http://www.e-journals.in
DOI:10.7598/cst2014.761

Chemical Science Transactions
2014, **3(2),** 608-613

RESEARCH ARTICLE

A Study of Acoustical and Transport Properties of Binary Mixtures of Dimethyl Sulphoxide and Acetonitrile with Water at 303.15 K

SANDARVE, UPASNA MAGOTRA and MEENA SHARMA*

Department of Chemistry, University of Jammu, Jammu 180 006, India
mlakhanpal89@rediffmail.com

Received 26 October 2013 / Accepted 22 November 2013

Abstract: Ultrasonic velocity (U) and density (ρ) of different concentrations of binary solutions of dimethyl sulphoxide (DMSO) and water and acetonitrile (ACN) and water have been studied at 303.15 K. From the experimental data various acoustical parameters such as isentropic compressibility (K_s), acoustic impedance (Z), intermolecular free length (L_f) and Rao's Constant (R) have been evaluated. Also hydrodynamic flow studies of different concentrations of experimental solvents through anisotropic cellulose acetate membrane are described and used to evaluate transport properties such as permeability coefficient (L_p) and frictional coefficient (F_{wm}) The results are discussed in the light of intermolecular interactions occurring in the solutions and also in terms of interactions between membrane and solution.

Keywords: Ultrasonic velocity, Isentropic compressibility, Acoustic impedance, Intermolecular free length, Rao's constant, Anisotropic cellulose acetate membrane, Permeability coefficient, Frictional coefficient.

Introduction

The thermodynamic and acoustic properties are very essential for understanding the physicochemical behavior of the binary and multi-component liquid mixtures. Ultrasonic investigations of liquid mixtures are of considerable importance in understanding the intermolecular interactions between the component molecules and finds applications in several industrial and technological processes. Such studies as a function of concentration scale are useful in giving insight into structure and bonding of the associated molecular complexes and other molecular processes[1]. References[2,3] related to the field of medicine, whereas references[4-7] based on studies on emulsions/microemulsions, polymer surfactants interactions and ultrasonic destruction of surfactants[8] are only a few cases to suggest versatility of the technique. On the other hand study of transport properties across membrane also provides information regarding molecular interactions as well as interactions of solute and solvent with the membrane. The survey of literature shows that the data on transport properties and acoustic properties are being increasingly studied for developing the correlation between the two[9-15]. The present investigation deals with the study of binary mixtures of water-acetonitrile and water-dimethyl sulphoxide across anisotropic cellulose acetate membrane. The membrane studied in the present work is of particular interest from biological point of view, since it behaves as a porous structure for hydrophillic solutes and as a lipophilic phase for those solutions with high partition coefficients, a behaviour resembling that found for membranes of living cells[16].

Experimental

DMSO (AR grade) was used as such. ACN (AR grade) after keeping over anhydrous calcium oxide for about 48 hours was shaken with phosphorus pentoxide and was distilled. Ordinary water distilled thrice over alkaline $KMnO_4$ and acidic $K_2Cr_2O_7$ in all glass apparatus was used for preparing the solutions. The specific conductance of this water was 1.30×10^{-4} Sm^{-1}.

The ultrasonic velocity, ‘U’ of solutions was measured by determining the wavelength of sound with the help of multi frequency ultrasonic interferometer (M-82S, Mittal Enterprises, India) at 7 MHz. The temperature of water surrounding the measuring cell was controlled and accuracy in the velocity measurement was ±0.05%. 5 mL specific gravity bottle was used to measure density, ‘ρ’ which was calibrated using triply distilled water. The specific gravity bottle containing the experimental solutions was immersed in a constant temperature bath controlled with in ±0.05 K. The weighing was performed in an analytical balance (Mettler Toledo) having an accuracy of 1.0×10^{-5}g. The ultrasonic velocity and density measurements were measured at least thrice for each sample and found to be repeatable within the precision limits. The anisotropic cellulose acetate membrane used in the present investigation was prepared by the apparatus and method as described elsewhere[17]. The apparatus was thoroughly cleaned with distilled water and dried. The membrane was kept in the solutions of different concentrations of the two experimental liquids for 48 hours. After 48 hours, membrane was again thoroughly cleaned with distilled water and dried. The membrane was found to be stable over entire range of DMSO concentration but it disintegrated above 50% concentration of ACN. Therefore, low concentrations for preparation of solutions were chosen. The apparatus and procedure used in the present investigation for evaluating transport properties is the same as described elsewhere[18].

