Journal of Chemical and Pharmaceutical Research, 2016, 8(5):783-791



Research Article

ISSN: 0975-7384 CODEN(USA): JCPRC5

Volumetric properties and molecular interactions of acetic acid in water at 298.15 K

Sneha Khobragade^{1*}, Sunil H. Ganatra² and Anushree A. Ujjankar³

Department of Chemistry, Institute of Science, R. T. Road, Civil Lines, Nagpur -440008 (MS)

ABSTRACT

Acetic acid, the first molecule in carboxylic acid series has $-CH_3$ group and shows unique property of solubility in aqueous solutions. Number of workers already reported that these acids make dimer or higher aggregation in aqueous solutions. To understand the volume properties, densities (ρ), are measured for acetic acid in water at 298.15 K. Values of experimental densities were used to calculate derived properties like apparent molal

volumes (ϕ_v) , apparent molal volumes at infinite dilution (ϕ_v) , limiting apparent molal volume (\overline{V}_2), volume of

ionisation(ΔV°), volume of dimers (ϕ_{v2}^{o}) and volume change due to dimerisation (ΔV_{D}°). To understand

solute-solute interaction, molecular dynamic (MD) simulation was performed for acetic acid in water at T=298.15K. It is reported that acetic acid prefers chain dimer in aqueous solution and the results are supported by the aggregation of acetate ions in simulation ensemble.

Keywords: Molecular Dynamic, Simulation, Dimer, Density, Acetic Acid

INTRODUCTION

Carboxylic acids from acetic acid to n-valeric acid show unique property of solubility in aqueous and non-aqueous solutions. It is already reported that these molecules shows hydrophobic interactions. The strength of hydrophobic interaction increases from acetic acid to n-valeric acid[1-4].

Number of workers already reported that these acids make dimer or higher aggregation in both solvents Like, Suzuki [5] who reported volumes of dimerisation in aqueous solutions on the basis of variation of conductance under pressure. Patil et.al.[6] have derived method to determine volumes of dimerisation using density and derived properties of binary solutions. This is convenient and efficient method, which gives results of very high accuracy.

Molecular dynamics, theoretical tools, provides valuable information about the molecular level interaction and various energy profiles of the system. It is also provide valuable information about the orientation of molecules and ions in ensemble and knowledge of possible void space created in system. The results obtained from experimental study and MD simulation can provide the valuable information about the reasons for unique behaviour of acetic acid in water.

EXPERIMENTAL SECTION

Acetic Acid (stated mass fraction purity 0.995) was obtained from Fluka AG and used without further purification. It was kept over activated molecular sieves of type 4.10^{-6} (4A) (Union Carbide) and filtered before use. Water was used as an aqueous medium, which was purified in laboratory using double distillation techniques. The purity of water was checked by conductivity. The verification of the purity of liquids again confirmed by measuring their densities at temperature 298.15 K and compared their values with standard literature. [7]

The densities of the pure liquids and their binary mixtures were measured at temperature 298.15 K with high precision vibrating-tube digital densimeter (model DMA 602) whose measurement cell temperature was controlled automatically within ± 0.01 K by circulating constant temperature (298.15 K) water. The precision in constant temperature of water was ascertained by measuring the temperatures using 1/100 Beckmann thermometer. Before each series of measurements, the densimeter was calibrated at temperature 298.15 K and atmospheric pressure with double distilled water and dry air. Densities, both water and dry air, at 298.15 K temperature is listed by the manufacturer in the instruction manual [8].

For standardization of this instrument A and B constants (Instrumental Constants) were calculated using air and pure water as standard materials. The observed densities are related using equation 1.

 $\rho = A + B\tau^2 \dots 1$

Where τ is time scale reading measured using densimeter. The uncertainty in the density measurements was better than $\pm 3 \times 10^{-2}$. kg m⁻³.

The densities of the all pure liquids were measured at 298.15 K and were compared with the literature values [9,10] and listed in Table 1.

