



Evaluation of the Polarity in Binary Liquid Mixtures as a Function of Volume Fraction

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The variation of solvatochromic polarity parameters as a function of mole fraction data may not represent the realistic environment of the solvatochromic probe molecule. This is because of the fact that the solvation environment of the solvatochromic probe molecules is not only determined by the number of individual solvent molecules around it but also by the size of those individual solvent molecules. In this regard we wish to understand the variation of E_T^N polarity parameter of binary liquid mixtures as a function of volume fractions. Representation of the E_T^N parameter as a function of volume fraction data leads to a completely different dataset for binary liquid mixtures where water is used as one of the solvents. These mixtures usually display negative deviations from linearity for the E_T^N values, when E_T^N values are plotted as a function of mole fraction values of the solvents. On the other hand, if the E_T^N values are plotted as a function of volume fraction values of the solvents in binary liquid mixtures containing water, these deviations are minimized to a large extent and even reversed to the positive deviations in some of these mixtures. This study gives an insight into a long lasting problem of understanding the negative deviations of the E_T^N values from linearity observed in binary liquid mixtures of water, as these deviations are either minimized or reversed into positive deviations when E_T^N values are plotted *versus* volume fraction of solvents. This study opens up a whole new discussion about the solvatochromic data of the solvent mixtures, whether this data must be represented as a function of mole fraction values or as a function of volume fraction of the solvents. The representation of the solvatochromic data as a function of volume fraction of solvents might lead to new insights in studying the solute-solvent interactions in binary solvent mixtures.

Keywords: Binary liquid mixture, Polarity, Volume fraction, Solvatochromic probe.

INTRODUCTION

Solvation plays a vital role in various chemical reactions taking place in the liquid phase and therefore studying the solvation process is essential for understanding the solvent effects on chemical processes [1]. Various biological processes including metabolism, signaling and transportation are also controlled by the solvation phenomenon [2,3]. Solvation refers to the interactions of solvent with dissolved solute molecules both ionized as well as uncharged. The nature of the interactions of solvent with solute molecules influences a large number of properties of the solute such as their colour, reactivity, solubility, *etc.* Similarly these interactions also influence the solvent properties such as the viscosity, polarity, density, *etc.*

The solvent effects on a chemical process can broadly be defined as the summation of solvent-solute interactions, solvent-solvent interactions and solute-solute interactions. One of the generic methods used to measure these intermolecular inter-

actions is the solvent polarity [4,5]. Polarity is an important solvent property for explaining the solvent effects on various chemical processes. Based on the polarity, solvents are generally classified into two categories *i.e.* polar and non-polar. Usually the polar solute molecules are dissolved best in polar solvents and non-polar solute molecules are dissolved best in non-polar solvents “like dissolves like”. Parameters like refractive index and dielectric constant are used to represent a variety of solvent properties. However, solvent polarity is a complex issue which largely arises due to the solvation of reactants, products as well as activated complex as a consequence of different specific and non-specific intermolecular interactions between the solute and solvent molecules [6].

It was pointed out by Reichardt & Welton [7] that the macroscopic measurement of dielectric constants only does not fully reflect the polarity of the solvent. So, in order to account for the various types of intermolecular interactions provided by the solvent molecules a number of solvent polarity scales

have been developed, based on the specific and non-specific interactions provided by the solvent molecules [7,8-18]. Most of these scales are based on the use of single spectroscopic data set for a probe molecule. The most commonly used solvatochromic polarity parameter is the E_T^N parameter which uses 2,6-diphenyl-4-(2,4,6-triphenyl-pyridin-1-ium)-1 phenolate or Reichardt's E_T (30) dye as solvatochromic indicator. Values of the E_T^N polarity parameter have been calculated for a large number of pure solvents as well as for binary liquid mixtures including ionic liquids [5,8,17,19-40]. Ionic liquids have received a great deal of attention in recent times because of their unique physico-chemical properties, for example high electrochemical and thermal stability, negligible volatility, high conductivity *etc.*, which allow their application as green substitutes for volatile organic solvents [41-45]. More importantly, the required properties for a particular application can be achieved with the ionic liquids simply by changing the cation or anion and therefore ionic liquids are often termed as designer solvents. Extensive studies have been carried out to attain the fundamental understanding of the physico-chemical, photochemical and electrochemical properties of ionic liquids over the past few years [46-48] and as a result, now they are being used in organic synthesis, catalysis, electrochemical studies, fabrication of inorganic materials and many other technological applications [49-53].

