

Isentropic Compressibility and Viscosity of Aqueous and Methanolic Calcium Chloride Solutions

Abdul Wahab and Sekh Mahiuddin*

Material Science Division, Regional Research Laboratory, Jorhat 785 006, Assam, India

Speeds of sound and viscosities of aqueous and methanolic calcium chloride solutions were measured as functions of concentration [$0.0040 \leq m/(\text{mol}\cdot\text{kg}^{-1}) \leq 7.151$ and $0.1903 \leq m/(\text{mol}\cdot\text{kg}^{-1}) \leq 3.252$ for aqueous and methanolic calcium chloride solutions, respectively] and temperature ($273.15 \leq T/\text{K} \leq 323.15$). Isentropic compressibility isotherms of aqueous calcium chloride solutions converge at $5.1 \text{ mol}\cdot\text{kg}^{-1}$. In the case of methanolic calcium chloride solutions, isentropic compressibility isotherms vary smoothly with the increase in concentration and converge at $5.66 \text{ mol}\cdot\text{kg}^{-1}$ on extrapolation. Total solvation numbers of calcium chloride in water and methanol media were estimated to be 10.9 and 5.5, respectively.

Introduction

The interactions and equilibria of ions in aqueous and nonaqueous media in different concentration regions are of immense importance to the technologist and theoretician as most of the chemical processes occur in these systems. The structure and existence of free ions, solvated ions, and ion pairs depend on concentration regions.¹

Various techniques² have been employed to study the solvation structure and dynamics of ions in aqueous and nonaqueous media. Despite extensive studies, ambiguities prevail with regard to the solvation structure and dynamics of Ca^{2+} ions as the reported values of the primary hydration number² scattered between 5.5 and 10. Furthermore, the hydration numbers^{3–5} exhibit a large discrepancy even at a common concentration ($\sim 1.1 \text{ mol}\cdot\text{kg}^{-1}$) of Ca^{2+} ion. However, molecular dynamic simulations^{3,6} reveal a much larger value of hydration numbers of 9.2–10 than that obtained by X-ray and neutron diffraction methods.^{3–5,7,8} On the other hand, Caminiti et al.⁹ inferred from the X-ray diffraction studies that the Ca^{2+} ion in water and in the concentration range of (~ 1.0 – 4.5) $\text{mol}\cdot\text{kg}^{-1}$ has essentially a coordination sphere of six water molecules. When the $\text{H}_2\text{O}/\text{salt}$ ratio approaches that of the solid hydrate ($\text{CaCl}_2\cdot 6\text{H}_2\text{O}$), the nearest-neighbor structure around the Ca^{2+} ion changes significantly due to the nonavailability of free water.

X-ray and neutron diffraction studies^{3,5,7,8} reveal that the Cl^- ion is bound with six water molecules, but computer simulations^{10–12} show a statistical dispersion of the number of hydrated water molecules of primary hydration shell in the range of 5.6–8.5. From the above discussion it seems that the hydration numbers may not reflect the true primary hydration number of the Ca^{2+} ion as the studies were performed in the concentration range far from the concentration at which the primary hydration shell of the Ca^{2+} ion is just saturated.

Vogrin and Malinowski¹³ found a consistent solvation phenomenon in methanol and water for CaCl_2 by NMR measurements and reported the total solvation numbers of 10.3 ± 0.6 and 9.9 ± 0.6 in the respective solvents. In

contrast, experimental¹⁴ and theoretical^{15,16} studies reveal that the solvation dynamics in methanol is strikingly different from that in water.

Among the many approaches² the acoustic method^{17–19} has proved to be an alternative technique to study the solvation of electrolyte in aqueous and nonaqueous media. In earlier papers,^{20,21} we reported that the isentropic compressibility isotherms converge at a particular concentration when the primary solvation shell of an electrolyte is saturated, resulting in a most ordered structure. On the other hand, the ion–solvent and ion–ion interactions and equilibria in different concentration regions have an influence on viscosity and electrical conductivity. Therefore, in this paper we report speeds of sound and viscosity of aqueous and methanolic calcium chloride solutions as functions of concentration and temperature.

Experimental Section

Calcium chloride (>97%, E. Merck, Mumbai, India) was recrystallized twice from double-distilled water and was kept in a desiccator under vacuum over P_2O_5 . Finally, calcium chloride was dried at 120°C under vacuum. Anhydrous methanol was prepared from A.R. grade methanol (>99.5%, Qualigens Fine Chemicals, Mumbai, India) as described elsewhere.²² All solutions were prepared by mass with $\pm 0.2\%$ uncertainty. Concentrations of the solutions were checked further by determining calcium by EDTA titration.

Densities, ρ , of all solutions were measured with an uncertainty of $\pm 10^{-4} \text{ g}\cdot\text{cm}^{-3}$ by using a single-stem graduated pycnometer of $\sim 9 \text{ cm}^3$ capacity. The pycnometer was calibrated by using double-distilled water.

Speeds of sound, u , in aqueous and methanolic calcium chloride solutions were measured with an uncertainty of $\pm 0.1 \text{ m}\cdot\text{s}^{-1}$ by using a variable path interferometer (multifrequency ultrasonic interferometer, M-83, Mittal Enterprises, New Delhi, India) at 2 MHz as described elsewhere.^{20,21}

Viscosities, η , of all solutions were measured with a Schott-Geräte AVS 310 unit equipped with Ubbelohde viscometers. Viscometers of different constants of (0.009595, 0.013103, 0.03004, and 0.1126) $\text{mm}^2\cdot\text{s}^{-2}$ were used to measure the efflux time in different concentration ranges. An average of five efflux times at each temperature was

* Author to whom correspondence should be addressed (fax 0091-376-370011; e-mail mahirrjlt@yahoo.com).

Table 1. Density Values for Aqueous and Methanolic Calcium Chloride Solutions as Functions of Concentration and Temperature

