Isentropic Compressibility of Aqueous and Methanolic Sodium Thiocyanate Solutions

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The speed of sound in aqueous and methanolic sodium thiocyanate solutions was measured as a function of temperature (~293.15 ≤ T/K ≤ 323.15) and concentration (~0.0146 ≤ m/(mol kg^{-1}) ≤ 17.328). The isentropic compressibility isotherms for aqueous sodium thiocyanate systems converge at a particular concentration characteristic of the primary hydration shell of the solute. For the methanolic sodium thiocyanate system isentropic compressibility isotherms vary smoothly with concentration. The primary solvation number of the thiocyanate ion has been estimated to be 12.8 in aqueous medium. The total primary solvation number of sodium thiocyanate in methanol medium was found to be 3.7.

Introduction

Electrolyte solutions either in aqueous or nonaqueous solvent have been of immense importance to the technologist and theoretician due to the different interactions and equilibria that exist in different concentration regions. The existence of ions, solvated ions, ion pairs, and free solvent depends on the concentration. The structures of the solvent around ions and/or solvation phenomenon have been studied, employing various techniques (Ohtaki and Radnai, 1993). Recent reports indicate that efforts have been made to study the solvation phenomena in aqueous (Ohtaki and Radnai, 1993; Kameda et al., 1994; Rudolph et al., 1995) and nonaqueous (Kameda et al., 1995; Schultz et al., 1996) electrolyte solutions in the dilute or in the intermediate concentration region, i.e., before and after the primary solvation region. Should that be the case, the solvation number obtained may not be the true primary solvation number but the number of solvent molecules around the ions, as reported by Kameda et al. (1994).

Depending on the techniques employed, the number of coordinated solvent molecules and the primary solvation number of SCN^- in aqueous sodium thiocyanate (Kameda et al., 1994) and methanolic tetrabutylammonium thiocyanate (Schultz et al., 1996) solutions have been reported as 2. On the other hand, experimental (Kahlow et al., 1989) and theoretical (Phelps et al., 1993; Roy and Bagchi, 1994) studies showed that methanol is strikingly different in its solvation dynamics from water.

Hinton and Amis (1971) and Ohtaki and Radnai (1993) reviewed the different approaches for studying the solvent structure around ions vis-à-vis wide differences in solvation number for the same cation and anion. Among the many approaches the acoustic method (Bockris and Saluja, 1972; Endo and Nomoto, 1981) seems to be an alternative proposition for studying the solvent structure around the ions. Recently, we reported that the speed of sound and isentropic compressibility isotherms in aqueous sodium nitrate and sodium thiosulfate solutions converge at a particular concentration which has been correlated with the primary hydration shell of the solute (Rohman and Mahiuddin, 1997). Beyond the concentration at which the isentropic compressibility converges, cospheres of the cation and anion start to overlap, leading to the liquid−liquid phase separation or ion-pair formation depending on the electrolyte and the solvent. In this paper we report the speed of sound and the isentropic compressibility of aqueous and methanolic sodium thiocyanate solutions as functions of concentration and temperature.

Experimental Section

Sodium thiocyanate (SD, AR grade) was recrystallized twice from conductivity water and was dried over P_2O_5. Methanol (E. Merck, LR grade) was treated with quick lime and was distilled after refluxing for about 4 h. Finally, anhydrous methanol was prepared by using a dry magnesium turning and iodine mixture as described elsewhere (Vogel, 1975). Only the middle fraction was used in our study. Triply distilled water was used to prepare aqueous solutions. All solutions were prepared by weight.

Speeds of sound (u) in sodium thiocyanate solutions were measured with an accuracy of ±0.1 m s^{-1} by using a variable path interferometer (multifrequency ultrasonic interferometer, M-83, Mittal Enterprises, New Delhi, India) at 2 MHz. The solution inside the cell was thermostated by circulating liquid from the thermostat. The sound wavelength, λ, in the solution was determined by measuring the positions of a series of standing waves over a distance of 40 wavelengths, and the speed of sound was calculated from $u = 2df/n$, where n is the number of waves, d is the distance traveled by the movable sound reflector, and f is the frequency of the sound.

Densities (ρ) of all solutions were measured accurately to ±0.01% by using a single stem, graduated and calibrated pycnometer (~9 cm^3) provided with a well-fitted glass stopper to prevent evaporation. The pycnometer was calibrated using triply distilled water.

All the measurements were made as functions of concentration (0.1400 ≤ m/(mol kg^{-1}) ≤ 17.328 and 0.0146 ≤ m/(mol kg^{-1}) ≤ 5.023 for aqueous and methanolic sodium