As mentioned earlier the E_T^N parameter has been measured for a variety of pure and mixed solvents. However, the interpretation of the E_T^N values in pure or in mixed solvents is different. The E_T^N value measures the polarity of the solvation microsphere surrounding the solvatochromic indicator. In a pure solvent, the composition of this microsphere is the same as in the bulk solvent, but this is not necessarily true for the mixed solvents. Generally, the polarity behaviour of binary liquid mixtures is discussed as a function of the mole fraction of solvent molecules. However, the mole fraction values of the solvent mixtures may not reflect the realistic picture of the solvation environment of the solvatochromic probe molecules. This is because of the different sizes of different solvent molecules. In the process of solvation, solute molecules are surrounded by a concentric shell of solvent molecules where solvent and solute molecules reorganize into the solvation complex. Solvation involves the bond formation *via* electrostatic interactions, hydrogen bonding and van der Waals forces. The solvent molecules having bigger size cover a larger surface area around the probe molecule and thus constitute relatively more portion of the solvation shell as compared to the solvent having smaller molecules (Fig. 1).

It may be understood from the above discussion that the solvation environment of the solvatochromic probe molecule can be represented more realistically in terms of surface area covered by the two solvents. Surface area covered by the solvent molecules around the probe molecule can be estimated by the volume fraction, higher the molar volume of solvent, bigger the surface area they cover around probe molecules. In order to understand the variation of E_T^N polarity parameter as a function of volume fraction of solvents, we have studied the binary liquid mixture of water with three types of solvents, (a) polar

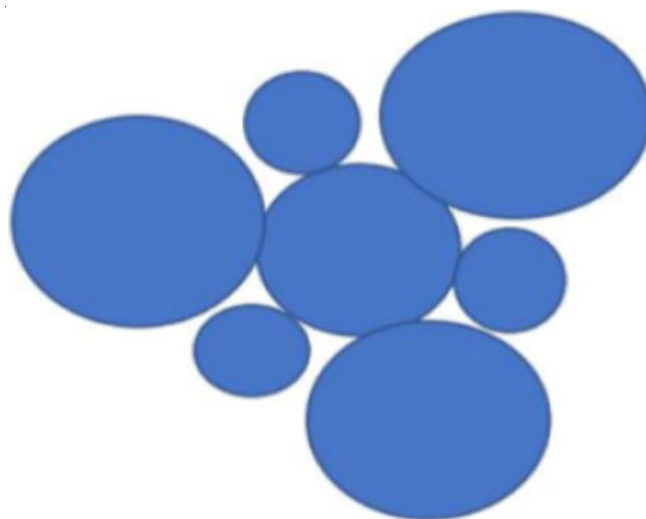


Fig. 1. Representation of the solvation environment of solvatochromic probe molecule. Bigger solvent molecules cover larger surface area of the solvation sphere

protic solvents; methanol and ethanol, (b) polar aprotic solvents, *e.g.* acetone and dimethylsulphoxide (DMSO) and (c) ionic liquid *e.g.* 1-butyl-3-methylimidazolium bromide ([Bmim]Br) and 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF₄]). Representation of the E_T^N parameter as a function of volume fraction data leads to a completely different results for binary liquid mixtures of water.

EXPERIMENTAL

1-Methylimidazole (99%) and *n*-butyl bromide (99%) used for the synthesis of ionic liquid were purchased from M/s Sigma-Aldrich and were distilled before use. The solvatochromic probe; 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate dye (90%), was purchased from M/s Sigma-Aldrich and used as obtained. Sodium tetrafluoroborate salt (98%) was procured from Merck and used as such. High-purity methanol (99.7%), ethanol (99%), acetone (99.5%), acetonitrile (99.8%) and DMSO (99.9%) were obtained from Merck and used as obtained. Milli Q water with a conductivity < 80 μ S/cm was used as the solvent throughout the experiments.

Synthesis of ionic liquids: Synthesis of the ionic liquids was done in accordance with the reported procedures [54,55]. First, 1-butyl-3-methylimidazolium bromide ([Bmim]Br) ionic liquid was synthesized by the reaction of 1-methylimidazole with *n*-butyl bromide (1.0:1.2 ratio) under reflux condenser at 60 °C for 12 h. After the completion of the reaction, excess of *n*-butyl bromide was removed by the multiple extractions using ethyl acetate as solvent. Leftover impurities were removed by putting the ionic liquid under ultrahigh vacuum at 60 °C for 10 h. Pure [Bmim]Br ionic liquid was obtained as a crystalline white coloured solid. For the synthesis of [Bmim][BF₄] ionic liquid, the reaction of [Bmim]Br ionic liquid was carried out with sodium tetrafluoroborate salt (in 1.0:1.2 ratio) using dichloromethane as solvent at room temperature for 24 h. Sodium bromide salt formed as the side product and excess of sodium tetrafluoroborate salt were removed by filtration through celite powder. Dichloromethane as solvent was removed by

rota-vapour. Leftover impurities were removed by using ultrahigh vacuum at 60 °C for 6 h. The characterization of the ionic liquids was done by ^1H NMR spectroscopy. Halide contents of [Bmim][BF₄] ionic liquid was found to be less than 50 ppm as obtained by Volhard titration method using a chloride-selective electrode [56]. Water content of both ionic liquids was measured with a Karl Fischer coulometer before making solutions and found to be less than 70 ppm.