Table 1. Densities of pure liquids at 298.15 K compared with literature values.			
Pure Liquids	ρ x 10 ⁻³ (Kg. m ⁻³)	Literature Values ρ x 10 ⁻³ (Kg. m ⁻³)	
		[7]	
Acetic Acid (CH ₃ COOH)	1.043	1.043	
Water	0.997046	0.997047	

The binary solutions of acetic acid were prepared fresh using double distilled water. All solutions were prepared on molality (*m*) basis. Densities (ρ) were obtained for binary solutions of acetic acid at temperature 298.15 K. The densities data were used for the calculation of the apparent molal volumes (ϕ_v) in $m^3 mol^{-1}$ using equation 2.

$$\phi_{\nu} = \left[\frac{1000(\rho - \rho_0)}{m.\rho.\rho_0}\right] - \left[\frac{M_2}{\rho}\right] \dots \dots 2$$

Whereas, M_2 is molecular weight of solute, ρ and ρ_0 are densities of solution and pure solvent respectively and m is the concentration of solution. The uncertainty in the calculation of apparent molal volumes (ϕ_v) is better than $\pm 0.5 \times 10^{-3} m^3 mol^{-1}$.

Table 2 depicts the molality (m), density (ρ), 1000(ρ - ρ_0) and apparent molal volumes (ϕ_v) of acetic acid in water at 298.15 K respectively.

Table 2. Properties of Acetic acid in water at 298.15 K				
Sr. No.	Molality (m)	$Density(\rho) \; x \; 10^{3} kg/m^3$	1000(ρ-ρ0)	$\phi_v x 10^{-3} m^3 mol^{-1}$
1	0.3132	0.9996	2.5570	51.8839
2	0.4102	1.0004	3.3290	51.8927
3	0.4706	1.0009	3.8020	51.9053
4	0.5773	1.0017	4.6270	51.9261
5	0.7163	1.0028	5.6890	51.9444
6	0.9574	1.0046	7.4840	51.9763
7	1.3359	1.0073	10.2030	52.0146

Various graphs are plotted to understand the behaviour of properties of binary solutions. Figure 1 shows the variation of density against molality at 298.15 K. The obtained data fitted to the polynomial equation with R² reported to be 0.999, whereas, figure 2 shows the variation of $1000(\rho-\rho_0)$ verses molality. The obtained data best fitted to polynomial equation with R² reported to be 0.998. Figure 3 shows the graph between calculated apparent molal volumes ϕ_{ν} and molality. The graphs extrapolated to zero concentration (m=0) to calculate apparent molal volumes at infinite dilution (ϕ_{ν}^{o}). The data fitted to polynomial equation and R² reported to be 0.997.



Figure 1. Variation of densities of acetic acid against molality at 298.15 K



Figure 2. Variation of $1000(\rho-\rho_0)$ of acetic acid against molality at 298.16 K



Figure 3. Apparent molal volumes of acetic acid in water at 298.15 K.

3. Calculation of volume of dimerisation

To calculate the volume of dimerisation of acetic acid in aqueous solution, it is necessary to know the volume change for the ionization (ΔV°). In present study, the volumes change for the ionization (ΔV°) of acetic acid were calculated using equation 3,

$$\Delta V^{\circ} = \phi_{v(HA)}^{o} - \phi_{v(NA)}^{o} - \left[\phi_{v(NA)}^{o} - \phi_{v(H^{+})}^{o}\right] \dots 3$$

Whereas, $\phi_{\nu}^{o}{}_{(HA)}^{o}$ is apparent molal volume of acid at infinite dilution, $\phi_{\nu}^{o}{}_{(NaA)}^{o}$ is apparent molal volume of sodium salt of acid i.e. sodium acetate at infinite dilution. $\phi_{\nu}^{o}{}_{(H^{+})}^{o}$ and $\phi_{\nu}^{o}{}_{(Na^{+})}^{o}$ are the apparent molal volumes of cations of acid and sodium salt of acid respectively at infinite dilutions.

