Thermochimica Acta 487 (2009) 1–7

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Densities and apparent molar volumes of myo-inositol in aqueous solutions of alkaline earth metal salts at different temperatures

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ARTICLE INFO

Article history:
Received 21 July 2008
Received in revised form 31 December 2008
Accepted 1 January 2009
Available online 15 January 2009

Keywords:
Apparent molar volumes
Myo-inositol
Alkaline earth metal chlorides

ABSTRACT

Apparent molar volumes (V_φ) of myo-inositol in water and in aqueous solutions of alkaline earth metal salt MCl_2 (M = Mg, Ca, Sr, Ba) under various concentrations and temperatures ranging from 293.15 K to 318.15 K have been measured by a precise vibrating-tube digital densimeter. The calculated partial molar volumes (V_φ^0) have been used to obtain the corresponding transfer partial molar volumes ($\Delta_{trs}V_\varphi^0$) of the polyol from water to various salt solutions. The experimental results show that V_φ^0 of myo-inositol increases with enhancement of salt concentration and ascension of temperature. The interpretation is that these results arise from the dominant interaction of MCl_2 with the charged centers of myo-inositol. $\Delta_{trs}V_\varphi^0$ of myo-inositol increases with enhancement of concentration of MCl_2 while decreases with the ascension of temperature. The change tendency of volume property of myo-inositol has been rationalized in the light of weak interactions between myo-inositol molecules, the polyol molecules and coexistent ions as well as the polyol molecules and solvent molecules with a cosphere overlap model applied.

1. Introduction

Myo-inositol (MI), a cyclic polyol, is the most biologically abundant stereo-isomer of the inositols. It is an essential nutrient for most living cells, including protozoa [1,2]. Kiyoshima et al. [3,4] also found the contents of MI and mannitol in both human and rat brain tissues. Inositol levels change in association with ischemic state and edema in animal models [5,6]. MI plays multiple important roles in all organisms [7] and it can be found in many biological fluids, which are not pure water but complicated aqueous solution containing many kinds of bio-molecules and ions. So investigating the influence of solvent components on properties of MI is essential for its research and biochemical engineering application. There are some investigations on properties of MI [8–10], but no systematic studies, to our best knowledge, exist on the voluminal properties of MI in alkaline earth metal salt solutions although ions of alkaline earth metals are often found in bio-system. As a continuation of our earlier work in obtaining thermodynamic data of aqueous solutions [9–13] of MI and for complete understanding of the influence of electrolytes on properties of the polyol, in this paper, we present the densities (ρ), apparent volumes (V_φ), apparent molar volume (V_φ^0) in aqueous MCl_2 (M = Mg, Ca, Sr, Ba) solutions and transfer molar volumes ($\Delta_{trs}V_\varphi^0$) from water to aqueous MCl_2 solutions at different temperatures (from 293.15 K to 318.15 K). Alkaline earth metal salts (MCl_2) have been chosen for this part study to observe the relative effects of the change of cation of electrolyte, especially change of radius of cation.

2. Experimental

2.1. Materials

Myo-inositol (MI) was a product of Aldrich, and the stated purity was better than 99%. It was dried under reduced pressure at 323 K before use. Magnesium chloride ($MgCl_2$), calcium chloride ($CaCl_2$), strontium chloride ($SrCl_2$) and barium chloride ($BaCl_2$) were all analytical reagents (purity > 99%) purchased from Shanghai Chemical Reagent Company (Shanghai, China), recrystallized from distilled water and dried under reduced pressure at 393 K before use. All of the reagents were stored over P_2O_5 in a vacuum desiccator for 72 h at room temperature prior to use. Twice-distilled water was used in the experiment. Solutions of different compositions were prepared by weight using a METTLER TOLEDO AG 135 analytical balance with a precision of $\pm 1 \times 10^{-5}$ g. All liquids were degassed with ultrasonic waves and used within 12 h of preparation.

2.2. Density measurements

The densities of solutions were determined by a vibrating-tube digital densimeter (DMA 5000 Anton Paar) thermostated

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doi:10.1016/j.tca.2009.01.003

Table 1
The densities (ρ) of MI—salt aqueous solutions and the apparent molar volumes (V_φ) of MI at different temperatures.

