal and in the case of mixtures the values of $r_1$and r_2 are different, depending upon the binary system used. Using this approach, on the basis of the experimental results on different systems, we arrived at the following empirical relationship for concentration-dependent line width

$$\Gamma(C) = \Gamma_c + \Gamma_i(\eta_c) \tag{6}$$

where the second term in eq 6 is expressed as

$$\Gamma_i(\eta_c) = \Gamma_i \exp\left[-a\left(1 - \frac{\mu_2\eta_c}{\mu_1\eta_{\text{solute}}}\right)\right] \tag{7}$$

The value of η_c may be evaluated in terms of the viscosities of the solute, η_{solute}, and of the solvent, η_{solvent}, as

$$\eta_c = \eta_{\text{solute}}C + \eta_{\text{solvent}}(1 - C) \tag{8}$$

To provide a physical basis for taking an exponential form for the second term in eq 7, an analogy may be drawn from the temperature dependence of the line width, where the temperature-dependent contribution to the line width is expressed by Rakov's relationship[27]

$$\Gamma(T) = \Gamma_0 + A\exp(-B/kT) \tag{9}$$

Since viscosity is also temperature-dependent, it is not out of place to draw such an analogy. A similar expression may be assumed for the line width variation as the function of the viscosity of the mixture as

$$\Gamma_i(\eta_c) = \Gamma_0 + A\exp(-B\eta_c) \tag{10}$$

The viscosity being an intrinsic property of the system, its influence on the line width is taken to modify the intrinsic line width itself. The parameter a in eq 7 is an adjustable parameter, which is basically vibrational mode dependent. It essentially depends on the polarizability of the mode. The value of a is, however, taken to be same at different concentrations for a particular solute–solvent system. If $a = 1$ is substituted in eq 7, the qualitative trend can still be fitted, but by adjusting this parameter, one can obtain a reasonably good quantitative agreement with the experimental results. Furthermore, for $\eta_{\text{solute}} > \eta_{\text{solvent}}$, eq 7 would lead to line narrowing, and for $\eta_{\text{solute}} < \eta_{\text{solvent}}$, it will give rise to line broadening with the decreasing mole fraction, C, of the solute or, in other words, after dilution. Thus our method, although based on an empirical model, seems to be working nicely for both positive or negative values of $\Delta\eta$. The applicability of the model has been tested both qualitatively and quantitatively for different systems.

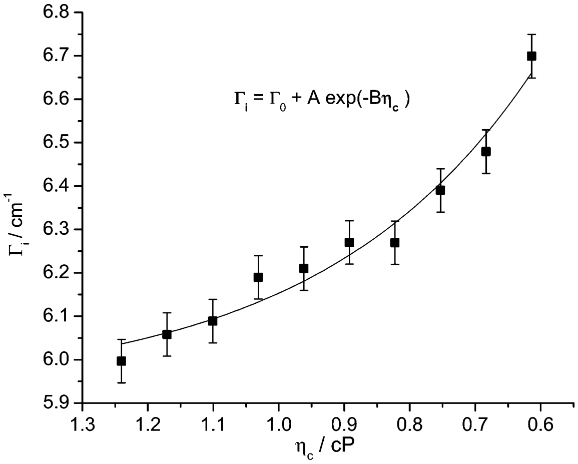

Figure 1. The values of Γ_I for ν(C≡N) stretching mode in the binary mixture $C_6H_5C{\equiv}N + CH_3OH$ obtained using the Bondarev and Mardaevea model (eqs 3 and 4) fitted to eq 9.

3. Applications to Interacting Systems

The applicability of the proposed relationship based on an empirical model has been tested in different cases, which fall under the category of interacting systems. We have chosen some hydrogen-bonded systems carefully, which are representative cases exhibiting different types of $\Gamma(C)$ vs C dependencies. The influence of microviscosity comes into play in terms of solute and solvent radii in the binary mixture. In the case of hydrogen-bonded systems,[23] the value of the van der Waals radius of the terminal atom through which the hydrogen bonding takes place was taken as the solute radius r_1 and similarly the value of the van der Waals radius of the terminal atom of the solvent participating in the hydrogen bonding was taken as the solvent radius r_2 for calculating the microviscosity using eq 5. It seems quite logical to take the van der Waals Radii of the two atoms forming the hydrogen bond.

