

Dielectric and thermodynamic study of binary systems of alcohols in H-bond acceptor media

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Abstract

Relative permittivity, refractive index, and density data were measured for binary mixtures containing alcohols and ketones in the mole fraction range of ($0 \leq x \leq 1$) at $T = (298.2 \text{ and } 308.2) \text{ K}$ and $P = 101.3 \text{ kPa}$. Comparative study was performed on the eighteen polar-polar binary systems of the {1-alkanols (ethanol, 1-butanol, 1-hexanol, 1-octanol and 1-decanol) + cyclic ketones (cyclopentanone, and cyclohexanone)}, {cyclohexanol + cyclic ketones (cyclopentanone and cyclohexanone)}, and {heavy alcohols (1-hexanol, 1-octanol, and 2-ethyl-1-hexanol) + linear ketones (methyl ethyl ketone, diethyl ketone)}. The analyses were performed by using Kumbharkhane, Winkelmann-Quitze, and Reis-Iglesias theories, leading to optical, electrical, and thermodynamic excess quantities. The effective and corrective Kirkwood- ϵ correlation factors are also calculated to investigate the formations of H-bonded structure in the mixtures. The inter molecular communications were explored through different overabundance parameters, namely, excess permittivity, abundance refractive index, abundance molar volumes, overabundance Helmholtz energies and overabundance Kirkwood connection factors. The excess properties of different physical quantities are also confirming the formation of hydrogen-bonded structure in these mixtures.

The thermodynamics of the hydrogen holding in 1-alcohol + water paired blends is contemplated utilizing sub-atomic dynamic (MD) reproduction and the polar and irritated chain type of the factual partner liquid hypothesis (polar PC-SAFT). The division of free monomers in unadulterated soaked fluid water is figured utilizing both TIP4P/2005 and iAMOEBA re-enactment water models. Results are contrasted with spectroscopic information accessible in the writing just as to polar PC-SAFT. Polar PC-SAFT models hydrogen bonds using single bondable association sites representing electron donors and electron acceptors. The distribution of hydrogen bonds in pure alcohols is computed using the OPLS-AA force field. Results are compared to Monte Carlo simulations available in the literature as well as to polar PC-SAFT. The analysis shows that hydrogen bonding in pure alcohols is best predicted using a two-site model within the SAFT framework. On the other hand, molecular simulations show that increasing the concentration of water in the mixture increases the average number of hydrogen bonds formed by an alcohol molecule. As a result, a transition in association scheme occurs at high water

concentrations where hydrogen bonding is better captured within the SAFT framework using a three-site alcohol model.

Hydrogen bonding is interesting molecular interaction in organic compound especially in aqueous medium. Occurring of H-bond between the molecules has been well defined by Arunan et al. The interaction between the lone pair of the electrons through-space overlaps the atomic orbital and the inconceivable present state concentrates on inter-nitrogen coupling that could be large enough to prevent symmetry lowering on formation. Based on various spectroscopic and molecular orbital calculations ensures the interaction is a 'through bond interaction' and precede a much longer coupling as expected. Through bond coupling is a magnitude of the distortive forces which compete with the through bond interaction to determine molecular geometry. The present work focuses the interaction between pyrazine + water mixture on various mole fractions and temperature. The presence of water leads to formation of hydrogen bonds between the lone pair exists in N-atoms and a water-hydrogen atom interacts in the various molecular states and the lone pair ion depleted and eliminating the additional hydrogen bonds that stabilizes the structural formation. The hydrogen bonding interactions and their effects on molecular spectral studies was established by Brealey and Kasha et al. Primary alcohol has been selected as a representative of strong proton donors introduced to binary to ensure the formation of typical molecular bonding.

Ostwald viscometer is a function of both dynamic viscosity and density used to determine the relationship between dynamic viscosity and density is called the kinematic viscosity and is defined as the ratio of dynamic viscosity and density. The accuracy of measurement is in the order of 10^{-3} gm. , at 0.1 MPa .

The complex permittivity spectra $\epsilon^*(\omega)$ Dielectric properties of the aqueous pyrazine are studied by Kaatze. It shows the variation in static permittivity with temperature for various mole fractions of pyrazine–binary mixture. Paradiazine in polar medium(water), has temperature disturbs the alignment of dipoles in an outer field is well pronounced one and the dielectric constant decreases with temperature and with increasing mole fraction due to dipolar molecules rotating or reorientation of ions. The value of ϵ_∞ was taken to be 4 for all solution studied, since for the frequency range considered here, ϵ' is not sensitive with respect to ϵ_∞ . The intermolecular bonding in the system contributes structural changes which in turn alter the dielectric properties. Intermolecular bonding as H-bond in aqueous pyrazine studied by Caminati et al

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estimated water molecules bound above the ring and also in the plane of the ring. The mechanism of interaction involved in formation of dimers and particularly the self-associative hydrogen bond pairs with alcohol group dominates it to be a polar. The electrostatic potential between negative oxygen and nitrogen is well balanced with positive carbon and hydrogen. The interaction with shifting of ions of the symmetrical heterocyclic molecule of pyrazine is compatible to flow of charges and movement of charges in oscillating electric field. The thermal effects are associated with dissipation of energy as dielectric loss in the medium that influence significant changes in their dielectric properties. The dielectric constant is strongly dependent on the structure. The electron shifting within molecules and orientation polarizability causes dielectric polarization in pyrazine with organic molecules. The effect of electronic shifting within molecules has rather weak temperature dependence than the orientation polarization. In the presence of lower order alcohol is a passive active medium with higher static permittivity in the applied electric field. The potential energy of orientations aligned with the field is lowered and orientations aligned against the field are raised. Therefore over a time excess molecule will align with the field and less energy is required to switch to orientations aligned with the field and more energy required to switch to orientations aligned against the field. The molecular energy need to be more than the any energy barrier within the system for a change in orientation rather with lower energy cannot change its orientation.