$m_{inositol}$/mol kg^{-1}	ρ/g cm^{-3}	V_φ/cm^3 mol^{-1}	ρ/g cm^{-3}	V_φ/cm^3 mol^{-1}	ρ/g cm^{-3}	V_φ/cm^3 mol^{-1}	ρ/g cm^{-3}	V_φ/cm^3 mol^{-1}	ρ/g cm^{-3}	V_φ/cm^3 mol^{-1}
	293.15 K		298.15 K		303.15 K		308.15 K		318.15 K	
H_2O										
0.09984	1.006205	99.46 ± 0.12	1.004972	100.59 ± 0.20	1.003508	101.61 ± 0.15	1.001835	102.58 ± 0.18	0.997362	103.98 ± 0.24
0.19881	1.014161	99.96 ± 0.21	1.012856	101.10 ± 0.12	1.011331	102.08 ± 0.12	1.009601	102.99 ± 0.12	1.005546	104.35 ± 0.13
0.29711	1.021023	100.46 ± 0.09	1.019662	101.50 ± 0.09	1.018083	102.48 ± 0.14	1.016307	103.52 ± 0.15	1.012215	104.77 ± 0.03
0.39659	1.029428	100.86 ± 0.15	1.027989	101.95 ± 0.17	1.026347	102.96 ± 0.11	1.024521	103.80 ± 0.18	1.020272	104.97 ± 0.11
0.49524	1.036371	101.28 ± 0.28	1.034883	102.35 ± 0.23	1.033191	103.38 ± 0.21	1.031312	104.35 ± 0.22	1.027054	105.36 ± 0.16
m_{MgCl_2} = 0.09953 mol kg^{-1}										
0.09929	1.014249	100.09 ± 0.22	1.012982	101.10 ± 0.19	1.011497	102.06 ± 0.11	1.009811	102.98 ± 0.12	1.005889	104.40 ± 0.15
0.19888	1.021770	100.65 ± 0.31	1.020442	101.71 ± 0.21	1.018897	102.57 ± 0.15	1.017159	103.53 ± 0.19	1.013155	104.93 ± 0.25
0.29722	1.028919	101.15 ± 0.16	1.027526	102.24 ± 0.23	1.025924	103.08 ± 0.16	1.024137	104.03 ± 0.07	1.020217	105.44 ± 0.20
0.39593	1.036658	101.65 ± 0.13	1.035200	102.72 ± 0.09	1.033543	103.49 ± 0.13	1.031700	104.52 ± 0.11	1.027487	105.91 ± 0.10
0.49559	1.043691	102.10 ± 0.06	1.042180	103.19 ± 0.15	1.040476	103.96 ± 0.20	1.038592	104.97 ± 0.13	1.034344	106.36 ± 0.09
m_{MgCl_2} = 0.29436 mol kg^{-1}										
0.09940	1.029884	100.51 ± 0.10	1.028553	101.56 ± 0.22	1.027024	102.58 ± 0.11	1.025317	103.48 ± 0.21	1.021186	104.79 ± 0.18
0.19866	1.036945	101.07 ± 0.19	1.035561	102.15 ± 0.11	1.033979	103.14 ± 0.07	1.032219	104.14 ± 0.10	1.028436	105.24 ± 0.15
0.29799	1.044176	101.58 ± 0.25	1.042727	102.65 ± 019	1.041093	103.64 ± 0.09	1.039285	104.64 ± 0.02	1.034854	105.54 ± 0.21
0.39604	1.051120	102.07 ± 0.22	1.049615	103.14 ± 0.16	1.047930	104.14 ± 0.13	1.046078	105.13 ± 0.21	1.041914	106.03 ± 0.10
0.49559	1.059591	102.52 ± 0.13	1.058023	103.59 ± 0.23	1.056284	104.59 ± 0.21	1.054388	105.59 ± 0.18	1.049746	106.29 ± 0.05
m_{MgCl_2} = 0.48305 mol kg^{-1}										
0.09942	1.044769	100.92 ± 0.26	1.043376	101.94 ± 0.30	1.041805	102.92 ± 0.11	1.040068	103.82 ± 0.21	1.035816	105.16 ± 0.20