<i>T</i> /K	$\rho/\text{kg}\cdot\text{m}^{-3}$	<i>T</i> /K	$\rho/\text{kg}\cdot\text{m}^{-3}$	<i>T</i> /K	$\rho/\text{kg}\cdot\text{m}^{-3}$	<i>T</i> /K	$\rho/\text{kg}\cdot\text{m}^{-3}$	<i>T</i> /K	$\rho/\text{kg}\cdot\text{m}^{-3}$	<i>T</i> /K	$\rho/\text{kg}\cdot\text{m}^{-3}$	<i>T</i> /K	$\rho/\text{kg}\cdot\text{m}^{-3}$
Aqueous Calcium Chloride													
0.0040 mol·kg ⁻¹		0.1987 mol·kg ⁻¹		0.5127 mol·kg ⁻¹		0.7085 mol·kg ⁻¹		1.021 mol·kg ⁻¹		1.546 mol·kg ⁻¹		2.084 mol·kg ⁻¹	
320.55	989.72	321.25	1006.7	320.20	1033.8	321.70	1049.2	319.90	1076.2	322.70	1117.4	323.65	1154.7
317.80	990.96	318.45	1007.9	317.20	1034.8	318.90	1050.5	316.90	1077.2	320.00	1118.8	320.90	1156.1
314.65	991.91	315.30	1008.9	314.35	1036.0	315.85	1051.9	314.00	1078.5	316.95	1119.8	318.05	1157.6
311.45	993.09	312.30	1010.1	311.00	1037.4	312.65	1052.9	310.70	1079.9	313.90	1121.2	314.90	1158.7
307.80	994.40	308.65	1011.4	307.65	1038.7	309.50	1054.1	307.15	1081.3	310.85	1122.7	311.85	1160.1
303.85	995.64	304.95	1012.7	303.95	1040.0	305.95	1055.5	303.70	1082.6	307.50	1124.1	308.70	1161.6
299.40	996.90	300.90	1014.0	299.70	1041.4	302.15	1056.8	299.85	1084.2	304.20	1125.5	305.35	1163.1
		295.90	1015.4			298.15	1058.2			300.60	1127.0	302.15	1164.5
										297.05	1128.4	298.50	1166.1
2.676 mol·kg ⁻¹		3.281 mol·kg ⁻¹		3.872 mol·kg ⁻¹		4.290 mol·kg ⁻¹		4.483 mol·kg ⁻¹		4.802 mol·kg ⁻¹		5.252 mol·kg ⁻¹	
323.25	1195.5	322.20	1235.1	322.90	1269.5	322.55	1293.5	321.80	1304.4	323.55	1324.6	320.90	1342.2
320.50	1197.0	319.25	1236.3	320.25	1271.1	319.85	1295.2	319.25	1306.0	320.90	1326.2	318.15	1343.9
317.50	1198.5	316.25	1237.8	317.45	1272.7	316.95	1296.8	316.30	1307.7	318.50	1327.6	315.35	1345.1
314.50	1199.6	313.35	1239.4	314.35	1273.9	313.90	1298.0	313.50	1309.3	315.80	1329.3	312.70	1346.7
311.65	1201.0	310.25	1241.0	311.60	1275.4	311.25	1299.6	310.75	1311.0	313.25	1330.8	309.75	1348.5
308.45	1202.6	307.20	1242.5	308.55	1277.1	308.25	1301.3	307.75	1312.2	310.65	1332.4	306.85	1350.2
305.25	1204.1	304.05	1244.3	305.55	1278.7	305.30	1302.9	305.00	1313.8	308.00	1334.1	304.10	1351.9
302.05	1205.6	301.00	1245.8	302.50	1280.3	302.35	1304.6	301.85	1315.5	305.55	1335.5	301.10	1353.8
298.55	1207.3	297.80	1247.5	299.35	1282.1	299.20	1306.4	298.95	1317.2			298.35	1355.5
5.475 mol·kg ⁻¹		5.783 mol·kg ⁻¹		5.991 mol·kg ⁻¹		6.629 mol·kg ⁻¹		7.151 mol·kg ⁻¹					
323.65	1351.4	323.50	1365.6	322.95	1380.3	323.85	1393.9	321.15	1433.2				
321.30	1352.9	321.15	1367.1	320.25	1382.0	321.15	1395.5	318.45	1435.0				
318.80	1354.3	318.55	1368.8	317.60	1383.8	318.75	1397.0	315.75	1436.8				
316.20	1355.9	316.15	1370.2	314.70	1385.1	316.10	1398.8	312.90	1438.2				
313.75	1357.4	313.60	1371.9	312.00	1386.7	313.60	1400.4	310.25	1439.9				
311.20	1359.1	311.10	1373.6	309.25	1388.6	311.10	1402.1	307.50	1441.8				
308.55	1360.7	308.50	1375.2	306.50	1390.3	308.40	1403.8	304.70	1443.6				
306.15	1362.3	305.95	1376.9	303.75	1392.1	306.05	1405.3	301.95	1445.4				
303.50	1364.0	303.50	1378.4	300.95	1394.0	303.45	1407.0	299.10	1447.4				
Methanolic Calcium Chloride													
0.1903 mol·kg ⁻¹		0.3798 mol·kg ⁻¹		0.7156 mol·kg ⁻¹		0.8753 mol·kg ⁻¹		1.208 mol·kg ⁻¹		1.274 mol·kg ⁻¹		1.311 mol·kg ⁻¹	
316.90	785.01	317.35	802.96	317.80	833.93	318.65	845.61	320.35	869.61	320.30	875.50	319.25	882.23
315.15	786.74	315.65	804.73	316.00	835.77	316.95	847.48	318.50	871.53	318.50	877.43	317.25	884.17
313.45	788.54	313.90	806.58	314.15	837.68	315.10	849.42	316.60	873.53	316.60	879.44	315.30	886.20
311.85	790.12	312.10	808.19	312.35	839.36	313.10	851.12	314.65	875.27	314.65	881.20	313.30	887.97
309.95	791.82	310.30	809.93	310.35	841.16	311.15	852.95	312.55	877.15	312.45	883.09	311.30	889.88
308.15	793.62	308.55	811.77	308.40	843.07	309.25	854.89	310.55	879.15	310.45	885.10	309.25	891.90
306.25	795.46	306.60	813.66	306.50	845.03	307.25	856.87	308.50	881.19	308.35	887.16	307.15	893.98
304.35	797.36	304.75	815.59	304.45	847.04	305.30	858.91	306.45	883.29	306.30	889.27	305.10	896.10
302.45	799.19	302.85	817.47	302.45	849.00	303.25	860.90	304.40	885.33	304.25	891.32	303.00	898.17
1.534 mol·kg ⁻¹		1.610 mol·kg ⁻¹		1.936 mol·kg ⁻¹		2.245 mol·kg ⁻¹		2.716 mol·kg ⁻¹		2.995 mol·kg ⁻¹		3.252 mol·kg ⁻¹	
318.80	894.92	317.80	908.80	323.15	926.84	320.70	952.06	318.80	987.35	322.65	1000.9	322.00	1012.4
316.95	896.90	315.85	910.80	321.25	928.93	318.40	954.16	316.50	989.52	320.15	1003.1	319.65	1014.6
314.95	898.95	313.80	912.89	319.05	931.00	316.25	956.35	314.10	991.79	317.70	1005.4	317.15	1016.9
312.95	900.75	311.80	914.72	317.00	932.85	314.05	958.26	311.85	993.77	315.30	1007.4	314.65	1018.9
310.95	902.68	309.70	916.68	314.90	934.88	311.80	960.32	309.40	995.91	312.80	1009.6	312.25	1021.1
308.75	904.74	307.60	918.77	312.80	936.99	309.55	962.51	306.95	998.17	310.35	1011.9	309.70	1023.5
306.70	906.84	305.55	920.90	310.60	939.28	307.25	964.74	304.55	1000.5	308.15	1014.2	307.20	1025.8
304.55	909.00	303.50	923.09	308.30	941.56	304.95	967.04	302.10	1002.9	305.65	1016.6	304.60	1028.3
302.45	911.10	301.30	925.22	306.15	943.70	302.60	969.27	299.65	1005.2	303.10	1019.0	302.10	1030.7

taken for calculating the dynamic viscosities for all solutions. The experimental uncertainties in viscosities were within $\pm 0.5\%$.

