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Comparative Study of Free Volume And Permeability Coefficient of Solutions of N-Acetyl-L-Cysteine in Ethanol-Water (1:4) System Across Cellulose Acetate Membrane At Various Temperatures

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ABSTRACT

Ultrasonic velocity has been measured in solutions of N-Acetyl-L-cysteine in ethanol-water (1:4) system at 6.0 MHz and at a temperature 308.15 K. The results are discussed in terms of different theories of propagation of ultrasonic waves. From the velocity, density and viscosity data values, various acoustical parameters namely, adiabatic compressibility(β_{ad}), intermolecular free length(L_f), free volume(V_f), relaxation time(τ), and specific acoustic impedance(Z) have been calculated. The values of free volume (V_f) so obtained were correlated with permeability coefficient (L_p) values of these aqueous solutions through cellulose acetate membrane at three different temperatures(303K, 308K, 313K). All these parameters have been discussed separately to throw light on the molecular association and structural reorganization between the amino-acid, alcohol and water molecules. The permeability coefficient (L_p) has been found to be independent of the hydraulic pressure but is a characteristic property of the membrane and depends on the concentration of the solute. The results showed that both permeability coefficient (L_p) and free volume (V_f) increases with increase in concentration and the data is found to be in accordance with their observed density (ρ) and viscosity (η) data.

Keywords: Ultrasonic velocity, structural reorganization, relative association, permeability coefficient, cellulose acetate membrane, activation parameters.

INTRODUCTION

Ultrasonic velocities of solutions of N-Acetyl-L-Cysteine in ethanol-water (1:4) system were measured at various concentrations. The ultrasonic interferometer method was used to measure the velocity; the relative error of measurement was kept within 0.1%. The density (ρ), viscosity (η), adiabatic compressibility (βad), intermolecular path length (L_f) and Free volume (V_f) were also estimated during the measurement. Ultrasonic spectrometry permits the study of complexation processes in solution and the extraction of specific relaxation parameters of chemical Equilibrium [1-2]. It is also possible to estimate the hydration number of the electrolyte solutions from the molar compressibility value at infinite dilution. Ions plays an important role in chemical and biological system, so the hydration of these ions in these systems is a key issue to understand the chemical and thermo dynamical processes [3]. Besides wide-spread well established studies of the compressibility behaviour of liquids in basic research, the adiabatic

compressibility has also been considered as an indicator with high potential in advanced medical diagnosis and as a process control parameter in the food industry [4] . Despite a large amount of works, there are not strict structural models of electrolyte solutions, not well substantiated parameters of ion hydration spheres. Dissolution of an electrolyte in water is accompanied by electrostriction of the solvent under the action of electrostatic fields of newly formed ions. Application of acoustic methods have showed extensive possibility in the fields of chemistry, biochemistry, chemical Engineering and process control for a fundamental understanding of many phenomenon in solutions and liquid system [5]. Permeability coefficient of electrolytic solutions at different concentration and temperatures was measured by using cellulose acetate membrane, under the driving force of a pressure gradient [6]. In this paper a detailed comparative study of Free volume (V_f) and Permeability coefficient (L_P) of different solutions of N-Acetyl-L-Cysteine in ethanol-water (1:4) system as a function of concentration was made.

MATERIALS AND METHODS

N-Acetyl-L-Cysteine and ethanol of AR grade was used for making different solutions with water which was distilled thrice over alkaline $KMnO_4$ in an all-glass apparatus. The specific conductance of water so obtained was 1.3×10^{-4} Ωcm^{-1}. The apparatus and procedure were the same as described elsewhere [7-8]. Ultrasonic velocities for these solutions were measured using 6.0 MHz ultrasonic interferometer (M-82S, Mittal Enterprises, New Delhi). The temperature was maintained at 308.15 K by using a thermostatic bath. Permeability coefficient measurement was carried out in a permeation cell which was kept in an air thermostat maintained at a desired temperature within $\pm$ 0.5^0 C. The thermometer was kept constant with the help of a contact thermometer an electronic relay type 1050 supplied by Anu Vidyut, Roorkee. The data of the rate of flow in the capillary were analysed in terms of volume flux which was further used to estimate permeability coefficient 'L_p' by using the relation as,

$$J_v = L_p \Delta P$$

where Jv is the volume flux per unit area of the membrane and ΔP is the pressure difference across the membrane. The hydrodynamic volume flux J_v of the solution through the membrane is estimated from the following relations.

$$Jv = \pi r^2 x / \pi R^2 t \quad \text{.....} \quad (1)$$

Where 'x' the distance moved in the capillary of the apparatus in time t, 'r' is the radius of the capillary and R is the radius of the membrane.