Measurement of E_T^N polarity parameter: For the measurement of E_T^N polarity parameter, first the stock solutions of the dye were prepared in all the solvents (except water). The methanolic solution of the dye was added to the ionic liquid dropwise and the contents were mixed thoroughly. Methanol was removed by placing the solution under ultrahigh vacuum at 50 °C for 6 h. These stock solutions of the solvatochromic probe were mixed in the proper volume fraction ratios under the inert atmosphere of nitrogen gas for the measurement of the E_T^N polarity parameter. These mixtures were transferred to the quartz cuvette and the spectra were recorded using Cary-50 UV-vis spectrophotometer. The temperature of the sample cell was kept constant at 25 ± 0.1 °C during the experiments. Once the frequency of absorption maximum (ν_{\max}) is obtained, the value of E_T (30) polarity parameter was calculated using eqn. 1 [5]:

$$E_T(30) = h\nu_{\max} N_A = 2.859 \times \nu_{\max} \text{ kcal mol}^{-1} \quad (1)$$

here h is Plank's constant, c is the velocity of light and N_A is Avogadro's number. Once the value of E_T (30) polarity parameter is known, the value of E_T^N polarity parameter can be calculated using eqn. 2 [5]:

$$E_T^N = \frac{E_T(30)_{\text{solvent}} - 30.7}{32.4} \quad (2)$$

[Bmim]Br ionic liquid is solid at room temperature, so the E_T^N value for this ionic liquid in pure state was calculated at higher temperature and the estimation of the E_T^N values at 25 °C was done by interpolation (Fig. 2).

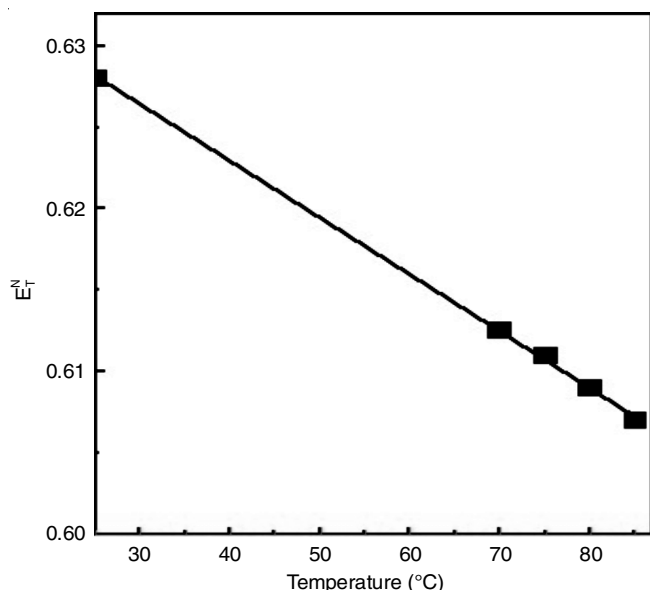


Fig. 2. Plot obtained for the prediction of E_T^N value of [Bmim]Br ionic liquid at 25 °C

RESULTS AND DISCUSSION

Generally, the polarity parameters such as E_T^N polarity parameter of binary solvent mixtures were calculated in the terms of mole-fractions of the solvents but as we have discussed earlier, the solvation environment of the solvatochromic probe molecules cannot be represented correctly by the mole-fraction values of these mixtures. This is because of the fact that the size of solvent molecules are different as represented in Fig. 1. It can be understood that most of the surface area of the surrounding environment of solvatochromic probe molecule in solvation sphere is occupied by larger solvent and very small surface area is available for the smaller solvent molecules. It can be inferred from this discussion that the mole-fraction value does not precisely represent the surrounding environment of the solvatochromic probe molecule. So the variation of the solvatochromic properties with the volume fraction values represents a more realistic picture of the solvation sphere of the dye molecules. The behaviour of the E_T^N values in binary liquid mixtures are determined in the form of the deviations from the linear behaviour, To understand the nature of deviations in these liquid mixtures, we have calculated the deviations of the E_T^N values from the ideal behaviour, the ΔE_T^N values. The ΔE_T^N values for both the mole fraction as well as volume fraction data can be measured as the difference between the experimentally observed E_T^N value and the E_T^N value expected from the ideal binary liquid mixture ($E_{T,\text{ideal}}^N$) using eqns. 3 and 4, respectively.