All of the measurements were made as functions of concentration [$0.0040 \leq m/(\text{mol}\cdot\text{kg}^{-1}) \leq 7.151$ and $0.1903 \leq m/(\text{mol}\cdot\text{kg}^{-1}) \leq 3.252$ for aqueous and methanolic calcium chloride solutions, respectively] and temperature ($273.15 \leq T/\text{K} \leq 323.15$). Thermostat units Schott-Geräte CT 1450, Lauda RLS 6D, or Julabo F 32 HP were used to maintain the temperature of solutions within ± 0.02 K.

Results and Discussion

The measured densities of aqueous and methanolic calcium chloride solutions are shown in Table 1 and were

found to be a linear function of temperature (Table 2) at a fixed concentration. In Figure 1, ρ versus m isotherms are plotted at 298.15 K along with the literature values. Experimental density values agree well with the reported values^{23–26} within $\pm 0.6\%$ at 298.15 K except with the values of Romanklw and Chou,²⁷ for which the deviation is $\pm 1.5\%$. However, the density values of Romanklw and Chou²⁷ deviate up to $\pm 1.8\%$ at higher concentrations from the reported values.^{25,26} The density values of methanolic solutions were comparable within $\pm 0.3\%$ with the reported values²⁸ at 286.02 K.

The measured values of speeds of sound in aqueous and methanolic calcium chloride solutions are presented in

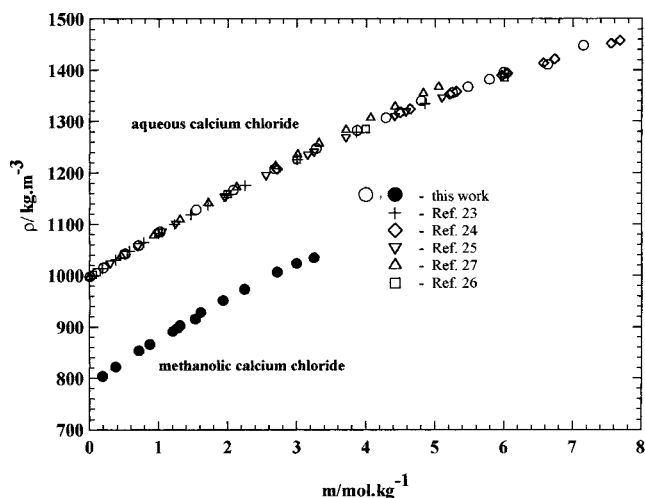


Figure 1. Plots of density, ρ , versus molality, m , isotherms at 298.15 K for aqueous and methanolic calcium chloride solutions.

Table 2. Least-Squares Fitted Values of the Constant Parameters of the Density Equation, $\rho = a - b(T/K - 273.15)$, for Aqueous and Methanolic Calcium Chloride Solutions

$m/\text{mol}\cdot\text{kg}^{-1}$	$a/\text{kg}\cdot\text{m}^{-3}$	$b/\text{kg}\cdot\text{m}^{-3}\cdot\text{K}^{-1}$	SD in $\rho/\text{kg}\cdot\text{m}^{-3}$
Aqueous Calcium Chloride			
0.0040	1006.0 ± 0.3	0.3386 ± 0.0083	0.1
0.1987	1023.5 ± 0.3	0.3456 ± 0.0074	0.2
0.5127	1051.6 ± 0.3	0.3784 ± 0.0071	0.1
0.7085	1067.8 ± 0.3	0.3776 ± 0.0071	0.2
1.021	1094.9 ± 0.2	0.4025 ± 0.0045	0.1
1.546	1138.8 ± 0.2	0.4300 ± 0.0047	0.1
2.084	1177.5 ± 0.2	0.4492 ± 0.0047	0.1
2.676	1219.3 ± 0.2	0.4723 ± 0.0045	0.1
3.281	1260.1 ± 0.2	0.5151 ± 0.0050	0.1
3.872	1295.8 ± 0.3	0.5262 ± 0.0064	0.1
4.290	1320.5 ± 0.3	0.5451 ± 0.0069	0.2
4.483	1331.4 ± 0.3	0.5512 ± 0.0073	0.2
4.802	1355.2 ± 0.1	0.6081 ± 0.0024	0.1
5.252	1370.2 ± 0.3	0.5892 ± 0.0081	0.2
5.475	1382.7 ± 0.2	0.6244 ± 0.0043	0.1
5.783	1397.9 ± 0.1	0.6421 ± 0.0027	0.1
5.991	1410.9 ± 0.4	0.6150 ± 0.0090	0.2
6.629	1426.6 ± 0.1	0.6468 ± 0.0030	0.1
7.151	1463.7 ± 0.3	0.6370 ± 0.0075	0.2
Methanolic Calcium Chloride			
0.1903	827.86 ± 0.17	0.9779 ± 0.0047	0.1
0.3798	847.01 ± 0.20	0.9955 ± 0.0052	0.1
0.7156	877.55 ± 0.20	0.9756 ± 0.0053	0.1
0.8753	890.24 ± 0.35	0.9770 ± 0.0094	0.1
1.208	915.75 ± 0.28	0.9761 ± 0.0071	0.1
1.274	921.46 ± 0.34	0.9720 ± 0.0085	0.1
1.311	927.27 ± 0.21	0.9774 ± 0.0054	0.1
1.534	939.74 ± 0.22	0.9795 ± 0.0059	0.1
1.610	953.04 ± 0.25	0.9908 ± 0.0068	0.1
1.936	976.15 ± 0.27	0.9853 ± 0.0064	0.1
2.245	997.18 ± 0.21	0.9502 ± 0.0053	0.1
2.716	1029.7 ± 0.2	0.9273 ± 0.0055	0.1
2.995	1046.6 ± 0.4	0.9263 ± 0.0093	0.2
3.252	1057.0 ± 0.3	0.9140 ± 0.0068	0.1

Table 3. Speeds of sound values in aqueous medium were in excellent agreement within $\pm 0.4\%$ with the literature values.²⁹ However, we could not compare the speeds of sound values for methanolic calcium chloride solutions due to lack of reported data.

The measured viscosities (Table 4) in aqueous calcium chloride solutions are comparable within $\pm 4.5\%$ at 298.15 K with the reported values.^{24–26,30} We could not compare the viscosities of methanolic calcium chloride solutions due to lack of literature values.

