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Solvation Behaviour of Some Copper(I) Nitrate Complexes in Dimethylsulfoxide and Nitromethane at 298 K

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The ultrasonic velocities of solutions of Bu_4NBPh_4, Bu_4NClO_4, $[Cu(AN)_4]NO_3$, $[Cu(BN)_4]NO_3$, $[Cu(Phen)_2]NO_3$, $[Cu(DMPhen)_2]NO_3$, $[Cu(Bipy)_2]NO_3$ and $[Cu(TU)_4]NO_3$ (where AN = acetonitrile, BN = benzonitrile, Phen = 1,10-phenanthroline, DMPhen = 2,9-dimethyl-1,10-phenanthroline, Bipy = 2,2′-bipyridyl and TU = thiourea) were measured in the concentration range 0.03-0.27 M in dimethylsulfoxide (DMSO), nitromethane (NM) and binary mixtures of DMSO + NM containing 0, 20, 40, 60, 80 and 100 mol% NM at 298 K in the present studies. Using ultrasonic velocity and density data, isentropic compressibility (κ_s) and apparent molal isentropic compressibility ($\kappa_{s,\phi}$) for electrolytes in DMSO + NM mixture have been calculated. Result shows that copper(I) electrolytes show less solvation in NM rich regions indicating structure breaking tendency of nitromethane. Extent of solvation in Cu(I) ions decreases in the order: $[Cu(AN)_4]^+ > [Cu(BN)_4]^+ > [Cu(TU)_4]^+ > [Cu(DMPhen)_2]^+ > [Cu(Phen)_2]^+ > [Cu(Bipy)_2]^+$.

Keywords: Ultrasonic velocity, Solvation study, Non-aqueous solvents, Binary mixture.

INTRODUCTION

The study of solvation behaviour of 1:1 electrolytes in the mixed solvents has generated a great interest in the field of chemistry [1-3]. A large number of alkali metals and tetraalkylammonium salt [4] have often been used for solvation studies as 1:1 electrolytes which are mostly solvated by purely electrostatic ion-dipole interaction. On the other hand, studies on highly ionic copper(I) salts are very rare. Studies of electrolyte solutions in mixed solvents have a wide range of industrial applications [5-9]. The stabilized copper salt solutions have been used as catalysts in many oxidation-reduction reactions [10-13]. Though solvation studies of Cu(I) salts were attempted in the recent years, however no attempt has been made to study the solvation behaviour of monovalent copper nitrate complexes in binary mixtures of dimethylsulfoxide (DMSO) and nitromethane (NM).

The dielectric constant and dipole moments of DMSO and NM are quite high, and so, it is expected that they would have a good tendency to solvate the ions. The molecular interactions studies can be best carried out by spectroscopic methods [14] but other parameters like dielectric constant, ultrasonic velocity, conductance, magnetic or viscosity measurements [15] have been widely used in evaluating the nature of solute-solute, solute-solvent and solvent-solvent interactions. In the present studies the ultrasonic velocity measurements have been adequately used in understanding the physico-chemical behaviour in liquid mixtures [16,17]. The ultrasonic velocities of solutions of Bu_4NBPh_4, Bu_4NClO_4, $[Cu(AN)_4]NO_3$, $[Cu(BN)_4]NO_3$, $[Cu(Phen)_2]NO_3$, $[Cu(DMPhen)_2]NO_3$, $[Cu(Bipy)_2]NO_3$ and $[Cu(TU)_4]NO_3$ have been measured in the concentration range 0.03-0.27 M in dimethylsulfoxide (DMSO), nitromethane (NM) and binary mixtures of DMSO + NM containing 0, 20, 40, 60, 80 and 100 mol% NM at 298 K in the present studies.

EXPERIMENTAL

Density and ultrasound velocity were measured by DSA 5000M from Anton Parr at 298 K and 1 atmospheric pressure. The sample was inserted in a long U-tube made of borosilicate glass that is excited to oscillate at its operating frequency of 2 MHz. Apparatus was calibrated at the beginning of every set of reading with distilled water and air. Accuracy in the density value was ± 1 × 10^{-5} g cm^{-3} and for ultrasonic velocity was ±

0.1 m s^{-1}. For calibration, the density and ultrasonic velocity of known liquids like water (ρ = 0.99705 g cm^{-3}, u = 1496.68 m s^{-1}) and acetonitrile (ρ = 0.77687 g cm^{-3} , u = 1280.9 m s^{-1}) were measured at 298 K and it agreed well with literature values of (ρ = 0.99707 g cm^{-3}) [18], (u = 1496.6 m s^{-1}) [19] for water and (ρ = 0.77685 g cm^{-3} , u = 1280.8 m s^{-1}) [20] for acetonitrile. The temperature control in DSA apparatus is ± 0.01 K.

