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Evidence of anomalous behavior of intermolecular interactions at low concentration of methanol in ethanol-methanol binary system

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ABSTRACT

At low concentrations of methanol in a binary system of ethanol and methanol, uniquely complex molecular interactions are reported here. Previous studies indicate that ethanol molecules form aggregates held together by hydrogen bonding (O–H–O) and also dispersive forces. Addition of small amount of methanol tends to break the hydrogen bond network of ethanol due to the larger polarity of methanol. This leads to the ethanol molecules becoming somewhat isolated from each other within a scaffolding network of methanol molecules, as seen from the present molecular dynamics simulations. This is an indication of a repulsive force that dominates among the two different alcohols. At higher molar concentration of methanol ($Xm > 0.3817$), the strength and extent (number) of formation of hydrogen bonds between ethanol and methanol increase. The geometry of molecular structure at high concentration favors the fitting of component molecules with each other. Intermolecular interactions in the ethanol-methanol binary system over the entire concentration range were investigated in detail using broadband dielectric spectroscopy, FTIR, surface tension and refractive index studies. Molecular dynamics simulations show that the hydrogen bond density is a direct function of the number of methanol molecules present, as the ethanol aggregates are not strictly hydrogen-bond constructed which is in agreement with the experimental results.

1. Introduction

Ethanol and methanol strongly self-associate due to hydrogen bonding [1–4]. These primary alcohols do not form azetropes when mixed with each other at any concentration ratios. They form extended hydrogen bond networks due to the similarity of hydrogen bonds in both of them [5]. However, methanol is dominated by hydrogen bond while ethanol, a higher homologue of methanol, is known to have a significant hydrophobic property due to the extra 'methylene' (CH2) group. Hence the behavior of ethanol-methanol binary system is far from ideal because both the hydrogen bond donating and accepting strengths are seem not to be identical [6].

Vast experimental information is available concerning the dielectric properties, excess volume parameters, FTIR spectra and refractive index of binary system of ethanol-water [7], methanol-water [7,8], methanol-higher alcohols [9], etc. All these systems show a deviation from ideal behavior for most physical and chemical properties at 50%. On the other hand, comparatively very few reports are available for the ethanol-methanol binary system. Albuquerque et al. [10] observed ideal behavior of the surface tension and density measurements of the ethanol-methanol binary system for all concentration ranges at 298.15 K. The current study is undertaken to understand the anomalous behavior of intermolecular interactions at low concentrations of methanol in ethanol-methanol system at 303 K. Dielectric, FTIR, surface tension, refractive index and molecular dynamics studies for this system is undertaken over the complete concentration range, with emphasis on concentration regions where anomalous behavior in properties is seen. The excess values of molar volume and refractive index, molar refraction and total partial pressure were determined using the experimental values. Complex impedance Cole-Cole plots were used to study the relaxation mechanism in the ethanol-methanol system.

Molecular dynamics simulations were done to verify the behavior of ethanol-methanol binary system. The structure of molecules and the number of hydrogen-bonded molecules determined from the simulations are used to interpret the experimental results of surface tension, density, refractive index and dielectric values relating hydrogen bond structure. It is understood from the present study that the methanol molecules are responsible for increase in hydrogen bond density and they play the role of a mediator in connecting ethanol molecules.

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Table 1
Variation of hydrogen bond density with the concentration of methanol.

Mole fraction of methanol	No. of et molecules	No. of met. molecules	No. of H-bonds	Box volume (nm^3)	Hydrogen bonds/ (nm^3)
0.1379	1000	132	33.71	80.4956624	0.41879275
0.1641	1000	152	38.834	77.857765	0.49878134
0.1899	1000	185	50.996	84.2252341	0.60547175
0.2153	1000	200	62.467	84.8753878	0.73598486
0.2402	1000	226	64.118	86.8064943	0.69175572
0.2467	1000	254	74.251	89.6014556	0.82868073
0.2889	1000	283	97.126	64.0920729	1.51541362
0.3126	1000	310	108.152	94.6536029	1.14260838
0.3360	1000	350	148.882	98.7398907	1.50782018
0.3590	1000	386	162.283	100.910922	1.60818073
0.3817	1000	441	196.457	105.081882	1.86956111
0.4899	1000	686	343.271	127.380453	2.69484832
0.5902	1000	1040	555.289	160.99895	3.44902249
0.6836	1000	1548	948.363	198.209334	4.784655358
0.7707	1000	2321	1604.325	251.864824	6.3678588
0.8521	1000	3939	3066.731	359.514916	8.53019128
0.9283	1000	9072	7765.461	696.126002	11.155252

2. Experimental Section

2.1. Materials

Methanol and ethanol were purchased from Sigma-Aldrich and Merck Emplura respectively. The purities of methanol and ethanol were 99.9%. The precision of the binary system was ±0.1 mg and they were measured using a weighing balance.