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Table 1. Density Values of Aqueous and Methanolic Sodium Thiocyanate 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 Sodium Thiocyanate											
0.1400 mol kg^{-1}		0.6628 mol kg^{-1}		0.9811 mol kg^{-1}		1.430 mol kg^{-1}		2.137 mol kg^{-1}		2.954 mol kg^{-1}	
322.15	992.69	322.25	1012.6	323.25	1023.1	323.90	1036.8	324.55	1059.0	323.70	1082.9
319.35	993.65	319.75	1013.6	321.15	1024.2	321.75	1037.8	322.55	1060.3	322.00	1084.1
316.40	994.92	317.15	1014.9	319.05	1025.3	319.55	1039.1	320.55	1061.4	320.25	1085.1
313.70	995.96	314.65	1016.0	316.95	1026.2	317.40	1040.2	318.45	1062.6	318.45	1086.5
310.80	997.11	312.05	1017.1	314.65	1027.6	315.25	1041.4	316.45	1063.6	316.60	1087.6
307.90	998.23	309.45	1018.3	312.35	1028.6	313.05	1042.6	314.35	1064.7	314.65	1088.9
304.95	999.20	306.95	1019.3	310.05	1029.8	310.85	1043.6	312.35	1065.9	312.75	1090.1
301.80	1000.3	304.15	1020.4	307.35	1031.0	308.65	1044.8	310.25	1066.9	310.85	1091.2
298.65	1001.4	301.15	1021.5	304.85	1032.0	306.35	1045.9	308.15	1068.3	308.90	1092.4
		298.15	1022.7	302.75	1033.2	304.05	1047.1	306.05	1069.4	306.90	1093.6
				300.45	1034.3			303.85	1070.6	304.90	1094.9
				297.70	1035.5			301.65	1071.8		
								299.55	1072.9		
								297.35	1074.1		
								295.15	1075.2		
4.062 mol kg^{-1}		4.860 mol kg^{-1}		5.921 mol kg^{-1}		7.054 mol kg^{-1}		7.849 mol kg^{-1}		8.547 mol kg^{-1}	
318.60	1118.6	324.60	1134.0	324.85	1157.4	324.65	1186.9	323.65	1197.6	323.40	1211.4
316.90	1119.7	322.90	1135.4	323.25	1158.6	323.10	1188.1	322.15	1198.8	321.65	1212.7
315.10	1121.1	321.25	1136.5	321.65	1159.9	321.45	1189.5	320.50	1200.3	320.05	1213.8
313.25	1122.2	319.50	1137.8	320.05	1161.0	319.70	1190.7	318.85	1201.5	318.25	1215.4
311.40	1123.5	317.85	1138.9	318.25	1162.2	318.00	1192.1	317.15	1202.9	316.60	1216.7
309.75	1124.6	314.35	1141.3	316.55	1163.5	316.40	1193.2	315.50	1204.1	314.80	1218.1
307.90	1125.8	312.65	1142.4	314.85	1164.6	314.75	1194.5	313.75	1205.3	313.05	1219.4
306.10	1127.0	310.85	1143.9	313.15	1166.1	312.95	1195.8	312.10	1206.6	311.30	1220.6
304.20	1128.1	309.10	1145.1	311.50	1167.3	311.35	1196.9	310.45	1207.8	309.50	1222.0
302.35	1129.5	307.20	1146.4	309.70	1168.6	309.55	1198.4	308.65	1209.3	307.70	1223.3
300.45	1130.7	305.45	1147.7	308.05	1169.9	307.85	1199.7	306.90	1210.6	305.90	1224.7
298.55	1132.0	303.65	1148.8	306.45	1171.1	305.95	1201.1	305.15	1212.0		
296.55	1133.3	301.70	1150.1	304.35	1172.4	304.20	1202.4	303.40	1213.3		
294.65	1134.4	299.80	1151.3	302.50	1173.7	302.55	1203.6	301.60	1214.5		
		297.95	1152.7	300.65	1175.0	300.70	1205.0	299.75	1215.9		
						299.00	1206.3	298.00	1217.2		
						297.15	1207.7	296.10	1218.6		
9.994 mol kg^{-1}		11.229 mol kg^{-1}		12.468 mol kg^{-1}		14.872 mol kg^{-1}		17.328 mol kg^{-1}			
323.45	1235.0	324.65	1254.1	323.85	1272.1	323.50	1301.0	319.35	1325.1		
321.75	1236.4	322.85	1255.3	322.15	1273.4	321.65	1302.3	317.55	1326.4		
320.05	1237.6	321.30	1256.8	320.50	1274.8	319.95	1303.8	315.70	1328.0		
318.25	1238.9	319.65	1258.0	318.85	1276.0	318.15	1305.1	313.95	1329.4		
316.45	1240.2	318.05	1259.3	316.95	1277.7	316.40	1306.4	312.05	1330.9		
314.75	1241.4	316.30	1260.6	315.30	1279.0	314.60	1307.8	310.25	1332.2		
313.05	1243.0	314.50	1261.8	313.55	1280.5	312.90	1309.1	308.60	1333.6		
		312.75	1263.5	311.65	1281.9	311.05	1310.8	306.75	1335.0		
311.40	1244.3	310.90	1264.8	309.95	1283.2	309.25	1312.1	304.85	1336.3		
309.50	1245.8	309.25	1266.3	308.05	1284.6	307.30	1313.6	302.95	1338.0		
307.85	1247.2	307.35	1267.7	306.30	1286.0	305.45	1315.1	301.20	1339.4		
306.00	1248.4	305.50	1268.9	304.55	1287.5	303.65	1316.4	299.15	1340.9		
304.25	1249.8	303.65	1270.4			301.85	1317.9	297.15	1342.5		
302.50	1251.1	301.85	1271.7			300.05	1319.3	295.35	1343.8		
300.60	1252.6	300.05	1273.2			298.15	1320.8	293.45	1345.3		
Methanolic Sodium Thiocyanate											
0.0146 mol kg^{-1}		0.1257 mol kg^{-1}		0.3876 mol kg^{-1}		0.6192 mol kg^{-1}		0.8693 mol kg^{-1}		1.102 mol kg^{-1}	
312.05	777.7	308.65	784.9	310.35	795.5	309.15	807.5	312.90	814.9	310.15	827.3
311.20	778.5	307.75	785.7	309.55	796.3	308.15	808.3	311.95	815.7	309.25	828.2
310.35	779.4	306.85	786.7	308.70	797.3	307.35	809.3	311.00	816.7	308.30	829.2
309.50	780.2	305.95	787.5	307.80	798.1	306.40	810.1	310.05	817.5	307.35	830.0
308.60	781.1	305.05	788.4	306.90	799.0	305.45	811.0	309.10	818.5	306.35	831.0
307.70	781.9	304.15	789.1	306.05	799.8	304.55	811.8	308.15	819.2	305.40	831.8
306.90	782.7	303.30	790.0	305.20	800.6	303.60	812.6	307.20	820.1	304.45	832.6
306.00	783.5	302.45	790.8	304.30	801.5	302.65	813.5	306.25	821.0	303.55	833.5
305.20	784.3	301.55	791.6	303.40	802.3	301.75	814.3	305.30	821.8	302.60	834.3
304.35	785.3	300.65	792.6	302.45	803.3	300.80	815.3	304.35	822.8	301.65	835.4
303.55	786.1	299.75	793.4	301.55	804.1	299.85	816.2	303.40	823.7	300.70	836.3
302.65	787.0	298.85	794.3	300.65	805.1	298.90	817.1	302.45	824.6	299.70	837.2
301.75	787.9	297.95	795.2	299.70	806.0	297.95	818.0	301.50	825.6	298.70	838.2
300.85	788.7	297.05	796.0	298.75	806.7	297.05	818.8	300.55	826.4	297.75	839.0
299.95	789.6	296.15	796.9	297.80	807.7			299.60	827.3		
299.05	790.4			296.90	808.5			298.65	828.2		
298.15	791.3							297.70	829.1		

Table 1. (Continued)