Values of ϕ_v^o for all sodium salt of acids are reported by Rao [11] and used as it is whereas, $\phi_{v(Na^+)}^o - \phi_{v(H^+)}^o$ which is equal to 1.24 as reported by many standard literatures [2, 3] used as it is. Calculated values of $\phi_{v(HA)}^o$, ΔV^o and their comparison with literature values are enlisted in table 3.

Table 3. Apparent molal Volumes at infinite dilution	$\phi^o_{v(HA)}$ and Volume change (ΔV	$^{\circ}$) for the ionization of acetic acid in water at
298.15 K		
		I ite meterne Maleren

Carboxylic Acid	$\phi^o_{ u(HA)} { m x10^{-3}} \ { m m^3 mol^{-1}}$	$\phi^{o}_{v (NaH)}$ x10 ⁻³ m ³ mol ⁻¹ [9]	$\Delta V^{\circ}_{\rm x10^{-3}}$ m ³ mol ⁻¹	Literature Values [2-3] ΔV° x10 ⁻³ m ³ mol ⁻¹
Acetic acid	50.16	39.22	11.44	11.3 11.5 10.9

Apparent molal volumes of un-dissociated molecules $\phi_{\nu(\mu)}$ calculated using equation 4,

$$\phi_{v(u)} = \phi_v - \alpha \Delta V^{\circ} \dots 4$$

Whereas ' α ' is degree of ionization which is calculated using equation 5,

Whereas K_i and m are the dissociation constant of an acid in the solution and the concentration of the solution respectively.

In case of aqueous solutions, volumes of un-dissociated ions are due to the contribution of apparent molal volume of monomer $\phi_{v(1)}$ and apparent molal volume of dimers $\phi_{v(2)}$. Volumes of monomer for all acids were calculated by plotting graph between $\phi_{v(u)}$ and $(1-\alpha)m$, on extrapolating it to y-axis gives the apparent molal volume of monomer $\phi_{v(1)}^o$ at infinite dilution. It is shown in figure 4.



Figure 4. Variation of $\phi_{v(u)}$ (un-dissociate ions) of acetic acid against $1 \cdot \alpha^*(m)$ in water at 298.15 K

Assuming only dimers are formed in the aqueous solutions of acids; volumes of dimer are calculated using equation 6.

 $\phi_{v(2)(aqua)} = 2[\phi_{v(1)} - (1 - \alpha - \beta).\phi_{v(1)}^{o}]/\beta.....6$

whereas ' β ' is degree of dimerisation and calculated using equation 7.

Whereas $a = 1 - \alpha$

 K_a = Dimension association constant of acid in water and is obtained from the work of Ganatra [12].

The limiting apparent molal volumes of dimers in aqueous was calculated using equation number 8.

$$\overline{V}_2 = 2.m_2/\rho_{pa}.....8$$

Whereas ρ_{pa} is the density of pure acid at 298.15 K.

Volume change due to dimerisation for solution was calculated using equation number 9.

$$\Delta V^{\circ}{}_{D} = \phi^{o}_{v2} - \overline{V_2}.....9$$

Table 4 shows the calculated values of ϕ_{v2}^{o} , \overline{V}_{2} and ΔV_{D}^{o} for acids in aqueous medium at 298.15 K constant temperature.

Table 4 Apparent molal volumes of dimmers at infinite dilution, Limiting apparent molal volumes of dimmers and Volume change due			
to dimerisation in aqueous solution at 298.15 K			
Carboxylic Acid	ϕ_{v2}^{o} x10 ⁻³ m ³ mol ⁻¹	$\overline{V}_2 $ x10 ⁻³ m ³ mol ⁻¹	$\Delta V^{\circ}{}_D$ x 10 ⁻³ m ³ mol ⁻¹
Acetic Acid	51.9	103.7	-11.3

MD Simulation of acetic acid in water

The simulation procedure is standardized with 375 water molecules using TIP4P force field. Outputs of the results were compared with the literature values. The water simulation results are comparable with literatures [13,14] and our previous work [15].

