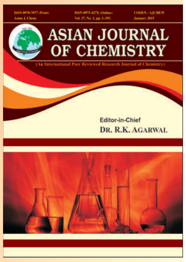
Asian Journal of Chemistry; Vol. 27, No. 3 (2015), 1173-1174

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.17408



NOTE

Cooperative Interactions in Methanol-Water Mixtures Studied by Microwave Dielectric Data

YONG-QIANG CHEN*, YING-SHU HUANG and BO YU

College of Electrical Engineering and Information Technology, Xihua University, Chengdu 610039, P.R. China

*Corresponding author: E-mail: cyqlqq@gmail.com

Received: 18 February 2014; *Accepted*: 7 May 2014; *Published online*: 19 January 2015; AJC-16750

Based on the dielectric data, the methanol-water mixtures in the water rich region (0-0.1) at 293, 298 and 303 K were performed. We estimated the cooperative interaction of methanol-water cluster by extended Froehlich theory. We get different aspect of the interaction of molecules, which help to understand the relaxation acts.

Keywords: Water-methanol mixture, H-bonds dynamic, Cooperative interactions.

A significant driving force behind dielectric studies of water H-bonded liquids is the goal of understanding the role of the H-bond in water[1-6]. Because the inherent ability to monitor the cooperative motion of a molecular ensemble makes dielectric relaxation spectroscopy (DRS) a valuable tool for investigating the structure and of aqueous solutions dominated by intermolecular H-bonds.

An extensive study of dielectric behaviours of polar solutes at low concentration (to minimize solute-solute interactions) in polar solvents has led to valuable information regarding hydrogen bonding and solute-solvent interaction. And the nature of H-bonding interactions and the mechanism of bound water are still not completely understood. To gain some insight into the nature of molecular interactions between the associating molecules, a dielectric study of methanol-water system would be helpful.

Theoretical background: The dipole moments of methanol and the formation of water clusters exist in the mixture. We outlined how to determine the number of the water molecules hydrogen bound to one methanol molecule by using extended Froehlich theory[7,8].

The Froehlich's function at temperature is described by as follow:

$$B(T) = \frac{1}{3\varepsilon_0 kT}\left(M^2\right) \tag{1}$$

Here is the absolute temperature k, is the Boltzmann constant, V is a volume with microscopic cells containing dipoles and in this function $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m. The electric dipole moment of this volume is defined as $M = \sum_{i=1}^{N} m_i$, with the average dipole moment of the ith cell m_i, and the brackets in eqn. 1 indicate a statistical averaging over all possible cell configurations.

To calculate the value (M^2) in eqn. 1 for the water-methanol, the random macroscopic dipole moment M can be written as

$$M = \sum_{i=1}^{N_1} \mu_1 + \sum_{k=1}^{N_2} \mu_2 \tag{2}$$

where $\mu_1 = 1.84$ D and $\mu_2 = 1.69$D are the dipole moments of water and methanol. The mean square random macroscopic dipole moment (eqn. 1) can be approximated by the following relationship:

$$(M^2) \cong N_1\mu_1^2 G_1 + N_2\mu_2^2 G_2 + 2N_2 N_{12}\mu_1\mu_2(\cos\theta_{12}) \tag{3}$$

In eqn. 3, $G_1 = 2.06$ and $G_2 = 1.0$ are the Kirkwood factors of water-water and methanol-methanol associates, respectively (G is used in the extended Froehlich theory. In this model we use G to estimate cooperative interactions of water-methanol dependent concentration. So we choose two symbols distinguishing their significances). N_{12} is the number of the water molecules hydrogen bound to one methanol molecule, θ_{12} is the angle between the hydration water and methanol dipoles. Substituting eqn. 3 into relationship (1) and considering B as a function of the concentration, we obtain:

$$\frac{B(x_2)}{B(0)} = 1 + \frac{x_1\mu_1^2 G_1}{x_2\mu_2^2 G_2} + 2\frac{x_1\mu_1 G_1}{x_2\mu_2 G_2} N_{12}(\cos\theta_{12}) \tag{4}$$

where $B(0)=\frac{n_2\mu_2^2G_2}{3\varepsilon_0 k}$ and X_1 as well X_2 as are the molar fraction of water and Methanol, respectively. $n_2 = X_1 \cdot N_A \cdot 10^3 m^{-3}$ is the number of water molecules, where $N_A = 60.22 \times 10^{23}$ mol^{-1} denotes Avogadro's number. And $N_{cl} = N_{12} \cos \theta_{12}$, the value of N_{cl} can be analytically expressed as

$$N_{cl}(x_2)=\frac{1}{2}\left|\left[\frac{B(x_1)}{B(0)}-1-\frac{x_1\mu_1^2G_1}{x_2\mu_2^2G_2}\right]\right|\frac{x_2\mu_2G_2}{x_1\mu_1} \qquad (5)$$

This formula allows us to calculate the value of N_{cl} for various concentrations X_2, using the experimental values of the Froehlich function $B(x_2)$.

