Compressibility Studies of Some Copper(I), Silver(I), and Tetrabutylammonium Salts in Acetonitrile + Adiponitrile Binary Mixtures[†]

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Ultrasonic velocities and densities of some copper(I), silver(I), and tetrabutylammonium salts have been measured in the concentration range of (0.002 to 0.28) m in binary mixtures of acetonitrile (AN) + adiponitrile (ADN) containing 1.0, 0.9, 0.8, 0.7, 0.6, and 0.5 mol fraction of AN at 298.15 K. The isentropic compressibility (κ_s) and apparent molal isentropic compressibility ($\kappa_{s,\phi}$) in various solvent systems have been calculated by using ultrasonic velocity (u) and partial molal volume (V_ϕ) data, respectively. Limiting apparent molal isentropic compressibilities ($\kappa^o_{s,\phi}$) for various salts have been evaluated from $\kappa_{s,\phi}$ versus $m^{1/2}$ plots and split into the contributions of individual ions $(\kappa^o_{s,\phi})_\pm$. The $(\kappa^o_{s,\phi})_\pm$ values for copper(I) and silver(I) ions are found to be negative over the entire solvent composition range which indicates strong solvation of these ions. The $(\kappa^o_{s,\phi})_\pm$ values becoming more and more negative with an increase in the ADN composition shows that the extent of solvation increases with an increase in ADN composition. The large and positive $(\kappa^o_{s,\phi})_\pm$ values for Bu_4N^+ and Ph_4B^- indicate some special type of interaction with the solvent molecules, which increases with the increase of ADN composition in the mixture.

Introduction

Numerous studies have shown that acoustical parameters like compressibility coupled with density are recently gaining importance in providing valuable information regarding ion−ion and ion−solvent interactions in pure and mixed solvents. Compressibility data are usually needed for predicting the pressure dependence properties of electrolyte solutions. Precise compressibility data of electrolytes in nonaqueous solvents are rare and in acetonitrile (AN) + adiponitrile (ADN) system are completely lacking. The electromotive force (emf),[1,2] solubility,[3−5] transport number,[6,7] Fourier transform infrared (FTIR),[8] NMR,[2,9−12] electron spin resonance (ESR),[13,14] conductance,[15,16] and viscosity[11,17,18] studies have been used to investigate the solvation behavior of ions in mixed solvents. The enthalpy[19] and Gibbs energy of transfer[20,21] from a reference solvent to a solvent mixture have also been used to provide meaningful information about the solvation of ions in mixed solvents. Solvation studies in mixed solvents using compressibility data are also available.[22,23] Detailed studies of the solvation behavior of monovalent cations show that all alkali metal cations are usually solvated by purely electrostatic ion−dipole interactions.[24,25] Copper(I) and silver(I) cations, on the other hand, are found to be solvated by a special type of interaction[26] with some solvents. This specific type of interaction is well-recognized for copper(I) and silver(I) cations in nitrile solvents where the dπ−pπ type of interaction of copper(I) and silver(I) has been recognized with a nitrile group of solvents.[21,26]

In continuation of our earlier studies of the stabilization of copper(I) salts[27−29] using AN as one of the components of binary mixtures, we report here the ultrasonic velocity measurements of copper(I), silver(I), and some other ions in AN + ADN binary mixtures. Both AN and ADN are dipolar aprotic solvents with almost similar relative permittivities (AN = 36.0 and ADN = 33.7) but different viscosities (AN = 0.341 mPa·s and ADN = 5.99 mPa·s). Both of the solvents, AN with one $-C\equiv N$ group and ADN with two $-C\equiv N$ groups, have the tendency to interact with the Cu(I) and Ag(I) ions. The present studies are expected to provide interesting results of the solvation behavior of the ions as one $-C\equiv N$ group in AN is changed to two $-C\equiv N$ groups in ADN. Such studies will find an application in finding a suitable solvent for the hydrometallurgical purification of copper.[26]