$$\Delta E_{T,\text{MF}}^N = E_T^N - E_{T,\text{ideal MF}}^N \quad (3)$$

$$\Delta E_{T,\text{VF}}^N = E_T^N - E_{T,\text{ideal VF}}^N \quad (4)$$

here $E_{T,\text{ideal}}^N$ can be measured for both the mole fraction and volume fraction data sets *via* eqns. 5 and 6, respectively.

$$E_{T,\text{ideal MF}}^N = E_T^N(1)x_1 + E_T^N(2)x_2 \quad (5)$$

$$E_{T,\text{ideal VF}}^N = E_T^N(1)VF_1 + E_T^N(2)VF_2 \quad (6)$$

here x_1 and x_2 represents the mole fractions of solvent (1) and solvent (2), respectively and VF_1 and VF_2 represents the volume fractions of solvent (1) and solvent (2), respectively. $E_T^N(1)$ and $E_T^N(2)$ represents the E_T^N values of the pure solvents (1) and (2), respectively. Values of the E_T^N polarity parameter of the solvents used in this study, in pure state are provided in Table-1.

TABLE-1
VALUES OF THE E_T^N POLARITY PARAMETER
OF THE PURE SOLVENTS USED IN THE STUDY

Solvent	E_T^N value
Water	1.000
Ethanol	0.675
Methanol	0.766
Acetone	0.379
DMSO	0.450
[Bmim]Br	0.628
[Bmim][BF ₄]	0.689

In this study, the variation of E_T^N values has been studied with volume fraction of the solvents in binary liquid mixtures of water with three different types of solvents, *viz.* polar protic

solvents, polar aprotic solvents and ionic liquids. We have also compared the behaviour of the E_T^N values as a function of volume fraction data to that of mole fraction data.

Polar protic solvents: In order to understand the variation of E_T^N values as a function of volume fraction of the solvents in the binary liquid mixtures of polar protic solvents, we have taken two types of solvent mixtures, *viz.* water-methanol and water-ethanol mixtures. Variation of the E_T^N values as a function of volume fraction (VF_w) and mole fraction (x_w) of water in the binary liquid mixtures of water with polar protic solvents is provided in Fig. 3.

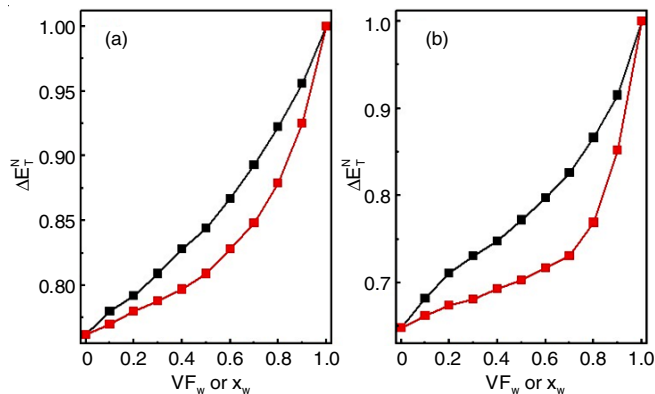


Fig. 3. E_T^N values as a function of VF_w (black) and x_w (red) in the binary liquid mixtures of H_2O with (a) methanol and (b) ethanol

It can be observed from Fig. 4 that the E_T^N values display less deviation from the ideal behaviour when plotted against VF_w in comparison to when plotted against x_w . Moreover, the highest value of deviation for water-methanol mixtures, when plotted against the mole fraction values (the highest $\Delta E_{T,MF}^N$) is about -0.081. On the contrary, the highest $\Delta E_{T,VF}^N$ was found to be only about -0.038. Similarly, the highest $\Delta E_{T,VF}^N$ (-0.068) was found to be significantly less than the highest $\Delta E_{T,MF}^N$ value (-0.163) for water-ethanol mixtures.

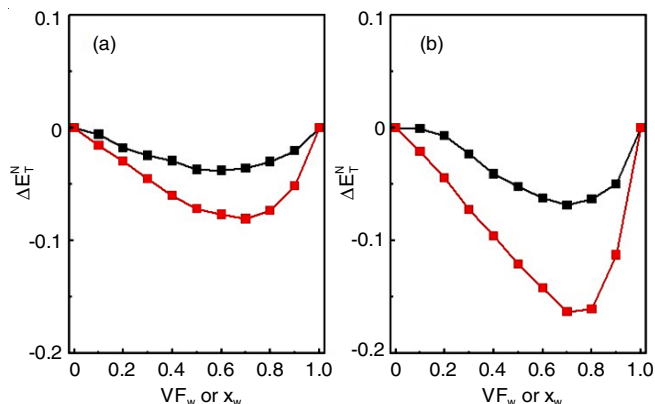


Fig. 4. ΔE_T^N values as a function of VF_w (black) and x_w (red) in the binary liquid mixtures of H_2O with (a) methanol and (b) ethanol

It thus can be concluded from this data that the negative deviations of the E_T^N values generally obtained in the binary liquid mixtures of water are minimized to a large extent when plotted against the volume fraction values of the solvents. Understanding the negative deviations of the E_T^N values from ideal

behaviour in the binary liquid mixtures where water is used as one of the components has been an unsolved problem to the researchers. However as we have seen in the water-methanol and water-ethanol mixtures, the negative deviations gets minimized when plotted the E_T^N values as a function of volume fraction values.

