PART II

ULTRASONIC STUDIES ON DILUTE SOLUTIONS OF WATER IN NONELECTROLYTES

CHAPTER 6

INTRODUCTION

6.1 Brief review of the experimental work carried out on the ultrasonic behaviour of aqueous nonelectrolytes

Aqueous nonelectrolytes exhibit extrema in many of their physical properties such as viscosity, partial molar volume, ultrasonic velocity and absorption as a function of concentration of the nonelectrolytes. The ultrasonic behaviour of aqueous nonelectrolytes has been studied extensively. A brief review of the work carried out on the ultrasonic velocity behaviour of aqueous solutions of nonelectrolytes is presented here.

The initial studies carried out by Tarasov *et al.* [1] and Smith and Eyring [2] revealed pronounced maxima in the ultrasonic velocity versus composition curves of aqueous solutions of organic liquids. These peculiarities were further confirmed by the studies carried out subsequently. A brief summary of the work carried out by different workers is presented in Table 6.1.1. The various studies detailed in this table indicate velocity maxima in all aqueous nonelectrolytes except in aqueous glycerol.

As the temperature is increased, the composition at which the velocity maximum occurs was found to shift towards lower concentrations of the nonelectrolyte. The magnitude of the velocity maximum is found to decrease with rise in temperature and the effect finally disappears in the temperature range 70-80°C. In solutions containing large amounts of organic solute, the velocity is found to decrease linearly with temperature as is found in the case of normal liquids. In the organic rich region the velocity is found to vary linearly with composition and this

Table 6.1.1

Non-electrolyte	Temperature range (%)	Authors	Reference
Methanol	27	Burton	[3]
	25	Kaulgud *et al.*	[4]
	25	Parshad	[5]
	25,30	Tiwari and Rajagopalan	[6]
	0-50	Emery and Gasse	[7]
	0,15,25	Dale *et al.*	[8]
	20-50	Kuhnkies and Schaaffs	[9]
	0-50	Emery *et al.*	[10]
	30	Bhadra and Basu	[11]
	0-100	Nozdrev and Lorinov	[12]
	25	Peace and Giacomini	[13]
	20	Jacobson	[14]
	-32 to -10	Sette	[15]
	25	Lara and Desnoyers	[16]
	25	Kiyohara and Benson	[17]
Ethanol	32.6	Parshad	[5]
	5-45	Giacomini	[18]
	20-60	Willard	[19]
	23	Willis	[20]
	27	Burton	[3]
	0,10,25	Storey	[21]

Non-electrolyte	**Temperature range (%)**	**Authors**	**Reference**
Ethanol	0-100	Nozdrev and Larinov	[12]
	20-50	Kuhnkies and Schaffs	[9]
	25	Lara and Desnoyers	[16]
	25	Kiyohara and Benson	[17]
	30	Bhadra and Basu	[11]
	0-30	Emery and Gasse	[7]
	0-50	Emery *et al.*	[10]
	25	Blandamer and Waddington	[22]
n-Propanol	22	Parshad	[5]
	25	Burton	[3]
	20-50	Kuhnkies and Schaaffs	[9]
	0-100	Nozdrev and Larinov	[12]
	25	Manohara Murthy and Subrahmanyam	[23]
	25	Kiyohara and Benson	[17]
	25	Venkata Ramana *et al.*	[24]
	25	Kaulgud *et al.*	[4]
	0,25	Treloar	[25]
	25	Nishikawa *et al.*	[26]
	0,15	Emery and Gasse	[27]
	0,25	Blandamer *et al.*	[28]
	50-80	Girija and Reddy	[29]

Non-electrolyte	Temperature range (%)	Authors	Reference
n-Propanol	25	Manucharov and Mikhailov	[30]
	60-80	Subrahmanyam and Manohara Murthy	[31]
	25	Blandamer and Waddington	[22]
	30	Bhadra and Basu	[11]
	38-70	Manohara Murthy and Subrahmanyam	[32]
Iso-propanol	25	Burton	[3]
	25	Venkata Ramana *et al.*	[24]
	25	Manucharov and Mikhailov	[30]
	20	Jacobson	[14]
	25	Blandamer *et al.*	[28]
	0,15	Gasse and Emery	[27]
	7-35	Oda *et al.*	[33]
n-Butanol	25-70	Manohara Murthy and Subrahmanyam	[34]
	25	Blandamer and Waddington	[22]
	55-80	Manohara Murthy and Subrahmanyam	[35]
t-Butanol	25	Ramakrishna *et al.*	[36]
	27	Burton	[3]
	10,25	Hammes and Knoche	[37]
	20-60	Arakawa and Takenaka	[38]