Experimental Section

AN and ADN (both 99.5 % from E. Merck) were purified as reported previously.[30] The purified solvents had the densities of (776.85 and 975.26) $kg \cdot m^{-3}$ and viscosities of (0.341 and 5.99) mPa·s, respectively, which agrees well with the literature values.[30] Tetraacetonitrile copper(I) perchlorate was prepared by the reduction of copper(II) perchlorate hexahydrate by copper metal powder in warm AN, following the method reported by Hathaway et al.[31] and Gill and Cheema.[32] Tetrabenzonitrile copper(I) perchlorate was prepared by the method already reported.[10] Bis(2,9-dimethyl-1,10-phenanthroline) copper(I) perchlorate was prepared by mixing a warm solution of 2,9-dimethyl-1,10-phenanthroline ligand with $[Cu(CH_3CN)_4]ClO_4$ in AN in the required proportion. The salt was precipitated out by adding toluene. The purity of the salts was checked by their elemental, chemical, and spectroscopic analysis. Tetrabutylammonium tetraphenylborate and tetrabutylammonium perchlorate were prepared and dried by the methods already reported.[33,34] All physical parameters like ultrasonic velocity, density, viscosity, and relative permittivity were measured at (298.15 ± 0.01) K. An ultrasonic time intervalometer, model UTI-101, fabricated by Innovative Instruments (Hyderabad) was used for the precise acoustical measurement of various binary mixtures

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Table 1. Relative Permittivity ε_r, Viscosity η, Density ρ, Ultrasonic Velocity u, and Isentropic Compressibility κ_s of AN (1) + ADN (2) Binary Mixtures at 298.15 K

x_1	ϵ_r	$\frac{\eta}{\mathrm{mPa \cdot s}}$	$\frac{\rho}{\mathrm{kg \cdot m^{-3}}}$	$\frac{u}{\mathrm{m \cdot s^{-1}}}$	$\frac{10^{-1}\,\kappa_s}{\mathrm{Pa^{-1}}}$
1.0	36.0	0.341	776.85	1270.15	79.70
0.9	35.5	0.506	818.58	1320.21	70.09
0.8	35.0	0.684	848.59	1378.73	61.99
0.7	34.5	1.057	870.00	1405.47	58.19
0.6	34.0	1.410	880.00	1445.39	54.39
0.5	33.7	1.610	892.51	1468.78	51.94

Table 2. Molality m, Density ρ, and Ultrasound Velocity u for Some Electrolytes in AN at 298.15 K

$\frac{m}{\mathrm{mol \cdot kg^{-1}}}$	$\frac{\rho}{\mathrm{kg \cdot m^{-3}}}$	$\frac{u}{\mathrm{m \cdot s^{-1}}}$
	Bu_4NBPh_4	
0.02541	786.40	1272.16
0.03943	791.67	1273.12
0.06096	800.13	1276.07
0.09374	813.28	1278.17
0.14285	833.50	1279.56
	Bu_4NClO_4	
0.02616	783.32	1272.36
0.04068	786.97	1273.17
0.06312	792.62	1275.21
0.09762	801.31	1276.78
0.15016	814.61	1278.23
	$[Cu(CH_3CN)_4]ClO_4$	
0.02538	787.25	1272.13
0.03962	793.19	1273.68
0.05890	801.28	1274.96
0.08537	812.53	1276.69
0.12538	828.76	1278.45
	$[Cu(C_6H_5CN)_4]ClO_4$	
0.02433	791.66	1273.56
0.03778	799.95	1274.25
0.05712	811.96	1275.23
0.08272	828.09	1277.09
0.11642	849.54	1279.18
	$[Cu(DMPhen)_2]ClO_4$	
0.02474	792.91	1273.25
0.03841	801.84	1274.51
0.05937	815.69	1275.86
0.08169	830.27	1277.35
0.12183	857.14	1279.66
	Bu_4NNO_3	
0.02174	781.56	1272.73
0.04144	785.96	1273.68
0.06482	791.21	1275.22
0.08753	796.37	1276.59
0.11385	802.45	1279.35
	$AgNO_3$	
0.02830	785.04	1272.02
0.04474	789.86	1273.54
0.06947	797.11	1275.33
0.09727	805.38	1277.68
0.12847	814.46	1279.51

Table 3. Molality m, Density ρ, and Ultrasound Velocity u for Some Electrolytes in AN (1) + ADN (2) at $x_1 = 0.9$ at 298.15 K

