Speed of Sound in Aqueous and Methanolic Lithium Nitrate Solutions

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Speeds of sound in aqueous and methanolic lithium nitrate solutions were measured as functions of concentration ($0.0181 \leq m/(\text{mol}\cdot\text{kg}^{-1}) \leq 21.818$) and temperature ($273.15 \leq T/\text{K} \leq 323.15$) at 2 MHz. The isentropic compressibility isotherms for aqueous lithium nitrate solutions converge at 3.75 $\text{mol}\cdot\text{kg}^{-1}$, and at this concentration the primary hydration shell of the solute has become just saturated. It has been estimated that there are 15 molecules of water in the primary hydration shell of lithium nitrate, and the calculated primary hydration number of the nitrate ion was found to be 9. For methanolic lithium nitrate solutions, the isentropic compressibility isotherms vary smoothly within the concentration and temperature ranges of study.

Introduction

Aqueous and nonaqueous electrolyte solutions have been of immense importance to the technologist and theoretician since most chemical processes occur in these systems. The existence of free ions, solvated ions, and ion pair depends on the concentration range. The structure of the solvent around ions has been studied by different techniques (Hinton and Amis, 1971; Ohtaki and Radnai, 1993).

The primary solvation number of Li^+ ion in aqueous medium has been reported and lies in the range of 3−9 (Hinton and Amis, 1971; Ohtaki and Radnai, 1993; Rudolph et al., 1995). Several techniques, notably X-ray diffraction (Okada et al., 1983; Yamanaka et al., 1993; Yamaguchi et al., 1995), neutron diffraction (Kameda and Uemura, 1993; Yamagami et al., 1994; Yamaguchi et al., 1995), Raman spectroscopy (Kameda et al., 1994), and simulation (Tamura et al., 1988; Pye et al., 1996) have been used to study the hydration structure of Li^+ ion in lithium halide solutions in the concentration ranges that are far away from the concentration at which the primary solvation shell is just saturated. On the other hand, the most frequently appearing hydration number of Li^+ ion has been reported as 4 in an aqueous system with a water to lithium halide ratio of 4, whereas, for the water to salt ratio > 4, the hydration number is 6 (Ohtaki and Radnai, 1993). It appears that the concentration dependence of the hydration number of Li^+ ion is not well understood.

Among the many approaches, speed of sound (Endo and Nomoto, 1981) seems to be an alternative technique for determining the hydration number, since the isentropic compressibility isotherms for aqueous systems converge (Onori, 1988; Rohman and Mahiuddin, 1997) at a particular concentration. At that concentration all the solvent molecules are involved in the solvation and have formed a rigid structure with a critical value of isentropic compressibility which is independent of temperature. The solvation phenomenon of salt in methanol seems to be quite different from that of water since solvation of the solute in methanol is slow (Roy and Bagchi, 1994). Therefore, in this paper we report the speed of sound and isentropic compressibility of aqueous and methanolic lithium nitrate solutions as functions of concentration and temperature.

Experimental Section

Materials. Lithium nitrate (>98%, E. Merck, Darmstadt, Germany) were recrystallized twice from triple distilled water and dried over P_2O_5 until use. Methanol (GR grade, E. Merck, Mumbai, India) was distilled after refluxing with quicklime for 4 h. Anhydrous methanol was prepared by distilling from a mixture of magnesium turning and iodine. Only the middle fraction was used in our study. Aqueous and methanolic lithium nitrate solutions were prepared by mass. Triple distilled water was used to prepare aqueous solutions.

Measurements. Speeds of sound in aqueous and methanolic lithium nitrate solutions were measured at 2 MHz by using a Multifrequency Ultrasonic Interferometer, M83 (Mittal Enterprises, New Delhi, India) as described elsewhere (Rohman et al., 1999). The interferometer was calibrated with triple distilled water using the reported values of the speed of sound (Kell, 1970; Del Grosso and Mader, 1972; De Lisi et al., 1990) at 298.15 K. Speeds of sound were measured both in ascending and descending order, and an average value was determined. The uncertainty in the speed of sound has been found to be within ±0.01%. The densities of both systems were measured by using a pycnometer with an accuracy of ±0.01%.

All the measurements were made as functions of concentration ($0.0181 \leq m/(\text{mol}\cdot\text{kg}^{-1}) \leq 21.818$ and $0.0184 \leq m/(\text{mol}\cdot\text{kg}^{-1}) \leq 8.542$ for aqueous and methanolic lithium nitrate solutions, respectively) and temperature ($273.15 \leq T/\text{K} \leq 323.15$). A Schott-Geräte thermostat CT-1450 or a Julabo F30VC circulator was used to maintain the temperature of the study to ±0.02 K in IPTS-68 scale.

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Table 1. Density Values for Aqueous and Methanolic Lithium Nitrate Solutions as Functions of Concentration and Temperature