Non-electrolyte	**Temperature range (%)**	**Authors**	**Reference**
t-Butanol	30-80	Raghunath	[39]
	25	Manohara Murthy and Subrahmanyam	[40]
	10,25	Baumgartner and Atkinson	[41]
	25	Manucharov and Mikhailov	[30]
	25-70	Manohara Murthy and Subrahmanyam	[34]
	55-80	Manohara Murthy and Subrahmanyam	[35]
	25	Nishikawa *et al.*	[26]
	25	Blandamer *et al.*	[42]
	25	Patil and Rout	[43]
	2-45	Stone and Pontinen	[44]
	25	Manohara Murthy and Subrahmanyam	[23]
	20-50	Endo and Nomoto	[45]
	15-90	Lisnyanskii *et al.*	[46]
	25	Asenbaum	[47]
	25	Kruus *et al.*	[48]
Iso-propanol	55-80	Manohara Murthy and Subrahmanyam	[35]
	25	Ramakrishna *et al.*	[36]
	25-70	Manohara Murthy and Subrahmanyam	[34]

Non-electrolyte	Temperatur e range (%)	Authors	Reference
Allyl alcohol	25	Blandamer *et al.*	[49]
	0	Treloar	[25]
	25	Niskikawa *et al.*	[26]
	50-80	Girija and Reddy	[29]
2-Bromo ethanol	25	Treloar	[25]
	0	Treloar	[25]
	25	Blandamer *et al.*	[50]
Butane-1,4-diol	25	Blandamer *et al.*	[50]
2-Chloro ethanol	0,25	Thamsen	[51]
	25	Blandamer *et al.*	[50]
	0,9,18,25	Thamsen	[52]
1-Chloro propanol	25	Treloar	[25]
2-Cyno ethanol	25	Blandamer *et al.*	[50]
Ethoxy ethanol	15-20	Shindo *et al.*	[53]
Ethoxy-n-propanol	15-20	Shindo *et al.*	[53]
Ethylene glycol	15,25,35	Kor and Bhatti	[54]
	25	Manohara Murthy and Subrahmanyam	[23]
	38-70	Manohara Murthy and Subrahmanyam	[32]
Glyceral	26	Willis	[20]
	30	Danusso and Natta	[55]

Non-electrolyte	Temperature range (%)	Authors	Reference
Glyceral	25	Manohara Murthy and Subrahmanyam	[25]
	25	Slie *et al.*	[56]
	20-60	Willard	[19]
	30-80	Raghunath	[39]
	25	Venkata Ramana *et al.*	[24]
	38-79	Manohara Murthy and Subrahmanyam	[32]
Iso-amyl alcohol	50-80	Girija and Reddy	[29]
	0-100	Nozdrev and Larinov	[57]
2-Iso-butoxy ethanol	0-30	Fanning and Kruus	[58]
Methoxy ethanol	15-20	Shindo *et al.*	[53]
2-Butoxy ethanol	25	Lara and Desnoyers	[16]
Pyridine	25	Manohara Murthy and Subrahmanyam	[59]
	38-70	Manohara Murthy and Subrahmanyam	[32]
	64-80	Subrahmanyam and Manohara Murthy	[31]
	15,25,35	Thomas and Stumpf	[60]
	20-80	Feng Tao	[61]
Ethylamine	0	Blandamer *et al.*	[62]
	20	Kaulgud and Patil	[63]

Non-electrolyte	**Temperatur e range (%)**	**Authors**	**Reference**
n-Propylamine	0	Blandamer *et al.*	[62]
	20	Kaulgud and Patil	[63]
Di-n-propyl-amine	0	Blandamer *et al.*	[62]
1,2-Propylene diamine	20	Kaulgud and Patil	[63]
Piperidine	20	Kaulgud and Patil	[63]
Ethanol amine	20	Kaulgud and Patil	[63]
	25	Blandamer *et al.*	[62]
	20	Kaulgud and Patil	[64]
Ethylene diamine	10-20	Sasaki and Arakawa	[65]
	20	Kaulgud and Patil	[63]
	0	Blandamer *et al.*	[62]
Iso-butyl amine	20	Kaulgud and Patil	[63]
	0	Blandamer *et al.*	[62]
	25	Nishikawa and Uchida	[66]
3-Methyl pyridine	20	Lisnyanskii and Manucharov	[67]
Methyl amine	20	Kaulgud and Patil	[63]
Dimethylamine	0,20	Kaulgud and Patil	[63]
Diethylamine	20	Kaulgud and Patil	[63]
	24.5, 45	Chynoweth and Schneider	[68]