The source and purity of the solvents are given in Table-1. DMSO (99.8%, E. Merck, India) and NM (99%, Loba Chemie, India) were purified according to the reported methods [21-23]. Tetrabutylammonium tetraphenylborate [Bu_4NBPh_4] and tetrabutylammonium perchlorate [Bu_4NClO_4] used as reference electrolytes were prepared and dried [24,25]. Copper(I) nitrate complexes like $[Cu(AN)_4]NO_3$, $[Cu(BN)_4]NO_3$, $[Cu(Phen)_2]NO_3$, $[Cu(DMPhen)_2]NO_3$, $[Cu(Bipy)_2]NO_3$ and $[Cu(TU)_4]NO_3$ have been synthesized in the present studies. Tetraacetonitrile copper(I) nitrate $[Cu(AN)_4]NO_3$, was synthesized by reduction of copper(II) nitrate trihydrate $[CuNO_3{\cdot}3H_2O]$ (99%, Merck) (5 g) with copper powder (99.7% from Lobachem) (3 g) in warm acetonitrile (40 mL) and heated for 10-20 min till the solution became colourless at 60-70 ºC. The colourless solution was filtered and on cooling white crystals separate. Crystals were dried and stored under vacuum. The synthesized tetraacetonitrile copper(I) nitrate crystals remained stable only for a short time and became blue in a few hours. However, copper(I) nitrate solution in dry acetonitrile remained stable and was used to synthesize other complexes with stronger ligands like phenanthroline, 2,9-dimethyl-1,10-phenanthroline (neocuproin), thiourea, bipyridyl. The physico-chemical analysis of the synthesized compounds are given in Table-2.

The density (ρ), viscosity (η), dielectric constant (ε), ultrasonic velocity (u) and isentropic compressibility (κ) of DMSO + NM binary mixture at different mol% of NM have been reported in Table-3.

RESULTS AND DISCUSSION

The ultrasonic velocities (u), density (ρ) of solutions of Bu_4NBPh_4, Bu_4NClO_4, $[Cu(AN)_4]NO_3$, $[Cu(BN)_4]NO_3$, $[Cu(Phen)_2]NO_3$, $[Cu(DMPhen)_2]NO_3$, $[Cu(Bipy)_2]NO_3$ and $[Cu(TU)_4]NO_3$ have been measured in the concentration range

TABLE-1
SOURCE AND PURITY OF SOLVENTS

Solvent	Provenance	CAS number	m.f.	Molar mass (g/mol)	Grade	Density[a] (g/cm^3)	Mass fraction purity	Water content
Dimethylsulfoxide	E. Merck	67-68-5	C_2H_6OS	78.13	ACS	1.0953	0.998[b]	0.0002[c]
Nitromethane	Loba Chemie	75-52-5	CH_3NO_2	61.04	LR	1.1295	0.980[b]	0.0025[c]

[a]Density at 298 K by Anton Parr density meter (DSA 5000 M) with a precision of 0.0004 g/cm^3; [b]From gas chromatography analysis; [c]Karl-Fischer Titration method.

TABLE-2
IUPAC NAMES, MOLECULAR MASS, PURIFICATION METHOD AND ELEMENTAL ANALYSIS OF THE ELECTROLYTES

Electrolytes	IUPAC name	Molecular mass (g)	Purification method	Elemental analysis (%): Calcd. (found)			
				C	H	N	S
$[Cu(AN)_4]ClO_4$	Tetraacetonitrilecopper(I) perchlorate	327.00	Recrystallization from dry acetonitrile	–	–	–	–
$[Cu(AN)_4]NO_3$	Tetraacetonitrile copper(I) nitrate	289.70	Recrystallization from dry acetonitrile	34.221 (33.13)	4.115 (4.14)	23.893 (24.16)	–
$[Cu(BN)_4]NO_3$	Tetrabenzonitrile copper(I) nitrate	537.66	Repeated washing with dry cyclohexane	63.768 (62.49)	3.584 (3.72)	12.677 (13.02)	–
$[Cu(Phen)_2]NO_3$	*bis*(1,10-Phenanthroline) copper(I) nitrate	485.92	Precipitation by dry cyclohexane	58.903 (59.27)	3.222 (3.29)	13.974 (14.4)	–
$[Cu(DMPhen)_2]NO_3$	*bis*(2,9-Dimethyl-1,10-phenanthroline) copper(I) nitrate	542.03	Precipitation by dry acetone	62.515 (61.98)	5.218 (4.42)	11.896 (12.91)	–
$[Cu(Bipy)_2]NO_3$	*bis*(2,2,-Bipyridyl) copper(I) nitrate	437.88	Recrystallization and dried under vacuum	53.876 (54.81)	3.591 (3.65)	15.576 (15.98)	–
$[Cu(TU)_4]NO_3$	Tetrathiourea copper(I) nitrate	429.98	Recrystallization and dried under vacuum	10.303 (11.16)	3.345 (3.72)	23.666 (29.3)	28.184 (29.77)

TABLE-3
DENSITY (ρ), VISCOSITY (η), DIELECTRIC CONSTANT (ε), ULTRASONIC VELOCITY (u) AND ISENTROPIC COMPRESSIBILITY (κ_o) FOR DMSO + NM MIXTURE at 298 K

Mol% NM	ρ (g cm^{-3})		η (mPa s)		ε		u (m s^{-1})		$\kappa_o \times 10^6$ bar^{-1}
	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.	
0	1.0953	1.09530 [26] 1.09533 [27]	1.99	1.99 [28] 2.00 [29]	46.7	46.7 [28,30]	1486.49	1486.74 [31]	41.32
20	1.0997		1.25		44.1		1438.27		43.96
40	1.1054		1.04		41.9		1403.33		45.94
60	1.1124		0.91		39.7		1370.19		47.88
80	1.1209		0.78		37.5		1342.88		49.47
100	1.1295	1.12958 [32]	0.612	0.615 [33,34]	35.07	36.3 [35]	1321.38	1320.41 [36]	50.71

0.03-0.27 mol kg^{-1} in dimethylsulfoxide (DMSO), nitromethane (NM) and binary mixture of DMSO + NM containing 0, 20, 40, 60, 80 and 100 mol% NM at 298 K (Table-4).