0.19910	1.051580	101.48 ± 0.31	1.050139	102.60 ± 0.19	1.048520	103.58 ± 0.23	1.046738	104.53 ± 0.14	1.042726	105.64 ± 0.06
0.29744	1.057685	101.98 ± 0.18	1.056195	103.10 ± 0.20	1.054530	104.08 ± 0.18	1.052706	105.03 ± 0.19	1.048616	105.94 ± 0.21
0.39637	1.066225	102.47 ± 0.09	1.064674	103.59 ± 0.08	1.062949	104.58 ± 0.12	1.061077	105.53 ± 0.18	1.056753	106.44 ± 0.15
0.49537	1.072521	102.93 ± 0.23	1.070918	104.05 ± 0.11	1.069156	105.03 ± 0.09	1.067244	105.98 ± 0.20	1.063010	106.67 ± 0.11
m_{MgCl_2} = 0.66604 mol kg^{-1}										
0.09979	1.059504	101.37 ± 0.16	1.058065	102.37 ± 0.06	1.056466	103.33 ± 0.12	1.054649	104.20 ± 0.12	1.050708	105.58 ± 0.12
0.19877	1.065944	101.84 ± 0.35	1.064456	102.93 ± 0.12	1.062806	103.89 ± 0.22	1.061005	104.86 ± 0.21	1.056993	105.98 ± 0.07
0.29775	1.072826	102.34 ± 0.29	1.071289	103.43 ± 0.0	1.069591	104.39 ± 0.23	1.067749	105.36 ± 0.19	1.063578	106.18 ± 0.18
0.39714	1.080434	102.83 ± 0.18	1.078838	103.93 ± 18	1.077096	104.89 ± 0.17	1.075220	105.86 ± 0.06	1.070885	106.67 ± 0.15
0.49524	1.086290	103.29 ± 0.07	1.084655	104.38 ± 0.13	1.082865	105.35 ± 0.19	1.080922	106.31 ± 0.25	1.078607	107.03 ± 0.21
m_{MgCl_2} = 0.93300 mol kg^{-1}										
0.09964	1.081295	101.70 ± 0.24	1.079789	102.68 ± 0.16	1.078142	103.63 ± 0.06	1.076357	104.49 ± 0.15	1.072082	105.89 ± 0.16
0.19804	1.087585	102.17 ± 0.16	1.086037	103.25 ± 0.11	1.084345	104.19 ± 0.20	1.082521	105.16 ± 0.19	1.079229	106.32 ± 0.18
0.29704	1.094391	102.67 ± 0.39	1.092781	103.75 ± 0.21	1.091040	104.69 ± 0.19	1.089190	105.66 ± 0.24	1.085116	106.55 ± 0.03
0.39602	1.100855	103.16 ± 0.26	1.099216	104.25 ± 0.09	1.097440	105.19 ± 0.12	1.095533	106.15 ± 0.08	1.092576	107.05 ± 0.12
0.49509	1.108289	103.62 ± 0.20	1.106596	104.70 ± 0.24	1.104781	105.65 ± 0.11	1.102846	106.61 ± 0.13	1.097715	107.50 ± 0.20
m_{CaCl_2} = 0.09955 mol kg^{-1}										
0.08931	1.014481	100.03 ± 0.11	1.013198	101.03 ± 0.06	1.01166	102.04 ± 0.21	1.009921	102.91 ± 0.17	1.005883	104.45 ± 0.15
0.19818	1.022356	100.55 ± 0.15	1.021006	101.66 ± 0.21	1.019448	102.67 ± 0.31	1.017690	103.57 ± 0.26	1.013652	104.48 ± 0.20
0.29770	1.030604	101.05 ± 0.13	1.029185	102.17 ± 0.11	1.027577	103.17 ± 0.14	1.025753	104.07 ± 0.13	1.021352	104.98 ± 0.18
0.39725	1.037054	101.54 ± 0.20	1.035582	102.66 ± 0.16	1.034159	103.67 ± 0.20	1.032058	104.57 ± 0.09	1.027855	105.47 ± 0.09
0.49555	1.045463	101.99 ± 0.07	1.043920	103.12 ± 0.02	1.042207	104.12 ± 0.11	1.040295	105.02 ± 0.18	1.035655	105.93 ± 0.06