To demonstrate that the exponential factor taken in eq 7 is justifiable, before dealing with the individual cases and explaining the concentration dependence of the line width, experimental data[7] on line width with concentration were used to obtain Γ_i using the Bondarev and Mardaeva[13] relationship (eq 4). The values of Γ_i thus obtained were fitted to eq 10, which has been depicted in Figure 1. This clearly justifies our viewpoint almost unambiguously in assuming an exponential form in eq 7.

We have selected three cases[7,22,28] where the influence of viscosity in modifying the line width exhibits different trends. In case of the $C_6H_5C{\equiv}N + CH_3OH$ system, the ν(C≡N) stretching mode was chosen. This bond (C≡N) is directly involved in the hydrogen-bond formation. As a result, although $\Delta\eta$ is large, its influence in not so appreciable, since it is neutralized by the strong interaction between the solute and the solvent molecules. In the second case of 2Cl-phenol + acrylonitrile, the ring-breathing mode of 2Cl-phenol is taken as the reference mode. In this case, the system is nearly noninteracting, but the $\Delta\eta$ value is also extremely small, and this leads to a very small change due to the effect of viscosity. In the third case of $C_4H_8O + H_2O$, the ν(C–C) stretching vibration was

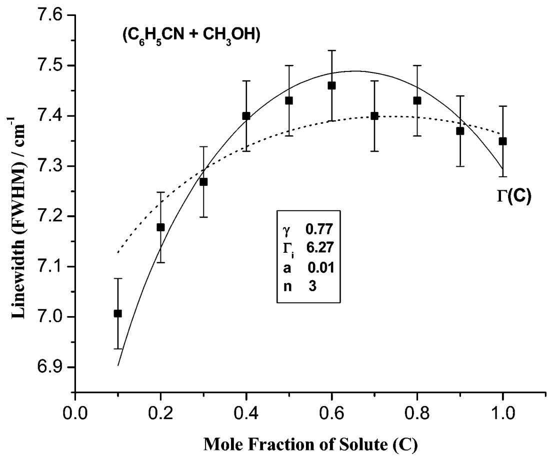

Figure 2. The experimental data points for the line width varying with concentration of the solute $C_6H_5C{\equiv}N$ at mole fraction C for the ν-($C{\equiv}N$) stretching mode in the binary mixture $C_6H_5C{\equiv}N + CH_3OH$ and fitted curves: (i) the solid line represents the fit obtained using eq 6 and (ii) the dashed line represents the fit obtained by varying n and replacing C with γC in eq 3.

chosen as the reference mode. Since this bond is not directly involved in hydrogen-bond formation, it may be considered as a less interacting system. However, $\Delta\eta = -0.4295$ cP, which is significant, and consequently, it causes an appreciable contribution to the line width. All the three cases have been discussed below in some detail.

In one of our recent studies[7] on $C_6H_5C{\equiv}N + CH_3OH$ for the $\nu(C{\equiv}N)$ stretching mode of $C_6H_5C{\equiv}N$, the value of $\Delta\Omega = 1.8$ cm^{-1}, whereas $\Gamma_i \sim 7$ cm^{-1}. In this case, the C≡N bond of the solute molecule forms a hydrogen bond with the H-atom of the solvent molecule. The values of r_1 and r_2 were taken as 1.5 and 1.2 Å, which are the van der Waals radii for N- and H-atoms, respectively. In this study, it was concluded that, although concentration fluctuation may be an important factor, the concentration dependence of both $\nu(C)$ and $\Gamma(C)$ showed a departure from what is expected on the basis of the concentration fluctuation model.[13] It was further concluded that the departure from the expected trend may be due to small contribution coming from some other factors. We used the empirical relationship proposed in this study to the for $\nu(C{\equiv}N)$ stretching mode of $C_6H_5C{\equiv}N$ studied earlier,[7] and the experimental data on $\Gamma(C)$ as a function of concentration could nicely be fitted, where the maximum in the $\Gamma(C)$ vs C plot is shifted to a C value larger than 0.5, as presented in Figure 2 (the dashed line curve represents the values of $\Gamma(C)$ without taking contribution due to microviscosity into account).