Using ultrasonic velocity and density data, isentropic compressibility (κ_s) for various electrolytes in DMSO + NM mixture have been calculated using eqn. 1:

TABLE-4
MEASURED VALUE OF DENSITY (ρ), ULTRASONIC VELOCITY (u) FOR Bu_4NBPh_4, Bu_4NClO_4, $[Cu(AN)_4]ClO_4$, $[Cu(AN)_4]NO_3$, $[Cu(BN)_4]NO_3$, $[Cu(Phen)_2]NO_3$, $[Cu(DMPhen)_2]NO_3$, $[Cu(bipy)_2]NO_3$ AND $[Cu(TU)_4]NO_3$ IN DMSO + NM BINARY MIXTURE AT 298 K

Conc. (mol Kg^{-1})	ρ (g cm^{-3})	u (m s^{-1})	$\kappa_s \times 10^6$ bar^{-1}	$K_{s,\phi}$ (cm^3 mol^{-1} bar^{-1})	Conc. (mol Kg^{-1})	ρ (g cm^{-3})	u (m s^{-1})	$\kappa_s \times 10^6$ bar^{-1}	$K_{s,\phi}$ (cm^3 mol^{-1} bar^{-1})	Conc. (mol Kg^{-1})	ρ (g cm^{-3})	u (m s^{-1})	$\kappa_s \times 10^6$ bar^{-1}	$K_{s,\phi}$ (cm^3 mol^{-1} bar^{-1})
Bu_4NBPh_4					**Bu_4NClO_4**					**$[Cu(AN)_4]ClO_4$**				
0 mol% NM					0 mol% NM					0 mol% NM				
0.0306	1.0950	1494.84	40.86	212.93	0.0334	1.0952	1494.97	40.85	128.55	0.0373	1.0955	1487.63	41.25	97.19
0.0731	1.0944	1503.63	40.41	211.55	0.0759	1.0947	1501.92	40.49	129.13	0.0798	1.0969	1489.49	41.09	95.94
0.1156	1.0934	1508.33	40.19	211.97	0.1184	1.0939	1504.10	40.41	130.29	0.1223	1.0977	1491.32	40.96	95.87
0.1581	1.0923	1514.91	39.89	211.68	0.1609	1.0929	1505.73	40.35	131.26	0.1648	1.0982	1509.73	39.95	94.01
0.2006	1.0911	1521.34	39.59	210.74	0.2034	1.0915	1508.84	40.24	132.33	0.2073	1.0992	1525.05	39.11	95.20
20 mol% NM					20 mol% NM					20 mol% NM				
0.0327	1.0993	1450.29	43.25	225.36	0.0369	1.0999	1449.09	43.70	133.48	0.0389	1.1002	1472.71	43.90	106.43
0.0752	1.0988	1458.15	42.80	223.02	0.0794	1.0988	1455.35	42.96	137.70	0.0814	1.1009	1441.06	43.74	105.96
0.1177	1.0982	1464.53	42.45	221.59	0.1219	1.0981	1457.41	42.87	138.14	0.1239	1.1010	1445.15	43.49	103.23
0.1602	1.0975	1469.97	42.17	220.62	0.1644	1.0972	1460.32	42.73	138.54	0.1664	1.1012	1457.98	42.71	102.46
0.2027	1.0967	1478.79	41.69	218.63	0.2069	1.0959	1465.44	42.49	139.04	0.2089	1.1017	1473.38	41.81	101.21
40 mol% NM					40 mol% NM					40 mol% NM				
0.0348	1.1051	1411.53	45.42	234.06	0.0404	1.1055	1407.23	45.67	140.32	0.0406	1.1055	1403.36	45.93	129.13
0.0773	1.1046	1420.54	44.86	231.92	0.0826	1.1046	1414.37	45.25	143.65	0.0831	1.1061	1404.75	45.81	116.85
0.1198	1.1041	1429.05	44.35	229.56	0.1251	1.1037	1417.20	45.11	144.77	0.1256	1.1066	1407.67	45.60	111.73
0.1623	1.1036	1435.30	43.98	227.84	0.1676	1.1028	1420.60	44.93	145.02	0.1681	1.1069	1417.89	44.93	111.66
0.2048	1.1032	1441.28	43.63	225.98	0.2101	1.1017	1422.95	44.83	145.61	0.2106	1.0710	1473.27	43.02	102.21
60 mol% NM					60 mol% NM					60 mol% NM				
0.0366	1.1117	1377.11	47.43	246.97	0.0433	1.1119	1374.92	47.57	150.72	0.0423	1.1121	1370.37	47.88	123.54
0.0791	1.1107	1384.27	46.98	245.75	0.0858	1.1104	1381.07	47.21	154.27	0.0848	1.1129	1371.45	47.77	125.58
0.1216	1.1096	1390.60	46.60	244.59	0.1283	1.1089	1386.05	46.94	155.11	0.1273	1.1133	1373.61	47.60	121.87
0.1641	1.1086	1396.71	46.24	242.96	0.1708	1.1074	1389.68	46.75	155.44	0.1698	1.1137	1380.49	47.11	117.72