2.2. Methods

Surface tension of the binary systems over the whole concentration range were measured using Rame-Hart contact angle goniometer. Pendant drop method was used in calculating the surface tension. The polar and dispersive parts of surface tension were calculated using the contact angle data. The mid infra-red spectra of the binary systems were measured by Fourier Transform Infra Red

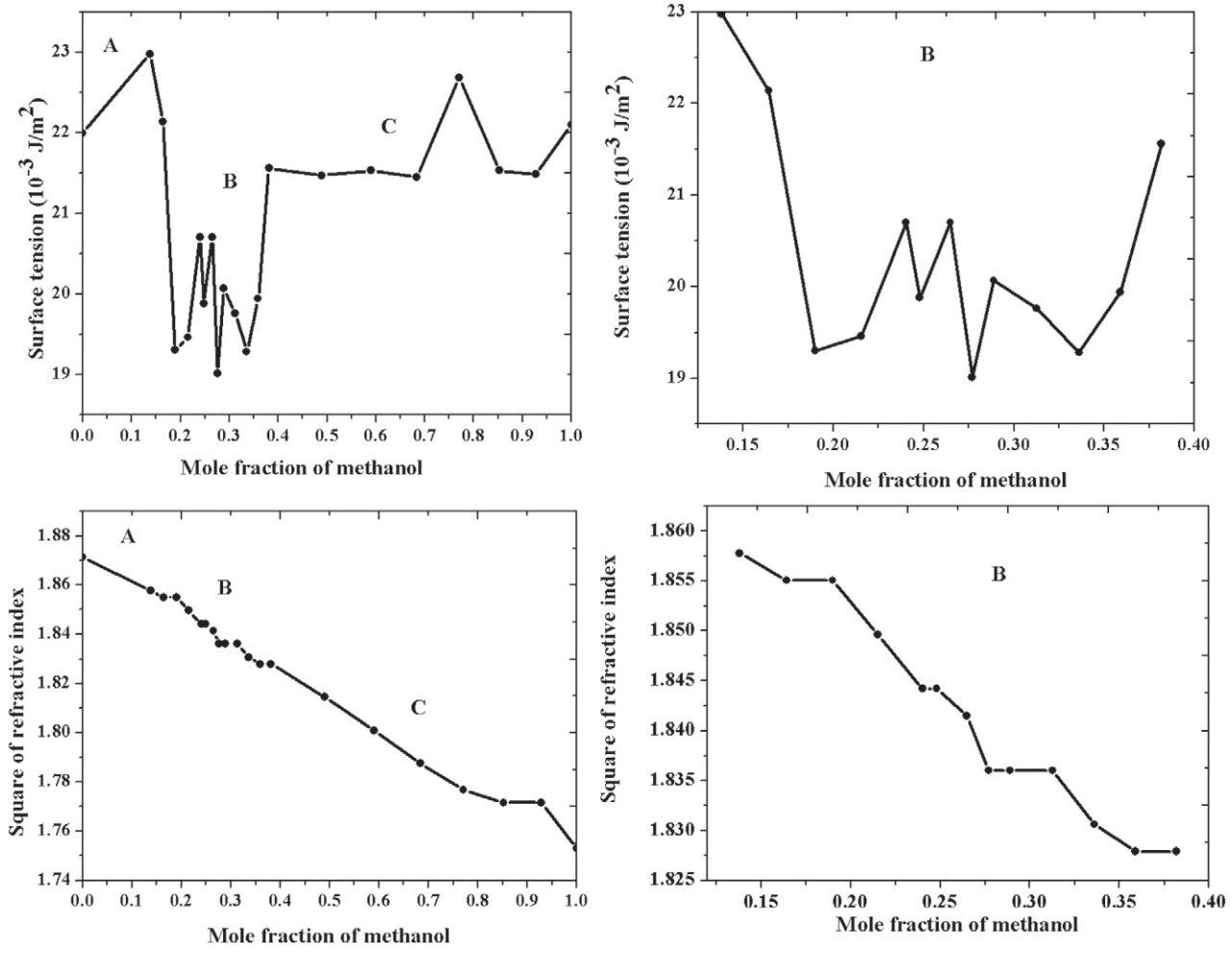

Fig. 1. Variation of surface tension and refractive index with mole fraction of methanol. The experimental error values of the measured properties are much smaller than the symbol size.