$\frac{m}{\mathrm{mol \cdot kg^{-1}}}$	$\frac{\rho}{\mathrm{kg \cdot m^{-3}}}$	$\frac{u}{\mathrm{m \cdot s^{-1}}}$
	Bu_4NBPh_4	
0.02435	827.59	1321.64
0.03779	832.91	1323.08
0.05846	841.43	1324.87
0.08993	854.69	1327.53
0.13721	875.93	1329.18
	Bu_4NClO_4	
0.02508	824.89	1322.97
0.03882	828.44	1323.82
0.06032	834.09	1324.79
0.09330	842.87	1326.45
0.12826	852.30	1328.39
	$[Cu(CH_3CN)_4]ClO_4$	
0.02456	830.37	1322.62
0.03843	837.09	1323.81
0.05861	846.96	1325.32
0.08361	859.26	1326.76
0.11073	872.64	1328.19
	$[Cu(C_6H_5CN)_4]ClO_4$	
0.02236	833.96	1322.25
0.03468	842.50	1323.54
0.05352	855.63	1324.69
0.07619	871.50	1325.92
0.10217	889.91	1326.96
	$[Cu(DMPhen)_2]ClO_4$	
0.02136	834.31	1322.23
0.03277	842.74	1324.29
0.04882	854.72	1325.61
0.07026	870.38	1327.15
0.09682	889.86	1328.78
	Bu_4NNO_3	
0.02848	824.89	1321.88
0.04533	828.73	1323.57
0.06416	833.18	1325.67
0.08461	838.07	1327.92
0.10328	842.83	1330.32
	$AgNO_3$	
0.03026	829.25	1321.70
0.05281	837.27	1323.08
0.07243	844.26	1324.96
0.10265	855.12	1326.71
0.13424	867.02	1328.75

and electrolyte solutions using pulse echo overlap technique at a fixed frequency of 2 MHz. An oscilloscope (60 MHz, from Philips India Limited) was coupled with the instrument to record signals for measuring ultrasonic velocities. Densities of solvent mixtures and solutions were measured using a Anton Paar digital density meter model 60 and calibrated cell model 602. Viscosities were measured by using an Ubbelohde suspended level viscometer by the method reported earlier.[18] The relative permittivities were measured at 2 MHz using a Radelkis Hungury OH-301 dielectrometer. The experimentally measured physical parameters of binary mixtures of AN + ADN are reported in Table 1. The uncertainty of the sound velocity, density, viscosity, relative permittivity, and isentropic compressibility was ± 0.02 $\mathrm{m \cdot s^{-1}}$, ± 0.01 $\mathrm{kg \cdot m^{-3}}$, ± 0.001 mPa·s, ± 0.1, and ± 0.04 $\mathrm{Pa^{-1}}$, respectively.

Results and Discussion

Compressibility Studies. Ultrasonic velocities (u) and densities (ρ) of Bu_4NBPh_4, Bu_4NClO_4, $[Cu(CH_3CN)_4]ClO_4$, $[Cu(C_6H_5CN)_4]ClO_4$, $[Cu(DMPhen)_2]ClO_4$, Bu_4NNO_3, and $AgNO_3$ have been measured at different salt concentrations in the concentration range (0.002 to 0.28) m in AN + ADN mixtures containing 1.0, 0.9, 0.8, 0.7, 0.6, and 0.5 mol fraction of AN at 298.15 K and are reported in Tables 2 to 7. The isentropic compressibilities (κ_s) of the electrolytes in each solvent system have been calculated by using the relation

$$\kappa_s = u^{-2}\rho^{-1} \qquad (1)$$

It has been found that the κ_s values decrease linearly with the increase in salt concentration in all of the cases, which indicates that the electrolytes are not associated in AN + ADN mixtures over the salt concentrations studied.

Table 4. Molality m, Density ρ, and Ultrasound Velocity u for Some Electrolytes in AN (1) + ADN (2) at $x_1 = 0.8$ at 298.15 K