In another example,[22] the ring breathing mode of 2Cl-phenol has been studied in the 2Cl-phenol + acrylonitrile mixture. Since the ring-breathing mode pertains to 2Cl-phenol, this was treated as the solute and the acrylonitrile was treated as the solvent. In this case the H-atom of the solute molecule forms a hydrogen bond with the N-atom of the solvent molecule. The values of r_1 and r_2 were taken to be 1.2 and 1.5 Å, respectively. Further, $\Delta\Omega$ is small ($\sim$1 cm^{-1}) and $\Gamma_i = 6.1$ cm^{-1} in this case. The small value of $\Delta\Omega$ causes a very small contribution to Γ_c in accordance with eq 3 due to concentration fluctuation. Further, $\Delta\eta$ is extremely small but positive (0.01). However, owing to a relatively large value of Γ_i compared to $\Delta\Omega$, the second term in eq 6 becomes significant and primarily decides the $\Gamma(C)$ vs C dependence, which shows a steady decrease of line width upon dilution. The experimental data points are again nicely fitted using the empirical relationship (eqs 6 and 7) and the results are presented in Figure 3 (dashed line curve represents similar result as in Figure 2). The calculated values of $\Gamma(C)$ according to our empirical model are in nice agreement with the experimental results.

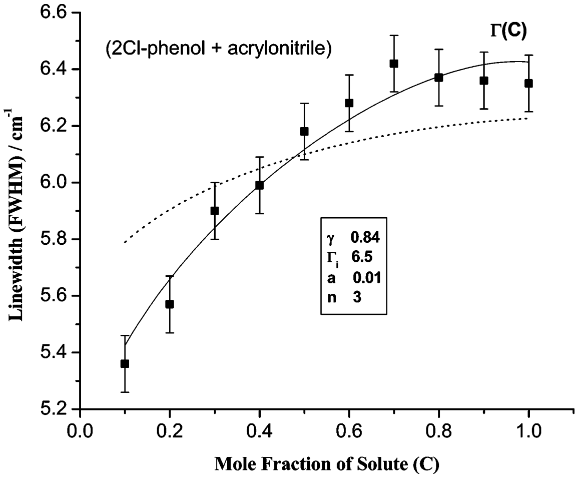

Figure 3. The experimental data points for the line width varying with concentration of the solute 2Cl-phenol at mole fraction C for the ring-breathing mode in the binary mixture 2Cl-phenol + acrylonitrile and fitted curves: (i) the solid line represents the fit obtained using eq 6 and (ii) the dashed line represents the fit obtained by varying n and replacing C with γC in eq 3.

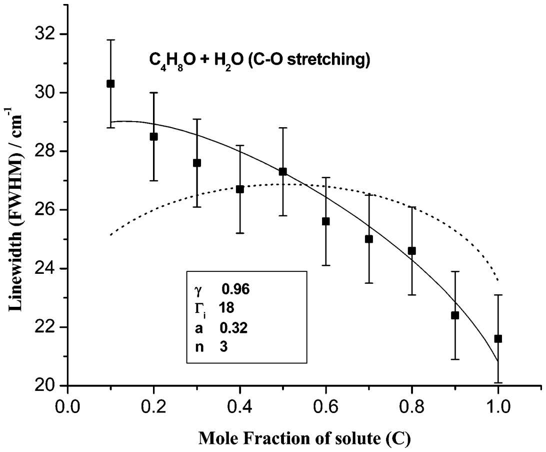

Figure 4. The experimental data points for the line width varying with concentration of the solute C_4H_8O in mole fraction C for the ν(C−C) stretching mode in the binary mixture $C_4H_8O + H_2O$ and fitted curves: (i) the solid line represents the fit obtained using eq 6 and (ii) the dashed line represents the fit obtained by varying n and replacing C with γC in eq 3.

In one of the recent studies[27] on $C_4H_8O + H_2O$, the ν(C−O) stretching mode of the C_4H_8O was investigated and the concentration dependence of the wavenumber shift and line width were studied in detail, and the values of $\Delta\Omega = 6.3$ and $\Gamma_i = 21$ cm^{-1} were obtained from the experimental data. Further, the O-atom of the solute molecule forms a hydrogen bond with the H-atom of the solvent molecule, and hence, the values of r_1 and r_2 were taken as 1.4 and 1.2 Å, which are the van der Waals radii for O- and H-atoms, respectively. The value of $\Delta\eta = -0.4295$ cP was obtained from a data bank.[29] Since Γ_i is appreciably large for the ν(C−O) stretching, the value of Γ_c in eq 3 becomes too small as compared to the viscosity-dependent contribution. As a consequence, the $\Gamma(C)$ exhibits a steady increase upon dilution. The experimental data points and the fitted curve are presented in Figure 4 (dashed line curve again represents similar result as in Figures 2 and 3). Thus it is clearly evident that the proposed relationships (eqs 6 and 7 together) based on empirical model work very nicely for this case also.