It thus can be inferred from this discussion that one of the prime reasons for the large negative deviations observed in the E_T^N values of the binary liquid mixtures of water might be, the way of depiction of the E_T^N values as a function of mole fraction values, which might not represent the true picture of the solvation environment of the solvatochromic probe. Alternately, if we plot the E_T^N values as a function of volume fraction values of the solvents, which also represents the realistic volume occupied by different solvents in the solvation shell, these negative deviations are minimized to a great extent. Thus the depiction of the E_T^N values as a function of volume fraction values might be the more appropriate way for studying the polarity behaviour of the binary liquid mixtures.

Polar aprotic solvents: To understand the behaviour of E_T^N values in the mixtures of water with polar aprotic solvents, we have plotted the E_T^N values as a function of VF_w and x_w for water-acetone and water-DMSO mixtures (Fig. 5).

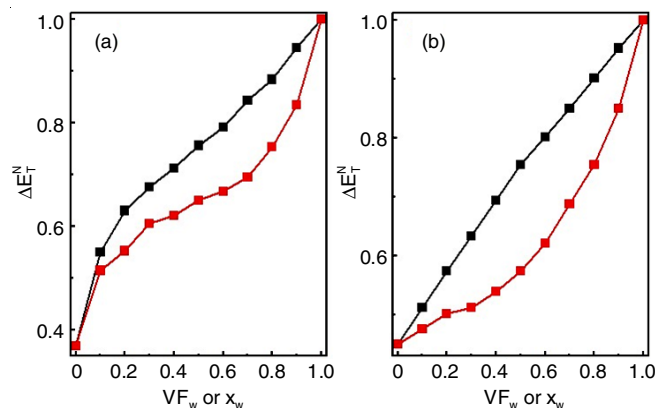


Fig. 5. E_T^N values as a function of VF_w (black) and x_w (red) in the binary liquid mixtures of H_2O with (a) acetone and (b) DMSO

It can be inferred from Fig. 5 that the E_T^N values when plotted against x_w , display both the positive and negative deviations from the ideal behaviour in different mole fraction regions for water-acetone mixtures, whereas they exhibit only negative deviations for water-DMSO mixtures. On the other hand, E_T^N values display the positive deviations from the linear behaviour when plotted as a function of VF_w in both water-acetone and water-DMSO mixtures. Nature of the deviations of E_T^N values (ΔE_T^N values) both as function of VF_w and x_w in these mixtures is represented in Fig. 6.

Since the positive deviations of the E_T^N values from the linear mixtures can be understood very easily with the help of preferential solvation of the dye molecules by more polar solvent [35], the behaviour of E_T^N values in the water-acetone and water-DMSO mixtures can be understood easily, just by plotting the E_T^N values against the volume fraction values of the solvents in place of mole fraction values. This suggests

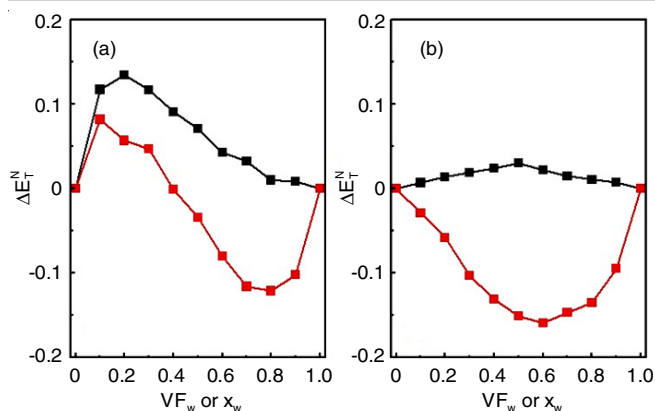


Fig. 6. ΔE_T^N values as a function of VF_w (black) and x_w (red) in the binary liquid mixtures of H_2O with (a) acetone and (b) DMSO

that it is more appropriate to study the E_T^N values as a function of volume fraction values for the binary liquid mixtures.

Ionic liquids: Variation of the E_T^N values as a function of both the volume fraction and mole fraction values of the solvents is provided in Fig. 7 for water-[Bmim]Br and water-[Bmim]-[BF₄] mixtures.