0.2066	1.1075	1403.07	45.86	241.31	0.2133	1.1071	1391.40	46.65	153.51	0.2123	1.1143	1388.88	46.52	115.92
80 mol %NM					80 mol %NM					80 mol %NM				
0.0383	1.1193	1349.29	49.07	262.58	0.0463	1.1192	1350.63	48.98	163.96	0.0439	1.1191	1344.59	49.42	140.50
0.0808	1.1177	1355.11	48.72	260.24	0.0888	1.1178	1355.91	48.66	162.39	0.0864	1.1201	1344.93	49.35	135.69
0.1233	1.1159	1361.91	48.32	259.22	0.1313	1.1165	1360.50	48.39	161.14	0.1289	1.1209	1347.21	49.15	129.53
0.1658	1.1142	1366.49	48.60	257.83	0.1738	1.1149	1364.22	48.19	161.33	0.1714	1.1216	1353.18	48.69	125.46
0.2083	1.1129	1370.15	47.86	256.28	0.2163	1.1148	1366.95	48.01	158.08	0.2139	1.1227	1357.91	48.30	119.74
100 mol% NM					100 mol% NM					100 mol% NM				
0.0405	1.1272	1326.35	50.43	273.79	0.0495	1.1271	1330.02	50.15	171.23	0.0456	1.1271	1323.11	50.68	142.77
0.083	1.2462	1328.85	50.35	274.88	0.0920	1.1257	1332.47	50.04	168.24	0.0881	1.1280	1323.39	50.61	128.06
0.1255	1.1225	1332.62	50.16	273.06	0.1345	1.1243	1335.78	49.85	166.77	0.1306	1.1299	1323.75	50.50	123.74
0.1681	1.1205	1334.74	50.09	272.29	0.1771	1.1233	1339.40	49.63	164.76	0.1731	1.1303	1329.74	50.03	118.81
0.2105	1.1186	1337.90	49.94	271.23	0.2195	1.1231	1342.57	49.39	161.71	0.2156	1.1307	1335.39	49.59	114.34
$[Cu(AN)_4]NO_3$					**$[Cu(BN)_4]NO_3$**					**$[Cu(Phen)_2]NO_3$**				
0 mol% NM					0 mol% NM					0 mol% NM				
0.0359	1.0923	1488.48	41.32	89.19	0.0317	1.0989	1502.30	40.32	-228.77	0.0305	1.0973	1491.43	40.97	159.07
0.0784	1.0924	1488.69	41.31	89.88	0.0696	1.1036	1536.78	38.36	-239.24	0.0730	1.1012	1494.95	40.63	152.06
0.1209	1.0931	1488.73	41.28	89.85	0.0948	1.1113	1557.02	37.11	-277.36	0.1155	1.1086	1499.23	40.13	137.84
0.1634	1.0938	1491.62	41.09	88.58	0.1251	1.1209	1566.37	36.36	-288.18	0.158	1.1186	1502.20	39.61	124.39
0.2059	1.0944	1499.07	40.66	87.49	0.2132	1.1748	1581.12	34.04	-294.61	0.2005	1.1264	1502.01	39.35	120.28
20 mol% NM					20 mol% NM					20 mol% NM				
0.0378	1.0965	1440.35	43.95	97.31	0.0338	1.1011	1453.71	42.97	195.12	0.0326	1.1023	1448.01	43.26	162.24
0.1181	1.0967	1440.47	43.94	96.27	0.0721	1.1017	1477.86	41.56	193.31	0.0751	1.1068	1451.23	42.89	154.98
0.1606	1.0975	1440.53	43.90	95.9	0.0983	1.1024	1491.54	40.77	189.61	0.1176	1.1141	1452.95	42.52	142.96
0.2031	1.0982	1442.66	43.75	95.29	0.1294	1.1029	1515.68	39.46	184.32	0.1601	1.1223	1453.03	42.20	134.44
0.2456	1.0988	1453.22	43.09	92.85	0.2167	1.1035	1539.06	38.26	180.88	0.2026	1.1338	1452.75	41.78	122.66
40 mol% NM					40 mol% NM					40 mol% NM				
0.0399	1.1015	1404.96	45.91	110.18	0.0362	1.1058	1425.64	44.49	212.29	0.0347	1.1077	1406.2	45.65	175.54
0.0824	1.1017	1406.24	45.90	106.27	0.0784	1.1063	1444.04	43.35	206.61	0.0772	1.1121	1407.73	45.37	166.21
0.1249	1.1022	1407.17	45.81	103.02	0.1011	1.1069	1468.17	41.91	198.48	0.1197	1.1182	1409.51	45.01	156.65
0.1674	1.1031	1408.52	45.69	100.78	0.1345	1.1074	1480.98	41.17	194.88	0.1622	1.1271	1409.69	44.65	144.55
0.2099	1.1043	1411.24	45.46	99.01	0.2199	1.1075	1503.55	39.94	190.77	0.2047	1.1339	1409.58	44.38	137.77