$\frac{m}{\text{mol}\cdot\text{kg}^{-1}}$	$\frac{\rho}{\text{kg}\cdot\text{m}^{-3}}$	$\frac{u}{\text{m}\cdot\text{s}^{-1}}$
	Bu_4NBPh_4	
0.02408	857.14	1380.34
0.03746	862.37	1381.29
0.05787	870.79	1382.63
0.08621	883.19	1383.85
0.12053	899.61	1385.37
	Bu_4NClO_4	
0.02369	854.33	1381.89
0.03876	858.31	1382.96
0.05735	863.28	1383.08
0.08517	870.85	1384.51
0.11862	880.24	1385.79
	$[Cu(CH_3CN)_4]ClO_4$	
0.01849	858.89	1381.49
0.02879	864.64	1383.01
0.04475	873.63	1384.85
0.06960	886.59	1387.88
0.09572	902.68	1390.26
	$[Cu(C_6H_5CN)_4]ClO_4$	
0.01726	861.88	1380.39
0.02634	868.84	1381.95
0.04330	881.85	1383.40
0.06628	899.59	1385.12
0.08953	917.36	1387.47
	$[Cu(DMPhen)_2]ClO_4$	
0.01923	864.39	1380.78
0.02762	871.33	1382.34
0.04375	884.61	1383.87
0.06513	902.19	1385.14
0.08528	917.93	1387.72
	Bu_4NNO_3	
0.02214	853.42	1380.92
0.03994	857.55	1381.80
0.06275	862.97	1383.56
0.08476	868.52	1385.73
0.10434	873.86	1388.09
	$AgNO_3$	
0.02578	859.49	1381.07
0.04358	866.94	1383.21
0.06895	877.52	1385.41
0.09273	887.58	1387.39
0.11632	0.89708	1389.46

Table 5. Molality m, Density ρ, and Ultrasound Velocity u for Some Electrolytes in AN (1) + ADN (2) at $x_1 = 0.7$ at 298.15 K

$\frac{m}{\text{mol}\cdot\text{kg}^{-1}}$	$\frac{\rho}{\text{kg}\cdot\text{m}^{-3}}$	$\frac{u}{\text{m}\cdot\text{s}^{-1}}$
	Bu_4NBPh_4	
0.02361	877.84	1407.27
0.03854	883.45	1409.16
0.05208	889.17	1411.76
0.07493	899.65	1413.89
0.10162	913.22	1416.32
	Bu_4NClO_4	
0.01955	874.61	1407.69
0.03089	877.49	1409.43
0.04757	881.93	1411.38
0.07352	888.92	1413.54
0.10341	897.61	1415.81
	$[Cu(CH_3CN)_4]ClO_4$	
0.01430	878.89	1407.98
0.02513	885.64	1408.91
0.04128	895.78	1410.27
0.05826	906.17	1411.73
0.08011	919.54	1412.25
	$[Cu(C_6H_5CN)_4]ClO_4$	
0.01850	885.77	1406.54
0.02961	895.28	1407.96
0.04538	908.72	1409.37
0.06517	925.62	1410.72
0.08369	940.81	1412.29
	$[Cu(DMPhen)_2]ClO_4$	
0.02216	889.04	1407.94
0.03435	900.81	1409.27
0.05281	917.51	1410.84
0.07326	935.66	1412.53
0.09486	953.28	1414.11
	Bu_4NNO_3	
0.03124	876.57	1407.31
0.05633	882.19	1408.65
0.07880	887.55	1410.12
0.09176	891.15	1411.42
0.11426	897.39	1412.83
	$AgNO_3$	
0.02017	879.82	1407.66
0.03494	887.02	1408.92
0.05408	896.18	1410.47
0.07845	907.74	1412.37
0.10419	919.35	1414.09

The apparent molal isentropic compressibility ($\kappa_{s,\phi}$) of these salts has been calculated by using partial molal volume (V_ϕ) and the following equations

$$V_\phi = \frac{M}{\rho} - \frac{[\rho - \rho_o]}{m\rho\rho_o} \tag{2}$$

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

where m is the molality, M is the molecular mass of the solute, κ_s and κ_o are the isentropic compressibilities of the solution and of pure solvent or solvent mixtures, and ρ and ρ_o are the densities of the solution and of pure solvent or solvent mixtures, respectively. The plots of $\kappa_{s,\phi}$ versus $m^{1/2}$ were linear in the concentration range studied. The limiting apparent molal isentropic compressibilities ($\kappa^o_{s,\phi}$) were obtained by extrapolation from the linear plots of $\kappa_{s,\phi}$ versus $m^{1/2}$ by the least-squares method using the equation