T/K	ρ/(kg·m^{-3})	T/K	ρ/(kg·m^{-3})	T/K	ρ/(kg·m^{-3})	T/K	ρ/(kg·m^{-3})	T/K	ρ/(kg·m^{-3})	T/K	ρ/(kg·m^{-3})
Aqueous Lithium Nitrate											
0.0181 mol.kg^{-1}		0.0254 mol.kg^{-1}		0.0383 mol.kg^{-1}		0.2402 mol.kg^{-1}		0.6480 mol.kg^{-1}		1.129 mol.kg^{-1}	
323.60	990.76	321.85	992.66	323.85	992.09	323.40	999.34	322.55	1014.0	321.55	1032.9
320.85	992.14	318.55	994.04	320.75	994.00	319.65	1000.7	318.55	1015.5	318.35	1034.1
317.55	993.40	314.95	995.30	317.15	995.41	315.15	1002.1	314.95	1016.7	315.10	1035.3
313.75	995.31	311.50	997.22	313.60	996.86	311.35	1003.4	311.55	1018.7	311.95	1036.8
310.30	996.72	307.55	998.63	310.15	998.20	307.65	1005.3	308.05	1020.1	308.55	1038.2
306.35	998.18	303.55	1000.1	306.30	999.59	303.15	1006.7	304.25	1021.6	305.15	1039.6
								300.75	1023.0		
1.537 mol·kg^{-1}		3.011 mol·kg^{-1}		4.502 mol·kg^{-1}		5.017 mol·kg^{-1}		5.500 mol·kg^{-1}		6.230 mol·kg^{-1}	
322.05	1045.4	322.15	1094.3	321.25	1137.6	322.25	1150.6	321.75	1161.9	322.85	1182.1
318.95	1046.6	319.55	1095.6	318.65	1139.1	319.65	1152.2	318.85	1163.4	320.15	1183.7
315.45	1048.1	317.05	1097.1	315.95	1140.7	316.65	1153.7	316.15	1165.1	317.35	1185.3
312.25	1049.5	314.15	1098.6	313.45	1142.1	313.95	1155.9	313.45	1166.5	314.75	1187.0
309.15	1050.9	311.35	1100.1	310.60	1143.4	310.95	1157.5	310.65	1168.8	311.85	1188.5
305.85	1052.3	308.25	1101.5	307.85	1144.7	308.15	1159.2	307.75	1170.4	309.35	1190.8
		305.05	1103.7	304.95	1146.3	305.45	1160.8	304.85	1172.1	306.40	1192.5
						302.45	1162.4	302.05	1173.7	303.45	1194.2
8.353 mol·kg^{-1}		10.308 mol·kg^{-1}		13.402 mol·kg^{-1}		16.611 mol·kg^{-1}		19.435 mol·kg^{-1}		21.818 mol·kg^{-1}	
322.35	1231.1	323.15	1270.9	322.15	1329.3	322.95	1379.0	322.45	1417.8	322.15	1447.6
319.75	1232.8	320.65	1272.6	319.80	1331.1	320.25	1380.5	320.05	1419.8	319.45	1449.6
317.25	1234.5	318.05	1274.4	316.95	1332.8	317.85	1382.1	317.35	1421.7	317.15	1451.6
314.50	1236.1	315.25	1276.0	314.25	1335.4	315.45	1384.1	314.95	1423.7	314.65	1453.4
311.55	1238.5	312.85	1278.5	311.75	1337.3	312.75	1386.0	312.40	1425.5	312.05	1456.2
308.05	1240.2	310.15	1280.3	309.25	1339.2	310.25	1387.9	309.80	1428.3	309.55	1458.3
306.10	1242.0	307.15	1282.1	306.65	1341.0	307.55	1389.6	307.30	1430.3	307.05	1460.4
		304.75	1283.9			304.95	1392.3	304.75	1432.4	304.45	1462.4
Methanolic Lithium Nitrate											
0.0184 mol·kg^{-1}		0.0661 mol·kg^{-1}		0.2540 mol·kg^{-1}		0.5966 mol·kg^{-1}		0.8740 mol·kg^{-1}		1.197 mol·kg^{-1}	
313.50	779.0	310.90	790.8	312.80	795.3	318.45	807.8	319.35	814.7	317.65	830.7
312.70	779.8	310.10	791.6	311.95	796.1	317.55	808.6	318.45	815.5	316.70	831.5
311.85	780.7	309.20	792.6	311.00	797.1	316.65	809.6	317.40	816.5	315.70	832.5
311.05	781.5	308.45	793.4	310.15	797.9	315.80	810.5	316.45	817.3	314.80	833.4
310.15	782.4	307.65	794.3	309.20	798.8	314.90	811.4	315.45	818.2	313.80	834.3
309.25	783.2	306.75	795.1	308.30	799.6	314.00	812.2	314.60	819.0	312.85	835.1
308.35	784.0	305.80	795.9	307.45	800.4	313.15	813.0	313.65	819.9	311.95	836.0
307.55	784.8	305.00	796.7	306.70	801.3	312.25	813.9	312.75	820.8	310.95	836.9
306.70	785.6	304.15	797.5	305.65	802.0	311.30	814.7	311.80	821.5	310.00	837.7
305.80	786.6	303.15	798.5	304.75	803.1	310.25	815.7	310.75	822.6	308.95	838.8
304.90	787.4	302.20	799.4	303.90	803.9	309.30	816.6	309.80	823.5	307.95	839.6
304.00	788.3	301.25	800.3	302.85	804.8	308.35	817.5	308.80	824.4	306.95	840.6
303.10	789.2	300.30	801.2	301.80	805.7	307.35	818.4	307.85	825.3	305.85	841.6
302.20	790.0	299.35	802.0			306.35	819.2	306.85	826.1	304.85	842.4
301.25	790.9	298.35	802.9			305.35	820.2	305.90	827.1	303.75	843.4
300.35	791.7	297.40	803.7			304.35	821.0	304.90	828.0	302.75	844.2
299.45	792.6	296.45	804.7			303.35	822.0	303.95	828.9	301.70	845.2
1.624 mol·kg^{-1}		2.167 mol·kg^{-1}		2.437 mol·kg^{-1}		2.875 mol·kg^{-1}		4.105 mol·kg^{-1}		5.425 mol·kg^{-1}	
319.50	837.0	319.55	870.6	317.55	879.0	319.15	894.0	319.50	932.2	323.30	970.8
318.50	837.8	318.50	871.5	316.45	879.9	318.15	894.9	318.35	933.1	322.05	971.8
317.50	838.9	317.35	872.6	315.35	881.0	317.15	896.0	317.15	934.3	320.80	973.0
316.50	839.7	316.25	873.5	314.25	881.9	316.10	896.9	315.95	935.2	319.55	974.0
315.50	840.7	315.15	874.5	313.15	882.9	315.05	898.0	314.75	936.3	318.25	975.1
314.50	841.5	314.20	875.3	312.05	883.7	313.95	898.8	313.55	937.2	317.05	976.1
313.50	842.4	313.10	876.2	310.95	884.7	312.85	899.8	312.35	938.2	315.65	977.1
312.55	843.3	312.05	877.2	309.85	885.6	311.75	900.7	311.15	939.2	314.40	978.1
311.55	844.1	310.95	878.0	308.75	886.5	310.65	901.6	309.90	940.1	313.15	979.1
310.55	845.1	309.85	879.1	307.65	887.6	309.45	902.8	308.65	941.3	311.80	980.3
309.55	846.0	308.75	880.1	306.50	888.5	308.30	903.7	307.40	942.3	310.50	981.3
308.50	847.0	307.60	881.1	305.35	889.6	307.15	904.8	306.15	943.4	309.20	982.5
307.45	848.0	306.45	882.1	304.20	890.6	306.00	905.8	304.85	944.4	307.95	983.6
306.50	848.8	305.30	882.9	393.05	891.4	304.80	906.6	303.55	945.3	306.55	984.5
305.35	849.8	304.10	883.9	301.90	892.4	303.55	907.7	302.20	946.4	305.10	985.7
304.35	850.7	303.00	884.9			302.35	908.6	300.85	947.4	303.85	986.7
303.25	851.6	301.85	885.9			301.15	909.7			302.55	987.9
6.265 mol·kg^{-1}		7.002 mol·kg^{-1}		7.807 mol·kg^{-1}		8.542 mol·kg^{-1}					
321.70	996.6	322.60	1015.2	322.15	1031.9	322.00	1052.4				
320.60	997.8	321.35	1016.4	320.95	1033.1	320.75	1053.4				
319.20	998.8	320.10	1017.4	319.45	1034.1	319.45	1054.5				
317.95	1000.0	318.80	1018.4	318.10	1035.2	318.00	1055.6				
316.40	1001.0	317.45	1019.5	316.70	1036.3	316.55	1056.6				
315.30	1002.0	316.00	1020.5	315.35	1037.3	315.05	1058.0				
314.00	1003.1	314.60	1021.8	313.95	1038.6	313.65	1059.1				
312.80	1004.0	313.35	1022.9	312.65	1039.7	312.10	1060.3				
311.40	1005.3	311.75	1024.1	310.95	1040.9	310.80	1061.5				
310.15	1006.4	310.35	1025.2	309.75	1042.0	309.40	1062.5				
308.70	1007.6	309.05	1026.2	308.30	1043.1	307.95	1063.4				
307.30	1008.7	307.70	1027.4	306.75	1044.3	306.50	1064.9				
305.90	1009.6	306.30	1028.5	305.45	1045.4	305.05	1066.1				
304.55	1010.8	304.85	1029.7								
303.30	1011.9										
301.85	1013.1										