60 mol% NM					60 mol% NM					60 mol% NM				
0.0421	1.1086	1372.72	47.86	111.11	0.0391	1.113	1395.63	46.13	217.12	0.0368	1.1157	1374.16	47.46	172.43
0.0846	1.1089	1372.8	47.85	108.59	0.0809	1.1134	1414.7	44.87	212.18	0.0793	1.1197	1380.67	46.85	168.69
0.1271	1.1091	1373.64	47.78	106.76	0.1045	1.1137	1436.84	43.49	205.59	0.1218	1.1235	1386.74	46.28	166.42
0.1696	1.1099	1374.33	47.70	104.96	0.1377	1.1141	1450.02	42.69	201.76	0.1643	1.1309	1392.51	45.59	155.08
0.2121	1.1118	1377.03	47.43	103.66	0.2212	1.1145	1478.13	41.07	194.98	0.2068	1.1347	1386.8	45.28	155.22
80 mol %NM					80 mol %NM					80 mol %NM				
0.0443	1.1162	1345.83	49.46	122.14	0.0421	1.1214	1363.19	47.98	225.51	0.0389	1.1239	1347.84	48.97	181.74
0.0868	1.1168	1346.05	49.42	118.20	0.0834	1.1219	1388.42	46.24	217.19	0.0814	1.1297	1349.96	48.57	167.45
0.1293	1.1171	1346.16	49.40	114.23	0.1077	1.122	1406.38	45.06	212.76	0.1239	1.1343	1351.64	48.25	165.66
0.1718	1.1181	1346.99	49.29	110.51	0.1406	1.1222	1429.77	43.59	205.64	0.1664	1.1429	1353.47	47.76	153.77
0.2143	1.1186	1347.59	49.22	107.97	0.2269	1.1223	1447.06	42.55	201.75	0.2089	1.1536	1354.79	47.23	141.95
100 mol% NM					100 mol% NM					100 mol% NM				
0.0465	1.1236	1325.11	50.68	131.66	0.0468	1.1302	1342.61	49.08	227.73	0.0411	1.1314	1324.68	50.37	198.07
0.0891	1.1242	1325.16	50.66	128.29	0.0889	1.1304	1367.17	47.32	221.32	0.0835	1.1355	1327.42	49.97	185.83
0.1315	1.1251	1325.21	50.61	125.44	0.1099	1.1309	1385.54	46.06	214.39	0.1261	1.1478	1329.56	49.28	153.42
0.1741	1.1256	1325.38	50.57	121.86	0.1421	1.1310	1400.09	45.11	210.72	0.1685	1.1496	1332.31	49.01	162.10
0.2165	1.1257	1325.81	50.53	119.09	0.2297	1.1313	1426.68	43.43	203.74	0.2111	1.1581	1335.93	48.38	152.86
$[Cu(DMPhen)_2]NO_3$					**$[Cu(bipy)_2]NO_3$**					**$[Cu(TU)_4]NO_3$**				
0 mol% NM					0 mol% NM					0 mol% NM				
0.028	1.0968	1502.12	40.41	-115.04	0.0335	1.0976	1491.47	40.96	140.01	0.0343	1.0988	1504.57	40.20	-174.89
0.0705	1.1011	1515.35	39.55	-61.58	0.0760	1.1011	1495.33	40.62	136.28	0.0768	1.1054	1514.38	39.45	-111.7
0.113	1.1037	1520.2	39.21	-2.03	0.1185	1.1055	1496.86	40.37	131.20	0.1193	1.1126	1519.93	38.91	-80.36
0.1555	1.1089	1519.64	39.04	29.11	0.1610	1.1117	1496.75	40.15	124.55	0.1618	1.1143	1520.04	38.84	-47.12
0.198	1.1123	1521.36	38.84	47.55	0.2035	1.1132	1498.65	39.99	125.18	0.2043	1.1155	1538.48	37.87	-38.85
20 mol% NM					20 mol% NM					20 mol% NM				
0.0301	1.1043	1440.75	43.62	159.21	0.0354	1.1029	1483.05	41.22	132.93	0.0362	1.1036	1451.45	43.01	129.39
0.0726	1.1099	1448.17	42.95	160.31	0.0779	1.1077	1496.51	40.31	125.36	0.0787	1.1096	1455.50	42.54	120.99
0.1151	1.1135	1449.59	42.74	166.20	0.1204	1.1145	1512.07	39.24	114.81	0.1212	1.1176	1457.60	42.12	111.44
0.1576	1.1229	1449.45	42.39	154.32	0.1629	1.1222	1526.75	38.23	106.38	0.1637	1.1281	1456.16	41.80	100.86
0.2001	1.1299	1449.72	42.11	150.86	0.2054	1.1204	1545.24	37.38	115.52	0.2062	1.1381	1454.29	41.55	95.32
40 mol% NM					40 mol% NM					40 mol% NM				
0.0322	1.1091	1405.22	45.66	181.52	0.0373	1.1076	1419.41	44.81	155.56	0.0381	1.1079	1412.29	45.25	151.37
0.0747	1.1167	1408.83	45.12	164.22	0.0798	1.1111	1425.89	44.27	149.18	0.0806	1.1129	1416.97	44.74	139.02
0.1172	1.1201	1410.93	44.85	171.6	0.1223	1.1163	1428.97	43.87	140.39	0.1231	1.121	1419.22	44.28	124.56
0.1597	1.1272	1413.09	44.43	164.97	0.1648	1.1233	1433.92	43.29	130.89	0.1656	1.1323	1416.44	44.02	110.03
0.2022	1.1328	1413.36	44.19	163.81	0.2073	1.1254	1437.06	43.03	134.05	0.2081	1.1435	1416.9	43.56	100.87
60 mol% NM					60 mol% NM					60 mol% NM				
0.0342	1.1164	1373.27	47.49	185.85	0.0392	1.1136	1389.11	46.54	171.49	0.0400	1.1155	1378.57	47.17	152.37
0.0767	1.1217	1376.67	47.04	181.59	0.0817	1.1167	1394.76	46.03	160.98	0.0825	1.1209	1381.87	46.40	139.44
0.1192	1.1273	1379.67	46.60	177.61	0.1242	1.1203	1397.88	45.68	158.23	0.1251	1.1286	1383.7	46.28	128.58
0.1617	1.1331	1381.63	46.23	174.19	0.1667	1.1251	1398.30	45.45	149.22	0.1675	1.1389	1383.3	45.88	115.69
0.2042	1.1374	1381.69	46.05	174.88	0.2092	1.1282	1399.32	45.26	148.43	0.2101	1.1489	1381.95	45.57	108.51
80 mol %NM					80 mol %NM					80 mol %NM				
0.0366	1.1242	1347.04	49.02	201.27	0.0411	1.1199	1359.79	48.29	198.17	0.0419	1.1229	1353.69	48.59	171.65
0.0791	1.1285	1349.68	48.64	196.67	0.0836	1.1229	1367.57	47.62	176.64	0.0844	1.13	1351.71	48.43	144.95
0.1216	1.1343	1352.52	48.19	188.51	0.1261	1.1246	1368.02	47.51	173.92	0.1269	1.1371	1352.66	48.06	135.07
0.1641	1.1392	1355.01	47.81	185.72	0.1686	1.1267	1369.98	47.29	170.91	0.1694	1.1463	1351.91	47.73	124.27
0.2066	1.1447	1353.94	47.65	182.85	0.2111	1.1298	1370.76	47.11	167.09	0.2119	1.1543	1350.61	47.49	119.78
100 mol% NM					100 mol% NM					100 mol% NM				
0.0389	1.1294	1331.40	49.95	240.73	0.0430	1.1311	1322.91	50.55	181.90	0.0438	1.1286	1325.46	50.44	200.30
0.0814	1.1291	1344.15	49.01	236.66	0.0855	1.1366	1323.77	50.21	160.95	0.0863	1.1299	1331.17	49.94	188.23
0.1239	1.1294	1356.80	48.09	231.10	0.1280	1.1369	1324.44	50.14	170.54	0.1288	1.1318	1336.80	49.44	181.24
0.1664	1.1296	1368.06	47.30	226.74	0.1705	1.1371	1325.02	50.09	175.50	0.1713	1.1381	1341.35	48.84	165.44
0.2089	1.1292	1379.82	46.51	223.77	0.2131	1.1440	1325.09	49.81	164.38	0.2138	1.1574	1349.70	47.43	128.86