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})
Methanolic Sodium Thiocyanate											
1.443 mol kg^{-1}		1.978 mol kg^{-1}		2.636 mol kg^{-1}		3.119 mol kg^{-1}		3.889 mol kg^{-1}		4.220 mol kg^{-1}	
312.35	840.1	317.30	856.3	316.20	881.5	317.25	897.6	315.80	925.0	313.20	936.2
311.35	841.0	316.35	857.2	315.25	882.4	316.15	898.5	314.65	926.0	312.05	937.2
310.40	842.0	315.35	858.3	314.25	883.5	315.10	899.6	313.55	927.1	311.00	938.3
309.45	842.9	314.35	859.1	313.25	884.4	314.00	900.5	312.45	928.0	309.90	939.3
308.50	843.8	313.30	860.1	312.25	885.4	312.95	901.5	311.40	929.1	308.80	940.3
307.55	844.6	312.30	860.9	311.25	886.3	311.85	902.4	310.30	930.0	307.75	941.2
306.60	845.5	311.35	861.8	310.20	887.2	310.80	903.3	309.20	931.0	306.65	942.2
305.60	846.4	310.35	862.8	309.20	888.2	309.75	904.3	308.10	932.0	305.50	943.2
304.65	847.2	309.35	863.6	308.20	889.0	308.70	905.1	307.05	932.9	304.40	944.1
303.65	848.3	308.35	864.7	307.10	890.1	307.60	906.3	305.95	934.1	303.25	945.3
302.70	849.2	307.35	865.6	306.05	891.1	306.50	907.3	304.85	935.0	302.15	946.3
301.70	850.2	306.35	866.6	304.95	892.1	305.45	908.3	303.75	936.1	301.05	947.4
300.65	851.1	305.35	867.6	303.85	893.1	304.35	909.3	302.65	937.2	299.95	948.5
299.65	852.0	304.30	868.4	302.80	894.0	303.25	910.2	301.50	938.1	298.75	949.4
298.65	853.0	303.35	869.4	301.70	895.0	302.15	911.3	300.30	939.2	297.65	950.5
297.65	853.9	302.35	870.3	300.65	895.9			299.10	940.1	296.50	951.5
		301.30	871.3	299.55	897.0						
4.844 mol kg^{-1}		5.023 mol kg^{-1}									
319.25	949.4	317.30	955.4								
318.00	950.4	316.25	956.4								
316.85	951.5	315.05	957.5								
315.75	952.5	313.95	958.6								
314.60	953.6	312.85	959.6								
313.50	954.5	311.70	960.5								
312.40	955.5	310.60	961.5								
311.35	956.5	309.55	962.6								
310.25	957.4	308.35	963.5								
309.15	958.7	307.15	964.7								
308.05	959.7	306.00	965.7								
306.90	960.8	304.95	966.8								
305.80	961.9	303.75	967.9								
304.65	962.8	302.55	968.9								
303.55	963.9	301.40	970.0								
302.45	964.9	300.25	971.0								
301.35	966.0	299.15	972.1								

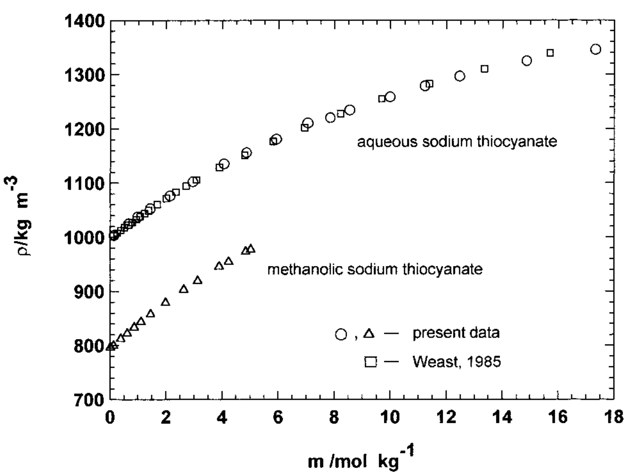

Figure 1. Plots of density (ρ) isotherms versus molality, (m) at 293.15 K for aqueous and methanolic sodium thiocyanate solutions.

thiocyanate solutions, respectively) and temperature ($\sim$293.15 $\leq T$/K $\leq$ 323.15). A Schott-Geräte thermostat type CT-1450 was used to maintain the temperature of the measurement to $\pm$0.02 K.

Results and Discussion

Experimental densities (ρ) of aqueous and methanolic sodium thiocyanate solutions are presented in Table 1 and are found to be a linear function of temperature at a

Table 2. Least-Squares Fitted Values of the Density Equation, $\rho = a - b((T/\mathrm{K}) - 273.15)$, for Aqueous and Methanolic Sodium Thiocyanate Solutions

m/(mol kg^{-1})	a/(kg m^{-3})	b/(kg m^{-3} K^{-1})	std dev in ρ/(kg m^{-3})
Aqueous Sodium Thiocyanate			
0.1400	1011.0 ± 0.2	0.3731 ± 0.0048	0.1
0.6628	1033.4 ± 0.2	0.4215 ± 0.0057	0.1
0.9811	1047.5 ± 0.2	0.4847 ± 0.0043	0.1
1.430	1063.3 ± 0.2	0.5220 ± 0.0038	0.1
2.137	1087.4 ± 0.1	0.5499 ± 0.0025	0.1
2.954	1115.1 ± 0.2	0.6351 ± 0.0053	0.1
4.062	1148.8 ± 0.1	0.6619 ± 0.0028	0.1
4.860	1170.1 ± 0.1	0.6975 ± 0.0032	0.1
5.921	1195.3 ± 0.2	0.7310 ± 0.0039	0.1
7.054	1225.8 ± 0.1	0.7531 ± 0.0017	0.1
7.849	1236.1 ± 0.1	0.7589 ± 0.0033	0.1
8.547	1250.0 ± 0.1	0.7700 ± 0.0029	0.1
9.994	1274.0 ± 0.2	0.7774 ± 0.0039	0.1
11.229	1294.3 ± 0.2	0.7815 ± 0.0037	0.1
12.468	1312.5 ± 0.1	0.7955 ± 0.0027	0.1
14.872	1340.5 ± 0.1	0.7885 ± 0.0028	0.1
17.328	1361.2 ± 0.1	0.7810 ± 0.0026	0.1
Methanolic Sodium Thiocyanate			
0.0146	815.9 ± 0.1	0.9831 ± 0.0038	0.1
0.1257	818.9 ± 0.1	0.9592 ± 0.0038	0.1
0.3876	831.5 ± 0.2	0.9647 ± 0.0048	0.1
0.6192	841.1 ± 0.1	0.9349 ± 0.0050	0.1
0.8693	852.0 ± 0.1	0.9361 ± 0.0038	0.1
1.102	862.2 ± 0.2	0.9414 ± 0.0053	0.1
1.443	876.9 ± 0.1	0.9384 ± 0.0033	0.1
1.978	897.6 ± 0.1	0.9351 ± 0.0038	0.1
2.636	921.4 ± 0.1	0.9230 ± 0.0035	0.1
3.119	937.5 ± 0.2	0.9063 ± 0.0044	0.1
3.889	964.0 ± 0.2	0.9153 ± 0.0042	0.1
4.220	972.9 ± 0.1	0.9168 ± 0.0038	0.1
4.844	992.2 ± 0.2	0.9330 ± 0.0044	0.1
5.023	995.8 ± 0.1	0.9151 ± 0.0029	0.1