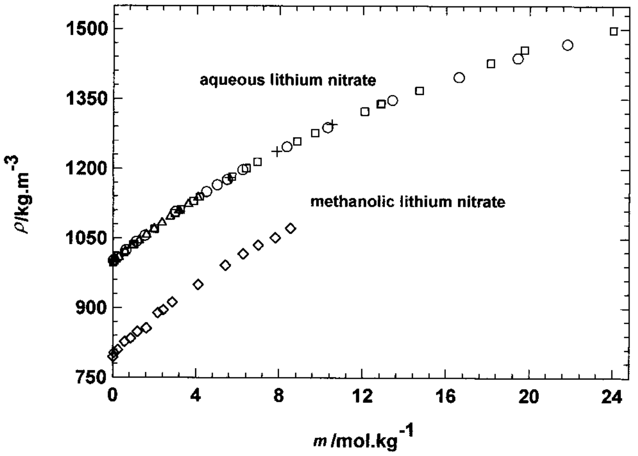

Figure 1. Plots of density (ρ/(kg·m^{-3})) isotherms versus concentration (m/(mol·kg^{-1})) at 298.15 K for aqueous and methanolic lithium nitrate solutions: (○,◇) this work; (Δ), Washburn (1928); (□), Campbell et al. (1955); (+) Wimby and Berntsson (1994).

Table 2. Least-Squares Fitted Values of the Density Equation $\rho = a - b(T - 273.15)$ for Aqueous and Methanolic Lithium Nitrate Solutions

m/(mol·kg^{-1})	a/(kg·m^{-3})	b/(kg·m^{-3}·K^{-1})	std dev in ρ
Aqueous Lithium Nitrate			
0.0181	1012.7 ± 0.4	0.4329 ± 0.0102	0.1
0.0254	1012.8 ± 0.5	0.4129 ± 0.0128	0.2
0.0383	1013.6 ± 0.8	0.4182 ± 0.0183	0.2
0.2402	1017.7 ± 0.9	0.3664 ± 0.0200	0.2
0.6480	1034.7 ± 0.4	0.4220 ± 0.0107	0.2
1.129	1052.8 ± 0.3	0.4132 ± 0.0067	0.1
1.537	1066.3 ± 0.2	0.4295 ± 0.0046	0.1
3.011	1120.7 ± 0.4	0.5404 ± 0.0106	0.1
4.502	1163.1 ± 0.4	0.5272 ± 0.0105	0.1
5.017	1180.2 ± 0.4	0.6035 ± 0.0097	0.2
5.500	1191.5 ± 0.4	0.6116 ± 0.0108	0.2
6.230	1213.4 ± 0.5	0.6336 ± 0.0132	0.2
8.353	1263.6 ± 0.6	0.6601 ± 0.0149	0.2
10.308	1306.5 ± 0.6	0.7132 ± 0.0153	0.2
13.402	1366.8 ± 0.7	0.7664 ± 0.0159	0.2
16.611	1415.2 ± 0.7	0.7346 ± 0.0182	0.3
19.435	1458.5 ± 0.6	0.8283 ± 0.0149	0.2
21.818	1489.2 ± 0.5	0.8543 ± 0.0135	0.2
Methanolic Lithium Nitrate			
0.0184	818.04 ± 0.11	0.9654 ± 0.0033	0.1
0.0661	826.98 ± 0.20	0.9524 ± 0.0066	0.1
0.2540	833.05 ± 0.25	0.9509 ± 0.0072	0.1
0.5966	850.34 ± 0.22	0.9354 ± 0.0057	0.1
0.8740	857.29 ± 0.10	0.9230 ± 0.0027	0.1
1.197	871.23 ± 0.15	0.9094 ± 0.0040	0.1
1.624	878.92 ± 0.12	0.9044 ± 0.0031	0.1
2.167	910.73 ± 0.13	0.8635 ± 0.0035	0.1
2.437	917.14 ± 0.15	0.8583 ± 0.0040	0.1
2.875	934.02 ± 0.22	0.8646 ± 0.0059	0.1
4.105	970.26 ± 0.17	0.8188 ± 0.0046	0.1
5.425	1011.9 ± 0.1	0.8176 ± 0.0033	0.1
6.265	1036.7 ± 0.2	0.8222 ± 0.0043	0.1
7.002	1055.3 ± 0.1	0.8097 ± 0.0036	0.1
7.807	1071.3 ± 0.2	0.8037 ± 0.0044	0.1
8.542	1091.9 ± 0.2	0.8089 ± 0.0037	0.1