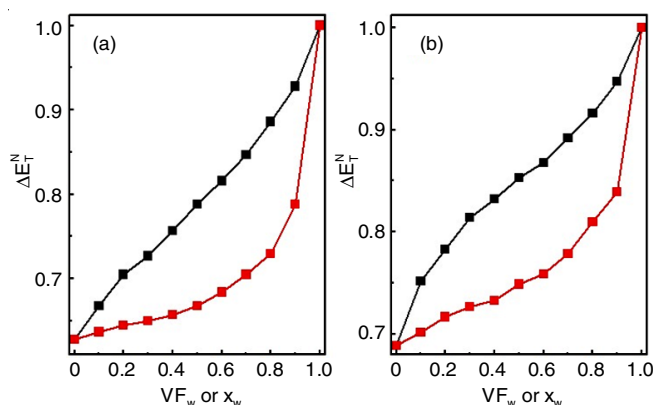


Fig. 7. E_T^N values as a function of VF_w (black) and x_w (red) in the binary liquid mixtures of H_2O with (a) [Bmim]Br and (b) [Bmim][BF₄]

As can be seen from Fig. 7 that the E_T^N values display large negative deviations when plotted against the mole fraction values of the solvents, however these deviations are much less pronounced when E_T^N values are plotted against the volume fraction of solvents. To clearly understand the nature of deviations in these mixtures, we have calculated the ΔE_T^N values both as function of VF_w and x_w . It is clear from Fig. 8 that the negative deviations of E_T^N values for mole fraction data in water-[Bmim]-[BF₄] mixtures convert into the positive deviations for most of the mole fraction range for volume fraction data. In water-[Bmim]Br mixtures though the deviations are primarily negative, they are much less pronounced for the volume fraction data in comparison to that of mole fraction data.

Following from this discussion, it is found that by studying the variation of E_T^N values as a function of volume fraction in the binary solvent mixtures rather than mole fraction could yield quite different results. Such results need to be analyzed from a completely different perspective since the nature of deviations in the values of E_T^N parameter has completely reversed for several binary liquid mixtures.

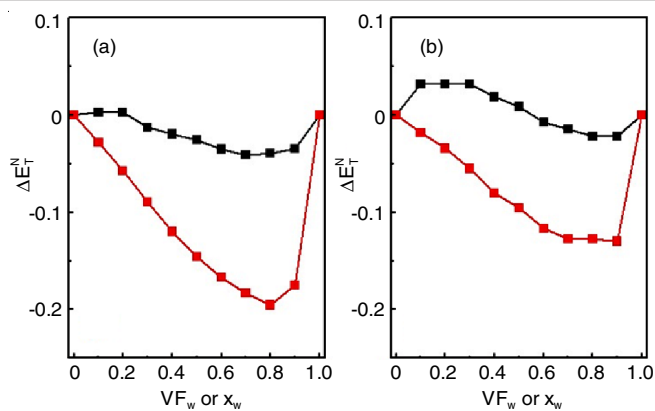


Fig. 8. ΔE_T^N values as a function of VF_w (black) and x_w (red) in the binary liquid mixtures of H_2O with (a) [Bmim]Br and (b) [Bmim][BF₄]

Conclusion

The purpose of this study indicates that the mole fraction values of the binary mixtures do not represent the realistic picture of the solvation environment of the solvatochromic probe molecules, rather the volume fraction values represent more realistic picture. The discussion from this study allows us to conclude that the variation of E_T^N values as a function of volume fraction data in binary solvent mixtures having water as one of the components, can have completely different trends in data when compared to that of mole fraction data. So the E_T^N values of binary liquid mixtures need to be analyzed from a completely different perspective. Large negative deviations observed in the E_T^N values when plotted against the mole fraction values of solvents in the binary liquid mixtures of water are minimized to a large extent when plotted against the volume fraction values. In some of the mixtures such as water-acetone, water-DMSO and water-[Bmim][BF₄], these negative deviations gets even reversed to the positive deviation. Since the researchers has not been able explain the negative deviations of the E_T^N values in the binary liquid mixtures satisfactorily, this study might provide an important insight to understand such unique behaviour. Possibly the E_T^N values must be represented as a function of volume fraction values and not as mole fraction values because the actual surrounding environment of the dye molecules is represented better by the volume fraction values of solvent. This study thus opens up a whole new discussion about the proper representation of the solvatochromic data whether, the solvatochromic data should be plotted against mole fraction values or the volume fraction values of the solvent.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