Table 3. Speeds of Sound as Functions of Concentration and Temperature for Aqueous and Methanolic Calcium Chloride Solutions

T/K	$u/\text{m}\cdot\text{s}^{-1}$	$u/\text{m}\cdot\text{s}^{-1}$	$u/\text{m}\cdot\text{s}^{-1}$	$u/\text{m}\cdot\text{s}^{-1}$	$u/\text{m}\cdot\text{s}^{-1}$	$u/\text{m}\cdot\text{s}^{-1}$	$u/\text{m}\cdot\text{s}^{-1}$
Aqueous Calcium Chloride							
	0.0040	0.1987	0.5127	0.7085	1.021	1.546	2.084
	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$
273.15	1402.2	1427.5	1462.8	1485.8	1511.1	1573.1	1616.1
278.15	1425.4	1451.3	1484.5	1503.9	1537.3	1588.7	1628.5
283.15	1443.4	1469.2	1501.7	1521.0	1550.8	1599.5	1639.0
288.15	1466.4	1486.8	1516.4	1535.1	1563.7	1611.2	1648.9
293.15	1476.2	1500.2	1530.5	1547.1	1574.9	1621.2	1656.7
298.15	1490.3	1514.0	1543.1	1559.3	1586.7	1627.9	1663.9
303.15	1502.2	1527.2	1553.7	1568.4	1596.7	1637.7	1670.8
308.15	1512.7	1536.0	1560.5	1577.5	1602.7	1644.0	1677.0
313.15	1520.8	1544.9	1568.6	1584.5	1610.3	1649.2	1681.2
318.15	1530.0	1552.2	1575.9	1591.9	1616.7	1652.3	1685.0
323.15	1541.6	1557.6	1581.3	1596.8	1620.7	1658.7	1688.5
	2.676	3.281	3.872	4.290	4.483	4.802	5.252
	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$
273.15	1659.3	1697.1	1730.1	1752.7	1761.8	1778.5	1800.2
278.15	1669.0	1704.3	1736.6	1755.5	1766.7	1783.9	1802.0
283.15	1677.1	1711.4	1742.1	1761.5	1772.3	1787.2	1802.5
288.15	1686.0	1718.0	1747.3	1767.6	1775.3	1789.7	1805.2
293.15	1692.7	1723.8	1752.4	1770.9	1780.1	1793.0	1809.3
298.15	1699.6	1730.0	1756.4	1773.2	1783.0	1795.4	1809.4
303.15	1705.2	1735.1	1760.7	1776.5	1786.5	1798.0	1810.2
308.15	1709.1	1738.9	1764.7	1777.6	1786.9	1799.2	1812.3
313.15	1714.4	1742.6	1767.4	1782.7	1789.9	1799.7	1813.4
318.15	1716.8	1745.5	1768.4	1784.3	1790.4	1801.4	1813.5
323.15	1720.6	1747.3	1770.9	1784.5	1791.5	1801.0	1821.1
	5.475	5.783	5.991	6.629	7.151		
	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$		
273.15	1803.6	1816.5					
278.15	1806.8	1818.3	1832.0				
283.15	1809.2	1820.5	1830.9	1841.4			
288.15	1811.2	1821.8	1834.0	1842.2			
293.15	1813.3	1823.9	1833.4	1842.6	1853.2		
298.15	1814.5	1824.1	1833.1	1842.7	1850.0		
303.15	1815.8	1825.8	1832.4	1842.6	1852.4		
308.15	1816.7	1825.3	1833.5	1841.8	1855.6		
313.15	1816.9	1825.0	1832.8	1841.7	1854.4		
318.15	1816.9	1824.6	1834.6	1840.9	1856.4		
323.15	1816.3	1823.7	1835.5	1839.4	1853.5		
Methanolic Calcium Chloride							
	0.1903	0.3798	0.7156	0.8753	1.208	1.274	1.311
	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$
273.15	1205.7	1226.8	1256.5	1268.2	1305.4	1305.0	1312.6
278.15	1188.6	1209.9	1239.8	1256.5	1288.9	1287.3	1295.0
283.15	1171.7	1192.9	1223.3	1241.3	1272.1	1269.2	1277.9
288.15	1155.2	1176.0	1206.1	1223.5	1254.4	1252.8	1260.8
293.15	1138.0	1159.9	1189.5	1206.8	1238.0	1236.3	1243.4
298.15	1121.3	1143.7	1173.2	1190.4	1221.9	1219.3	1226.8
303.15	1104.5	1127.0	1156.7	1173.6	1205.1	1204.0	1211.0
308.15	1088.1	1110.4	1140.3	1156.2	1189.6	1185.5	1194.5
313.15	1071.9	1094.2	1124.3	1140.6	1173.0	1169.4	1178.5
318.15	1055.7	1077.9	1108.5	1122.1	1156.8	1153.2	1163.0
323.15	1039.2	1060.3	1092.8	1107.0	1140.4	1136.2	1145.7
	1.534	1.610	1.936	2.245	2.716	2.995	3.252
	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$
273.15	1324.1	1341.0	1363.7	1390.5	1409.9	1427.8	1446.8
278.15	1302.6	1323.8	1346.1	1373.7	1392.8	1411.2	1429.6
283.15	1285.0	1305.8	1328.6	1356.2	1376.9	1394.8	1414.2
288.15	1267.0	1289.0	1311.4	1339.3	1356.5	1374.4	1398.2
293.15	1249.7	1272.2	1294.5	1322.2	1345.0	1362.2	1382.2
298.15	1232.0	1255.2	1274.7	1305.6	1327.7	1346.7	1366.3
303.15	1215.2	1239.1	1260.4	1289.2	1311.8	1328.9	1351.2
308.15	1198.8	1222.8	1243.9	1272.0	1296.1	1308.6	1335.0
313.15	1182.3	1207.1	1227.6	1257.3	1280.4	1296.4	1322.7
318.15	1166.2	1189.8	1209.5	1239.4	1264.9	1282.1	1302.7
323.15	1150.6	1170.2	1192.5	1222.1	1249.5	1266.4	1288.8

The isentropic compressibilities, κ_s , in aqueous and methanolic solutions were computed by using the following relationship:

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

The κ_s versus m isotherms at three temperatures for aqueous and methanolic calcium solutions are illustrated in Figures 2 and 3, respectively. An isothermal equation of the form

Table 4. Viscosities of Aqueous and Methanolic Calcium Chloride Solutions as Functions of Concentration and Temperature