The various activation parameters namely enthalpy of activation (ΔH^*), entropy of activation (ΔS^*) and free energy of activation (ΔG^*) have been evaluated. The energy of activation, E_n for the flow is obtained by the slopes of the plots of log L_p v/s 1/T which is always a straight line. The activation energy may be equated to the enthalpy of activation ΔH^* by applying the theory of absolute reaction rates. From this value, the entropy of activation, ΔS^* may be estimated from the Eyring's rate equation for flow i.e.,

$$\Delta S^* = \frac{\Delta H^*}{T} + R \log\left(\frac{Nh}{\eta \bar{V}}\right) \quad \text{.....} \quad (2)$$

Where 'η' is the viscosity of the permeating liquid, $\bar{V}$ is the molar volume of the permeating liquid, 'N' is the Avogadro's number, 'h' is the Planck's constant and 'R' is the gas constant. This equation is a result of eyring's rate equation. The activation free energy, ΔG^* may be estimated from the equation,

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad \text{.....} \quad (3)$$

A number of acoustical parameters have been computed from ultrasonic velocity, density and viscosity values using standard equations [4-15] which are summarized below.

The adiabatic compressibility(β_{ad}) has been estimated from the relation,

$$\beta_{ad} = (\rho C_u)^{-1} \quad \text{.....} \quad (4)$$

where C_u is the ultrasonic velocity and ρ is the density of the liquid under consideration measured as described elsewhere [9].

The intermolecular path length (L_f) of the liquid was determined by using the relation,

$$L_f = K_T \sqrt{\beta_{ad}} \quad \text{.....} \quad (5)$$

Where K_T is the temperature dependent constant.
Free volume(V_f) has been estimated by using the relation,

$$V_f = \left[\frac{M_{eff} \times C_u}{K \times \eta}\right]^{3/2} \quad \text{..... (6)}$$

where M_{eff} is the effective molecular weight, K = 4.28×10^9 and η is the viscosity of the solution under consideration.
Molar sound speed or Rao's constant(R) has been calculated using relation,

$$R = C_u^{1/3} \times V \quad \text{..... (7)}$$

where V is molar volume and is calculated using relation, $V = \frac{M_{eff}}{\rho}$
Molar compressibility or Wada's constant(W) has been calculated using the relation,

$$W = \beta_{ad}^{-1/7} \times V \quad \text{..... (8)}$$

Shear relaxation time(τ) has been calculated using the relation,

$$\tau = \frac{4}{3\beta_{ad} \times \pi} \quad \text{..... (9)}$$

Specific acoustic impedance(Z) has been calculated using the relation,

$$Z = C_u \times \rho \quad \text{..... (10)}$$

Classical sound absorption $\left(\alpha/f^2\right)_{class.}$ can be estimated from the relation,

$$\left(\alpha/f^2\right)_{class.} = \frac{8\pi^2\eta}{3\rho C_u^3} \quad \text{..... (11)}$$

Internal pressure (π_i) was estimated by using the relation,

$$\pi_i = bRT\left(\frac{K\eta}{C_u}\right)^{1/2}\left(\frac{\rho^{2/3}}{M_{eff}^{7/6}}\right) \quad \text{..... (12)}$$

where b is cubic packing which is assumed to be 2 for all liquids.
Molar cohesive energy(MCE) has been estimated using the relation,

$$MCE = \pi_i \times V \quad \text{..... (13)}$$

Relative association (R_A) from the relation,

$$R_A = \left(\frac{\rho}{\rho_0}\right)\left(\frac{C_u}{C_{uo}}\right)^{1/3} \quad \text{..... (14)}$$

Where C_{uo} is the ultrasonic velocity of the solvent and ρ_o is the density of solvent.
Solvation number(S_n) has been calculated using the relation,

$$S_n = \left(\frac{n_s}{n_i}\right)\left(1 - \frac{\beta}{\beta_0}\right) \quad \text{..... (15)}$$

where n_s is the number of moles of solvent in mol kg^{-1}, n_i is the number of moles of solute in mol kg^{-1}, β is the adiabatic compressibility of solution at a particular temperature and β_o is the adiabatic compressibility of solvent at a particular temperature.