Table 3. Speed of Sound (u) as a Function of Concentration and Temperature for Aqueous and Methanolic Sodium Thiocyanate 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 Sodium Thiocyanate											
0.1400 mol kg^{-1}		0.6628 mol kg^{-1}		0.9811 mol kg^{-1}		1.430 mol kg^{-1}		2.137 mol kg^{-1}		2.954 mol kg^{-1}	
293.15	1491.2	293.15	1518.1	293.15	1535.3	293.15	1556.3	293.15	1594.0	293.15	1632.4
298.15	1504.2	298.15	1529.2	298.15	1546.2	298.15	1565.0	298.15	1599.9	298.15	1635.9
303.15	1515.7	303.15	1538.8	303.15	1555.0	303.15	1572.3	303.15	1604.6	303.15	1638.5
308.15	1525.8	308.15	1547.2	308.15	1562.1	308.15	1578.3	308.15	1608.9	308.15	1640.4
313.15	1534.2	313.15	1553.9	313.15	1568.1	313.15	1583.5	313.15	1611.9	313.15	1641.6
317.95	1541.1	317.95	1559.0	317.95	1572.3	317.95	1586.8	317.95	1613.9	317.95	1641.9
323.15	1547.0	323.15	1563.9	323.15	1576.8	323.15	1590.1	323.15	1615.0	323.15	1641.5
4.062 mol kg^{-1}		4.860 mol kg^{-1}		5.921 mol kg^{-1}		7.054 mol kg^{-1}		7.849 mol kg^{-1}		8.547 mol kg^{-1}	
293.15	1687.2	293.15	1720.3	293.15	1756.2	293.15	1805.3	293.15	1821.1	293.15	1837.8
298.15	1687.2	298.15	1718.8	298.15	1754.0	298.15	1799.9	298.15	1815.6	298.15	1831.6
303.15	1686.7	303.15	1716.8	303.15	1750.5	303.15	1794.3	303.15	1809.4	303.15	1824.7
308.15	1685.7	308.15	1714.2	308.15	1746.3	308.15	1788.7	308.15	1802.6	308.15	1817.3
313.15	1684.3	313.15	1711.2	313.15	1741.7	313.15	1782.1	313.15	1795.6	313.15	1810.6
317.95	1682.4	317.95	1708.5	317.95	1737.6	317.95	1776.8	317.95	1789.6	317.95	1801.7
323.15	1679.9	323.15	1704.5	323.15	1732.9	323.15	1769.3	323.15	1781.8	323.15	1795.0
9.994 mol kg^{-1}		11.229 mol kg^{-1}		12.468 mol kg^{-1}		14.872 mol kg^{-1}		17.328 mol kg^{-1}			
293.15	1875.8	293.15	1907.8	293.15	1933.4	293.15	1958.4	293.15	1978.7		
298.15	1868.3	298.15	1898.7	298.15	1923.5	298.15	1945.9	298.15	1967.8		
303.15	1860.3	303.15	1889.9	303.15	1913.5	303.15	1934.9	303.15	1956.9		
308.15	1852.0	308.15	1881.0	308.15	1903.5	308.15	1925.0	308.15	1946.2		
313.15	1842.4	313.15	1871.9	313.15	1893.8	313.15	1914.8	313.15	1935.0		
317.95	1835.9	317.95	1863.5	317.95	1884.9	317.95	1905.0	317.95	1925.2		
323.15	1825.1	323.15	1851.6	323.15	1874.9	323.15	1892.5	323.15	1912.8		
Methanolic Sodium Thiocyanate											
0.0146 mol kg^{-1}		0.1257 mol kg^{-1}		0.3786 mol kg^{-1}		0.6192 mol kg^{-1}		0.8693 mol kg^{-1}		1.102 mol kg^{-1}	
293.15	1138.1	293.15	1137.4	293.15	1154.1	293.15	1168.9	293.15	1181.4	293.15	1195.6
298.15	1122.8	298.15	1122.0	298.15	1138.7	298.15	1152.8	298.15	1165.1	298.15	1179.6
303.15	1107.3	303.15	1106.2	303.15	1123.5	303.15	1137.1	303.15	1149.4	303.15	1164.4
308.15	1091.4	308.15	1090.2	308.15	1108.3	308.15	1121.8	308.15	1134.0	308.15	1149.5
313.15	1075.8	313.15	1073.9	313.15	1092.7	313.15	1106.7	313.15	1117.5	313.15	1135.1
317.95	1060.4	317.95	1060.0	317.95	1078.5	317.95	1092.1	317.95	1105.3	317.95	1121.0
323.15	1043.7	323.15	1043.5	323.15	1062.3	323.15	1076.2	323.15	1088.3	323.15	1104.7
1.443 mol kg^{-1}		1.978 mol kg^{-1}		2.636 mol kg^{-1}		3.119 mol kg^{-1}		3.889 mol kg^{-1}		4.220 mol kg^{-1}	
293.15	1215.4	293.15	1239.6	293.15	1273.4	293.15	1285.6	293.15	1329.0	293.15	1328.7
298.15	1199.6	298.15	1224.2	298.15	1257.0	298.15	1272.7	298.15	1313.9	298.15	1315.0
303.15	1184.4	303.15	1209.3	303.15	1241.5	303.15	1258.7	303.15	1299.1	303.15	1301.2
308.15	1169.5	308.15	1194.8	308.15	1226.5	308.15	1244.1	308.15	1284.7	308.15	1287.3
313.15	1153.8	313.15	1179.9	313.15	1212.4	313.15	1229.4	313.15	1270.7	313.15	1272.6
317.95	1141.1	317.95	1166.7	317.95	1198.6	317.95	1215.8	317.95	1257.3	317.95	1260.2
323.15	1124.7	323.15	1151.3	323.15	1185.2	323.15	1201.7	323.15	1243.8	323.15	1244.2
4.844 mol kg^{-1}		5.023 mol kg^{-1}									
293.15	1348.4	293.15	1356.4								
298.15	1333.4	298.15	1341.7								
303.15	1319.0	303.15	1327.4								
308.15	1305.0	308.15	1313.4								
313.15	1291.0	313.15	1299.4								
317.95	1279.0	317.95	1286.5								
323.15	1263.9	323.15	1272.7								

particular concentration, presented in Table 2. Densities of aqueous sodium thiocyanate solutions were compared with the reported data (Weast, 1985) by plotting ρ vs m isotherms in Figure 1 and are comparable within $\pm 0.2\%$. For methanolic sodium thiocyanate solution we could not make a comparison due to a lack of reported data.

Speeds of sound (u) and the calculated isentropic compressibilities (κ_s) from the following relation

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

where ρ is the density of the solution, for aqueous and methanolic sodium thiocyanate solutions are presented in Tables 3 and 4, respectively.

Even though the available expressions (Horvath, 1985; Millero et al., 1987; Kumar, 1993; Rohman and Mahiuddin, 1997) fit the values of the speed of sound, they may not be universal. A polynomial equation up to second degree in temperature, T, of the type

$$Y(u,\kappa_s) = a_n + b_n((T/\mathrm{K}) - 273.15) + c_n((T/\mathrm{K}) - 273.15)^d \qquad (2)$$

where Y refers either the speed of sound or the isentropic compressibility, a_n, b_n, and c_n are concentration dependent parameters, and d is a constant, explains the temperature dependence of both the speed of sound and the isentropic compressibility with reasonable accuracy. For the speed of sound $n = 1$, and for the isentropic compressibility $n = 2$. The computed values of the parameters of eq 2 for the speed of sound and the isentropic compressibility are presented in Tables 5 and 6, respectively. By inserting the concentration dependence of a_n, b_n, and c_n parameters in

Table 4. Isentropic Compressibilities (κ_s) as Functions of Concentration and Temperature for Aqueous and Methanolic Sodium Thiocyanate Solutions