<i>T/K</i>	$\eta/\text{mPa}\cdot\text{s}$	$\eta/\text{mPa}\cdot\text{s}$	$\eta/\text{mPa}\cdot\text{s}$	$\eta/\text{mPa}\cdot\text{s}$	$\eta/\text{mPa}\cdot\text{s}$	$\eta/\text{mPa}\cdot\text{s}$	$\eta/\text{mPa}\cdot\text{s}$
Aqueous Calcium Chloride							
	0.0040	0.1987	0.5127	0.7085	1.021	1.546	2.084
	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$
273.15	1.811	1.885	2.017	2.106	2.279	2.656	3.086
278.15	1.536	1.606	1.727	1.816	1.967	2.313	2.682
283.15	1.321	1.388	1.501	1.572	1.718	2.022	2.352
288.15	1.151	1.213	1.318	1.391	1.516	1.789	2.084
293.15	1.014	1.071	1.165	1.233	1.348	1.596	1.859
298.15	0.9013	0.9543	1.043	1.104	1.209	1.437	1.671
303.15	0.8079	0.8552	0.9364	0.9966	1.094	1.296	1.513
308.15	0.7294	0.7732	0.8497	0.9026	0.9905	1.179	1.377
313.15	0.6625	0.7041	0.7740	0.8242	0.9040	1.080	1.260
318.15	0.6055	0.6446	0.7114	0.7558	0.8324	0.9934	1.158
323.15	0.5560	0.5902	0.6559	0.6989	0.7694	0.9343	1.070
	2.676	3.281	3.872	4.290	4.483	4.802	5.252
	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$
273.15	3.792	4.763	6.028	7.252	7.999	9.811	11.49
278.15	3.291	4.131	5.221	6.231	6.859	8.349	9.721
283.15	2.890	3.613	4.538	5.426	5.926	7.170	8.301
288.15	2.564	3.196	3.995	4.748	5.212	6.256	7.195
293.15	2.285	2.848	3.541	4.199	4.595	5.489	6.294
298.15	2.055	2.556	3.169	3.745	4.098	4.861	5.553
303.15	1.860	2.306	2.864	3.360	3.672	4.334	4.933
308.15	1.693	2.097	2.587	3.033	3.304	3.892	4.456
313.15	1.549	1.915	2.361	2.765	2.993	3.521	3.965
318.15	1.423	1.759	2.162	2.523	2.732	3.196	3.593
323.15	1.318	1.624	1.992	2.308	2.500	2.915	3.270
	5.475	5.783	5.991	6.629			
	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$			
273.15	12.97	15.23	18.23	22.16			
278.15	10.94	12.75	15.14	18.26			
283.15	9.341	10.82	12.80	15.32			
288.15	8.122	9.276	10.92	12.99			
293.15	7.044	8.035	9.430	11.13			
298.15	6.202	7.041	8.223	9.573			
303.15	5.496	6.241	7.277	8.449			
308.15	4.907	5.553	6.428	7.455			
313.15	4.424	4.965	5.722	6.599			
318.15	4.009	4.471	5.139	5.898			
323.15	3.623	4.043	4.649	5.279			
Methanolic Calcium Chloride							
	0.1903	0.3798	0.7156	0.8753	1.208	1.274	1.311
	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$
273.15	0.9929	1.357	2.063	2.385	3.380	3.835	3.976
278.15	0.9901	1.461	2.022	2.142	2.977	3.352	3.473
283.15	0.8381	1.360	1.814	1.914	2.628	2.951	3.107
288.15	0.7728	1.249	1.573	1.719	2.332	2.608	2.743
293.15	0.7165	1.162	1.400	1.523	2.080	2.312	2.422
298.15	0.6639	1.069	1.254	1.444	1.878	2.064	2.156
303.15	0.6173	0.9959	1.132	1.322	1.667	1.815	1.976
308.15	0.5736	0.9197	1.047	1.198	1.503	1.632	1.771
313.15	0.5336	0.8505	0.9373	1.091	1.360	1.475	1.596
318.15	0.4974	0.7890	0.8576	0.9978	1.232	1.336	1.443
323.15	0.4646	0.7307	0.7862	0.9152	1.120	1.214	1.308
	1.534	1.610	1.936	2.245	2.716	2.995	3.252
	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$
273.15	4.929	5.762	8.678	12.33	21.76	30.59	34.23
278.15	4.271	4.956	7.345	10.25	17.69	24.80	28.24
283.15	3.722	4.296	6.242	8.626	14.53	20.10	22.59
288.15	3.256	3.751	5.375	7.319	12.00	15.98	18.50
293.15	2.831	3.295	4.623	6.267	10.10	13.20	15.31
298.15	2.603	2.942	4.034	5.465	8.562	11.12	12.78
303.15	2.402	2.660	3.503	4.747	7.343	9.323	10.74
308.15	2.139	2.369	3.088	4.153	6.339	7.985	9.196
313.15	1.905	2.105	2.732	3.647	5.499	6.892	7.810
318.15	1.714	1.884	2.431	3.221	4.809	5.997	6.770
323.15	1.546	1.694	2.175	2.861	4.223	5.239	5.900

reported earlier^{20,21} was used to fit the concentration dependence of isentropic compressibilities. In eq 2, a_1 , b_1 , and c_1 are the temperature dependent parameters, d is a constant parameter, and m is the concentration in $\text{mol}\cdot\text{kg}^{-1}$. The least-squares fitted values of the parameters of eq 2 are listed in Table 5. It is evident from Table 5 and Figures 2 and 3 that eq 2 fits the isentropic compressibility isotherms within $\pm 0.7\%$ except at $1.546 \text{ mol}\cdot\text{kg}^{-1}$, at which the deviation was within $\pm 1.3\%$ for aqueous calcium chloride solutions. However, the deviation in methanolic calcium chloride solutions was within $\pm 4.1\%$. From Figure

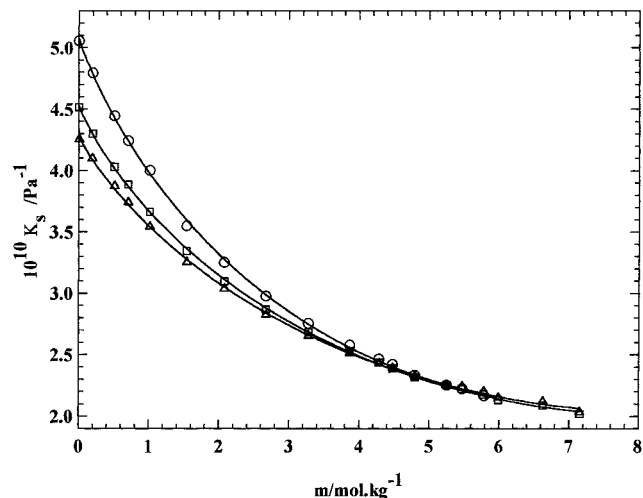


Figure 2. Variation of isentropic compressibility, κ_s , with molarity, m , at (○) 273.15 K, (□) 298.15 K, and (△) 323.15 K for aqueous calcium chloride solutions [symbols and solid curves represent experimental and calculated (from eq 2) values, respectively].