$$\kappa_s = \frac{1}{u^2\rho} \quad (1)$$

The compressibility of a solvent is higher than that of a solute and it decreases with increase in concentration. The isentropic compressibility (κ_s) decreases with increase in concentration because as the concentration of solutes increases, a larger portion of solvent molecules being electrostatic attract towards solute molecules and the amount of solvent molecules in the bulk decreases causing the compressibility to decrease.

The partial molal volume (V_ϕ) and apparent molal isentropic compressibility ($\kappa_{s,\phi}$) of the electrolytes were calculated using eqns 2 and 3, respectively.

$$V_\phi = \frac{M}{\rho} - \frac{10^3[\rho - \rho_o]}{m\rho\rho_o} \quad (2)$$

$$\kappa_{s,\phi} = V_\phi\kappa_s + \frac{10^3[\kappa_s - \kappa_o]}{m\rho_o} \quad (3)$$

where ρ and ρ_o are the densities of the electrolyte solution and of the pure solvent respectively. κ_s and κ_o are the corresponding isentropic compressibility's, M is the molecular mass of the electrolytes and m is the molal concentration.

The limiting apparent molal isentropic compressibilities ($\kappa^o_{s,\phi}$) were obtained by extrapolating from the linear graphs of $\kappa_{s,\phi}$ *vs.* $m^{½}$ by the least square method (Fig. 1) using the equation and the values of $\kappa^o_{s,\phi}$ is given in Table-5.

$$\kappa_{s,\phi} = \kappa^o_{s,\phi} + A_{s,\phi} + A_{s,\phi} m^{½} \quad (4)$$

where $\kappa^o_{s,\phi}$ is the intercept and $A_{s,\phi}$ is the slope.

Table-5 shows that $\kappa^o_{s,\phi}$ values for all the copper(I) nitrate complexes and the reference electrolytes increases (more positive) as the composition of nitromethane increases. In order to obtain more information regarding the tendency of each ion to produce structural or solvation effects, $\kappa^o_{s,\phi}$ values for the