Results and Discussion

The measured densities (ρ) of aqueous and methanolic lithium nitrate solutions are presented in Table 1 and are found to be a linear function of temperature (Table 2). For aqueous lithium nitrate solutions, densities are comparable within ±0.4% (Figure 1) with the reported values (Washburn, 1928; Campbell et al., 1955; Wimby and Berntsson, 1994). We could not compare the density data for methanolic lithium nitrate due to a lack of reported values.

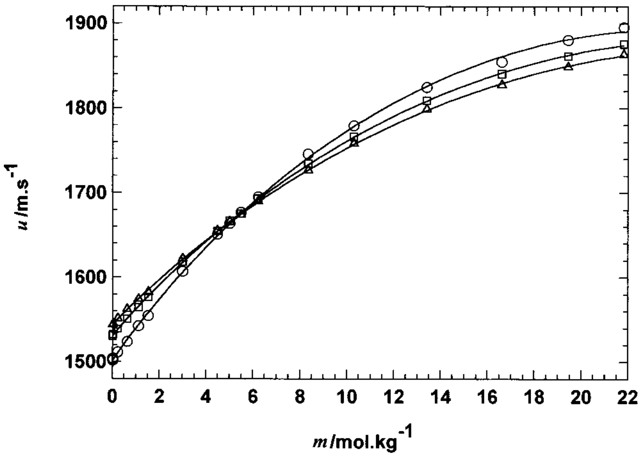

Figure 2. Variation of speed of sound (u/(m·s^{-1})) with concentration (m/(mol·kg^{-1})) at 298.15 K (○), 313.15 K (□), and 323.15 K (Δ) for aqueous lithium nitrate solutions. Symbols and solid curves are observed and calculated (from eq 2) values, respectively.

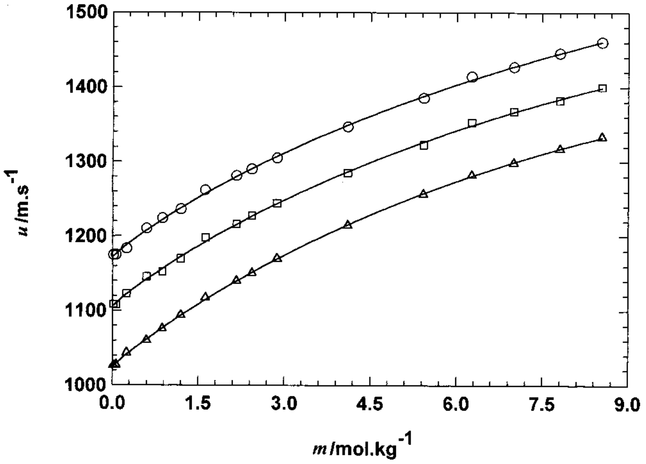

Figure 3. Variation of speed of sound (u/(m·s^{-1})) with concentration (m/(mol·kg^{-1})) at 273.15 K (○), 298.15 K (□), and 323.15 K (Δ) for methanolic lithium nitrate solutions. Symbols and solid curves are observed and calculated (from eq 2) values, respectively.

Values of the speed of sound (u) in aqueous and methanolic lithium nitrate solutions as functions of temperature and concentration are presented in Table 3, and the u versus m isotherms are illustrated in Figures 2 and 3, respectively. The isentropic compressibilities (κ_s) of the systems were calculated from

$$\kappa_s = 1/(u^2\rho) \qquad (1)$$

where u is the speed of sound, ρ is the density of the solutions, and the κ_s vs m isotherms for aqueous and methanolic lithium nitrate solution are illustrated in Figures 4 and 5, respectively.

In our earlier paper (Rohman et al., 1999) the following equation

$$Y = A + Bm + Cm^n \qquad (2)$$

was used to fit the concentration dependence of the speed of sound and isentropic compressibility of electrolyte solutions at a particular temperature. In eq 2, Y refers either to the speed of sound or the isentropic compressibility, A, B, and C are the temperature-dependent parameters, n is the adjustable parameter, and m is the concentration. Equation 2 is similar to the equation used by Millero et al.