T/K	$\kappa_s \times 10^{10}$/Pa^{-1}	T/K	$\kappa_s \times 10^{10}$/Pa^{-1}	T/K	$\kappa_s \times 10^{10}$/Pa^{-1}	T/K	$\kappa_s \times 10^{10}$/Pa^{-1}	T/K	$\kappa_s \times 10^{10}$/Pa^{-1}	T/K	$\kappa_s \times 10^{10}$/Pa^{-1}
Aqueous Sodium Thiocyanate											
0.1400 mol kg^{-1}		0.6628 mol kg^{-1}		0.9811 mol kg^{-1}		1.430 mol kg^{-1}		2.137 mol kg^{-1}		2.954 mol kg^{-1}	
293.15	4.481	293.15	4.233	293.15	4.088	293.15	3.921	293.15	3.656	293.15	3.404
298.15	4.412	298.15	4.181	298.15	4.040	298.15	3.888	298.15	3.639	298.15	3.399
303.15	4.354	303.15	4.137	303.15	4.004	303.15	3.861	303.15	3.627	303.15	3.398
308.15	4.304	308.15	4.101	308.15	3.977	308.15	3.841	308.15	3.617	308.15	3.400
313.15	4.265	313.15	4.074	313.15	3.956	313.15	3.826	313.15	3.613	313.15	3.405
317.95	4.235	317.95	4.056	317.95	3.943	317.95	3.819	317.95	3.613	317.95	3.414
323.15	4.211	323.15	4.039	323.15	3.931	323.15	3.813	323.15	3.617	323.15	3.426
4.062 mol kg^{-1}		4.860 mol kg^{-1}		5.921 mol kg^{-1}		7.054 mol kg^{-1}		7.849 mol kg^{-1}		8.547 mol kg^{-1}	
293.15	3.094	293.15	2.923	293.15	2.746	293.15	2.534	293.15	2.470	293.15	2.398
298.15	3.103	298.15	2.937	298.15	2.762	298.15	2.557	298.15	2.492	298.15	2.422
303.15	3.114	303.15	2.952	303.15	2.781	303.15	2.581	303.15	2.517	303.15	2.448
308.15	3.126	308.15	2.970	308.15	2.803	308.15	2.606	308.15	2.544	308.15	2.476
313.15	3.141	313.15	2.990	313.15	2.827	313.15	2.633	313.15	2.572	313.15	2.502
317.95	3.157	317.95	3.008	317.95	2.849	317.95	2.657	317.95	2.597	317.95	2.534
323.15	3.176	323.15	3.032	323.15	2.874	323.15	2.689	323.15	2.629	323.15	2.562
9.994 mol kg^{-1}		11.229 mol kg^{-1}		12.468 mol kg^{-1}		14.872 mol kg^{-1}		17.328 mol kg^{-1}			
293.15	2.258	293.15	2.149	293.15	2.063	293.15	1.968	293.15	1.898		
298.15	2.284	298.15	2.176	298.15	2.091	298.15	2.000	298.15	1.925		
303.15	2.310	303.15	2.203	303.15	2.119	303.15	2.028	303.15	1.952		
308.15	2.338	308.15	2.231	308.15	2.148	308.15	2.055	308.15	1.979		
313.15	2.370	313.15	2.260	313.15	2.177	313.15	2.084	313.15	2.008		
317.95	2.394	317.95	2.287	317.95	2.204	317.95	2.111	317.95	2.034		
323.15	2.431	323.15	2.324	323.15	2.235	323.15	2.146	323.15	2.067		
Methanolic Sodium Thiocyanate											
0.0146 mol kg^{-1}		0.1257 mol kg^{-1}		0.3856 mol kg^{-1}		0.6192 mol kg^{-1}		0.8693 mol kg^{-1}		1.102 mol kg^{-1}	
293.15	9.696	293.15	9.666	293.15	9.244	293.15	8.899	293.15	8.598	293.15	8.295
298.15	10.02	298.15	9.993	298.15	9.552	298.15	9.202	298.15	8.891	298.15	8.569
303.15	10.37	303.15	10.34	303.15	9.871	303.15	9.512	303.15	9.187	303.15	8.844
308.15	10.74	308.15	10.71	308.15	10.21	308.15	9.830	308.15	9.492	308.15	9.126
313.15	11.13	313.15	11.11	313.15	10.56	313.15	10.16	313.15	9.831	313.15	9.413
317.95	11.52	317.95	11.47	317.95	10.91	317.95	10.49	317.95	10.10	317.95	9.704
323.15	11.97	323.15	11.91	323.15	11.31	323.15	10.87	323.15	10.49	323.15	10.05
1.443 mol kg^{-1}		1.978 mol kg^{-1}		2.636 mol kg^{-1}		3.119 mol kg^{-1}		3.889 mol kg^{-1}		4.220 mol kg^{-1}	
293.15	7.889	293.15	7.405	293.15	6.830	293.15	6.581	293.15	5.987	293.15	5.934
298.15	8.142	298.15	7.633	298.15	7.045	298.15	6.748	298.15	6.155	298.15	6.087
303.15	8.399	303.15	7.864	303.15	7.260	303.15	6.934	303.15	6.327	303.15	6.247
308.15	8.662	308.15	8.099	308.15	7.477	308.15	7.133	308.15	6.501	308.15	6.414
313.15	8.949	313.15	8.350	313.15	7.692	313.15	7.341	313.15	6.678	313.15	6.595
317.95	9.199	317.95	8.585	317.95	7.909	317.95	7.543	317.95	6.854	317.95	6.757
323.15	9.525	323.15	8.867	323.15	8.134	323.15	7.762	323.15	7.040	323.15	6.968
4.844 mol kg^{-1}		5.023 mol kg^{-1}									
293.15	5.649	293.15	5.560								
298.15	5.805	298.15	5.710								
303.15	5.961	303.15	5.861								
308.15	6.119	308.15	6.015								
313.15	6.283	313.15	6.175								
317.95	6.432	317.95	6.328								
323.15	6.620	323.15	6.498								

eq 2 and on rearranging, we obtained an isothermal equation of the type

$$Y(u,\kappa_s) = a'_n + b'_n m + c'_n m^{d_1} \qquad (3)$$

to explain the concentration dependence of the speed of sound and the isentropic compressibility. In eq 3, a'_n, b'_n, and c'_n are temperature dependent parameters and d_1 is a constant. The computed values of these parameters for the speed of sound and the isentropic compressibility are presented in Tables 7 and 8, respectively. Equation 3 so obtained is equivalent to the equation proposed by Kumar (1993) but up to the second degree.