Non-electrolyte	**Temperature range (%)**	**Authors**	**Reference**
Diethylamine	0	Blandamer *et al.*	[62]
	25	Blandamer *et al.*	[49]
Cyclicamines	20	Kaulgud and Patil	[63]
Diethylamine	0	Andreae *et al.*	[69]
Triethylamine	10-28	Chynoweth and Schneider	[68]
	25	Blandamer *et al.*	[49]
	0	Blandamer *et al.*	[62]
	0-25	Yun	[70]
	51-80	Manohara Murthy and Subrahmanyam	[71]
	9.5-19.5	Alfrey and Schneider	[72]
	12.5-18	Harada	[73]
	-2 to 20	Garland and Chiu-Nonlai	[74]
Di-n-butyl-amine	50-80	Subbarangaiah	[75]
Di-n-propyl-amine	51-80	Manohara Murthy and Subrahmanyam	[71]
	45-70	Manohara Murthy and Subrahmanyam	[76]
n-Propylamine	20	Kaulgud and Patil	[63]
n-Butylamine	20	Kaulgud and Patil	[63]
Benzylamine	20	Kaulgud and Patil	[63]
Ethylene diamine	20	Kaulgud and Patil	[63]

Non-electrolyte	Temperature range (%)	Authors	Reference
Di-isopropyl amine	45-70	Manohara Murthy and Subrahmanyam	[76]
	51-80	Manohara Murthy and Subrahmanyam	[71]
1,3-Propan diamine	10-20	Sasaki and Arakawa	[65]
Hexa methylene tetramine	20-50	Nomoto and Endo	[77]
	22-50	Endo	[78]
Diamines	20	Kaulgud and Patil	[63]
Iso-propyl amine	20	Kaulgud and Patil	[63]
	0	Blandamer *et al.*	[62]
Urea	60-80	Prabhakara Rao and Reddy	[79]
	-10-20	Beauregard and Barrett	[80]
	20-40	Arakawa and Takenaka	[81]
	10-25	Hammes and Schimmel	[82]
	50-70	Girija and Reddy	[83]
	20	Singh	[84]
Propio nitrile	30-75	Subbarangaiah	[75]
Acetonitrile	0,25,35	Blandamer *et al.*	[85]
	25	Blandamer and Waddington	[86]
	30-75	Subbarangaiah	[87]
	25	Armitage *et al.*	[88]

Non-electrolyte	Temperature range (%)	Authors	Reference
Propylene oxide	10,25	Baumgartner and Atkingson	[41]
Acetamide	60-80	Krishna *et al.*	[89]
	20-50	Endo	[90]
Dimethyl sulfoxide	20	Dickson and Kruus	[91]
	35	Pillai *et al.*	[92]
	30-75	Subbarangaiah	[75]
	25-35	Bowen *et al.*	[93]
Diethoxy methane	10-30	Takenaka and Arakawa	[94]
1,1-Diethoxy ethane	10-30	Takenaka and Arakawa	[94]
1,2-dimethoxy ethane	10-30	Takenaka and Arakawa	[94]
Dimethyl urea	50-70	Girija and Reddy	[95]
	20-50	Endo	[78]
	60-80	Krishna *et al.*	[89]
Formaldehyde	55-80	Girija and Reddy	[83]
Formamide	40-80	Subbarangaiah	[75]
	20-50	Endo	[78]
	25	Venkata Ramana *et al.*	[24]

Non-electrolyte	**Temperature range (%)**	**Authors**	**Reference**
Monobutyl glycol ether	28.5	Burton	[3]
N,N-Dimethyl acetamide	20-100	Nomoto and Endo	[77]
	25	Silber and Cervantes	[96]
N,N-Dimethyl formamide	25,35	Kawaizumi *et al.*	[97]
	30-80	Subbarangaiah	[75]
	25	Venkata Ramana *et al.*	[24]
p-Dioxane	23	Burton	[3]
	10,25	Hammes and Knoche	[37]
	25	Manohara Murthy and Subrahmanyam	[40]
	30-80	Raghunath	[39]
	20-60	Arakawa Takenaka	[38]
p-Dioxane	25	Ramakrishna *et al.*	[36]
Tetrahydro furan	25	Venkata Ramana *et al.*	[24]
	25	Manohara Murthy and Subrahmanyam	[59]
	25	Kiyohara *et al.*	[17]

behaviour persisted at all temperatures. In the water rich region, the velocity temperature curves for aqueous nonelectrolytes are similar to that of the pure water.