Table 3. Speeds of Sound as Functions of Concentration and Temperature in Aqueous and Methanolic Lithium Nitrate Solutions

T/K	u/(m·s^{-1})	T/K	u/(m·s^{-1})	T/K	u/(m·s^{-1})	T/K	u/(m·s^{-1})	T/K	u/(m·s^{-1})	T/K	u/(m·s^{-1})
Aqueous Lithium Nitrate											
0.0181 mol·kg^{-1}		0.0254 mol·kg^{-1}		0.0383 mol·kg^{-1}		0.2402 mol·kg^{-1}		0.6480 mol·kg^{-1}		1.129 mol·kg^{-1}	
298.15	1503.4	298.15	1501.6	298.15	1504.0	298.15	1511.4	298.15	1523.5	298.15	1542.1
303.15	1513.4	303.15	1513.2	303.15	1514.7	303.15	1521.6	303.15	1534.5	303.15	1550.7
308.05	1521.5	307.95	1522.5	308.15	1524.1	307.95	1529.9	307.85	1542.5	307.95	1558.1
313.15	1530.4	313.15	1532.0	313.15	1532.3	313.15	1538.6	313.15	1550.3	313.15	1564.3
317.85	1537.1	317.85	1538.1	317.85	1538.9	317.85	1544.9	317.85	1558.7	317.85	1569.5
323.15	1543.7	323.15	1544.6	323.15	1545.0	323.15	1551.2	323.15	1561.9	323.15	1574.0
1.537 mol·kg^{-1}		3.011 mol·kg^{-1}		4.502 mol·kg^{-1}		5.017 mol·kg^{-1}		5.500 mol·kg^{-1}		6.230 mol·kg^{-1}	
298.15	1554.2	298.15	1606.9	298.15	1650.5	298.15	1663.4	298.15	1676.8	298.15	1694.9
303.15	1563.2	303.15	1611.5	303.15	1652.2	303.15	1665.0	303.15	1676.7	303.15	1694.5
307.85	1570.3	307.95	1615.3	307.95	1653.4	307.85	1666.0	307.85	1676.6	307.95	1694.0
313.15	1576.2	313.15	1618.2	313.15	1654.4	313.15	1666.4	313.15	1675.2	313.15	1692.7
317.85	1579.7	317.85	1620.6	317.85	1654.6	317.85	1666.4	317.85	1675.2	317.85	1691.4
323.15	1582.4	323.15	1621.8	323.15	1654.7	323.15	1665.6	323.15	1673.6	323.15	1689.6
8.353 mol·kg^{-1}		10.308 mol·kg^{-1}		13.402 mol·kg^{-1}		16.611 mol·kg^{-1}		19.435 mol·kg^{-1}		21.818 mol·kg^{-1}	
298.15	1745.6	298.15	1779.0	298.15	1824.5	298.15	1854.3	298.15	1880.1	298.15	1895.2
303.15	1742.1	303.15	1774.5	303.15	1819.5	303.15	1850.4	303.15	1873.8	303.15	1888.6
307.95	1737.9	307.85	1770.5	307.95	1813.9	307.85	1846.3	307.85	1867.4	307.85	1882.0
313.15	1734.0	313.15	1766.0	313.15	1809.0	313.15	1840.3	313.15	1861.2	313.15	1875.6
317.85	1730.8	317.85	1762.9	317.85	1804.3	317.85	1835.5	317.85	1855.2	317.85	1870.0
323.15	1726.4	323.15	1758.1	323.15	1798.7	323.15	1827.3	323.15	1848.7	323.15	1863.3
Methanolic Lithium Nitrate											
0.0184 mol·kg^{-1}		0.0661 mol·kg^{-1}		0.2540 mol·kg^{-1}		0.5966 mol·kg^{-1}		0.8740 mol·kg^{-1}		1.197 mol·kg^{-1}	
273.15	1174.9	273.15	1175.2	273.15	1183.4	273.15	1210.5	273.15	1224.3	273.15	1236.4
278.15	1164.7	278.15	1163.8	278.15	1177.4	278.15	1197.2	278.15	1209.4	278.15	1225.8
283.15	1149.3	283.15	1151.5	283.15	1161.5	283.15	1193.7	283.15	1194.7	283.15	1214.6
288.15	1138.1	288.15	1137.1	288.15	1151.9	288.15	1171.2	288.15	1182.6	288.15	1199.9
293.15	1120.6	293.15	1122.6	293.15	1135.1	293.15	1157.4	293.15	1165.8	293.15	1188.2
298.15	1108.5	298.15	1108.2	298.15	1122.6	298.15	1145.5	298.15	1152.3	298.15	1169.7
303.15	1091.8	303.15	1093.9	303.15	1106.0	303.15	1125.3	303.15	1136.8	303.15	1153.7
308.15	1076.0	308.15	1077.5	308.15	1090.5	308.15	1109.0	308.15	1121.8	308.15	1140.2
313.15	1058.2	313.15	1060.7	313.15	1072.6	313.15	1090.0	313.15	1106.8	313.15	1123.1
318.15	1042.8	318.15	1044.4	318.15	1057.8	318.15	1074.8	318.15	1091.5	318.15	1108.2
323.15	1026.4	323.15	1027.1	323.15	1043.3	323.15	1060.1	323.15	1076.1	323.15	1093.6
1.624 mol·kg^{-1}		2.167 mol·kg^{-1}		2.437 mol·kg^{-1}		2.875 mol·kg^{-1}		4.105 mol·kg^{-1}		5.425 mol·kg^{-1}	
273.15	1262.0	273.15	1281.4	273.15	1290.0	273.15	1305.1	273.15	1347.0	273.15	1385.5
278.15	1250.0	278.15	1264.7	278.15	1276.4	278.15	1295.6	278.15	1336.3	278.15	1372.2
283.15	1236.3	283.15	1255.2	283.15	1263.2	283.15	1281.2	283.15	1324.1	283.15	1362.3
288.15	1224.2	288.15	1243.3	288.15	1252.5	288.15	1269.2	288.15	1311.9	288.15	1349.3
293.15	1208.3	293.15	1229.4	293.15	1240.8	293.15	1255.6	293.15	1298.0	293.15	1337.6
298.15	1198.2	298.15	1216.3	298.15	1227.3	298.15	1244.3	298.15	1285.1	298.15	1322.7
303.15	1177.0	303.15	1198.8	303.15	1209.8	303.15	1226.3	303.15	1271.0	303.15	1310.3
308.15	1164.1	308.15	1185.3	308.15	1195.9	308.15	1213.4	308.15	1257.3	308.15	1297.1
313.15	1146.9	313.15	1169.3	313.15	1179.2	313.15	1197.4	313.15	1242.7	313.15	1283.2
318.15	1132.5	318.15	1154.7	318.15	1165.2	318.15	1183.9	318.15	1228.6	318.15	1269.9
323.15	1117.7	323.15	1140.1	323.15	1150.8	323.15	1169.9	323.15	1214.6	323.15	1256.6
6.265 mol·kg^{-1}		7.002 mol·kg^{-1}		7.807 mol·kg^{-1}		8.542 mol·kg^{-1}					
273.15	1414.4	273.15	1427.2	273.15	1445.5	273.15	1460.4				
278.15	1401.1	278.15	1416.5	278.15	1432.7	278.15	1451.0				
283.15	1390.2	283.15	1401.9	283.15	1420.7	283.15	1436.8				
288.15	1376.2	288.15	1392.1	288.15	1407.4	288.15	1423.9				
293.15	1367.4	293.15	1381.6	293.15	1396.7	293.15	1411.5				
298.15	1352.9	298.15	1367.8	298.15	1382.1	298.15	1400.1				
303.15	1337.2	303.15	1353.9	303.15	1369.8	303.15	1386.3				
308.15	1333.4	308.15	1340.4	308.15	1356.8	308.15	1373.2				
313.15	1307.8	313.15	1326.1	313.15	1343.6	313.15	1358.7				
318.15	1295.1	318.15	1312.4	318.15	1330.3	318.15	1346.6				
323.15	1282.4	323.15	1298.6	323.15	1317.2	323.15	1333.5				