As examples, complex dielectric spectra from the literature for methanol-water in the water rich region (0-0.1) Fig.1.

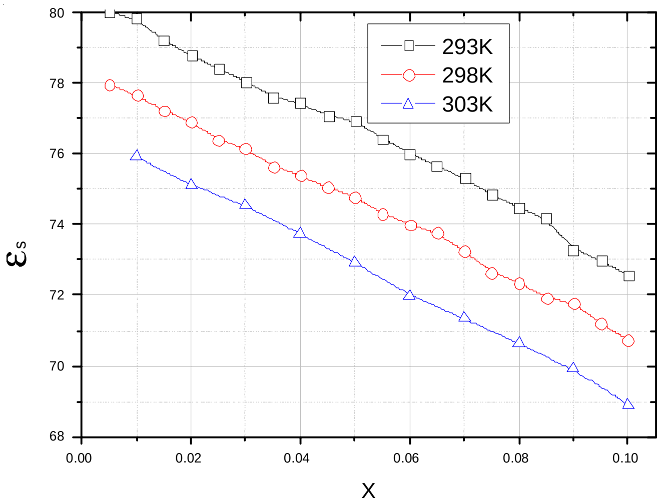


Fig. 1. Concentration dependence of the static dielectric constant for water-methanol mixture

Fig. 1 shows static dielectric constant of the water-methanol mixture temperature variation as a function of concentration. There is a slight temperature difference and decreased as a function of concentration. Fig. 2 shows that at dilute methanol solution the number of bound water molecules around with one methanol molecule. This confirms that a new scale of cooperativity existed due to the interaction of water clusters with methanol dipoles. The number of water clusters is affected by the dipole of methanol molecule and to show the differing effects of methanol fraction. The number of water molecules associated with the methanol decreases with methanol fraction. Water clusters contributed to the dielectric constant of mixture are consisted of tiny unit of hydrogen bonding to water molecules.

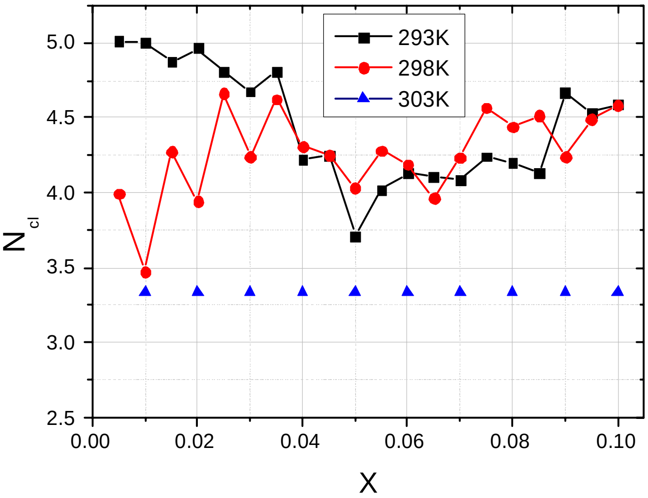


Fig. 2. Concentration dependence of the number of cluster molecules for water-methanol mixture

Conclusion

The clusters of water molecules affected by dipolar methanol molecule can be estimated by expanding Kirkwood-Froehlich theory applying to macroscopic dipole moment parameter. The number of water clusters of molecules change with the increasing of methanol molecules is observed.

The extended Froehlich theory focus on cooperative interaction of water-Methanol cluster, which provide valuable insights into the underlying mechanism of the relaxation acts.

REFERENCES

1. L.P. Singh and R. Richert, *Phys. Rev. Lett*., **109**, 167802 (2012).
2. H. Fröhlich, Theory of Dielectrics, Clarendon Press, Oxford (1958).
3. C.J.F. Böttcher, O.C. van Belle, P. Bordewijk and A. Rip, Theory of Electric Polarization, Elsevier, Amsterdam (1973).
4. C.J.F. Böttcher and P. Bordewijk, Theory of Electric Polarization, Vol. II, Elsevier Scientific Publishing Company, Amsterdam, Oxford, New York (1978).
5. J.N. Murrell and A.D. Jenkins, Properties of Liquids and Solutions, Wiley & Sons, edn 2 (1994).
6. J.B. Hasted, Aqueous Dielectrics, Chapman and Hall, London (1973).
7. T. Sato, A. Chiba and R. Nozaki, *J. Chem. Phys*., **112**, 2924 (2000).
8. E. Levy, A. Puzenko, U. Kaatze, P.B. Ishai and Y. Feldman, *J. Chem. Phys*., **136**, 114502 (2012).