

Hydrogen Bond Dynamics of Water-Acetone Mixtures Studied by The Complex Permittivity

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The complex permittivity of water-acetone mixtures, over the entire concentration range, have been measured using the resonant cavity perturbation method at 298 K. It was noticed that the permittivity gradually decreased with increasing concentration of acetone in water, whereas the relaxation time decreased with increasing concentration and temperature. The observed values of the dielectric parameters confirm that H-bonded molecular interactions decrease the number of effective parallel aligned dipoles with the formation of complexes in water-acetone mixtures.

Key Words: Binary mixture, Permittivity, Debye equation, Mixture formula.

INTRODUCTION

Microwave heating has attracted interest in the chemical industry for its ability to provide targeted heating of liquids rapidly and uniformly¹. For better application of microwaves in the chemical industry, the interaction between microwaves and the mixtures needs to be further studied. Usually, the permittivity describes a material's ability to absorb, transmit and reflect electromagnetic energy. Thus, it is important to know the permittivity of liquid mixtures at microwave frequencies. The obvious importance of water as a solvation medium has fueled a tremendous effort to understand the properties of aqueous solutions. Adding to the scientific interest in water are its peculiarities as a solvent—namely, its effectiveness in solvating ionic and dipolar substances²⁻⁴. These properties of water have a large bearing on biological systems and other chemical systems of practical importance and are related to the highly associating nature of water through its ability to form hydrogen bonds⁵. We shall restrict our attention in this article to binary mixtures of water with acetone, of which has large dipole moments. Consequently, it would be desirable to apply the resonant cavity perturbation method to study dynamics of hydrogen bond at water-acetone mixture.

EXPERIMENTAL

The measurement system (Fig. 1) consists of a vector network analyzer Agilent E8362 BandaH105 rectangular resonant wave guide cavity. The rectangular resonant cavity technique is based on the electromagnetic field perturbation of a resonant cavity by the insertion of a small sample and is a popular technique for measuring the permittivity by using the

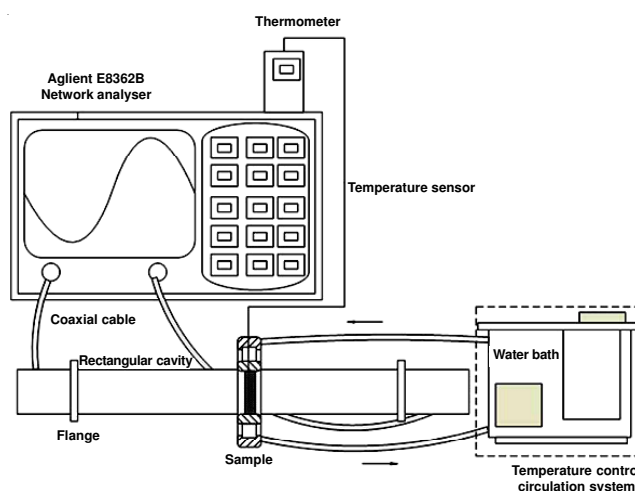


Fig. 1. Measurement systems

perturbation formula⁶. A temperature controller system with a water bath and thermostat was used to maintain the temperature constant within ± 0.5 K. The sample cell was surrounded by a heat insulating container through which the constant temperature water was circulated. The temperature at the cell was checked using a thermometer sensor. The dielectric properties of water-acetone mixtures with different volume ratios were measured at 298 K.

RESULTS AND DISCUSSION

We find reasonable agreement between the measured and the available experimental dielectric constant for all the compositions of water-acetone mixtures.

The excess dielectric constant and inverse relaxation time less than 1 indicates that one of the mixture constituent molecules acts as 'structure-breaker' and hence there is a decrease in the total number of aligned effective dipoles that contributed to the mixture dielectric polarization and solute-solvent interactions produce a field such that the effective dipoles rotate more slowly.

An array of experiments and theories have revealed the dielectric path ways and timescales associated with different aspects of the hydrogen-bond dynamics of bulk water and aqueous solution⁷⁻⁹. This implies that a new formula needs to be formulated to include hydrogen bond contributions. The static permittivity for the mixtures can be explained using the Luzar model by assuming the formation of two types of hydrogen-bonded dimers. The Kirkwood correlation factor g_i for a mixture can be expressed as:

$$\frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{9\epsilon_0} = \frac{4\pi}{9kT} \sum_{i=1}^2 g_i \rho_i \mu_i \quad (1)$$

where $i = 1$ and 2 represent solvent or water, respectively. Here, μ_i is the dipole moment of an solvent or water molecule, ρ_i is the density and g_i is the Kirkwood correlation factor for the i th liquid component. The interpretation of the dielectric phenomena in terms of the Kirkwood correlation factor is very difficult for a mixture of associated compounds. It is impossible to separate the average correlation factors g_1 and g_2 from a single value of the static dielectric constant without any assumptions. Kirkwood-Frohlich theory must be applied to media containing two species of molecules and the cross-correlation terms must be taken into account to separate g_1 and g_2 when considering only the hydrogen-bond contribution to the dipole-dipole correlation. In the present approach, the Kirkwood correlation factors for individual species $i = 1$ and 2 are modified and these new correlations are described by the following relations:

$$g_1 = 1 + Z_{11} \cos \phi_{11} + Z_{12} \cos \phi_{12} \left(\frac{\mu_1}{\mu_2} \right) \quad (2)$$