Results and Discussion

From the measured values of ultrasonic velocity and density at a temperature of 303.15 K the various acoustic and thermodynamic parameters have been used to understand different kinds of association, the molecular spacing, molecular motion and various types of intermolecular interactions and their strength, influenced by the size in pure components and in the mixtures.

Isentropic compressibility $K_s = \left(1/\rho U^2 \right)$ where ρ denotes density and U denotes ultrasonic velocity.

Acoustic Impedance $Z = \rho U$

Intermolecular length $L_f = K_s K_J^{1/2}$

Where K_J is temperature dependent Jacobson constant which is equal to 2.075×10^{-6} at 303.15 K

Rao's constant $R = \left(M / \rho \right) U^{1/3}$

Permeability coefficient $L_P = J_V / \Delta P$

Where ΔP is the applied pressure difference. L_p has the character of mobility and represents the velocity of the fluid per unit pressure difference for the unit cross-sectional area of membrane.

Frictional coefficient $F_{wm} = \Phi_w V_w / L_p \delta$

Where '$\overline{V}_w$' is the water content of the membrane and is expressed as the volume fraction of the total membrane volume, 'Φ_w' is numerically equal to the fraction of membrane surface available for the permeation of the solution. It was determined by the method described by Ginzberg and Katchalsky[19] and the value obtained was 0.9947 in the case of anisotropic cellulose acetate membrane, δ is the thickness of the membrane and its value in the given case is 0.42×10^{-5} m, $\overline{V}_w$ is the molar volume of water.

From Table 1 it can be observed that ultrasonic velocity increases with increase in concentration of aqueous solutions of DMSO however it is observed that there is decrease in isentropic compressibility and intermolecular free length this is attributed to the fact that in pure DMSO, there is dipole–dipole as well as the usual dispersive interaction but when second component which is polar in nature is added the dipole-dipole interaction between unlike polar molecules is most likely which result in contraction of volume and the mixture becomes less compressible and intermolecular free length also decreases.

Table 1. Density, ultrasonic velocity, isentropic compressibility, acoustic impedance, intermolecular free length and Rao's constant for DMSO at 303.15K

Concentration in %	ρ kgm^{-3}	U ms^{-1}	$K_s x10^{-10}$, m^2N^{-1}	$Zx10^6$, $kgm^{-2}s^{-1}$	$L_f x10^{-11}$, m	R, m^3mol^{-1} ms^{-1}
10	1.0138	1554	4.0846	1.5754	4.1936	892.7080
15	1.0204	1576.9091	3.9411	1.6091	4.1193	891.2679
20	1.0288	1599.8181	3.7978	1.6459	4.0438	888.2516
25	1.0365	1622.7272	3.6639	1.6820	3.9718	885.8442
30	1.0431	1638	3.5731	1.7086	3.9224	882.9880
35	1.0519	1663.4545	3.4356	1.7499	3.8460	880.1179
40	1.0602	1676.1818	3.3571	1.7771	3.8018	875.4462
45	1.0677	1692.7272	3.2687	1.8073	3.7516	872.1506
50	1.0746	1695.2727	3.2380	1.8217	3.7329	866.9867

From Table 2 it is observed that for ACN there is an increase in ultrasonic velocity up to 15% concentration and then it starts decreasing this may be attributed to the fact that although the water and the acetonitrile liquids mix very well in all proportions, they do not intermingle on the molecular basis. The structure of the acetonitrile (a typical aprotic solvent) - water (the most well-known protic solvent) solution[20] may rather be described as the intermixture of *clusters* consisting of a few tens of each molecular species. The formation of clusters is also supported by isentropic compressibility data. The intermolecular free length can be related to the space filling ability assuming that the molecules are incompressible hard spheres having uniform radius since the intermolecular free length increases with increase in concentration of ACN this further supports the formation of clusters due to which the space between the molecules increases and hence intermolecular free length increases.