According to Parshad [5] when alcohol is added to water a dynamical equilibrium among different associations is established and practically destruction of water associations takes place without much appreciable formation of water-alcohol groups. Therefore the number of molecules randomly distributed increases. The decrease of number of associations produces an increase of cohesive energy involved in sound propagation and determines the increase in velocity.

Endo and Nomoto [45] studied the ultrasonic velocity behaviour of a large number of aqueous nonelectrolytes as a function of concentration of the organic solutes in the temperature range 20 to 50°C. They determined the concentration of the organic solute at which ultrasonic velocity in the solution is independent of temperature and thereby derived some important conclusions regarding the solute-solvent molecular ratio of the long range ordered structure, assumed to exist in dilute aqueous solutions.

The ultrasonic velocity behaviour of aqueous nonelectrolytes has been utilized in classifying the organic solutes as structure makers (promotion/stabilization of the hydrogen bonded structure of water) and structure breakers (disruption of the hydrogen bonded structure). In solutions of water + t-butanol, n-propanol, p-dioxine, methyl alcohol, ethyl alcohol, pyridine, formamide N-methylformamide, dimethylformamide, dimethylsulphoxide, tetrahydrofuran etc., the velocity maxima are found to occur in the water rich region [3,5,13,16,21,23,36,40,59,90,93,97]. This behaviour has been attributed to stabilization or promotion of the hydrogen bonded structure of water leading to the formation of clathrate hydrates or complexes. For systems like water + ethylene glycol, the velocity maximum is found [23] at the intermediate composition and this behaviour has been attributed to the destablization of the hydrogen bonded structure of water by the solute.

Water exhibits ultrasonic velocity maximum at 74°C [19] apart from a density maximum at 3.98°C, isothermal compressibility minimum at 45°C, adiabatic compressibility minimum at 64°C and heat capacity minimum at 35°C. These peculiarities can be explained on the basis of the two state model of water common to many theories which are detailed in Section 1.2.

The effect of nonelectrolytes on the temperature of sound velocity maximum in water (TSVM) has been studied extensively [98-111] by determining ultrasonic velocity over a temperature range of $\simeq$ 5°C on either side of TSVM in aqueous solutions of nonelectrolytes containing very small amount of the nonelectrolyte. In most cases the structural contribution to the shift in TSVM after evaluating the dilution effect have been obtained. The data of concentration dependence of observed shifts and structural shifts have been utilized to classify the solutes as structure makers and structure breakers.

The review presented above highlights the usefulness of ultrasonic velocity data in understanding the solute-solvent interactions in aqueous nonelectrolytes.

In completely miscible systems of water and nonelectrolytes, ultrasonic velocity measurements have been carriedout throughout the composition range. In sparingly soluble systems, the velocity measurements were confined of the water rich region only. The ultrasonic velocity measurements in the case of completely miscible systems, are extensive only in the water rich region in view of the peculiarities exhibited by these systems in the water rich region. In the organic rich region, the number of measurements are less and not extended to the infinite dilution of water in the organic solute. Most of the data simply show a linear variation in the mole fraction range of 0.9 to 1.0 of the organic solute in water.

Recently density and partial molar volume measurements have been made of water in organic liquids at infinite dilution [112] with a view to understand the structure and molecular interactions between water and organic solute molecules.

Literature survey indicates that ultrasonic velocity measurements in the organic rich region of aqueous nonelectrolytes are scanty. An initial attempt has been made by Ramakrishna *et al.* [36] to understand the structure of dilute solutions of water in a few nonelectrolytes from measurements of ultrasonic velocity and evaluation of excess sound velocity. As an extension of this type study, the author has taken up the studies on the ultrasonic velocity behaviour of dilute solutions of water in a large number of nonelectrolytes and the results are presented and discussed in the forthcoming chapters.