m_{CaCl_2} = 0.29303 mol kg^{-1}										
0.08964	1.032410	100.43 ± 0.12	1.031014	101.46 ± 0.15	1.029438	102.46 ± 0.19	1.027658	103.36 ± 0.08	1.023612	104.73 ± 0.20
0.19829	1.039702	101.07 ± 0.20	1.038247	102.17 ± 0.13	1.036638	103.19 ± 0.14	1.034781	104.16 ± 0.21	1.030664	105.39 ± 0.19
0.29722	1.047753	101.58 ± 0.10	1.046237	102.67 ± 0.19	1.044555	103.68 ± 0.21	1.042675	104.66 ± 0.23	1.038204	105.56 ± 0.06
0.39699	1.054536	102.07 ± 0.18	1.052970	103.17 ± 0.09	1.051267	104.18 ± 0.09	1.049316	105.16 ± 0.19	1.045044	106.06 ± 0.18
0.49630	1.061614	102.53 ± 0.15	1.059988	103.62 ± 0.21	1.058246	104.64 ± 0.23	1.056242	105.61 ± 0.08	1.051895	106.51 ± 0.11
m_{CaCl_2} = 0.48148 mol kg^{-1}										
0.08911	1.049069	100.85 ± 0.09	1.047575	101.86 ± 0.23	1.045922	102.85 ± 0.32	1.04407	103.76 ± 0.32	1.039511	105.22 ± 0.12
0.19877	1.056515	101.55 ± 0.16	1.054963	102.67 ± 0.12	1.053265	103.72 ± 0.12	1.051363	104.65 ± 0.12	1.047161	105.72 ± 0.19
0.29764	1.064074	102.04 ± 0.21	1.062464	103.17 ± 0.09	1.060719	104.23 ± 0.15	1.058772	105.15 ± 0.09	1.054506	106.02 ± 0.15
0.39703	1.071265	102.54 ± 0.13	1.069609	103.67 ± 0.17	1.067811	104.72 ± 0.08	1.065832	105.65 ± 0.13	1.061086	106.52 ± 0.06
0.49504	1.076781	102.99 ± 0.18	1.075092	104.12 ± 0.25	1.073274	105.17 ± 0.24	1.071238	106.09 ± 0.14	1.066837	106.97 ± 0.11
m_{CaCl_2} = 0.69410 mol kg^{-1}										
0.08942	1.069354	101.28 ± 0.22	1.067343	102.26 ± 0.29	1.065378	103.24 ± 0.35	1.065312	104.10 ± 0.25	1.062213	105.56 ± 0.06
0.19888	1.076623	102.00 ± 0.13	1.075863	103.10 ± 0.09	1.074165	104.12 ± 0.11	1.072912	105.08 ± 0.12	1.071514	105.97 ± 0.14
0.29817	1.084431	102.50 ± 0.19	1.083537	103.61 ± 0.12	1.081296	104.63 ± 0.16	1.079604	105.58 ± 0.04	1.078543	106.47 ± 0.20
0.39679	1.091463	102.99 ± 0.07	1.088635	104.10 ± 0.18	1.087171	105.12 ± 0.06	1.086575	106.07 ± 0.13	1.085381	106.97 ± 0.08
0.49584	1.097243	103.45 ± 0.11	1.095467	104.55 ± 0.21	1.093976	105.58 ± 0.22	1.092795	106.53 ± 0.08	1.091164	107.21 ± 0.10
m_{CaCl_2} = 0.93763 mol kg^{-1}										
0.08990	1.093944	101.57 ± 0.23	1.092196	102.59 ± 0.31	1.090348	103.47 ± 0.26	1.088321	104.36 ± 0.29	1.083103	106.01 ± 0.12
0.19890	1.098618	102.40 ± 0.16	1.096843	103.48 ± 0.16	1.094967	104.53 ± 0.20	1.092912	105.52 ± 0.18	1.088508	106.50 ± 0.14
0.29751	1.104820	102.90 ± 0.11	1.103007	103.98 ± 0.05	1.101109	105.03 ± 0.07	1.09901	106.02 ± 0.27	1.094556	106.91 ± 0.04