Table 2. Density, ultrasonic velocity, isentropic compressibility, acoustic impedance, intermolecular free length, Rao's constant for ACN at 303.15 K

Concentration in %	ρ kgm^{-3}	U ms^{-1}	$K_s x10^{-10}$, m^2N^{-1}	$Zx10^6$, $kgm^{-2}s^{-1}$	$L_f x10^{-11}$ m	R m^3mol^{-1}, ms^{-1}
10	0.9879	1546.3630	4.2332	1.5277	4.2691	480.5402
15	0.9783	1551.4545	4.2467	1.5178	4.2762	485.7889
20	0.9707	1547.6363	4.3011	1.5023	4.3033	489.1900
25	0.9611	1536.1815	4.4091	1.4764	4.3571	492.8555
30	0.9518	1522.8888	4.5302	1.4495	4.4164	496.2299
35	0.9402	1503.0909	4.7077	1.4132	4.5021	500.1654
40	0.9286	1491.0000	4.8441	1.3845	4.5669	505.0513
45	0.9147	1469.7373	5.0611	1.3444	4.6681	510.2756
50	0.9052	1444.5454	5.2941	1.3076	4.7744	512.6692

From Table 3 and 4 it was inferred that for both the binary mixtures with increase of pressure hydrodynamic permeability and frictional coefficient increases but permeability coefficient decreases for a particular concentration. However if we compare different concentrations of aqueous solutions of DMSO it is observed that hydrodynamic permeability decreases with increase in concentration this is because the dipole-dipole interaction between water and DMSO increases with increasing concentration which reduces the interaction of aqueous solution of DMSO with cellulose acetate membrane. For ACN also it is observed that hydrodynamic permeability decreases with increasing concentration which suggests the formation of acetonitrile-water clusters which cannot permeate through small pores of cellulose acetate membrane. This is further supported by frictional coefficient data.

Table 3. Transport properties of aqueous solution of DMSO at 303.15K

Pressure difference ΔP x 10^3 Nm^{-2}	Hydrodynamic Permeability J_vx 10^{-4} ms^{-1}	Permeability coefficient Lp x 10^{-7} $m^3N^{-1}s^{-1}$	Frictional Coefficient F_{wm} x 10^9, $mNmol^{-1}s$
At 10% DMSO aq. Solution			
0.90	2.93	3.27	13.02
1.29	3.93	3.04	14.05
1.69	4.90	2.89	14.73
2.09	5.73	2.74	15.56
2.49	6.22	2.50	17.05
At 20% DMSO aq. Solution			
0.91	1.95	2.14	19.97
1.32	2.65	2.01	21.26
1.73	3.28	1.90	22.50
2.14	3.64	1.70	25.03
2.54	4.02	1.58	26.98
At 30% DMSO aq. Solution			
0.93	1.49	1.60	26.73
1.35	2.07	1.54	27.70

Contd…

1.76	2.56	1.45	29.36
2.18	3.05	1.40	30.43
2.59	3.59	1.39	30.78
At 40% DMSO aq. Solution			
1.17	1.12	0.96	44.27
1.68	1.55	0.92	46.29
2.20	1.88	0.85	50.04
2.72	2.24	0.82	51.74
3.24	2.60	0.80	53.09
At 50% DMSO aq. solution			
1.19	0.72	0.61	70.00
1.71	0.99	0.58	73.63
2.24	1.24	0.55	77.23
2.77	1.44	0.52	81.82
3.29	1.61	0.49	87.00