$$g_2 = 1 + Z_{21} \cos \phi_{21} \left(\frac{\mu_2}{\mu_1} \right) \quad (3)$$

where $Z_{11} = 2 \langle n_{HB_{11}} \rangle$, $Z_{12} = 2 \langle n_{HB_{12}} \rangle$ and $Z_{21} = - \langle n_{HB_{12}} \rangle / 2$, are the average numbers of hydrogen bonds between water-water, solvent-water and solvent-solvent pairs, respectively. ϕ_{11} , ϕ_{12} and ϕ_{21} are the average angles between neighbouring dipoles of solvent-solvent, solvent-water and water-water pairs, respectively and \cos is taken to be $1/3$. The average number of hydrogen bonds [$\langle n_{HB_{11}} \rangle$, $\langle n_{HB_{22}} \rangle$ and $\langle n_{HB_{12}} \rangle$] per solvent molecule for $1i$ pairs ($i = 1$ or 2) has been determined using the following relation⁷:

$$\langle n_{hb}^{li} \rangle = \frac{n_{li} \omega_{li}}{n_i} \quad (4)$$

where $\omega^{li} = 1/[1 + \alpha 1i \exp(\beta E_{1i})]$ is the probability of bond formation between solvent or water. n_i is the number density of solvent molecules, $\beta = 1/kT$ and $\alpha 1i$ are the statistical volume ratios of the two subvolumes of the phase space related to the

nonhydrogen-bonded and hydrogen-bonded pairs. These hydrogen-bonded pairs have only two energy levels, E_{11} and E_{12} , for 11 and 12 pair-formed bonds, respectively. The values of $\langle n_{HB_{12}} \rangle$ and $\langle n_{HB_{11}} \rangle$ depend on the number densities of the hydrogen-bonded pairs between solvent or water (n_{12}) and between solvent molecules ($n_{11} = 2n_1 - n_{12}$), respectively. These can be calculated, during which water-water (11 pair) and solvent-water (12 pair) are formed.

The concentration dependence of the static dielectric constants is calculated using eqns. 2 and 3 and is compared with experimental data. Here, the parameters μ required in eqns. are the dipole moments of molecules solvent. The polarizability, static volume ratio, number of hydrogen bonds and bonding energy are the fitting parameters. We calculated the average number of hydrogen-bonded water-water pairs, $\langle n_{HB}^{11} \rangle_v$ and water-solvent pairs, $\langle n_{HB}^{12} \rangle_v$, per unit volume ($/cm^3$) using

$$\langle n_{BH}^{11} \rangle_v = \frac{C_1 \rho_{mix} N_A n_{BH}^{11}}{M_1} \quad (5)$$

$$\langle n_{HB}^{12} \rangle_v = \frac{C_1 \rho_{mix} N_A n_{HB}^{12}}{M_1} \quad (6)$$

Here, solvent is the weight fraction of solvent, ρ_{mix} (g/cm^3) is the density of the mixtures, N_A is the Avogadro number and M_1 is the molecular weight of solvent. For instance, it is important to analyze the behaviour of the average number of hydrogen bond $\langle N_{HB} \rangle$ per molecule in function of the molar fraction of water in the mixture for acetone at 298 K and 1 atm. A direct analysis of Table-1 shows that acetone has roughly only one hydrogen-bond per molecule. But the most remarkable aspect is the fact that water-water hydrogen-bond does not behave in a similar way for each mixture. In the case of acetone an exponential behaviour is observed. This implies that water prefer self-association in the case of acetone, which is a consequence of the fact that acetone are able to accept only one hydrogen-bond. This behaviour was also reported by Venables and Schmuttenmaer⁴.

TABLE-1
THREE DEBYE DIELECTRIC CONSTANTS OF WATER-ACETONE BINARY MIXTURES AND THE AVERAGE NUMBER OF HYDROGEN-BONDED WATER-WATER PAIRS, $\langle n_{HB}^{11} \rangle_v$ AND WATER-ACETONE PAIRS, (AT 298 K)

x	ϵ_0	ϵ_0^1	τ (ps)	ϵ_∞	$\langle n_{HB}^{11} \rangle_v$	$\langle n_{HB}^{12} \rangle_v$
0	20	20.7	4.3	1.81	0	1.0
0.1	22.70	24.3	7.5	1.83	0.63	1.52
0.2	25.5	(x = 0.25) 32.9	9.2	1.85	1.12	1.28
0.3	28.5	-	12.3	1.85	1.55	1.15
0.4	29.7	-	13.5	1.85	1.83	1.01
0.5	32.5	38.6	14.1	1.86	2.14	0.96
0.6	36.4	-	14.6	1.87	2.37	0.83
0.7	45.26	-	13.8	1.86	2.66	0.51
0.8	56.6	64.0	12.4	1.83	2.93	0.36
0.9	68.2	73.2	11.6	1.81	3.22	0.17
1.0	79.7	-	8.2	1.78	3.53	0.00

Our data are compared to microwave data from Ref. 4 (ϵ_0^1).

Conclusion

The composition dependence of the dielectric relaxation behaviour at microwave frequencies of water-acetone were measured and are reported over the whole composition range at 298 K. It was noticed that the permittivity gradually decreased with increasing concentration of methanol in ethanol, where as the relaxation time decreased with increasing concentration. The observed values of the dielectric parameters confirm that H-bonded molecular interactions decrease the number of effective parallel aligned dipoles with the formation of complexes in liquid water-acetone mixtures.

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