- M. Havenith, *Angew. Chem. Int. Ed.*, **55**, 1218 (2016); <https://doi.org/10.1002/anie.201510614>
- D.J. Gordon, J.J. Balbach, R. Tycko and S.C. Meredith, *Biophys. J.*, **86**, 428 (2004); [https://doi.org/10.1016/S0006-3495\(04\)74119-3](https://doi.org/10.1016/S0006-3495(04)74119-3)
- S.B. Prusiner, *Proc. Natl. Acad. Sci. USA*, **95**, 13363 (1998); <https://doi.org/10.1073/pnas.95.23.13363>
- C. Dimroth, C. Reichardt, T. Siepmann and F. Bohlmann, *Justus Liebigs Ann. Chem.*, **661**, 1 (1963); <https://doi.org/10.1002/jlac.19636610102>
- C. Reichardt, *Chem. Rev.*, **94**, 2319 (1994); <https://doi.org/10.1021/cr00032a005>
- C. Reichardt, *Angew. Chem. Int. Ed. Engl.*, **4**, 29 (1965); <https://doi.org/10.1002/anie.196500291>
- C. Reichardt and T. Welton, *Solvents and Solvent Effects in Organic Chemistry*, Wiley-VCH: Weinheim (2011).
- E.M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958); <https://doi.org/10.1021/ja01546a020>
- E.M. Kosower, *J. Am. Chem. Soc.*, **80**, 3261 (1958); <https://doi.org/10.1021/ja01546a021>
- E.M. Kosower, *J. Am. Chem. Soc.*, **80**, 3267 (1958); <https://doi.org/10.1021/ja01546a022>
- F.W. Fowler, A.R. Katritzky and R.J.D. Rutherford, *J. Chem. Soc. B*, 460 (1971); <https://doi.org/10.1039/j29710000460>
- V. Gutmann and E. Wychara, *Inorg. Nucl. Chem. Lett.*, **2**, 257 (1966); [https://doi.org/10.1016/0020-1650\(66\)80056-9](https://doi.org/10.1016/0020-1650(66)80056-9)
- M.J. Kamlet and R.W. Taft, *J. Am. Chem. Soc.*, **98**, 377 (1976); <https://doi.org/10.1021/ja00418a009>
- R.W. Taft and M.J. Kamlet, *J. Am. Chem. Soc.*, **98**, 2886 (1976); <https://doi.org/10.1021/ja00426a036>
- Y. Marcus, *Chem. Soc. Rev.*, **22**, 409 (1993); <https://doi.org/10.1039/cs9932200409>
- M.H. Abraham, P.L. Grellier, D.V. Prior, J.J. Morris and P.J. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 521 (1990); <https://doi.org/10.1039/p29900000521>
- C. Reichardt, *Green Chem.*, **7**, 339 (2005); <https://doi.org/10.1039/b500106b>
- M.J. Kamlet, J.L. Abboud and R.W. Taft, *J. Am. Chem. Soc.*, **99**, 6027 (1977); <https://doi.org/10.1021/ja00460a031>
- J.G. Dawber, J. Ward and R.A. Williams, *J. Chem. Soc., Faraday Trans. 1*, **84**, 713 (1988); <https://doi.org/10.1039/f19888400713>
- E. Bosch and M. Roses, *J. Chem. Soc., Faraday Trans.*, **88**, 3541 (1992); <https://doi.org/10.1039/FT9928803541>
- R.D. Skwierzynski and K.A. Connors, *J. Chem. Soc., Perkin Trans. 2*, 467 (1994); <https://doi.org/10.1039/P29940000467>
- M. Roses, C. Rafols, J. Ortega and E. Bosch, *J. Chem. Soc., Perkin Trans. 2*, 1607 (1995); <https://doi.org/10.1039/P29950001607>
- J. Ortega, C. Rafols, E. Bosch and M. Roses, *J. Chem. Soc., Perkin Trans. 2*, 1497 (1996); <https://doi.org/10.1039/P29960001497>
- K.A. Fletcher, S.N. Baker, G.A. Baker and S. Pandey, *New J. Chem.*, **27**, 1706 (2003); <https://doi.org/10.1039/b305965k>
- K.A. Fletcher and S. Pandey, *J. Phys. Chem. B*, **107**, 13532 (2003); <https://doi.org/10.1021/jp0276754>
- T.W. Bentley and I.S. Koo, *Org. Biomol. Chem.*, **2**, 2376 (2004); <https://doi.org/10.1039/B408052C>
- C. Reichardt, *Pure Appl. Chem.*, **76**, 1903 (2004); <https://doi.org/10.1351/pac200476101903>
- A. Sarkar and S. Pandey, *J. Chem. Eng. Data*, **51**, 2051 (2006); <https://doi.org/10.1021/je0601560>