(1982, 1987) but with less adjustable parameters. The computed values of A, B, C, and n parameters for speed of sound and isentropic compressibility are presented in Tables 4 and 5, respectively. From Figures 2–5 and Tables 4 and 5 it is apparent that eq 2 fits the concentration dependence of the speed of sound and isentropic compressibility isotherms within ±0.4% and ±1.2% accuracy, respectively.

The u vs m isotherms for aqueous lithium nitrate (Figure 2) converge at a particular concentration (5.3 mol·kg^{-1}) and then diverge in a reverse way. It may be presumed that at 5.3 mol·kg^{-1} there is some kind of structural transition as found in other aqueous systems (Rohman and Mahiuddin, 1997; Rohman et al., 1999). Millero et al., (1985) reported a transition in $\Delta u/m$ vs $m^{1/2}$ isotherms; $\Delta u = u - u_0$, and u_0 is the speed of sound of water and related to the primary hydration structure around the ions. In our system we fail to observe any such transition or inflection in $\Delta u/m$ vs $m^{1/2}$ isotherms. From Figure 2 it is apparent that the concentration at which u vs m isotherms converge is independent

Table 4. Least-Squares Fitted Values of the Parameters of Equation 2 for the Speed of Sound in Aqueous and Methanolic Lithium Nitrate Solutions

T/K	A/(m·s^{-1})	B/(m·s^{-1}·kg·mol^{-1})	C/(m·s^{-1}·kg^{n}·mol^{-n})	n	std dev in u
			Aqueous Lithium Nitrate		
298.15	1501.0 ± 1.2	41.36 ± 0.46	−3.168 ± 0.065	1.65 ± 0.12	2.7
313.15	1530.2 ± 0.4	33.92 ± 0.16	−2.374 ± 0.022	1.66 ± 0.09	1.0
323.15	1543.3 ± 0.5	29.62 ± 0.19	−1.736 ± 0.023	1.70 ± 0.06	1.1
			Methanolic Lithium Nitrate		
273.15	1171.6 ± 1.5	85.15 ± 2.56	−28.15 ± 1.41	1.28 ± 0.16	2.6
298.15	1105.6 ± 1.7	78.38 ± 2.38	−20.77 ± 1.12	1.35 ± 0.17	2.9
323.15	1024.4 ± 0.9	72.12 ± 1.07	−12.88 ± 0.39	1.48 ± 0.10	1.7

Table 5. Least-Squares Fitted Values of the Parameters of Equation 2 for Isentropic Compressibility of Aqueous and Methanolic Lithium Nitrate Solutions

T/K	$A \times 10^{10}$/Pa^{-1}	$B \times 10^{10}$/(Pa^{-1}·kg·mol^{-1})	$C \times 10^{10}$/(Pa^{-1}·kg^{n}·mol^{-n})	n	std dev in $\kappa_s \times 10^{10}$
			Aqueous Lithium Nitrate		
298.15	4.452 ± 0.012	−1.119 ± 0.020	0.7149 ± 0.0144	1.11 ± 0.06	0.02
313.15	4.307 ± 0.008	−0.8408 ± 0.0111	0.4916 ± 0.0075	1.13 ± 0.06	0.02
323.15	4.250 ± 0.006	−0.6941 ± 0.0086	0.3725 ± 0.0054	1.15 ± 0.04	0.01
			Methanolic Lithium Nitrate		
273.15	8.911 ± 0.019	−5.619 ± 0.117	4.372 ± 0.100	1.07 ± 0.05	0.03
298.15	10.30 ± 0.03	−5.617 ± 0.121	4.098 ± 0.099	1.09 ± 0.10	0.04
323.15	12.38 ± 0.02	−6.834 ± 0.090	4.854 ± 0.073	1.09 ± 0.05	0.03