Table 1 (*Continued*)

$m_{inositol}$/mol kg^{-1}	ρ/g cm^{-3}	V_φ/cm^3 mol^{-1}	ρ/g cm^{-3}	V_φ/cm^3 mol^{-1}	ρ/g cm^{-3}	V_φ/cm^3 mol^{-1}	ρ/g cm^{-3}	V_φ/cm^3 mol^{-1}	ρ/g cm^{-3}	V_φ/cm^3 mol^{-1}
	293.15 K		298.15 K		303.15 K		308.15 K		318.15 K	
0.39763	1.110486	103.40 ± 0.15	1.108639	104.47 ± 0.17	1.106709	105.52 ± 0.12	1.104577	106.52 ± 0.11	1.100070	107.45 ± 0.16
0.49592	1.117920	103.85 ± 0.05	1.116028	104.93 ± 0.22	1.114063	105.98 ± 0.24	1.111896	106.97 ± 0.15	1.107135	108.19 ± 0.20
m_{SrCl_2} = 0.09897 mol kg^{-1}										
0.10067	1.020147	99.99 ± 0.09	1.018836	100.99 ± 0.09	1.017307	101.99 ± 0.09	1.015578	102.88 ± 0.13	1.011582	104.35 ± 0.10
0.19848	1.027726	100.48 ± 0.12	1.026346	101.55 ± 0.15	1.024763	102.56 ± 0.15	1.022982	103.48 ± 0.10	1.018905	104.62 ± 0.14
0.29764	1.034918	100.98 ± 0.18	1.033483	102.05 ± 0.13	1.031842	103.06 ± 0.21	1.030014	103.98 ± 0.09	1.025851	104.92 ± 0.16
0.39637	1.042344	101.48 ± 0.14	1.040848	102.56 ± 0.21	1.038151	103.55 ± 0.06	1.037278	104.47 ± 0.20	1.032982	105.42 ± 0.08
0.49540	1.049196	101.93 ± 0.16	1.047643	102.10 ± 0.24	1.045898	104.01 ± 0.13	1.043981	104.93 ± 0.03	1.039657	105.87 ± 0.15
m_{SrCl_2} = 0.28887 mol kg^{-1}										
0.09975	1.047075	100.39 ± 0.13	1.045609	101.41 ± 0.23	1.043942	102.42 ± 0.15	1.042098	103.32 ± 0.30	1.037955	104.64 ± 0.05
0.19796	1.053908	101.02 ± 0.15	1.052395	102.15 ± 0.16	1.050691	103.08 ± 0.11	1.048809	104.04 ± 0.10	1.044571	105.07 ± 0.14
0.29755	1.061631	101.52 ± 0.08	1.060063	102.65 ± 0.11	1.058305	103.58 ± 0.16	1.056378	104.54 ± 0.21	1.052064	105.45 ± 0.19
0.39758	1.068402	102.02 ± 0.20	1.066754	103.14 ± 0.08	1.064912	104.08 ± 0.20	1.062995	105.04 ± 0.05	1.058221	105.94 ± 0.09
0.49507	1.074548	102.47 ± 0.19	1.072880	103.59 ± 0.21	1.071035	104.53 ± 0.26	1.069032	105.49 ± 0.15	1.064584	106.29 ± 0.16
m_{SrCl_2} = 0.46906 mol kg^{-1}										
0.10003	1.073783	100.81 ± 0.08	1.072177	101.84 ± 0.20	1.070754	102.83 ± 0.19	1.068804	103.75 ± 0.10	1.064512	105.13 ± 0.06
0.19892	1.080796	101.53 ± 0.11	1.079145	102.62 ± 0.18	1.077321	103.64 ± 0.04	1.075338	104.55 ± 0.09	1.070935	105.75 ± 0.09
0.29770	1.087952	102.03 ± 0.15	1.086251	103.12 ± 0.16	1.084383	104.14 ± 0.12	1.082361	105.05 ± 0.15	1.077901	105.96 ± 0.11
0.39648	1.095746	102.52 ± 0.20	1.093983	103.62 ± 0.06	1.092066	104.63 ± 0.06	1.090011	105.55 ± 0.16	1.085199	106.45 ± 0.19
0.49546	1.100599	102.98 ± 0.11	1.098811	104.07 ± 0.12	1.096864	105.09 ± 0.22	1.094772	106.00 ± 0.21	1.090248	106.90 ± 0.14
m_{SrCl_2} = 0.64118 mol kg^{-1}										
0.09918	1.097111	101.24 ± 0.21	1.095385	102.25 ± 0.15	1.093504	103.24 ± 0.36	1.091471	104.09 ± 0.36	1.086998	105.49 ± 0.09