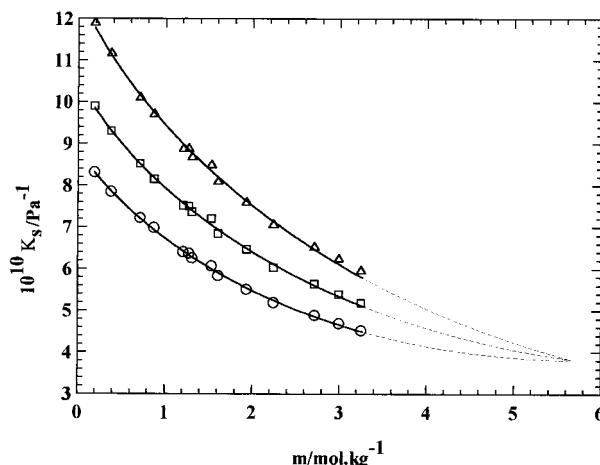


Figure 3. Variation of isentropic compressibility, κ_s , with molarity, m , at (○) 273.15 K, (□) 298.15 K, and (△) 323.15 K for methanolic calcium chloride solutions [symbols and solid curves represent experimental and calculated (from eq 2) values and broken curves represent the extrapolated isentropic compressibility values, respectively].

$$\kappa_s = a_1 + b_1 m + c_1 m^d \quad (2)$$

2 and Table 5, it has been observed that the isentropic compressibility isotherms for calcium chloride in aqueous medium converge at $5.1 \text{ mol}\cdot\text{kg}^{-1}$ with $\kappa_{s,h} = 2.275 \times 10^{-10} \text{ Pa}^{-1}$ ($\kappa_{s,h}$ is the isentropic compressibility of the hydrated sphere) and are independent of temperature. Millero et al.³¹ reported a transition at $5.9 \pm 0.5 \text{ mol}\cdot\text{kg}^{-1}$ in the isotherms of $(u - u_0)/m$ versus $m^{1/2}$, where u_0 is the speed of sound of pure water, and suggested that the transition was correlated to the hydration structure of Ca^{2+} ions. However, we could not find such a transition in the $(u - u_0)/m$ versus $m^{1/2}$ plot for the present system.

At $5.1 \text{ mol}\cdot\text{kg}^{-1}$, no free water exists in the solution and all of the water molecules are involved in the primary hydration shell of calcium chloride, resulting in a rigid structure due to strong and predominant ion-solvent interactions. At this critical concentration the inherent structure and hydrogen bonding in the bulk water are collapsed.³² The isentropic compressibility value $\kappa_{s,h} = 2.275 \times 10^{-10} \text{ Pa}^{-1}$ at the critical concentration is much lower than that of free water ($\kappa_s = 4.477 \times 10^{-10} \text{ Pa}^{-1}$). This

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

T/K	$10^{10} a_1/\text{Pa}^{-1}$	$10^{10} b_1/\text{Pa}^{-1}\cdot\text{kg}\cdot\text{mol}^{-1}$	$10^{10} c_1/\text{Pa}^{-1}\cdot\text{kg}^d\cdot\text{mol}^{-d}$	d	SD in $10^{12} \kappa_s/\text{Pa}^{-1}$
Aqueous Calcium Chloride					
273.15	5.081 ± 0.020	-2.837 ± 0.777	1.744 ± 0.756	1.167 ± 0.058	1.98
298.15	4.535 ± 0.012	-3.179 ± 0.849	2.318 ± 0.839	1.102 ± 0.032	1.29
323.15	4.280 ± 0.016	-1.689 ± 0.409	0.9604 ± 0.3923	1.184 ± 0.057	1.67
Methanolic Calcium Chloride					
273.15	8.880 ± 0.082	-5.005 ± 1.736	2.859 ± 1.652	1.209 ± 0.092	4.00
298.15	10.64 ± 0.15	-12.71 ± 18.49	10.00 ± 18.33	1.080 ± 0.132	6.98
323.15	12.84 ± 0.28	-19.33 ± 43.14	15.90 ± 42.88	1.063 ± 0.158	13.7

implies that the water molecules are rigidly held in the primary hydration sphere of calcium chloride.

In the case of methanolic calcium chloride solutions the κ_s versus m isotherms decrease smoothly and do not converge within the experimental concentration and temperature ranges of the study. However, on extrapolation the isotherms converge at $5.66 \text{ mol}\cdot\text{kg}^{-1}$ with $\kappa_s = 3.80 \times 10^{-10} \text{ Pa}^{-1}$. It is obvious from Figures 2 and 3 that the calcium chloride solutions in methanol are more compressible than those in water at a particular concentration and temperature. These indicate a different solvation dynamics of an electrolyte in methanol in comparison to water due to the fact that methanol exhibits weak ion-solvent interactions due to its poor hydrogen bonding capability and characteristic structure. It has both hydrophilic, $-\text{OH}$, and hydrophobic, $-\text{CH}_3$, groups and can form only two hydrogen bonds. On the other hand, water can participate in the formation of maximally four hydrogen bonds with the anions and other water molecules in the primary hydration sphere.

We have reported an empirical equation^{20,21} to estimate the primary hydration/solvation number, n_h , of solute as follows:

$$n_h = (\kappa_{s,\phi} - \kappa_{s,h} V_\phi) / [V_1(\kappa_{s,h} - \kappa_{s,1})] \quad (3)$$

In eq 3, $\kappa_{s,\phi}$ is the conventional apparent molal isentropic compressibility³³ of the solution, V_ϕ is the apparent molal volume of the solute, and $\kappa_{s,1}$ and V_1 are the isentropic compressibility and molar volume of the solvent, respectively. The values of apparent molal volume, V_ϕ , and apparent molal isentropic compressibilities, $\kappa_{s,\phi}$, which are required to calculate the values of n_h of both aqueous and methanolic calcium chloride solutions, are given in Tables 1S and 2S (Supporting Information), respectively. The estimated hydration/solvation numbers of calcium chloride in water and methanol media are depicted in Figure 4. The primary hydration number of calcium chloride in water at $5.1 \text{ mol}\cdot\text{kg}^{-1}$ was found to be 10.9 and is in excellent agreement with the number of available water molecules (10.9) per mole of the solute at that concentration.