$$\kappa_{s,\phi} = \kappa^o_{s,\phi} + A_{s,\phi}m^{1/2} \tag{4}$$

The $\kappa^o_{s,\phi}$ values for various salts thus obtained are reported in Table 8. The $\kappa^o_{s,\phi}$ values for these electrolytes are not available in AN + ADN mixtures; therefore, a comparison of our values could not be made. In pure AN, the $\kappa^o_{s,\phi}$ values for Bu_4NBPh_4 ($107.4\cdot10^{-3}$ $\text{m}^3\cdot\text{mol}^{-1}\cdot\text{TPa}^{-1}$) and for Bu_4NClO_4 ($22.4\cdot10^{-3}$ $\text{m}^3\cdot\text{mol}^{-1}\cdot\text{TPa}^{-1}$) are in good agreement with the literature values obtained by adding individual ionic values[35] ($108.0\cdot10^{-3}$ $\text{m}^3\cdot\text{mol}^{-1}\cdot\text{TPa}^{-1}$ and $20.0\cdot10^{-3}$ $\text{m}^3\cdot\text{mol}^{-1}\cdot\text{TPa}^{-1}$, respectively). A perusal of Table 8 shows that $\kappa^o_{s,\phi}$ values for $[Cu(CH_3CN)_4]ClO_4$, $[Cu(C_6H_5CN)_4]ClO_4$, $[Cu(DMPhen)_2]ClO_4$, and $AgNO_3$ are negative in AN + ADN binary mixtures at all compositions of the solvent mixtures and increase with an increase in ADN composition. A negative value indicates strong solvation effects for these salts in AN + ADN binary mixtures. $\kappa^o_{s,\phi}$ values for Bu_4NBPh_4, Bu_4NClO_4, and Bu_4NNO_3 are positive and large and increase in magnitude with an increase in mole fraction of ADN.

Evaluation of Limiting Ionic Apparent Molal Isentropic Compressibilities ($\kappa^o_{s,\phi}$)$_\pm$. To have better insight regarding the tendency of each ion to produce structural or solvation effects, the $\kappa^o_{s,\phi}$ values for the salts have been split into the contribution of individual ions ($\kappa^o_{s,\phi}$)$_\pm$ values. As reported earlier,[36−39] the $\kappa^o_{s,\phi}$ values are additive and can be directly split into the contribution of individual ions. There is no definite method of

Table 6. Molality m, Density ρ, and Ultrasound Velocity u for Some Electrolytes in AN (1) + ADN (2) at $x_1 = 0.6$ at 298.15 K

$\frac{m}{\text{mol}\cdot\text{kg}^{-1}}$	$\frac{\rho}{\text{kg}\cdot\text{m}^{-3}}$	$\frac{u}{\text{m}\cdot\text{s}^{-1}}$
	Bu_4NBPh_4	
0.02436	887.38	1447.24
0.04553	894.11	1449.17
0.06729	902.61	1451.35
0.08582	911.41	1453.81
0.10286	921.46	1456.45
	Bu_4NClO_4	
0.02595	885.71	1446.63
0.04012	889.21	1448.58
0.05734	893.78	1450.73
0.07857	899.74	1452.89
0.10237	906.96	1455.42
	$[Cu(CH_3CN)_4]ClO_4$	
0.02014	893.84	1447.24
0.03560	904.53	1449.32
0.05362	916.76	1451.57
0.07307	929.66	1453.91
0.09325	942.31	1456.09
	$[Cu(C_6H_5CN)_4]ClO_4$	
0.01553	894.21	1447.13
0.02861	906.14	1448.24
0.04138	917.44	1449.53
0.05427	928.52	1450.87
0.06801	939.57	1452.39
	$[Cu(DMPhen)_2]ClO_4$	
0.01431	893.91	1447.26
0.02617	905.51	1448.92
0.03842	917.29	1450.35
0.05163	929.70	1451.97
0.06837	945.01	1453.42
	Bu_4NNO_3	
0.03179	886.12	1446.87
0.05316	890.63	1448.18
0.07689	895.96	1449.76
0.10261	902.34	1451.35
0.12879	909.61	1453.09
	$AgNO_3$	
0.01429	887.88	1446.61
0.02219	892.03	1447.94
0.03451	898.44	1449.26
0.04927	905.69	1450.77
0.06252	911.23	1452.19