RESULTS AND DISCUSSION

The survey of literature showed that the transport properties and acoustic properties are being increasingly studied for developing the correlation between the two. Many attempts are being made to formulate a relationship between these properties. The necessary data of estimated and calculated acoustic parameters at three different concentrations(0.5%, 1.0% and 1.5%) and at a constant temperature 308.15K has been summarized in tables 1-4 and figures 1-2.

Table 1 Ultrasonic velocity(C_u), density(ρ), viscosity(η), adiabatic compressibility(β_{ad}), of aqueous solutions of N-Acetyl-L-Cysteine in ethanol-water (1:4) system at different concentrations and at a constant temperature 308.15K.

Conc. (c)	$C_u \times 10^{-3}$ (ms^{-1})	$\rho \times 10^{-3}$ (kgm^{-3})	$\eta \times 10^{3}$ ($kgm^{-1}s^{1}$)	$\beta_{ad} \times 10^{-10}$ ($N^{-1}m^{2}$)
0.5%	0.9408	1.669	0.7929	3.816
1.0%	0.9142	1.588	0.7342	4.338
1.55	0.8853	1.527	0.6931	4.844

Table 2 Intermolecular free length(L_f), free volume(V_f),Shear relaxation time(τ), specific acoustic impedance(Z), of aqueous solutions of D-Mannitol at different concentrations and at a constant temperature 308.15K.

Conc. (c)	$L_f \times 10^{11}$ (m)	$V_f \times 10^{4}$ (m^3mol^{-1})	$\tau \times 10^{-13}$ (s)	$Z \times 10^{-6}$ ($kgm^{-2}s^{-1}$)
0.5%	4.092	4.326	0.441	1.570
1.0%	4.363	4.696	0.419	1.452
1.55	4.611	4.879	0.397	1.352

Table 3 Permeability Coefficient for aqueous solutions of D-Mannitol at different concentrations and temperatures across cellulose acetate membrane.

L_p x 10^{12} ($m^3N^{-1}S^{-1}$) , C_1 = 0.5%

Pressure difference ΔP x 10^{-3}(Nm^{-2})	Temperature in Kelvin (K)		
	303	**308**	**313**
5.895	1.65	1.70	1.89
5.419	1.62	1.63	1.76
4.825	1.56	1.58	1.68
4.108	1.49	1.53	1.64
3.764	1.40	1.49	1.61

C_2 = 1.0%

Pressure difference ΔP x 10^{-3}(Nm^{-2})	Temperature in Kelvin (K)		
	303	**308**	**313**
5.895	1.48	1.52	1.72
5.419	1.45	1.49	1.69
4.825	1.43	1.48	1.64
4.108	1.39	1.44	1.63
3.764	1.38	1.42	1.59

C_3 = 1.5%

Pressure difference ΔP x 10^{-3}(Nm^{-2})	Temperature in Kelvin (K)		
	303	**308**	**313**
5.895	1.35	1.45	1.61
5.419	1.31	1.42	1.52
4.825	1.30	1.41	1.48
4.108	1.29	1.37	1.43
3.764	1.21	1.36	1.39

Table 4 Enthalpy of activation, entropy of activation and free energy of activation of activation of aqueous solutions of D-Mannitol at different concentrations, and different temperatures across cellulose acetate membrane

Concentration (c)	$\Delta H^* \times 10^{-3}$ **(Jmole^{-1})**	**ΔS^* (JK^{-1}mole^{-1})**	$\Delta G^* \times 10^{-4}$ **(Jmole^{-1})**
0.5%	4.54	-52.88	2.109
1.0%	5.29	-60.21	2.414
1.5%	6.05	-72.51	2.875

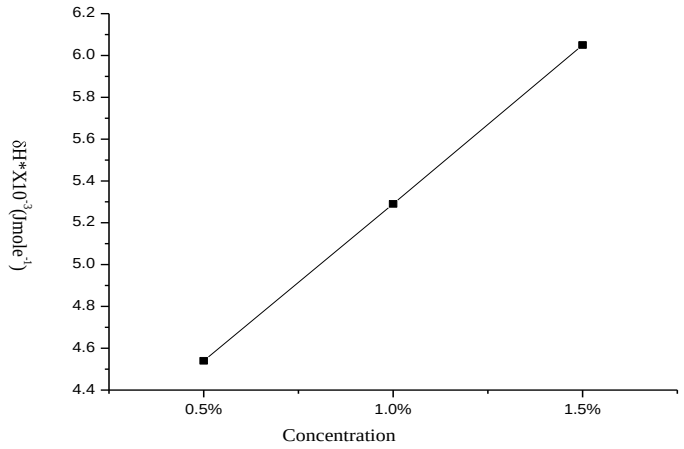

Fig 1: Plot of enthalpy of activation(ΔH*) versus concentration for N-Acetyl-L-Cysteine+ethanol+water systems at different concentrations and temperatures.