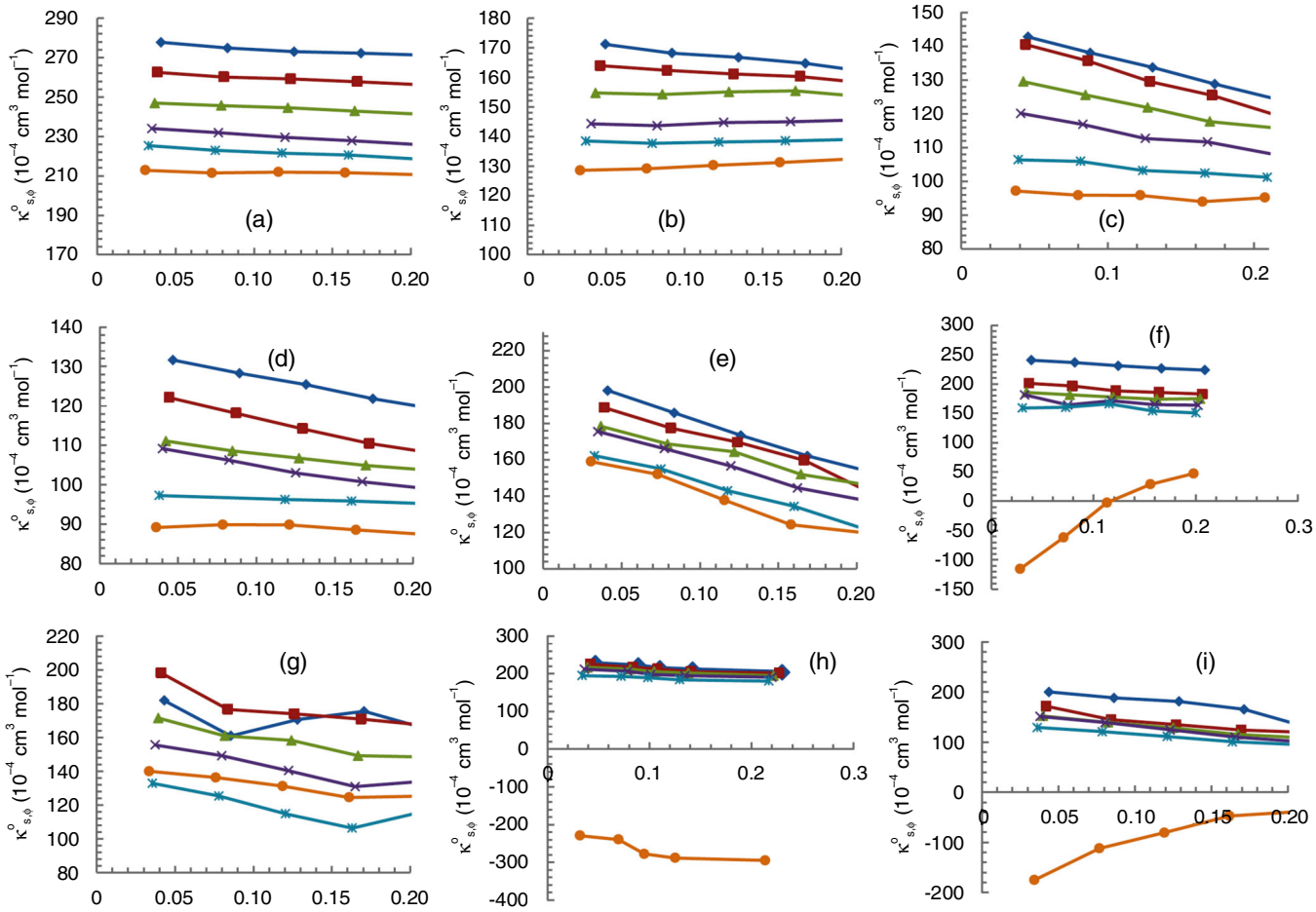

Fig. 1. Plot of limiting apparent molal isentropic compressibility ($\kappa^o_{s,\phi}$) *versus* $m^{1/2}$ for Bu_4NBPh_4 (a), Bu_4NClO_4 (b), $[Cu(AN)_4]ClO_4$ (c), $[Cu(AN)_4]NO_3$ (d), $[Cu(BN)_4]NO_3$ (e), $[Cu(Phen)_2]NO_3$ (f), $[Cu(DMPhen)_2]NO_3$ (g), $[Cu(Bipy)_2]NO_3$ (h), $[Cu(TU)_4]NO_3$ (i) in binary mixture of DMSO + NM at 298 K. ◆ 100 mol%; ■ 80 mol%; ▲ 60 mol%; × 40 mol%; ✳ 20 mol%; ● 0 mol% NM.

TABLE-5
LIMITING APPARENT MOLAL ISENTROPIC COMPRESSIBILITIES[a] ($\kappa^o_{s,\phi}$ / 10^{-4} cm^3 mol^{-1} bar^{-1}) FOR SOME COPPER(I) ELECTROLYTES IN DMSO + NM BINARY MIXTURE AT 298 K

Solutions	mol% nitromethane (NM)					
	0	20	40	60	80	100
Bu_4NBPh_4	224.88	229.67	240.04	251.47	267.10	277.66
Bu_4NClO_4	125.40	134.64	143.25	151.35	168.91	179.56
$[Cu(AN)_4]ClO_4$	183.19	185.59	191.69	201.25	206.26	222.31
$[Cu(AN)_4]NO_3$	182.86	184.18	188.71	193.61	201.67	209.14
$[Cu(BN)_4]NO_3$	-189.90	204.90	225.70	233.00	242.60	247.50
$[Cu(Phen)_2]NO_3$	188.92	191.73	204.72	207.46	210.69	256.39
$[Cu(DMPhen)_2]NO_3$	-208.17	94.09	122.41	194.58	215.75	254.82
$[Cu(Bipy)_2]NO_3$	154.17	155.49	181.60	189.11	201.87	295.75
$[Cu(TU)_4]NO_3$	-264.44	163.37	181.09	188.20	208.45	253.63

[a]Maximum uncertainity in these values is ± 1.5 × 10^{-4} cm^3 mol^{-1} bar^{-1}.