TABLE 1: Calculated Values of Γ_i, Γ_c, $\Gamma_i(\eta_c)$, and $\Gamma(C)$ Using Eqs 5 and 6 for Three Different Types of Binary Systems: (i) Showing a Shift of the Maximum from $C = 0.5$, (ii) Monotonously Increasing, and (iii) Monotonously Decreasing upon Dilution[a]

	$C_6H_5C{\equiv}N + CH_3OH$[b] $\Gamma_i = 6.27$ cm^{-1}			2Cl-phenol + acrylonitrile[c] $\Gamma_i = 6.5$ cm^{-1}			$C_4H_8O + H_2O$[d] $\Gamma_i = 18$ cm^{-1}		
C	Γ_c	$\Gamma_i(\eta_c)$	$\Gamma(C)$	Γ_c	$\Gamma_i(\eta_c)$	$\Gamma(C)$	Γ_c	$\Gamma_i(\eta_c)$	$\Gamma(C)$
0.1	0.65	6.25	6.90	0.41	4.95	5.36	2.51	26.51	29.02
0.2	0.89	6.25	7.14	0.56	5.04	5.60	3.36	25.61	28.97
0.3	1.04	6.26	7.30	0.65	5.13	5.78	3.86	24.73	28.59
0.4	1.13	6.26	7.39	0.70	5.22	5.92	4.15	23.88	28.03
0.5	1.19	6.27	7.46	0.74	5.31	6.05	4.26	23.07	27.33
0.6	1.22	6.27	7.49	0.75	5.40	6.15	4.22	22.27	26.49
0.7	1.21	6.27	7.48	0.74	5.50	6.24	4.01	21.51	25.52
0.8	1.18	6.28	7.46	0.70	5.60	6.30	3.60	20.78	24.38
0.9	1.12	6.28	7.40	0.64	5.70	6.34	2.93	20.06	22.99
1	1.01	6.28	7.29	0.55	5.80	6.35	1.67	19.38	21.05

[a] C is the mole fraction of the solute, Γ_i is the intrinsic line width in neat liquid, Γ_c is the contribution to line width due to concentration fluctuation alone, $\Gamma_i(\eta_c)$ is the intrinsic line width corrected for varying viscosity at different mole fraction of the solute, and $\Gamma(C)$ is the total line width at the mole fraction of the solute. [b] $\Delta\Omega = 1.8$ cm^{-1}, $\Delta\eta = 0.6995$ cP. [c] $\Delta\Omega = 1.1$ cm^{-1}, $\Delta\eta = 0.01$ cP. [d] $\Delta\Omega = 6.3$ cm^{-1}, $\Delta\eta = -0.4295$ cP.

4. Conclusions

To explain the concentration-dependent variation of isotropic Raman line width, the relationships (eqs 6 and 7 together) based on an empirical model using a new approach have been suggested. The proposed model has two contributions, Γ_c, which is due to concentration fluctuation, and a microviscosity-dependent term, both the contributions being additive. The model has been applied successfully in several cases, where experimental data are precisely known. The fitted curves in three different cases are presented in Figures 2–4, and the results obtained from the fitting are presented in Table 1, which clearly show that the empirical relationships suggested in this study explain quantitatively the concentration dependence of the line width in a variety of cases, such as a maximum in the $\Gamma(C)$ vs C plot and a monotonic increase or decrease of $\Gamma(C)$ as a function of C in a given class of hydrogen-bonded systems. To the best of our knowledge, this is the first study where the concentration fluctuation model given initially by Bondarev and Mardaeva[13] and the concept of microviscosity in the solute–solvent system have been combined together to explain the different trends of concentration-dependent line width variation. Some representative examples have been explored in order to test the applicability of the proposed empirical relationships. An important implication of the proposed empirical model, in our viewpoint, is that in some favorable cases it can even predict the type of line width vs concentration dependence, if the viscosities of the solute and the solvent are known precisely and vice versa.

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References and Notes

(1) Morresi, A.; Mariani, L.; Distefano, M. R.; Giorgini, M. G. *J. Raman Specrosc.* **1995**, *26*, 179–216.

(2) Asthana, B. P.; Kiefer, W. In: *Vibrational Spectra and Structure*; Durig, J. R., Ed.; Elsevier: Amsterdam, 1993; Vol. 20, p 69–157 (and references therein).