Kanno³⁴ studied the Raman spectra of $\sim 5.6 \text{ mol}\cdot\text{kg}^{-1}$ aqueous CaCl_2 solutions and could not observe the symmetric stretching band. The author suggested that the chloride ions enter into the primary hydration sphere of Ca^{2+} ions and destroy the six water molecule hydration sphere of the Ca^{2+} ion. On the other hand, the hydration number of the Ca^{2+} ion has not been reported precisely except the perturbed hydration shell of the Ca^{2+} ion.^{4,5,35,36}

To split the total hydration number of calcium chloride into the individual ionic contributions, we need the primary hydration number of either cation or anion. Recently, density functional theory approach³⁷ and X-ray diffraction study³⁶ showed that the coordination number of Ca^{2+} ion is 7. Therefore, selecting the primary hydration number

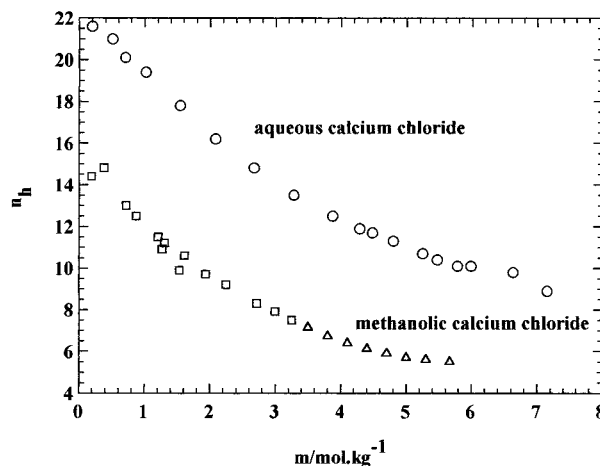


Figure 4. Variation of hydration/solvation number, n_h , with molality, m , for (○) aqueous calcium chloride and (□, △) methanolic calcium chloride solutions (circles and squares are experimental and triangles are extrapolated values, respectively).

of the Ca^{2+} ion as 7, as a reference, the primary hydration number of the Cl^- ion is estimated to be 1.95, which is lower than the reported values.^{7,8,12}

The total hydration number of calcium chloride in methanol at $5.66 \text{ mol}\cdot\text{kg}^{-1}$ using eq 3 is estimated to be 5.5, which is much smaller than that in aqueous medium. Due to lack of reliable reported primary hydration numbers of either Ca^{2+} or Cl^- ions, we could not split the total hydration number of calcium chloride in methanol.

Furthermore, we have calculated the shear relaxation time, τ , for both the aqueous and methanolic calcium chloride solutions using the relationship³⁸

$$\tau = 4\kappa_s\eta/3 \quad (4)$$

and the plots of τ versus m at different temperatures are shown in Figures 5 and 6, respectively. It is evident from Figure 5 that the variation of τ with concentration in different temperature regions is different. τ versus m is nearly linear up to ~ 3.5 , 3, and $1.5 \text{ mol}\cdot\text{kg}^{-1}$ at 323.15, 298.15, and 273.15 K, respectively, for aqueous calcium chloride solutions. Such a variation of τ with concentration is expected due to the fact that the hydrogen bonds are reinforced at low temperature^{32,36} and because of the existence of different complexes of Ca^{2+} ion³⁷ in aqueous solution. A similar explanation may also hold for methanolic calcium chloride solutions.

Acknowledgment

We express our gratitude to the Director of the laboratory for the facilities and interest in this work.

Supporting Information Available:

Tables of apparent molal volumes and apparent molal isentropic compressibility of aqueous and methanolic calcium

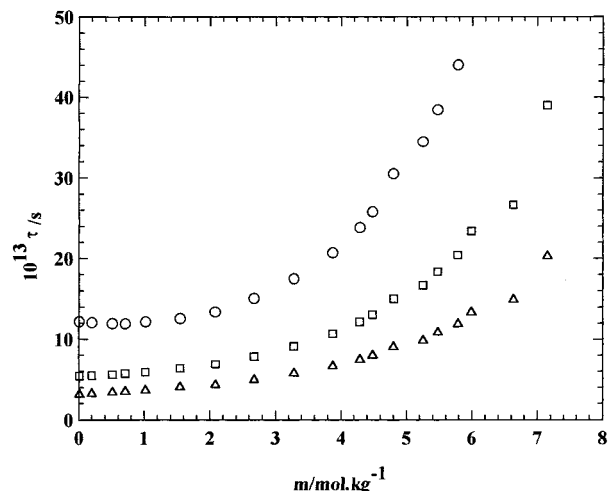


Figure 5. Variation of shear relaxation time, τ , with molality, m , at (○) 273.15 K, (□) 298.15 K, and (△) 323.15 K for aqueous calcium chloride solutions.

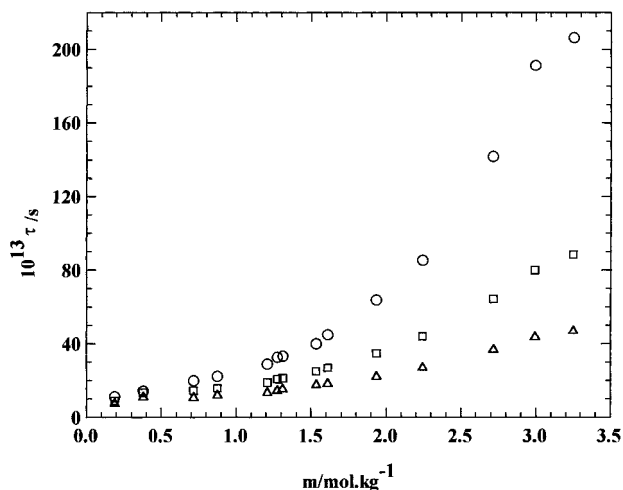


Figure 6. Variation of shear relaxation time, τ , with molality, m , at (○) 273.15 K, (□) 298.15 K, and (△) 323.15 K for methanolic calcium chloride solutions.