TABLE-6
LIMITING MOLAL IONIC ISENTROPIC COMPRESSIBILITIES $(\kappa^{o}_{s,\phi})_{\pm}$ / 10^{-4} cm^3 mol^{-1} bar^{-1} FOR SOME COPPER(I) ELECTROLYTES IN DMSO + NM BINARY MIXTURE AT 298 K

Solutions	mol% nitromethane (NM)					
	0	20	40	60	80	100
Bu_4N^+	101.07	103.22	107.88	113.02	120.04	124.79
Ph_4B^-	123.81	126.45	132.16	138.45	147.06	152.87
ClO_4^-	24.33	31.42	35.37	38.33	48.87	54.77
NO_3^-	24.00	30.01	32.39	30.69	44.28	41.60
$[Cu(AN)_4]^+$	158.86	154.17	156.32	162.92	157.39	167.54
$[Cu(BN)_4]^+$	-213.90	174.89	193.31	202.31	198.32	205.90
$[Cu(Phen)_2]^+$	164.92	161.72	172.33	176.77	166.41	214.79
$[Cu(DMPhen)_2]^+$	-232.17	64.08	90.02	163.89	171.47	213.22
$[Cu(Bipy)_2]^+$	130.17	125.48	149.21	158.42	157.59	254.15
$[Cu(TU)_4]^+$	-288.44	133.36	148.70	157.51	164.17	212.03

salts are split into the contribution of individual ions *i.e.* $(\kappa^{o}_{s,\phi})$ ± values.

Evaluation of limiting ionic apparent molal isentropic compressibilities: Since, it is known that the $\kappa^{o}_{s,\phi}$ values are additive [19,37] and can be split into the contribution of individual ions. There is no standard approach of splitting $\kappa^{o}_{s,\phi}$ values into its ionic components, though some approaches have been tested [38]. The method earlier used was reported for acetonitrile [39] which is based upon $(\kappa^{o}_{s,\phi})_{\pm}$ values for Ph_4B^- = 0, but this is less appropriative method because the size of Ph_4B^- = 0.535 nm, even larger than Bu_4N^+ = 0.50 nm and therefore, its compressibility contribution cannot be taken as zero. Millero [40] used Ph_4AsBPh_4 as reference electrolyte to split the partial molal volumes of electrolytes into its ionic components.

A model based on Bu_4NBPh_4 assumption, suggested by Gill *et al*. [19,37], in which they have recommended the use of reference electrolyte Bu_4NBPh_4 to achieve the splitting of $\kappa^{o}_{s,\phi}$ values into their ionic components $(\kappa^{o}_{s,\phi})_{\pm}$ with the help of the following equations is taken in a present work:

$$\frac{\kappa^{o}_{s,\phi}(Bu_4N^+)}{k^{o}_{s,\phi}(Ph_4B^-)} = \frac{r_c^3(Bu_4N^+)}{r_c^3(Ph_4B^-)} = \frac{(5.00)^3}{(5.35)^3} \quad (5)$$

and $$\kappa^{o}_{s,\phi}(Ph_4B^-) + \kappa^{o}_{s,\phi}(Bu_4N^+) = \kappa^{o}_{s,\phi}(Bu_4NBPh_4) \quad (6)$$

where r_c refers to the crystallographic radius of the ions.

The $(\kappa^{o}_{s,\phi})_{\pm}$ values of copper(I) electrolytes are reported in Table-6, which shows that the $(\kappa^{o}_{s,\phi})_{\pm}$ values for $[Cu(AN)_4]^+$, $[Cu(BN)_4]^+$, $[Cu(Phen)_2]^+$, $[Cu(DMPhen)_2]^+$, $[Cu(Bipy)_2]^+$ and $[Cu(TU)_4]^+$ increases *i.e.* it becomes more positive in magnitude as the composition of co-solvent increases. The $(\kappa^{o}_{s,\phi})_{\pm}$ values for Bu_4N^+, Ph_4B^-, ClO_4^- is positive and also increases as it moves to NM rich regions. The NO_3^- values are negative but it becomes less negative as we move to NM rich regions. The large values of $(\kappa^{o}_{s,\phi})_{\pm}$ arise either from the free space present in the solution between the ions and the solvent molecules or from any kind of conformational changes in the structure of ions. Thus positive $(\kappa^{o}_{s,\phi})_{\pm}$ values shows weak structural effects which arises due to less or no solute-solute and solvent-solvent interactions. Cu^+ electrolytes are therefore weakly solvated in DMSO + NM mixture and the extent of solvation decreases with the increase of NM composition in the mixtures.

Conclusions

The ultrasonic velocities of solutions of Bu_4NBPh_4, Bu_4NClO_4, $[Cu(AN)_4]NO_3$, $[Cu(BN)_4]NO_3$, $[Cu(Phen)_2]NO_3$, $[Cu(DMPhen)_2]NO_3$, $[Cu(Bipy)_2]NO_3$ and $[Cu(TU)_4]NO_3$ in binary mixture of dimethylsulfoxide (DMSO) and nitromethane shows that these copper(I) electrolytes show less solvation in nitromethane rich regions. This shows the structure breaking tendency of nitromethane, which is due to the absence of any kind of interaction between the solvents. The large values of $(\kappa^{o}_{s,\phi})_{\pm}$ arise either from the free space present in the solution between the ions and the solvent molecules or from any kind of conformational changes in the structure of ions. Thus, extent of solvation in Cu(I) ions decreases in the order: $[Cu(AN)_4]^+ > [Cu(BN)_4]^+ > [Cu(TU)_4]^+ > [Cu(DMPhen)_2]^+ > [Cu(Phen)_2]^+ > [Cu(Bipy)_2]^+$. It seems that extent of solvation is further less for chelating ligands like phenanthroline, 2,9-dimethyl-1,10-phenanthroline, thiourea and bipyridyl in nitromethane regions indicating conformational changes in these electrolytes.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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