(3) Asthana, B. P.; Takahashi, H.; Kiefer, W. *Chem. Phys. Lett*. **1983**, *94*, 41–47.

(4) Morresi, A.; Sassi, P.; Paolantoni, M.; Santini, S.; Cataliotti, R. S. *Chem. Phys.* **2000**, *254*, 337–347.

(5) Deckert, V.; Asthana, B. P.; Kiefer, W.; Purrucker, H.-G.; Laubereau, A. *J. Raman Spectrosc.* **2000**, *31*, 805–811.

(6) Asthana, B. P.; Deckert, V.; Shukla, M. K.; Kiefer, W. *Chem. Phys. Lett.* **2000**, *326*, 123–128.

(7) Raghuvansh (nee Bhriguvansh), P.; Srivastava, S. K.; Singh, R. K.; Schlücker, S.; Kiefer, W. *Phys. Chem. Chem. Phys*. **2004**, *6*, 531–536.

(8) Ojha, A. K.; Srivastava, S. K.; Koster, J.; Shukla, M. K.; Leszczynski, J.; Asthana, B. P.; Kiefer, W. *J. Mol. Struct.* **2004**, *689*, 127–135.

(9) Srivastava, S. K.; Ojha, A. K.; Koster, J.; Shukla, M. K.; Leszczynski, J.; Asthana, B. P.; Kiefer, W. *J. Mol. Struct.* **2003**, *661–662*, 11–21.

(10) Singh, R. K.; Bhriguvansh, P.; Asthana, B. P.; Verma, A. L. *Chem. Phys. Lett.* **1998**, *296*, 611–618.

(11) Singh, R. K.; Asthana, B. P.; Verma, A. L.; Pathak, C. M. *Chem. Phys. Lett*. **1997**, *278*, 35–40.

(12) Asthana, B. P.; Kiefer, W.; Knapp, E. W. *J. Chem. Phys.* **1984**, *81*, 3774–3778.

(13) Bondarev, F.; Mardaeva, A. I. *Opt. Spectrosc.* **1973**, *35*, 286–288.

(14) Van Woerkom, P. C. M.; Bleyser, J. D.; de Zwart, M.; Leyte, J. C. *Chem. Phys.* **1974**, *4*, 236–248.

(15) Fischer, S. F.; Laubereau, A. *Chem. Phys. Lett*. **1978**, *55*, 189–196.

(16) Laubereau, A.; Asthana, B. P.; Deckert, V. *Chem. Phys*. (to be published).

(17) Schweizer, K. S.; Chandler, D. *J. Chem. Phys.* **1982**, *76*, 2296–2314.

(18) Fujiyama, T.; Kakimoto, M.; Suzuki, T. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 606.

(19) Knapp, E. W.; Fischer S. F. *J. Chem. Phys.* **1982**, *76*, 4730–4735.

(20) Bratos, S.; Tarjus, G. *Phys. Rev. A* **1985**, *32*, 2431–2438.

(21) Tarjus, G.; Bratos, S. *Phys. Rev. A* **1986**, *34*, 4202–4210.

(22) Srivastava, S. K.; Ojha, A. K.; Sinha, P. K.; Asthana, B. P.; Singh, R. K. *J. Raman Spctrosc.* **2006**, *37*, 68–75.

(23) Bhattacharjee, D.; Ghose (Purukayastha), A.; Mishra, T. N.; Nandy, S. K. *J. Raman Spectosc.* **1996**, *27*, 457–461.

(24) Rothschild, W. G. *Dynamics of Molecular Liquids*; John Wiley & Sons: New York, 1984, p 286.

(25) Keutel, D.; Seifert, F.; Oehme, K. L.; Asenbaum, A.; Musso, M. *Phys. Rev. Lett.* **2000**, *85*, 3850–3853.

(26) Frolov, V. V. In *Nuclear Magnetic Resonence*; Borodin, P. M., Ed.; Amerind: New Delhi, 1975; 13.

(27) Singh, R. K.; Asthana, B. P.; Bist, H. D. *Chem. Phys. Lett.* **1993**, *209*, 390–396.

(28) Ojha A. K.; Srivastava, S. K.; Peica, N.; Schlücker, S.; Asthana, B. P.; Kiefer, W. *J. Mol. Struct.* **2005**, *735–736*, 349–357.

(29) Physical Properties of Liquids. In *Catalogue TriMan Chemical "Fine chemicals and custom synthesis*"; TriMan: Jakarta, Indonesia, 2004.