The simulation of acetic acid in water activated by selecting correct ensemble, followed by adding water molecules, cations (H^+) and anions(CH_3COO^-). In present study, we have simulated the $CH_3COO^- + H^+ + H_2O$ molecules at 298.15 K with the fixed number of molecules. The basic MD simulations were performed in Molden software [16] with Optimized Potentials for Liquid Simulations (OPLS) force field [17, 18]. Three files created for simulation process. The data file possessed molecular arrangement description, Force-Field file provided the force field values and input file was containing basic simulation parameters and commands. After simulation the results were stored in logfile. The supplied input parameters are listed in table 5.

Table 5. Simulation of acetic acid in water: Basic parameters.			
S. No.	Parameter	Value	
1	Number of water molecule	185	
2	Number of acetate molecule	10	
3	Volume of structure	8000 A ³	
4	Density of structure	0.808071 gm/cm ³	
5	Total mass	3893.074462 amu	

Figure 5 shows the arrangement of acetic acid in water before simulation of at 298 K and 101.325 kilopascal (kPa). In the ensemble, acetate ions randomly distributed, however water molecules are in lattice.



Water molecules are in blue & gold colour. Acetate ions in green colour: Acetate molecule. Acetate ions randomly distributed, however water molecules are in lattice



Figure 6 show the coordinates and arrangment of molecuels after simulation. In figure 6, the selected pink color molecules are acetate molecules. These molecules initially kept at random position, but after simulation they come closer to one another and make big void space in center. It is also reported that water molecules prefere exit from central space where all acetate molecules tries to aggregates. There are certain acetate molecules still at random space. Figure 7 depicts void space and aggregation of acetate ions in center of ensemble. Figure 8 shows the central acetate ion and its orentatin in three dimentional space. It clerally shows its affinity with surrounding acetate ions.



The selected molecule and all pink color molecules are acetate molecules. These molecules initially kept at random position, but after simulation they come closer to one another and make big void space in center.

Figure 6. Arrangement of molecules after simulation



Molecular position after simulation. The selected structure shows the void space at center and surrounding this space nearly all acetate molecules arrange (aggregate). Before simulation all these molecules were randomly placed in ensemble.





The selected molecules in pink colour are acetate ion. It is seen from this configuration that the acetate ions are aggregationg and orienting towards methyly group of ion.

Figure 8. Configuration of central acetate ion and its surrounding after simulation

Simulation activated with energy minimization, which brought the system energy to lowest possible. The process was performed for 5000 steps and as it converged, the process stops and accepted for futher analysis. Figure 9 (A) depicting the graph, which shows the systematic decrease of system energy to lowest possible values.

Once the system is ready for the simulation, moleculear random movement for 50,000 steps were performed. Before that the system were constrained with certain basic values like, temperature, pressure, allocation of KE to each molecules or ion etc. Figure 9 (B) shows the energy profile of the system. It depicts Kinetic energy profile, Total energy profile, Potential energy profile. Initially these energy changes to certain level, but onwards the trend of all three energies are same and nearly constant.

Figure 9 (C) depicting the Radial distribution function for central carbon atom of acetate ion. For first shell, within the distance of 1 A° , the normalized RDF values goest 87. For second shell, within 1.75 A^{\circ} the normalized RDF values goes upto 55. Since then, it constantly decreases.



DISCUSSION

Experimental results from present study reveal that the apparent molal volume of acetic acid varies very little as function of concentration of total acid in water at 298.15 K. This indicates negligible solute-solvent association in solution. Almost zero slopes help in extrapolating the line for infinite dilution.

The study of volume changes ΔV° for ionization of carboxylic acids in water at 298.15 K, shown in table 3, supports our approach as values are in excellent agreement with those reported in literatures [2, 3].

Acetic acid has highest solubility, but as we increase $-CH_2$ group to the existing acid the solubility decreases which is due to hydrophobic interaction. On adding $-CH_2$ group the hyrophobicity increases and hence decreases in solubility [1].

This is also clearly reflected in MD simulation studies. In case of acetic acid in water, it shows void space at center and surrounding this space nearly all acetate molecules arrange (aggregate in chain).