Table 4. Transport properties of aqueous solution of ACN at 303.15 K

Pressure difference $\Delta P \times 10^3$ Nm^{-2}	Hydrodynamic permeability $J_v \times 10^{-4}$ ms^{-1}	Permeability coefficient $Lp \times 10^{-7}$ $m^3N^{-1}s^{-1}$	Frictional coefficient $F_{wm} \times 10^9$ $mNmol^{-1}s$
At 10% ACN aq. Solution			
1.08	3.83	3.54	12.06
1.57	5.36	3.42	12.45
2.05	6.99	3.41	12.49
2.53	8.49	3.35	12.71
3.01	9.74	3.23	13.19
At 20% ACN aq. Solution			
1.07	3.36	3.15	13.54
1.54	4.75	3.08	13.83
2.02	6.18	3.06	13.92
2.49	7.31	2.94	14.52
2.96	8.58	2.89	14.73
At 30% ACN aq. Solution			
1.05	2.60	2.48	17.22
1.52	3.51	2.32	18.40
1.98	4.27	2.15	19.80
2.45	4.99	2.04	20.92
2.91	5.75	1.97	21.61
At 40%ACN aq. Solution			
1.03	1.95	1.90	22.44
1.48	2.66	1.80	23.72
1.94	3.18	1.64	25.96
2.39	3.74	1.56	27.26
2.85	3.97	1.39	30.60
At 50%ACN aq. Solution			
1.00	1.27	1.26	33.70
1.45	1.66	3.04	37.13
1.89	1.92	2.89	42.13
2.34	2.29	2.74	43.50
2.78	2.53	2.50	46.85

References

1. Thirumaran S and Earnest Jayakumar J, *Indian J Pure Appl Phys.*, 2009, **47**, 265-272.
2. Schermuly R, Schemehl T, Gunther A, Graimminger F, Seeger W and Walmrath D, *Am J Respir Crit Care Med.,* 1997, **156(2)**, 445.
3. Wanger M H, Freidrich S W, Mollenhauer I, Obiaden M and Boenick U, *Bio Phys Chem*., 2000, **84(1)**, 35-43; DOI:10.1016/S0301-4622(99)00144-1
4. Hickey S, Lawrence M J, Hagan S A and Buckin V*, Langmuir*, 2006, **22(13)**, 5575-5583; DOI:10.1021/la052735t
5. Becu L, Manneville S and Colin A, *Phys Rev Lett.,* 2006, **76**, 138.
6. Mehta S K and Kawaljet, *Phys Rev E Stat Nonlin Soft Matter Phys.*, 2002, 65.
7. Brasllev M and Grfesex F, *J Colloid Interface Sci.,* 2002, **251(1)**, 78-84; DOI:10.1006/jcis.2002.8383
8. Weavers L K, Gimyang F P J, Limei A Y, Rathman and James F, *Benzene Environ Res.,* 2005, **77(3)**, 259-267.
9. Blokhra R L and Awasthi A, *Ind J Pure Appl Phys*., 1992, **30(12)**, 760-763.
10. Blokhra R L and Nag A, *Ind J Pure Appl Phys*., 1991, **29**, 756-759.
11. Thornton A W, Nairn K M, Hill J A and Hill J M, *J Membr Sci.*, 2009, **338(1-2)**, 29-37; DOI:10.1016/j.memsci.2009.03.053
12. Thornton A W, Nairn K M, Hill A J, Hill J M and Huang Y, *J Membr Sci.*, 2009, **338(1-2)**, 38-42; DOI:10.1016/j.memsci.2009.03.057
13. Mondal S, Hu J L and Yong Z, *J Membr Sci*., 2006, **280(1-2)**, 427-432; DOI:10.1016/j.memsci.2006.01.047
14. Gedde W U, Larson P T, Edsberg L, Angelstok A and Hedenqvist M, *Polymer*, 1996, **37(14)**, 2887-2902; DOI:10.1016/0032-3861(96)89384-0
15. Wijmans J G, *J Membr Sci*., 2004, **237(1-2)**, 39-50; DOI:10.1016/j.memsci.2004.02.028
16. Dipolo R, Shaafi R I and Solomon A K, *J Gen Phys.,* 1970, **55(1)**, 63-76; DOI:10.1085/jgp.55.1.63
17. Sharma M, Slathia M, Sharma A, Sharma S and Gupta D, *Res J Chem Environ*., 2005, **9**, 64-65.
18. Sharma M, Sharma A K and Lal R, *Res J Chem Environ.*, 2010, **14(3)**, 75.
19. Ginzberg B Z and Katchalsky A, *J Gen Physiol.*, 1963, **47**, 403.
20. Ahn D and Lee S, *Bull Korean Chem Soc.,* 2007, **28**, 725.