The concentration dependencies of the isentropic compressibility isotherms for aqueous and methanolic sodium thiocyanate solutions are illustrated in Figures 2 and 3, respectively. From Figures 2 and 3 and Tables 7 and 8 it is evident that eq 3 can explain the concentration dependence of the isentropic compressibility within ±2% and ±0.8% accuracy for aqueous and methanolic sodium thio-

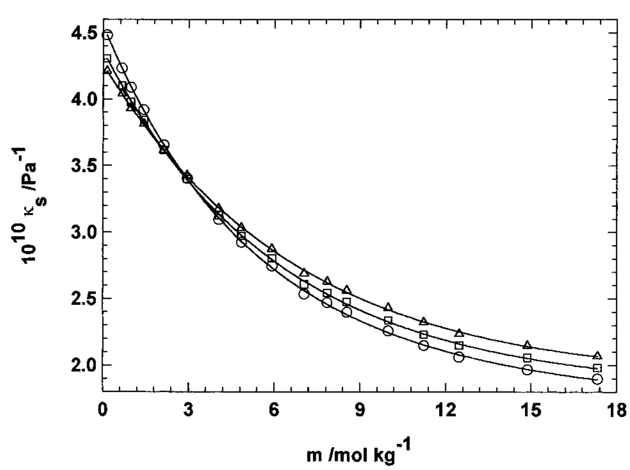

Figure 2. Variation of isentropic compressibility (κ_s) with molality (m) at 293.15 K (○), 308.15 K (□), and 323.15 K (△) for aqueous sodium thiocyanate solutions (symbols and solid curves represent experimental and calculated (from eq 3) values, respectively).

Table 5. Least-Squares Fitted Values of the Parameters of Equation 2 for the Speed of Sound for Aqueous and Methanolic Sodium Thiocyanate Solutions

m/(mol kg^{-1})	a_1/(m s^{-1})	b_1/(m s^{-1})	$c_1 \times 10^2$/(m s^{-1} K^{-d})	d	std dev in u/(m s^{-1})
		Aqueous Sodium Thiocyanate			
0.1400	1424.3 ± 0.4	3.951 ± 0.026	−3.113 ± 0.038	1.99 ± 0.07	0.1
0.6628	1458.4 ± 1.6	3.673 ± 0.102	−4.636 ± 0.218	1.90 ± 0.25	0.3
0.9811	1481.3 ± 2.4	3.309 ± 0.149	−3.419 ± 0.261	1.95 ± 0.39	0.4
1.430	1513.3 ± 1.2	2.478 ± 0.067	−0.935 ± 0.005	2.18 ± 0.47	0.2
2.137	1560.8 ± 0.9	2.010 ± 0.053	−1.524 ± 0.061	2.05 ± 0.22	0.2
2.954	1611.4 ± 0.6	1.352 ± 0.034	−1.499 ± 0.048	2.00 ± 0.14	0.1
4.062	1682.1 ± 0.3	0.448 ± 0.016	−0.948 ± 0.022	2.01 ± 0.06	0.1
4.860	1724.6 ± 0.6	−0.136 ± 0.032	−0.102 ± 0.008	2.42 ± 0.28	0.2
5.921	1764.3 ± 1.4	−0.120 ± 0.094	−2.944 ± 0.401	1.73 ± 0.19	0.4
7.054	1822.7 ± 2.2	−0.732 ± 0.144	−0.876 ± 0.274	1.93 ± 0.47	0.3
7.849	1843.2 ± 1.9	−0.993 ± 0.117	−0.591 ± 0.214	1.94 ± 1.11	0.3
8.547	1861.6 ± 3.9	−0.971 ± 0.300	−3.142 ± 1.944	1.63 ± 0.81	0.6
9.994	1904.1 ± 3.4	−1.320 ± 0.201	−0.317 ± 0.179	2.12 ± 2.07	0.6
11.229	1939.6 ± 3.2	−1.523 ± 0.189	−0.329 ± 0.194	2.08 ± 1.96	0.6
12.468	1975.6 ± 1.1	−2.166 ± 0.063	0.251 ± 0.072	2.05 ± 0.85	0.2
14.872	2002.1 ± 4.4	−2.261 ± 0.272	0.163 ± 0.390	2.00 ± 4.05	0.8
17.328	2020.3 ± 1.7	−2.056 ± 0.101	−0.122 ± 0.096	2.10 ± 1.55	0.3
		Methanolic Sodium Thiocyanate			
0.0146	1199.2 ± 1.3	−3.011 ± 0.075	−0.181 ± 0.099	2.02 ± 0.95	0.2
0.1257	1202.3 ± 2.5	−3.331 ± 0.234	2.181 ± 2.678	1.50 ± 0.76	0.4
0.3876	1213.8 ± 0.9	−2.843 ± 0.140	−6.759 ± 4.564	1.26 ± 0.15	0.3
0.6192	1234.1 ± 1.2	−3.338 ± 0.071	0.370 ± 0.101	2.00 ± 0.72	0.2
0.8693	1249.5 ± 5.1	−3.943 ± 0.686	19.22 ± 15.44	1.34 ± 0.44	0.7
1.102	1257.3 ± 2.1	−3.463 ± 0.348	16.33 ± 12.16	1.24 ± 0.25	0.4
1.443	1280.7 ± 3.6	−5.385 ± 1.414	166.1 ± 98.7	1.08 ± 0.10	0.5
1.978	1301.7 ± 2.3	−3.257 ± 0.179	2.227 ± 1.218	1.62 ± 0.63	0.3
2.636	1344.8 ± 1.1	−3.864 ± 0.067	1.907 ± 0.138	1.91 ± 0.33	0.2
3.119	1338.7 ± 2.6	−2.256 ± 0.358	−15.90 ± 10.04	1.29 ± 0.29	0.5
3.889	1394.5 ± 1.3	−3.621 ± 0.107	5.545 ± 0.769	1.61 ± 0.14	0.2
4.220	1379.8 ± 3.0	−1.881 ± 0.498	−34.88 ± 18.80	1.22 ± 0.13	0.4
4.844	1410.8 ± 3.1	−3.380 ± 0.242	3.682 ± 1.526	1.64 ± 0.86	0.4
5.023	1418.4 ± 0.9	−3.337 ± 0.068	3.597 ± 0.444	1.63 ± 0.21	0.1

Table 6. Least-Squares Fitted Values of the Parameters of Equation 2 for Isentropic Compressibility for Aqueous and Methanolic Sodium Thiocyanate Solutions