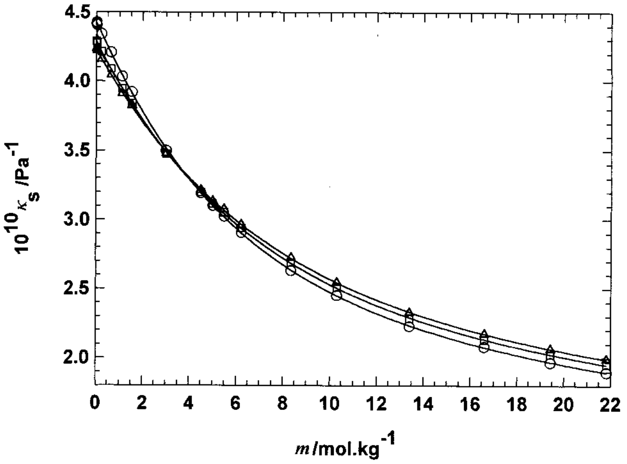

Figure 4. Variation of isentropic compressibility (κ_s/Pa^{-1}) with concentration (m/(mol·kg^{-1})) at 298.15 K (○), 313.15 K (□), and 323.15 K (Δ) for aqueous lithium nitrate solutions. Symbols and solid curves are observed and calculated (from eq 2) values, respectively.

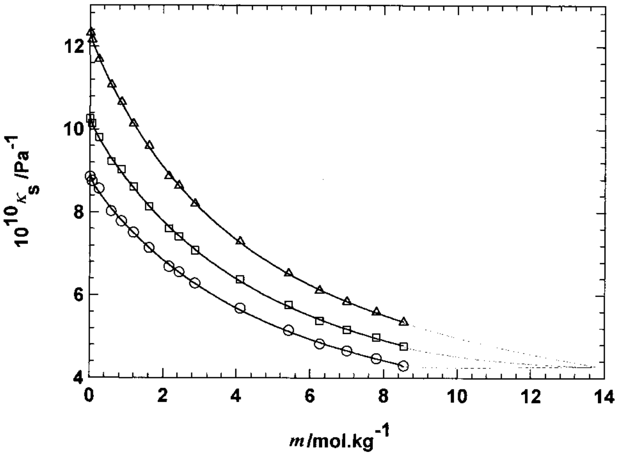

Figure 5. Variation of isentropic compressibility (κ_s/Pa^{-1}) with concentration (m/(mol·kg^{-1})) at 273.15 K (○), 298.15 K (□), and 323.15 K (Δ) for methanolic lithium nitrate solutions. Symbols and solid curves are observed and calculated (from eq 2) values, respectively.

of temperature which, in turn, suggests that the solvation shell around the ions formed a rigid structure. To correlate the concentration with the solvation phenomena, it is worthwhile to consider the isentropic compressibility of the systems. For methanolic lithium nitrate systems u vs m isotherms do not converge and vary smoothly (Figure 3). It may be presumed that the solvation phenomena of lithium nitrate in water and methanol may be of different origin.

The κ_s vs m isotherms (Figure 4) for aqueous lithium nitrate systems converge at 3.75 mol·kg^{-1}. As the concentration of the system increases, the number of water molecules around the ions decreases and a situation is reached where all the water molecules are involved in the solvation forming a rigid structure. Such a situation arises only when the primary solvation shell of the solute is completed with a critical isentropic compressibility value and independent of temperature. The isentropic compressibility, κ_s, at 3.75 mol·kg^{-1} becomes $K_{s,h}$, ($K_{s,h}$ is the isentropic compressibility of the primary hydration shell of the solute at 3.75 mol·kg^{-1}) with a value of 3.341×10^{-10} Pa^{-1} (Figure 4), which is ~1.2 times higher than the aqueous sodium chloride (Onori, 1988) and sodium nitrate and sodium thiosulfate (Rohman and Mahiuddin, 1997), comparable with sodium thiocyanate ($K_{s,h} = 3.35 \times 10^{-10}$ Pa^{-1}) (Rohman et al., 1999) solutions, and smaller in comparison to free water ($\kappa_s = 4.477 \times 10^{-10}$ Pa^{-1}). Even though the $K_{s,h}$ value suggests the existence of strong interactions in aqueous lithium nitrate solution but smaller in magnitude in comparison to aqueous sodium nitrate and sodium thiosulfate solutions (Rohman and Mahiuddin, 1997).

The κ_s vs m isotherms for methanolic lithium nitrate system (Figure 5) decrease smoothly with concentration without converging. From Figures 4 and 5 it is apparent that the methanolic lithium nitrate system is more compressible in comparison to the aqueous systems at a particular concentration and temperature. The κ_s of methanolic lithium nitrate solution at 3.75 mol·kg^{-1} (the concentration at which κ_s for the aqueous lithium nitrate system converges, Figure 4) are found to be (5.8−7.6) × 10^{-10} Pa^{-1} (Figure 5); even at the highest experimental concentration it is (4.3−5.4) × 10^{-10} Pa^{-1} and temperature dependent. Methanol forms a chain or ring structure in the medium through −OH group but not a three-dimensional structure like that of water, and the planar NO_3^- ions would fit less well into the methanol structure. On the other hand, the globular methyl group hinders methanol from efficiently solvating Li^+ and NO_3^- ions (Zhao and Freeman, 1995). Both these effects govern the smooth variation of κ_s vs m isotherms (Figure 5) with higher compressibility in methanolic lithium nitrate systems.

The isentropic compressibility of aqueous electrolyte solution is due to about 64% configurational and 36% vibrational compressibility (Davis and Litovitz, 1965; Slie et al., 1966). In dilute solution the isentropic compressibility is predominantly governed by the configurational part, whereas in the concentrated solution it is due to the vibrational parts. At 3.75 mol·kg^{-1}, for aqueous lithium nitrate solution (Figure 4) the water structure has totally collapsed since all the water molecules take part in the solvation. As a result the isentropic compressibility isotherms converge (Figure 4) at this concentration. Beyond 3.75 mol·kg^{-1}, vibrational compressibility dominates over configurational, which increases with an increase in temperature at a particular concentration due to thermal motion. Owing to this fact reversibility of the isentropic compressibility isotherms beyond 3.75 mol·kg^{-1} for aqueous lithium nitrate solution occurs (Figure 4). In methanolic lithium nitrate solution the isentropic compressibility increases with the increase in temperature at a particular concentration; therefore, it is the vibrational compressibility which contributes to the isentropic compressibility within the concentration and temperature range of the study.