Table 7. Molality m, Density ρ, and Ultrasound Velocity u for Some Electrolytes in AN (1) + ADN (2) at $x_1 = 0.5$ at 298.15 K

$\frac{m}{\text{mol}\cdot\text{kg}^{-1}}$	$\frac{\rho}{\text{kg}\cdot\text{m}^{-3}}$	$\frac{u}{\text{m}\cdot\text{s}^{-1}}$
	Bu_4NBPh_4	
0.02450	898.57	1470.12
0.04515	904.71	1471.64
0.07167	914.50	1473.39
0.09605	925.56	1475.72
0.12034	939.46	1480.03
	Bu_4NClO_4	
0.02108	896.78	1469.87
0.03983	901.07	1471.04
0.05734	905.60	1472.29
0.07826	911.53	1473.75
0.10109	919.10	1475.12
	$[Cu(CH_3CN)_4]ClO_4$	
0.01347	902.61	1469.96
0.02436	910.63	1471.46
0.03671	919.57	1473.05
0.04953	928.21	1474.79
0.07285	943.35	1476.41
	$[Cu(C_6H_5CN)_4]ClO_4$	
0.01128	903.69	1470.12
0.02438	916.53	1471.79
0.03825	929.83	1473.37
0.05248	942.89	1474.94
0.06436	952.96	1476.87
	$[Cu(DMPhen)_2]ClO_4$	
0.01219	905.11	1470.00
0.02130	914.41	1471.36
0.03424	927.57	1472.69
0.04717	939.86	1474.13
0.06123	952.61	1476.22
	Bu_4NNO_3	
0.01972	896.01	1470.31
0.04159	900.42	1472.48
0.06392	905.40	1473.84
0.08779	911.83	1475.37
0.10751	918.37	1477.92
	$AgNO_3$	
0.01526	901.93	1469.64
0.02839	910.12	1471.13
0.04319	918.34	1472.71
0.05987	927.27	1474.22
0.08068	938.30	1476.45

Table 8. Limiting Apparent Molal Isentropic Compressibilities,[a] $\kappa^{o}_{s,\phi}$, for Some Electrolytes in AN (1) + ADN (2) Mixtures at Different x_1 at 298.15 K

	$10^3\ \kappa^{o}_{s,\phi}/\text{m}^3\cdot\text{mol}^{-1}\cdot\text{TPa}^{-1}$					
salt	1.0	0.9	0.8	0.7	0.6	0.5
Bu_4NBPh_4	107.4 (108.0)[b]	124.8	143.2	167.6	196.4	231.7
Bu_4NClO_4	22.4 (20.0)[b]	33.1	45.2	58.7	72.7	90.1
$[Cu(CH_3CN)_4]ClO_4$	−211.7	−230.4	−252.7	−278.2	−306.3	−337.6
$[Cu(C_6H_5CN)_4]ClO_4$	−219.5	−237.1	−262.9	−291.9	−319.8	−353.2
$[Cu(DMPhen)_2]ClO_4$	−278.9	−294.2	−312.7	−333.4	−356.1	−381.3
Bu_4NNO_3	26.2	34.7	43.8	55.6	68.9	86.5
$AgNO_3$	−217.8	−233.0	−257.8	−283.2	−317.2	−346.4

[a] The uncertainty of $\kappa^{o}_{s,\phi}$ values is $\pm\ 2.5\cdot10^{-3}\ \text{m}^3\cdot\text{mol}^{-1}\cdot\text{TPa}^{-1}$. [b] Ref 35.

splitting $\kappa^{o}_{s,\phi}$ values into ionic components, and consequently some approaches[36] have been suggested by some workers. The method already used in AN is based upon $(\kappa^{o}_{s,\phi})_{\pm}$ for $Ph_4B^- = 0$. This method is less appropriate because the size of Ph_4B^- ion is large (0.535 nm),[37] even larger than the Bu_4N^+ ion (0.50 nm). Therefore, its compressibility contribution cannot be taken as zero. Millero[38] has split the partial molal volumes of electrolytes into ionic components using Ph_4AsBPh_4 as a reference electrolyte. A similar model based on the Bu_4NBPh_4 assumption was suggested by Gill and co-workers,[39] in which they recommended the use of the reference electrolyte Bu_4NBPh_4 to split the $\kappa^{o}_{s,\phi}$ values into its ionic contributions $(\kappa^{o}_{s,\phi})_{\pm}$ with the help of the following equations

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

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

where r_c refers to the crystallographic radius of the ions. This model has also been used in the present work. Using eqs 5 and 6, $\kappa^{o}_{s,\phi}$ values for Bu_4NBPh_4 were split into the ionic contribution for Bu_4N^+ and Ph_4B^- ions. By using these $(\kappa^{o}_{s,\phi})_{\pm}$ values, $(\kappa^{o}_{s,\phi})_{\pm}$ values for all other ions have been calculated on the basis of additive principle and are reported in Table 9.

