May-July, 2012, Vol.2.No.3, 1200-1205. e- ISSN: 2249 –1929

Journal of Chemical, Biological and Physical Sciences

An International Peer Review E-3 Journal of Sciences

Available online at www.jcbsc.org

Section A: Chemical Sciences

CODEN (USA): JCBPAT

Research Article

Ion-Solvent and Ion-Ion Interactions of Toluene-4-Sulfonic Acid in Mixed Media

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***Received: 25 April 2012; Revised: 17 May 2012;* Accepted: 22 May 2012**

ABSTRACT

Densities (ρ) and speeds of sound (u) of ternary mixtures of toluene-4-sulfonic acid in 70 % (v/v) acetone-water and 70% (v/v) ethanol-water mixtures for different concentrations of sulfonic acid were measured at 300 K. Apparent molar volume (ϕ_v) and adiabatic compressibility (Ks) of solutions were determined from the measured densities and sound velocities of solutions and solvent mixtures. The limiting infinite dilution apparent molar volume (ϕ^0_v) was evaluated from the Masson's relation. Data has been discussed in terms of ion-ion and ion-solvent interactions.

Keywords:

INTRODUCTION

Toluene-4-sulfonic acid (TSA) is used as a catalyst for manufacturing of pharmaceutical products such as Naproxen, Persantin, Ciprofloxacin etc., in adhesives of food packaging, as an acid catalyst for esterification, acetylation, polymerization, hydrolysis, dehydration, alkylation, in plasticizers industries as an esterification catalyst.

Study of molecular interactions in ternary system of organic compounds has great theoretical and practical applications [1-2]. TSA is soluble in water, ethanol and other polar solvents and it dissociates easily in aqueous media to produce H^+ and SO_3^- ions. Ternary system of TSA with water and ethanol or acetone shows deviations from ideality behavior. In its dilute solution, these ions are apart and hence inter-ionic attractions are less. As concentration increases, the inter-ionic attraction increases. At the same time, a) polar solvents align the ions with their oppositely charged part and b) there are solvent-solvent interactions e.g. intermolecular hydrogen bonding in water, water and ethanol etc. therefore, the monitoring the variations in these interactions is an interesting way to understand the overall picture of the ternary systems.

The qualitative information about molecular interactions in solutions can be collected from the measurement of ultrasonic velocity and related properties [3-6]. The ion-ion, ion-solvent and solvent-solvent interactions can be studied by the measurement of relative viscosity and ultrasonic velocity of an electrolyte in solutions. Structure making and breaking properties of solutes can be understood from this type of the study [7-9]. Molecular interactions in solution have been studied by many workers by measurement of sound velocity and density [10-13].

No work has been reported on the measurement of density and sound velocity of toluene-4-sulfonic acid in mixed media, therefore, the present work is carried out to study the molecular interactions of TSA and solvent mixtures at 300 K.

EXPERIMENTAL

Acetone and ethanol used were of analytical reagent grade and purified before use [14]. Toluene-4-sulfonic acid (TSA) was recrystallized before use. The binary mixtures of acetone-water (X_w=0.58, X_a=0.42) and ethanol-water (X_w=0.52, X_e=0.48) were prepared in precalibrated 250 mL volumetric flask by adding appropriate quantities of solvents. Doubly distilled water was used for preparation of all the solutions. Solutions of TSA (Mol. Wt. 172.02 g/mole) were prepared by adding accurate amount of it in binary solvent mixtures. All the glassware's used in during the experiment were of Pyrex quality. Weighing was done on single pan, electronic balance.

Densities were measured by using bicapillary pycnometer. The pycnometer was of Borosil make and of various volumes. The accuracy of pycnometer was 0.0003 $g\cdot cm^{-3}$. The ultrasonic velocities were measured by using ultrasonic interferometer (Mittal Enterprises, Model-F-81) with accuracy of ± 0.03% and constant frequency (2 MHz). Ultrasonic interferometer was calibrated with doubly distilled water at 300 K. The uncertainty of concentration was 0.0002 $mol\cdot dm^{-3}$. Special thermostatic arrangement was made for measurement of ultrasonic velocity. All the calculations were performed on personal computer using excel programme.

RESULTS AND DISCUSSION

The measured densities (ρ) and sound velocities (u) and calculated apparent molar volume (ϕ_v) and adiabatic compressibility (K_s) are reported in Table 1. It can be observed from this Table that densities of solutions increased and sound velocities decreased with increase in concentration of TSA. The existence of molecular association between the components of the liquid mixtures can be understood from the decrease in ultrasonic velocity (u) with concentration of TSA.

Adiabatic compressibility (K_s) of solutions was calculated [15-16] by following eq. 1.

$$K_s = (u^2 \times \rho)^{-1} .....(1)$$

Where, ρ=density of solution and u=sound velocity

The adiabatic compressibility of solutions increased with concentration of sulfonic acid, which may be due strengthening of ion-ion interactions, since at higher concentrations the ions will be closer to each other and attracts by Columbic forces. Its values are higher in 70% acetone-water than in 70% ethanol-water mixture.