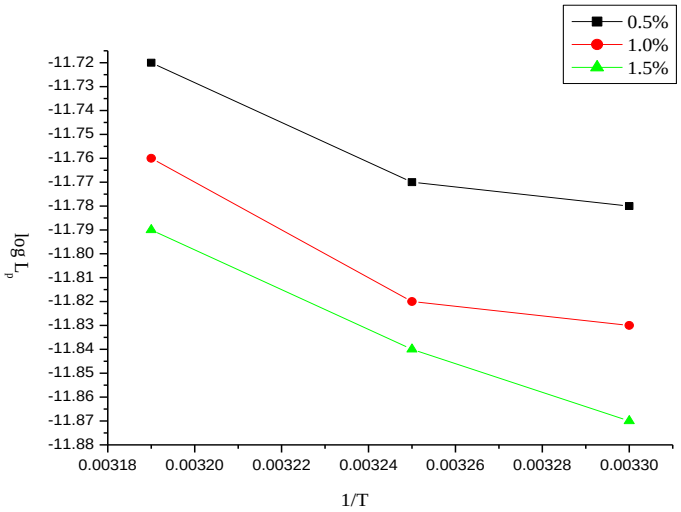

Fig 2: Plot of log Lp versus 1/T for N-Acetyl-L-Cysteine+ethanol+water systems at different concentrations and temperatures.

The ultrasonic velocity (C_u) is found to decrease with the increase in solute concentration. This indicates that when amino acids are dissolved, the water structure is disturbed initially, followed by a structural reorganization leaving the molecules in closely fitting helical cavities [10]. The density(η) and viscosity(ρ) values shows a decreasing trend with increasing concentration which again indicates the existence of

molecular interactions occurring in these solutions. Adiabatic compressibility(β_{ad}) increases with increase in concentration which confirms the formation of cations NH_3^+ and anions COO^-. The water molecules are attached to the ions strongly by the electrostatic forces of attraction. Intermolecular free length(L_f) increases with increase in solute concentration suggesting that there is a significant interaction between solute and solvent molecules and thus a structure promoting behaviour on addition of solute. The increase in free volume(V_f) with rise in concentration also confirms the ion-solvent interactions. Specific acoustic impedance(Z) is governed by the inertial and elastic properties of the medium. When a plane ultrasonic wave is set up in a liquid, the pressure and hence density of the liquid shows a periodic variation with distance from the source along the direction of propagation. Specific acoustic impedence decreases with increasing concentration of solute which indicates that molecular interactions are associative in nature. The activation data shows that permeability coefficient decreases with increase in concentration in all the cases. These results are in accordance with the fact that the permeability is inversely proportional to viscosity [11]. The increase in permeability with increase in temperature is also explained on the basis of same fact. The data in these tables indicates that the entropy of activation ΔS^* decreases with increase in concentration. The negative values of ΔS^* suggests that the flow of solutions through the membranes is more ordered which may be attributed to the greater membrane-solution interaction [12].

APPLICATIONS

N-acetyl-L-cysteine comes from the amino acid L-cysteine. Amino acids are the building blocks of proteins. N-acetyl-L-cysteine has many uses as medicine. It helps to prevent crusting in people with tracheostomy, acetaminophen poisoning, reducing mucus and helping with breathing in various lung conditions and cystic fibrosis. The studies of these solution systems across membranes is helpful in establishing major molecular mechanism by which amino acids are transported across cell membranes as these transport proteins may therefore participate in metal ion homoeostasis and toxicity. Also study of activation parameters reveal the enhanced stability of these ternary systems which indicate the use of these membranes as good battery separators.

CONCLUSIONS

The estimated and calculated acoustical and transport parameters and their values show the presence of specific molecular interactions between the solute and the solvent at different concentrations. Hence, it is concluded that, the association in this mixture is the result of structural reorganisation in the aqueous alcoholic amino acid solutions. The study of transport properties of these solutions across cellulose acetate membrane reflects the utility of the membranes in battery separators. The dependence of ultrasonic velocity and other derived parameters on composition is an indication of the presence of molecular interactions between amino acid, alcohol and water molecules.

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