Onori (1988) derived the following relation between conventional apparent molal isentropic compressibility, $K_{s,\phi}$ (Blandamer, 1998; Buwalda et al., 1998), and the product of the isentropic compressibility, $K_{s,1}$ and molar volume, V_1, of the solvent to estimate the hydration number, n_h,

$$K_{s,\phi} = K_{s,h}V_h - n_h K_{s,1} V_1 \tag{3}$$

In eq 3, $K_{s,h}$ and V_h are the isentropic compressibility of the hydrated sphere and the volume of 1 mol of hydrated solute, respectively. The calculated primary hydration number, n_h, of lithium nitrate in aqueous medium using eq 3 was found to be 17.9 at 3.75 mol·kg^{-1}, which is ~21% higher than the available water, 14.8 at the same concentration. The isentropic compressibility isotherms of aqueous lithium nitrate solutions converge at 3.75 mol·kg^{-1} with $K_{s,h} = 3.341 \times 10^{-10}$ Pa^{-1}, and it is suggested that all the available water molecules are in the primary hydration shell.

The apparent molal volume, V_ϕ, of the solution as proposed by Onori (1988) is given by

$$V_\phi = -n_h V_1 + V_h \tag{4}$$

Inserting the value of V_h (eq 4) into eq 3 and rearranging we obtain an expression for the hydration/solvation number

$$n_h = [K_{s,\phi} - K_{s,h}V_\phi]/[V_1(K_{s,h} - K_{s,1})] \tag{5}$$

Equation 5 has a concentration limitation in its application to estimate the hydration number (Onori, 1988). The primary hydration number at 3.75 mol·kg^{-1} (Figure 6) using eq 5 was found to be 15, and the estimated primary hydration number was found to be in good agreement with the available water molecules per mole of solute at that concentration.

The hydration structure of Li^+ ion in aqueous medium has been investigated using X-ray and neutron diffraction, simulation, and Raman spectroscopy techniques (Okada et al., 1983; Tamura et al., 1988; Yamanaka et al., 1993; Kameda and Uemura, 1993; Yamagami et al., 1994; Kameda et al., 1994; Yamaguchi et al., 1995; Pye et al., 1996) and the hydration number of Li^+ ion distributed over the range of 3−9. On the other hand, Pye et al. (1996) theoretically calculated that there are four molecules of water around the Li^+ ion in the first hydration shell. The frequently appearing coordination number of Li^+ ion has been reported (Ohtaki and Radnai, 1993) as 4−5 in the system with the water to salt ratio of 4, but for the system with water/salt > 4 it is 6. In the present system where the κ_s isotherm converges (at 3.75 mol·kg^{-1}, Figure 4), water to salt ratio is 14.8. Considering the primary hydration number of solute can be split into the constituent ions (Endo and Nomoto, 1981) and the primary hydration number of Li^+ ion is 6 as a reference (Ohtaki and Radnai, 1993), the primary hydration number of NO_3^- ion is calculated to be 9. The estimated primary hydration number of NO_3^- ion is in good agreement with the reported value (Ohtaki and Radnai, 1993).

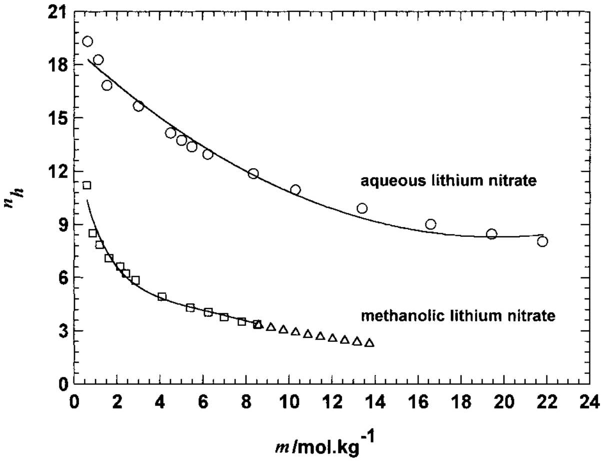

Figure 6. Variation of hydration/solvation number, n_h, with concentration (m/(mol·kg^{-1})) for aqueous (○) and methanolic (□, Δ) lithium nitrate solutions at 298.15 K. Circles and squares are obsereved, solid curves are calculated (from polynomial equation up to second degree), and triangles are extrapolated values, respectively.

In methanolic lithium nitrate solution the isentropic compressibility isotherms (Figure 5) vary smoothly within the concentration and temperature ranges of the study. On extrapolation the isentropic compressibility isotherms converge beyond the experimental concentration range at 13.75 mol·kg^{-1} with $K_{s,h} = 4.327 \times 10^{-10}$ Pa^{-1} (Figure 5). The calculated solvation numbers, n_h, at 298.15 K using eq 5 are presented in Figure 6. Accordingly there are 2.3 molecules of methanol in the primary solvation shell of lithium nitrate, which is much smaller than in aqueous medium. A reliable primary solvation number of either Li^+ ion or NO_3- ion in methanol is lacking in the literature, and we could not make a comparison.

From the above discussions it is apparent that at a particular concentration the primary solvation number becomes equal to the number of available solvent molecules per mole of solute. This situation is reached in electrolyte solution only when the isentropic compressibility isotherms converge at a particular concentration because of the fact that the primary solvation shell of the solute is completed and the solvent molecules are rigidly bound in the primary solvation shell due to the strong ion−solvent interaction. As a result the primary solvation shell attains some critical isentropic compressibility value and is independent of temperature.

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