Before simulation all these molecules were randomly placed in ensemble. This is due to water molecules try to retain their orginal conformation and hence doing so, replaces acetate molecules.

Water molecules try to retain their hydrogen bonding configuration, but the charge on acetate ion, do provide interaction with hydrogen of water molecules. This is clearly depicting from the figure 6. It is also reported that acetate ions are still interactiong with water molecules.

The most important feature reported is of void space. Figure 7 clearly reveals the presence of void space, where acetate ions are accumulated. To be clear, all acetate ions are not accumulated in center, but it clearly reflect the property of these ions to aggregates.

The values of volume change due to ionisation of acetic acid in water is $11.37 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$ at 298.15 K. This positive change in volume is also reflected in our simulation study where it shows the creation of some void spaces.

Graciela Ruderman et al. [19] support the multiple structure of acetic acid and that too depends on concentration. It is proposed that at lower concentration, the possibility of having dimer of acetic acid (two acetate ions in association) is negligible, whereas it is reported that there is linear (chain) dimer formation in case of concentration higher than 0.5M.

In present study, it is reported that the acetate molecules are forming aggregation but this study has not extended to understand the possibility of forming hydrogen bonds. As the distance between two acetate ions are less than $3A^{\circ}$ and hence there is definitely the possibility of making hydrogen bonds, but his needs to be confirmed with additional study. With this limited knowledge of simulation, it is concluded that the acetate ions do make linear dimmers and even polymer having number of acetate ions combines using hydrogen bonds. The orientation of acetate ions shows unique feature, where -CH3 groups of different ions faces each other. This may be due to hydrophobic properties of methyl group. The formation of chain dimer is also reported in our experimental study and confirmed from the study of Ganatra [12].

REFERENCES

[1] A Ben-Nam in "Water and aqueous solutions: Introduction to a molecular theory", Plenum Press, New York, **1974.**

[2] W. Kauzmann, Adv. Protein Chem., 14, 1959, 1.

[3] C. Tanford in "The Hydrophobic Effect : Formation of micelles and biological membrane", Wiley Interscience, New York, **1980**.

[4] E. M. Arnett in "Physico-chemical processes in mixed aqueous solvent system", Ed. F. Frank, London: Heinemann, **1967**, 105.

[5] Keizo Suzuki, Yoshihiro Tangiguchi and Takashi Watanabe, J. Phys. Chem., 77, 1973, 1918

[6] K. J. Patil & G. R. Mehta, Ind. J. Chem., 25A, 1986,319.

[7] H. Holland, J. Chem. Soc, Fraday Trans., 1973, 1180

[8] User Manual, DMA 602 Densimeter, 1992.

[9] H. Hoiland, J. Chem. Soc, Faraday Trans., 71, 1975,797-802.

[10] W. Kauzmann, A., Bodansky and J. Rasper, J. Ame. Chem. Soc., 84, 1962, 1777.

[11] K. S. M. Rao, Ph.D. Thesis, Submitted to Nagpur University, 1985

[12] SH Ganatra, Ph.D. Thesis, Nagpur University, Nagpur, 1991.

[13] Vega & de Miguel. J Chem Phys, **2007**. 126(15),154707.

[14] Vega et al. Faraday Discuss, 2009, 141, 251.

[15] A. Ujjankar; SH Ganatra & S Khobragade. *International Journal of Research and Analytical Reviews*, **2016**, 3 (1), 60-65.

[16] G Schaftenaar; and JH Noordik. J. Comput.-Aided Mol. Design, 2000, 14, 123.

[17] WL Jorgensen; J Tirado-Rives. J. Am. Chem. Soc. 1988, 110 (6), 1657–1666.

[18] WL Jorgensen; DS Maxwell; J Tirado-Rives. J. Am. Chem. Soc. 1996, 118 (45): 11225–11236.

[19] Graciela Ruderman et al. Journal of Solution Chemistry, 1998, Vol. 27, No. 10, pp. 935-948.