chloride solutions as functions of concentration and temperature. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- Marcus, Y. *Ion Solvation*; Wiley: Chichester, U.K., 1985; Chapter 4.
- Ohtaki, H.; Radnai, T. Structure and Dynamics of Hydrated Ions. *Chem. Rev.* **1993**, *93*, 1157–1204.
- Licheri, G.; Piccaluga, G.; Pinna, G. X-ray Diffraction Study of the Average Solute Species in CaCl_2 Aqueous Solutions. *J. Chem. Phys.* **1976**, *64*, 2437–2441.
- Hewish, N. A.; Neilson, G. W.; Enderby, J. E. Environment of Ca^{2+} Ions in Aqueous Solvent. *Nature* **1982**, *297*, 138–139.
- Probst, M. M.; Radnai, T.; Heinzinger, K.; Bopp, P.; Rode, B. M. Molecular Dynamics and X-ray Investigation of an Aqueous CaCl_2 Solution. *J. Phys. Chem.* **1985**, *89*, 753–759.
- Pálinkás, G.; Heinzinger, K. Hydration Shell Structure of the Calcium Ion. *Chem. Phys. Lett.* **1986**, *126*, 251–254.
- Cummings, S.; Enderby, J. E.; Howe, R. A. Ion Hydration in Aqueous Calcium Dichloride Solutions. *J. Phys. C: Solid State Phys.* **1980**, *13*, 1–8.
- Cummings, S.; Enderby, J. E.; Neilson, G. W.; Newsome, J. R.; Howe, R. A.; Howells, W. S.; Soper, A. K. Chloride Ions in Aqueous Solutions. *Nature* **1980**, *287*, 714–716.
- Caminiti, R.; Licheri, G.; Paschina, G.; Piccaluga, G.; Pinna, G. X-ray Diffraction and Structural Properties of Aqueous Solutions of Divalent Metal-Chlorides. *Z. Naturforsch. A* **1980**, *35a*, 1361–1367.
- Chandrasekhar, J.; Spellmeyer, D. C.; Jorgensen, W. L. Energy Component Analysis for Dilute Aqueous Solutions of Li^+ , Na^+ , F^- and Cl^- Ions. *J. Am. Chem. Soc.* **1984**, *106*, 903–910.
- Marchese, F. T.; Beveridge, D. L. Pattern Recognition Approach to the Analysis of Geometrical Features of Solvation: Application to the Aqueous Hydration of Li^+ , Na^+ , K^+ , F^- , and Cl^- . *J. Am. Chem. Soc.* **1984**, *106*, 3713–3722.
- Bounds, D. G. A Molecular Dynamics Study of the Structure of Water Around the Ions Lithium (1+), Sodium (1+), Potassium (1+), Calcium (2+), Nickel (2+) and Chloride. *Mol. Phys.* **1985**, *54*, 1335–1355.
- Vogrin, F. J.; Malinowski, E. R. Solvation Number of Strong Electrolytes in Methanol Determined From Temperature Effects on Proton Shift. *J. Am. Chem. Soc.* **1975**, *97*, 4876–4879.
- Kahlow, M. A.; Jarzeba, W.; Kang, T. J.; Barbara, P. F. Femto-second Resolved Solvation Dynamics in Polar Solvents. *J. Chem. Phys.* **1989**, *90*, 151–158.
- Phelps, D. K.; Weaver, M. J.; Ladanyi, B. M. Solvent Dynamic Effects in Electron Transfer: Molecular Dynamics Simulation of Reactions in Methanol. *Chem. Phys.* **1993**, *176*, 575–588.
- Roy, S.; Bagchi, B. Microscopic Theory of Ion Solvation Dynamics in Liquid Methanol. *J. Chem. Phys.* **1994**, *101*, 4150–4155.
- Bockris, J. O'M.; Saluja, P. P. S. Ionic Solvation Numbers from Compressibilities and Ionic Vibration Potentials Measurements. *J. Phys. Chem.* **1972**, *76*, 2140–2151.
- Endo, H.; Nomoto, O. Structural Absorption of Ultrasonic Waves in Aqueous Solutions of Alkali Halides. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 217–226.
- Onori, G. Ionic Hydration in Sodium Chloride Solutions. *J. Chem. Phys.* **1988**, *89*, 510–516.
- Rohman, N.; Dass, N. N.; Mahiuddin, S. Isentropic Compressibility of Aqueous and Methanolic Sodium Thiocyanate Solutions. *J. Chem. Eng. Data* **1999**, *44*, 465–472.
- Rohman, N.; Dass, N. N.; Mahiuddin, S. Speeds of Sound and viscosities of Potassium Thiocyanate in Water, Methanol, and Propylene Carbonate. *Aust. J. Chem.* **2000**, *53*, 463–469.
- Vogel, A. I. *A Textbook of Practical Organic Chemistry*, 3rd ed.; ELBS: Longman, U.K., 1975; p 268.
- Washburn, E. W., Ed. *International Critical Tables of Numerical Data, Physics, Chemistry, and Technology*; McGraw-Hill: New York, 1928; Vol. III, p 72.
- Lyons, P. A.; Riley, J. F. Diffusion coefficients for Aqueous Solutions of Calcium Chloride and Cesium Chloride at 25 °C. *J. Am. Chem. Soc.* **1954**, *76*, 5216–5220.
- Goncalves, F. A.; Kestin, J. The Viscosity of CaCl_2 Solutions in the Range 20–50 °C. *Ber. Bunsen-Ges. Phys. Chem.* **1979**, *83*, 24–27.
- Isono, T. Density, Viscosity, and Electrolytic Conductivity of Concentrated Aqueous Electrolyte Solutions at Several Temperatures. Alkaline-Earth Chlorides, LaCl_3 , Na_2SO_4 , NaNO_3 , NaBr , KNO_3 , KBr , and $\text{Cd}(\text{NO}_3)_2$. *J. Chem. Eng. Data* **1984**, *29*, 45–52.
- Romankiw, L. A.; Chou, I.-M. Densities of Aqueous NaCl , KCl , MgCl_2 , and CaCl_2 Binary Solutions in the Concentration Range 0.5–6.1 m at 25, 30, 35, 40, and 45 °C. *J. Chem. Eng. Data* **1983**, *28*, 300–305.
- International Critical Tables of Numerical Data, Physics, Chemistry, and Technology*; Washburn, E. W., Ed.; McGraw-Hill: New York, 1929; Vol. V, p 14.
- Onori, G. Adiabatic Compressibility and Local Structure in Aqueous Solutions of Strong II–I Electrolytes. *Acoust. Lett.* **1990**, *14*, 7–16.
- International Critical Tables of Numerical Data, Physics, Chemistry, and Technology*; Washburn, E. W., Ed.; McGraw-Hill: New York, 1928; Vol. III, p 140.
- Millero, F. J.; Fernandez, M.; Vinokurova, F. Transitions in the Speed of Sound in Concentrated Aqueous Electrolyte Solutions. *J. Phys. Chem.* **1985**, *89*, 1062–1064.
- Kanno, H.; Hiraishi, J. Raman Spectroscopic Study of Aqueous LiX and CaX_2 Solutions ($\text{X} = \text{Cl}, \text{Br}, \text{and I}$) in the Glassy State. *J. Phys. Chem.* **1983**, *87*, 3664–3670.
- Blandamer, M. J. Apparent Molar Isentropic Compression. A Critical Commentary. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 1057–1062.
- Kanno, H. Correlation of the Raman ν_1 Bands of Aqueous Divalent Metal Ions with the Cation-Hydrated Water Distance. *J. Raman Spectr.* **1987**, *18*, 301–304.

- (35) Yamaguchi, T.; Shun-ichi, H.; Ohtaki, H. X-ray Diffraction Study of Calcium(II) Chloride Hydrate Melts: $\text{CaCl}_2 \cdot \text{RH}_2\text{O}$ ($R = 4.0, 5.6, 6.0,$ and 8.6). *Inorg. Chem.* **1989**, *28*, 2434–2439.
- (36) Smirnov, P.; Yamagami, M.; Wakita, H.; Yamaguchi, T. An X-ray Diffraction Study on Concentrated Aqueous Calcium Nitrate Solutions at Subzero Temperatures. *J. Mol. Liq.* **1997**, *73*, 305–316.
- (37) Pavlov, M.; Siegbahn, P. E. M.; Sandström, M.; Hydration of Beryllium, Magnesium, Calcium, and Zinc Ions Using Density Functional Theory. *J. Phys. Chem. A* **1998**, *102*, 219–228.
- (38) Kinsler, L. E.; Frey, A. R. *Fundamentals of Acoustics*; Wiley Eastern: New Delhi, India, 1978; p 224.

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