The apparent molar volume (ϕ_v) for different solutions were determined [17-18] from measured densities of solutions (ρ), solvent mixture (ρ_0), molar mass of solute (M=172.02 $g\cdot mol^{-1}$) and concentration of solute (c) using following eq. 2.

$$\phi_v = \frac{M}{\rho_0} - \frac{10000 \times (\rho - \rho_0)}{c \times \rho_0} .....(2)$$

The apparent molar volume (ϕ_v) is a function of temperature and composition [19]. At infinite dilution, it is equal to the partial molar volume. It can be seen that, apparent molar volume largely decreases with increase in concentration of the TSA for both the systems. Thus, volume occupied by TSA solution decreases as concentration of TSA increases due to strengthening of the force of attraction between TSA and solvent molecules. So, the volume occupied by the pure solvent or solvent mixture is more than the solution of TSA because solvent molecules get strongly attracted to the TSA molecule. This is supported by the ϕ^0_v values, which are positive for both the media, due to strong ion-solvent interactions. The ϕ^0_v value is more in ethanol-water mixture due to strong ion-solvent interactions and enhanced electrostriction in it than acetone-water. Also, strengthening of ion-ion interactions upon increase in concentration occur due to decrease in the distance between ions. Apparent molar volume varies with concentration of solution according to Masson's relation [20], given by eq. 3.

$$\phi_v = \phi_v^{\ 0} + S_v \times \sqrt{m} .....(3)$$

From the plot of ϕ_v versus $c^{1/2}$, (Figure 1 and 2) the partial molar volume at infinite dilution (□$^0{}_v$), which represents the ion-solvent interactions and S_v, which represents ion-ion interactions were determined from an intercept and slope of the curve respectively. The values ϕ^0_v and S_v are reported in **Table 1**.The experimental slopes (S_v) values are negative for both media, which may be due to vanishing of ion-ion attractive force at infinite dilution. The ion-ion interactions decrease with dilution which can be attributed to increase in distance between ions at infinite dilution. The ion-solvent interactions are much stronger than the ion-ion interactions due to greater magnitude of values of ϕ^0_v than S_v.

Table-1: Measured density, sound velocity and calculated acoustical properties of TSA in 70% (v/v) acetone-water and ethanol-water mixtures

c (mole·dm^{-3})	ρ (g·cm^{-3})	u (m·s^{-1})	Ks (bar^{-1}·10^{-5})	ϕ_v (cm^3·mole^{-1})	ϕ^0_v (cm^3·mole^{-1})	S_v
70% (v/v) acetone-water						
0.0041	0.8793	1491.1	5.115	88.957		
0.0058	0.8795	1486.4	5.147	74.126		
0.0071	0.8797	1472.7	5.242	60.037	173.18	-1323.0
0.0107	0.8803	1465.8	5.287	33.980		
0.0150	0.8811	1456.3	5.351	12.928		
70% (v/v) ethanol-water						
0.0043	0.8806	1485.4	5.147	145.788		
0.0086	0.8814	1479.6	5.182	53.346		
0.0095	0.8817	1462.9	5.300	28.741	231.22	-1828.6
0.0107	0.8820	1454.6	5.358	12.987		
0.0145	0.8826	1449.4	5.393	7.717		
0.0197	0.8834	1441.8	5.446	5.013		

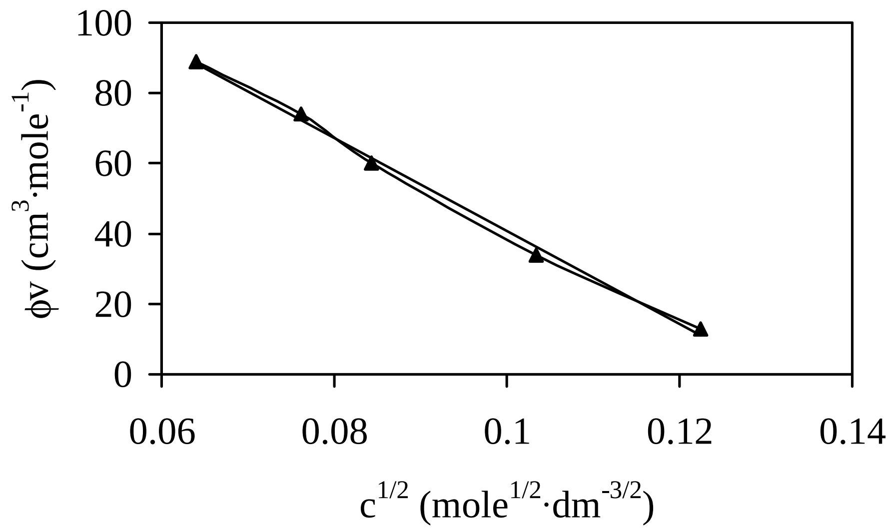

Fig.1: Variation of ϕ_v with concentration of TSA solutions a) in acetone-water mixture.