- A. Sarkar, S. Trivedi, G.A. Baker and S. Pandey, *J. Phys. Chem. B*, **112**, 14927 (2008); <https://doi.org/10.1021/jp804591q>
- G.G. Fortunato, P.M. Mancini, M.V. Bravo and C.G. Adam, *J. Phys. Chem. B*, **114**, 11804 (2010); <https://doi.org/10.1021/jp103677q>
- S. Trivedi, N.I. Malek, K. Behera and S. Pandey, *J. Phys. Chem. B*, **114**, 8118 (2010); <https://doi.org/10.1021/jp102217u>
- H. Salari, M. Khodadadi-Moghaddam, A.R. Harifi-Mood and M.R. Gholami, *J. Phys. Chem. B*, **114**, 9586 (2010); <https://doi.org/10.1021/jp103476a>
- C. Chiappe, C.S. Pomelli and S. Rajamani, *J. Phys. Chem. B*, **115**, 9653 (2011); <https://doi.org/10.1021/jp2045788>
- A. Ali, M. Ali, N.A. Malik, S. Uzair and A.B. Khan, *J. Chem. Eng. Data*, **59**, 1755 (2014); <https://doi.org/10.1021/je400908z>
- V. Beniwal and A. Kumar, *ChemPhysChem*, **16**, 1026 (2015); <https://doi.org/10.1002/cphc.201402825>
- M.R. Islam, F. Warsi, A.B. Khan, T. Kausar, I. Khan and M. Ali, *J. Chem. Eng. Data*, **64**, 1140 (2019); <https://doi.org/10.1021/acs.jced.8b01068>
- S. Thawarkar, N.D. Khupse and A. Kumar, *J. Solution Chem.*, **49**, 210 (2020); <https://doi.org/10.1007/s10953-020-00952-w>
- A. Duereh and H. Inomata, *J. Mol. Liq.*, **320**, 114394 (2020); <https://doi.org/10.1016/j.molliq.2020.114394>
- S. Morales, C. Pastenes, V.G. Machado and M.C. Rezende, *J. Mol. Liq.*, **343**, 117644 (2021); <https://doi.org/10.1016/j.molliq.2021.117644>
- X. Yao, R. Fang, H. Zhao, A. Farajtabar, A. Jouyban and W.E. Acree Jr., *J. Mol. Liq.*, **349**, 118515 (2022); <https://doi.org/10.1016/j.molliq.2022.118515>
- S. Zein El Abedin and F. Endres, *Acc. Chem. Res.*, **40**, 1106 (2007); <https://doi.org/10.1021/ar700049w>
- J. Dupont, *Acc. Chem. Res.*, **44**, 1223 (2011); <https://doi.org/10.1021/ar2000937>
- R.D. Rogers and K.R. Seddon, *Science*, **302**, 792 (2003); <https://doi.org/10.1126/science.1090313>
- T.L. Greaves and C.J. Drummond, *Chem. Rev.*, **108**, 206 (2008); <https://doi.org/10.1021/cr068040u>
- E.W. Castner Jr. and J.F. Wishart, *J. Chem. Phys.*, **132**, 120901 (2010); <https://doi.org/10.1063/1.3373178>
- G.A. Baker, S.N. Baker, S. Pandey and F.V. Bright, *Analyst*, **130**, 800 (2005); <https://doi.org/10.1039/b500865b>
- E.W. Castner Jr., J.F. Wishart and H. Shirota, *Acc. Chem. Res.*, **40**, 1217 (2007); <https://doi.org/10.1021/ar700169g>
- Z. Hu and C.J. Margulis, *Acc. Chem. Res.*, **40**, 1097 (2007); <https://doi.org/10.1021/ar700046m>
- J.P. Hallett and T. Welton, *Chem. Rev.*, **111**, 3508 (2011); <https://doi.org/10.1021/cr1003248>
- V.I. Parvulescu and C. Hardacre, *Chem. Rev.*, **107**, 2615 (2007); <https://doi.org/10.1021/cr050948h>
- C. Bouvy, G.A. Baker, H. Yin and S. Dai, *Cryst. Growth Des.*, **10**, 1319 (2010); <https://doi.org/10.1021/cg9013575>
- T. Tsuda and C.L. Hussey, *Interface*, **16**, 42 (2007); <https://doi.org/10.1149/2.F050711F>
- K. Bhattacharyya, *J. Phys. Chem. Lett.*, **1**, 3254 (2010); <https://doi.org/10.1021/jz1012438>
- J.S. Wilkes, J.A. Levisky, R.A. Wilson and C.L. Hussey, *Inorg. Chem.*, **21**, 1263 (1982); <https://doi.org/10.1021/ic00133a078>
- W. Ogihara, T. Aoyama and H. Ohno, *Chem. Lett.*, **33**, 1414 (2004); <https://doi.org/10.1246/cl.2004.1414>
- A. Stark, P. Behrend, O. Braun, A. Muller, J. Ranke, B. Ondruschka and B. Jastorff, *Green Chem.*, **10**, 1152 (2008); <https://doi.org/10.1039/b808532c>