m/(mol kg^{-1})	$a_2 \times 10^{10}$/Pa^{-1}	$b_2 \times 10^{12}$/(Pa^{-1} K^{-1})	$c_2 \times 10^{14}$/(Pa^{-1} K^{-d})	d	std dev in $\kappa_s \times 10^{12}$/Pa^{-1}
		Aqueous Sodium Thiocyanate			
0.1400	4.884 ± 0.002	−2.821 ± 0.015	11.16 ± 0.09	1.66 ± 0.09	0.03
0.6628	4.568 ± 0.011	−2.618 ± 0.094	18.16 ± 0.86	1.55 ± 0.67	0.14
0.9811	4.392 ± 0.012	−2.717 ± 0.119	30.91 ± 1.67	1.45 ± 0.83	0.15
1.430	4.109 ± 0.006	−1.203 ± 0.036	1.548 ± 0.066	1.94 ± 0.62	0.09
2.137	3.769 ± 0.005	−0.737 ± 0.029	0.866 ± 0.041	2.00 ± 0.54	0.08
2.954	3.468 ± 0.004	−0.605 ± 0.027	3.939 ± 0.157	1.66 ± 0.45	0.05
4.062	3.081 ± 0.002	−0.017 ± 0.014	0.418 ± 0.020	2.00 ± 0.42	0.04
4.860	2.881 ± 0.004	0.149 ± 0.024	0.271 ± 0.029	2.03 ± 0.89	0.06
5.921	2.685 ± 0.007	0.244 ± 0.045	0.269 ± 0.064	2.00 ± 2.18	0.12
7.054	2.458 ± 0.006	0.329 ± 0.037	0.234 ± 0.046	2.03 ± 1.39	0.09
7.849	2.384 ± 0.008	0.381 ± 0.048	0.244 ± 0.076	1.97 ± 2.96	0.12
8.547	2.307 ± 0.009	0.411 ± 0.006	0.217 ± 0.085	1.98 ± 2.33	0.14
9.994	2.168 ± 0.010	0.401 ± 0.059	0.217 ± 0.074	2.03 ± 2.35	0.16
11.229	2.046 ± 0.008	0.430 ± 0.047	0.139 ± 0.044	2.10 ± 2.96	0.14
12.468	1.951 ± 0.004	0.552 ± 0.023	0.044 ± 0.048	1.90 ± 1.85	0.05
14.872	1.862 ± 0.011	0.523 ± 0.067	0.084 ± 0.095	2.00 ± 1.96	0.18
17.328	1.801 ± 0.005	0.458 ± 0.028	0.134 ± 0.037	2.02 ± 1.89	0.08
		Methanolic Sodium Thiocyanate			
0.0146	8.582 ± 0.021	4.727 ± 0.128	4.426 ± 0.198	1.98 ± 0.49	0.33
0.1257	8.506 ± 0.041	5.071 ± 0.252	4.006 ± 0.421	1.96 ± 1.41	0.64
0.3856	8.251 ± 0.046	4.208 ± 0.280	4.282 ± 0.449	1.97 ± 2.19	0.72
0.6192	7.824 ± 0.038	4.967 ± 0.224	1.943 ± 0.281	2.03 ± 1.74	0.61
0.8693	7.547 ± 0.087	4.897 ± 0.513	1.632 ± 0.617	2.04 ± 5.34	1.41
1.102	7.320 ± 0.032	4.534 ± 0.193	1.789 ± 0.273	2.00 ± 1.81	0.51
1.443	7.021 ± 0.203	4.079 ± 1.150	0.998 ± 0.921	2.14 ± 13.4	3.45
1.978	6.609 ± 0.028	3.560 ± 0.182	3.286 ± 0.459	1.86 ± 1.62	0.42
2.636	5.990 ± 0.015	4.117 ± 0.010	0.759 ± 0.334	1.80 ± 1.75	0.22
3.119	5.960 ± 0.031	2.689 ± 0.195	2.338 ± 0.354	1.94 ± 1.75	0.49
3.889	5.347 ± 0.011	3.040 ± 0.070	1.198 ± 0.178	1.86 ± 1.30	0.16
4.220	5.406 ± 0.028	2.322 ± 0.168	1.652 ± 0.248	1.99 ± 2.41	0.44
4.844	5.077 ± 0.026	2.720 ± 0.160	0.906 ± 0.290	1.94 ± 4.64	0.40
5.023	5.001 ± 0.008	2.651 ± 0.050	0.834 ± 0.087	1.95 ± 0.99	0.13

cyanate solutions, respectively. In aqueous sodium thiocyanate (Figure 2) it is interesting to note that the isentropic compressibility, κ_s, isotherms converge at a particular concentration and then diverge. Similar variation in κ_s vs m isotherms has been observed in aqueous sodium nitrate and sodium thiosulfate solutions (Rohman and Mahiuddin,

Table 7. Least-Squares Fitted Values of the Parameters of Equation 3 for the Speed of Sound for Aqueous and Methanolic Sodium Thiocyanate Solutions

T/K	a'_1/(m s^{-1})	b'_1/(m s^{-1} kg mol^{-1})	c'_1/(m s^{-1} kg^{d_1} mol$^{-d_1}$)	d_1	std dev in u/(m s^{-1})
		Aqueous Sodium Thiocyanate			
293.15	1480.0 ± 2.0	59.59 ± 0.67	−2.896 ± 0.065	1.83 ± 0.09	3.4
298.15	1494.1 ± 1.8	54.77 ± 0.61	−2.239 ± 0.051	1.88 ± 0.10	3.2
308.15	1517.2 ± 1.7	46.25 ± 0.51	−1.246 ± 0.031	2.00 ± 0.12	3.0
323.15	1540.1 ± 1.6	36.94 ± 0.43	−0.521 ± 0.015	2.19 ± 0.16	2.9
		Methanolic Sodium Thiocyanate			
293.15	1133.6 ± 2.1	57.03 ± 1.79	−1.097 ± 0.150	2.53 ± 0.78	3.5
298.15	1118.3 ± 1.8	55.78 ± 1.40	−0.570 ± 0.069	2.87 ± 0.79	3.1
308.15	1086.9 ± 1.7	56.62 ± 1.32	−0.580 ± 0.065	2.87 ± 0.80	2.9
323.15	1039.5 ± 1.8	59.32 ± 1.51	−0.855 ± 0.097	2.70 ± 0.68	3.1

Table 8. Least-Squares Fitted Values of the Parameters of Equation 3 for the Isentropic Compressibility for Aqueous and Methanolic Sodium Thiocyanate Solutions

T/K	$a'_2 \times 10^{10}$/Pa^{-1}	$b'_2 \times 10^{11}$/(Pa^{-1} kg mol^{-1})	$c'_2 \times 10^{12}$/(Pa^{-1} kg^{d_1} mol$^{-d_1}$)	d_1	std dev in $\kappa_s \times 10^{12}$/Pa^{-1}
		Aqueous Sodium Thiocyanate			
293.15	4.619 ± 0.015	−23.59 ± 0.42	180.5 ± 3.4	1.07 ± 0.04	2.2
298.15	4.541 ± 0.014	−17.72 ± 0.30	125.5 ± 2.3	1.09 ± 0.06	2.0
308.15	4.407 ± 0.017	−9.685 ± 0.147	52.55 ± 0.93	1.16 ± 0.06	1.7
323.15	4.293 ± 0.010	−6.170 ± 0.085	24.68 ± 0.43	1.24 ± 0.06	1.5
		Methanolic Sodium Thiocyanate			
293.15	9.792 ± 0.029	−16.46 ± 0.42	28.30 ± 1.45	1.65 ± 0.20	4.5
298.15	10.12 ± 0.03	−16.63 ± 0.38	25.08 ± 1.20	1.71 ± 0.19	4.3
308.15	10.85 ± 0.03	−18.70 ± 0.42	30.45 ± 1.36	1.68 ± 0.18	4.6
323.15	12.09 ± 0.03	−23.01 ± 0.51	44.64 ± 1.86	1.61 ± 0.16	5.1