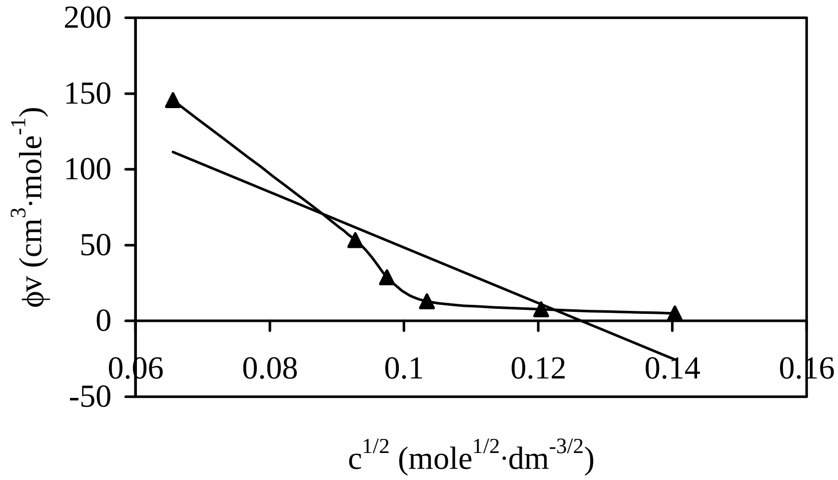

Fig.2: Variation of ϕ_v with $c^{1/2}$ of TSA solutions in ethanol-water mixture.

Structure of TSA after optimization with point charge distribution as obtained by Gaussian 09, ground state, restricted Hartree Fock method using 3-21G basis set is pictorially shown in Figure 3.

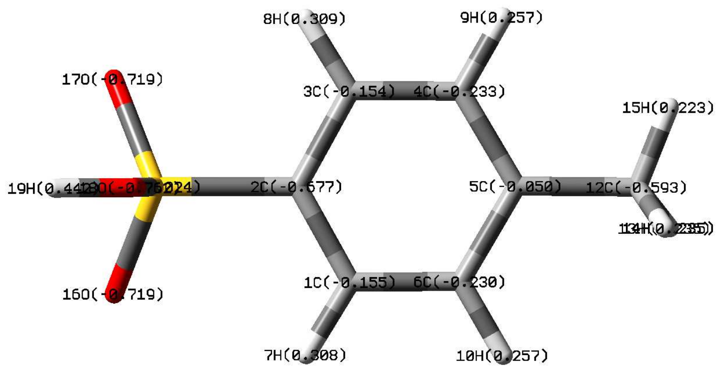

Fig.3: Optimized structure of TSA with Mulliken type atomic point charge distribution.

High charge density lies on the $–SO_3^-$ part of the molecule which interacts with water and other polar solvents in its dilute solutions showing strong ion-solvent interactions. Various types of interactions in ternary system are summarized in Figure 4.

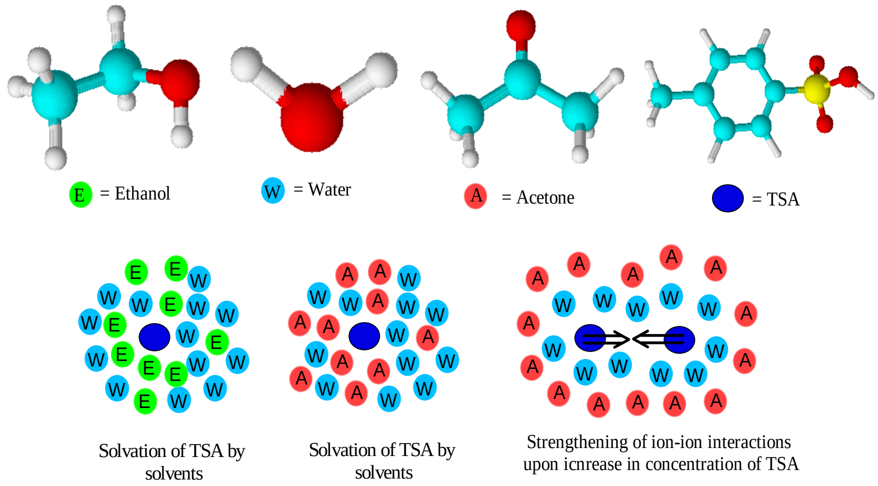

Fig.4: Optimized structures of solvents and TSA molecule showing ion-solvent, ion-ion and solvent-solvent interactions.

CONCLUSIONS

It can be concluded from results obtained in present work that both ion-ion and ion-solvent interactions are present and they dominates each other as concentration of the TSA changes. Strong ion-solvent interactions are present in both acetone-water and ethanol-water media in dilute solutions. Highly acidic $–SO_3H$ group present in TSA dissociates into ions and shows ion-solvent interactions. Ion-ion interaction strengthens with increase in TSA concentration. Enhanced electrostriction was found in ethanol-water media than acetone-water media.

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