Negative $(\kappa^{o}_{s,\phi})_{\pm}$ values are generally obtained due to stronger ion−solvent interactions involving electrostatic ion−dipole or

Table 9. Limiting Ionic Apparent Molal Isentropic Compressibilities $(\kappa^{o}_{s,\phi})_{\pm}$ for Some Ions in AN (1) + ADN (2) Mixtures at Different x_1 at 298.15 K

	$10^3\ (\kappa^{o}_{s,\phi})_{\pm}/\mathrm{m^3 \cdot mol^{-1} \cdot TPa^{-1}}$					
ion	1.0	0.9	0.8	0.7	0.6	0.5
Bu_4N^+	48.3	56.1	64.4	75.3	87.8	104.1
$[Cu(CH_3CN)_4]^+$	−185.8	−207.4	−233.5	−261.6	−291.2	−323.6
$[Cu(C_6H_5CN)_4]^+$	−193.6	−214.1	−243.7	−275.3	−304.7	−339.2
$[Cu(DMPhen)_2]^+$	−253.0	−271.2	−293.5	−316.8	−341.0	−367.3
Ag^+	−195.7	−211.6	−237.2	−263.5	−298.3	−328.8
NO_3^-	−22.1	−21.4	−20.6	−19.7	−18.9	−17.6
Ph_4B^-	59.1	68.7	78.8	92.3	108.6	127.6
ClO_4^-	−25.9	−23.0	−19.2	−16.6	−15.1	−14.0

some special type of interactions, while positive values are obtained mostly for tetraalkylammonium ions due to hydrophobic or dispersive interactions. The results of Table 9 show that the $(\kappa^{o}_{s,\phi})_{\pm}$ values for $[Cu(CH_3CN)_4]^+$, $[Cu(C_6H_5CN)_4]^+$, $[Cu(DMPhen)_2]^+$, and Ag^+ are large and negative which indicate that these ions have strong ion−solvent interactions which increase with the increase in ADN composition. The $(\kappa^{o}_{s,\phi})_{\pm}$ values for Bu_4N^+ and Ph_4B^- ions are positive and large at all compositions of the mixtures. The positive and large $(\kappa^{o}_{s,\phi})_{\pm}$ values for Bu_4N^+ and Ph_4B^- indicate some special type of ion−solvent interactions which may take place because of solvophobic, dispersion, or solvent−solvent interactions. Special interaction of Ph_4B^- with AN through dispersion forces was also reported by Bose and Kundu[40] from conductance measurements. The solvophobic interaction increases with the increase in ADN composition due to the increased chain length in ADN. ClO_4^- and NO_3^- have small negative $(\kappa^{o}_{s,\phi})_{\pm}$ values in pure AN and increase with the increase in ADN composition in AN + ADN mixtures. The magnitude of $(\kappa^{o}_{s,\phi})_{\pm}$ values in all of these cases is, however, small, indicating the poor solvation of these ions in AN + ADN mixtures. The ion−solvent interactions for these ions change from weak electrostatic interaction to a special type of interaction in the ADN-rich region of the binary mixtures.

Conclusion

The large and negative $(\kappa^{o}_{s,\phi})_{\pm}$ values for $[Cu(CH_3CN)_4]^+$, $[Cu(C_6H_5CN)_4]^+$, $[Cu(DMPhen)_2]^+$, and Ag^+ indicate strong ion−solvent interaction. Extent of ion−solvent interaction for these ions increases with the increase of ADN composition in AN + ADN binary mixtures. ClO_4^- and NO_3^- are poorly solvated in present solvent system. Bu_4N^+ and Ph_4B^- show a special type of interaction in AN + ADN binary mixtures.

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