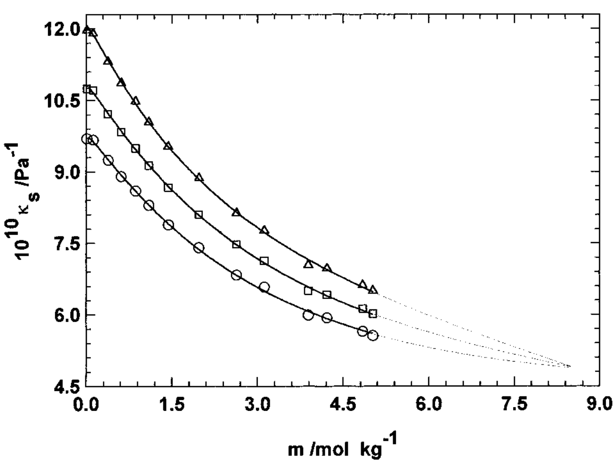

Figure 3. Variation of isentropic compressibility (κ_s) with molality (m) at 293.15 K (○), 308.15 K (□), and 323.15 K (△) for methanolic sodium thiocyanate solutions (symbols and solid curves represent experimental and calculated (from eq 3) values and the broken curves represent the extrapolated isentropic compressibility values, respectively).

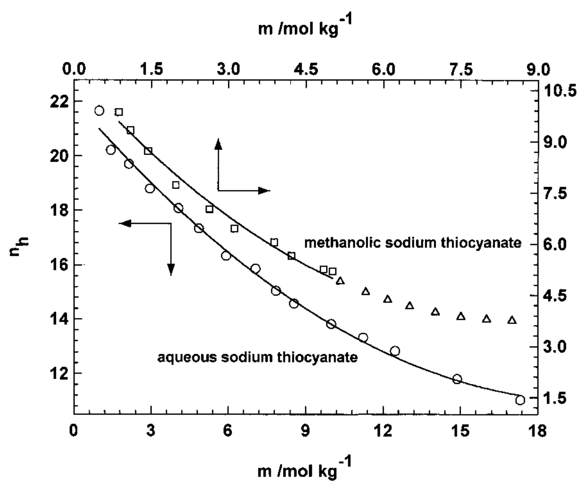

Figure 4. Variation of hydration/solvation number (n_h) with molality (m) for (○) aqueous sodium thiocyanate and (□, △) methanolic sodium thiocyanate solutions (circles and squares are experimental, solid curves are calculated (from polynomial equation up to second degree), and triangles are extrapolated values, respectively).

1997). In the case of methanolic sodium thiocyanate solution κ_s vs m isotherms (Figure 3) vary smoothly and do not converge within the concentration and temperature range of this study. It may be presumed that the solvent structure around sodium thiocyanate would be different when water and methanol are used as solvent.

From Figure 2 it is apparent that the κ_s isotherms possess a critical κ_s value at 3.0 mol kg^{-1} which is independent of temperature and is related to the primary solvation of the solute (Endo and Nomoto, 1981). Beyond this concentration, overlap of cospheres of cation and anion occurs leading to the solvent shared, separated, and contact ion pairs (Marcus, 1985) due to the strong and predominant ion−ion interactions. In dilute solution the isentropic compressibility is predominantly governed by the 64% configurational part arising from the network structure of bulk water, whereas in the concentrated solution it is due to the 36% vibrational arising from the thermal vibration (Slie et al., 1966). Beyond 3.0 mol kg^{-1} vibrational compressibility dominates, which increases with an increase in temperature due to the thermal motion at a particular concentration resulting in reversibility of the isentropic compressibility isotherms (Figure 2). For methanolic sodium thiocyanate solution isentropic compressibilities (Figure 3) increase with an increase in temperature. It may be presumed that the vibrational compressibility predominantly contributes to the isentropic compressibility within the concentration and temperature range of this study.

Onori (1988) derived the following relation between the 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 the molar volume, V_1, of the solvent to estimate the total hydration number, n_h, of the solute

$$K_{s,\phi} = K_{s,h}V_h - n_hK_{s,1}V_1 \quad (4)$$

In eq 4, $K_{s,h}$ and V_h are the isentropic compressibility of the solution at which isentropic compressibility isotherms converge and the volume of 1 mol of the hydrated solute, respectively. The estimated primary hydration number at 3.0 mol kg^{-1} was found to be 25.1 and was ~36% higher than the available water per mole of solute at 3.0 mol kg^{-1}. On extrapolation, the primary hydration number of aqueous sodium chloride (Onori, 1988) was found to be 10.3 at 5.5 mol kg^{-1}, which is ~2% higher than the available water molecules. Alternatively, the apparent molal volume, V_ϕ of the solution as proposed by Onori (1988) is given by

$$V_\phi = -n_hV_1 + V_h \quad (5)$$

With inserting the value of V_h (eq 5) into eq 4 and upon rearrangement, an expression for the total hydration number, n_h, of the following form can be obtained

$$n_h = (K_{s,\phi} - K_{s,h}V_\phi)/[V_1(K_{s,h} - K_{s,1})] \quad (6)$$

The total hydration number calculated from eq 6 within its limit of validity (Onori, 1988) for the aqueous sodium thiocyanate at 298.15 K has been illustrated in Figure 4. The primary hydration number corresponding to 3.0 mol kg^{-1} (Figure 2) for the aqueous sodium thiocyanate was found to be 18.8 (Figure 4) and is in good agreement with the available number of water molecules per mole of solute at 3.0 mol kg^{-1}. Similarly for aqueous sodium chloride the primary hydration number was estimated to be 10.1 at 5.5 mol kg^{-1}, which is also in good agreement with the available water molecules at that concentration. Therefore, eq 6 can be used to estimate the hydration/solvation number with a better confidence level as far as the primary hydration/solvation number is concerned.

Considering the primary solvation number of Na^+ is 6 as a reference in aqueous medium (Caminiti et al., 1980; Ohtaki and Radnai, 1993) and the solvation number can be divided between the constituent ions (Endo and Nomoto, 1981), the primary solvation number of SCN^- is estimated to be 12.8. which is much higher than the reported coordination number (1.8 ± 0.2) obtained by Kameda et al. (1994). The large difference in the primary solvation number may be due to the concentration difference.

For the methanolic sodium thiocyanate system, the isentropic compressibility isotherms converge beyond the experimental concentration range at 8.6 mol kg^{-1} with $K_{s,h} = 4.9 \times 10^{-10}$ Pa^{-1} (Figure 3). The calculated total solvation number, n_h, at 298.15 K using eq 6 is illustrated in Figure 4. As discussed above the primary solvation number at 8.6 mol kg^{-1} was found to be 3.7, which is much smaller than in aqueous medium and in good agreement with the available number of methanol molecules per mole of solute. The primary solvation number of Na^+ in methanol is lacking, and we are not able to separate the primary solvation number into an ionic contribution.

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