0.19888	1.105805	101.91 ± 0.19	1.104031	102.99 ± 0.20	1.102079	104.00 ± 0.19	1.099905	104.96 ± 0.21	1.095917	105.98 ± 0.12
0.29753	1.112890	102.41 ± 0.08	1.111077	103.49 ± 0.13	1.109105	104.50 ± 0.13	1.106992	105.47 ± 0.15	1.102874	106.38 ± 0.21
0.39631	1.117575	102.90 ± 0.20	1.115704	103.99 ± 0.09	1.113339	104.99 ± 0.18	1.111185	105.96 ± 0.19	1.106394	106.88 ± 0.19
0.49551	1.124558	103.36 ± 0.23	1.122657	104.44 ± 0.14	1.120619	105.45 ± 0.23	1.118452	106.41 ± 0.22	1.113645	107.13 ± 0.11
m_{SrCl_2} = 0.91565 mol kg^{-1}										
0.10008	1.137973	101.55 ± 0.23	1.136047	102.58 ± 0.32	1.122993	103.50 ± 0.41	1.131828	104.39 ± 0.23	1.127446	105.81 ± 0.12
0.19829	1.144433	102.24 ± 0.16	1.142479	103.32 ± 0.12	1.140394	104.31 ± 0.25	1.138187	105.26 ± 0.16	1.133389	106.26 ± 0.08
0.29832	1.150230	102.74 ± 0.18	1.148243	103.82 ± 0.15	1.146423	104.81 ± 0.13	1.143879	105.76 ± 0.25	1.138749	106.66 ± 0.13
0.39657	1.156125	103.23 ± 0.09	1.154101	104.32 ± 0.46	1.151957	105.31 ± 0.19	1.149788	106.26 ± 0.14	1.144714	107.16 ± 0.20
0.49500	1.161197	103.69 ± 0.25	1.159149	104.77 ± 0.11	1.156972	105.76 ± 0.21	1.154687	106.70 ± 0.23	1.149801	107.41 ± 0.26
m_{BaCl_2} = 0.09824 mol kg^{-1}										
0.08955	1.025131	99.92 ± 0.26	1.023804	100.92 ± 0.21	1.022254	101.92 ± 0.19	1.020524	102.83 ± 0.19	1.016498	104.17 ± 0.16
0.19840	1.033377	100.43 ± 0.14	1.031984	101.54 ± 0.19	1.030381	102.66 ± 0.05	1.028581	103.58 ± 0.12	1.024466	104.68 ± 0.11
0.29722	1.040818	100.93 ± 0.13	1.039362	102.04 ± 0.13	1.037704	103.16 ± 0.13	1.03586	104.09 ± 0.11	1.031661	104.98 ± 0.21
0.39635	1.048271	101.43 ± 0.18	1.046752	102.53 ± 0.16	1.045041	103.66 ± 0.15	1.043152	104.58 ± 0.23	1.038872	105.48 ± 0.17
0.49522	1.054788	101.88 ± 0.30	1.053221	102.98 ± 0.25	1.051461	104.11 ± 0.23	1.049527	105.04 ± 0.24	1.045176	105.73 ± 0.23
m_{BaCl_2} = 0.28388 mol kg^{-1}										
0.08911	1.064173	100.40 ± 0.09	1.062648	101.39 ± 0.12	1.066934	102.39 ± 0.32	1.059046	103.28 ± 0.35	1.054661	104.67 ± 0.25
0.19906	1.071698	100.96 ± 0.15	1.070123	102.03 ± 0.15	1.068357	103.08 ± 0.16	1.06642	104.01 ± 0.12	1.062073	105.19 ± 0.30
0.29779	1.079581	101.46 ± 0.23	1.077940	102.54 ± 0.12	1.076233	103.58 ± 0.11	1.074245	104.51 ± 0.24	1.069922	105.39 ± 0.25
0.39642	1.084764	101.96 ± 0.30	1.083088	103.03 ± 0.20	1.081233	104.07 ± 0.17	1.079214	105.01 ± 0.16	1.074731	105.89 ± 0.13
0.49579	1.093801	102.41 ± 0.21	1.092064	103.49 ± 0.18	1.090159	104.53 ± 0.08	1.088094	105.46 ± 0.22	1.083527	106.34 ± 0.18
m_{BaCl_2} = 0.45658 mol kg^{-1}										
0.09964	1.104506	100.80 ± 0.25	1.102786	101.82 ± 0.32	1.100901	102.83 ± 0.23	1.098859	103.73 ± 0.25	1.093027	105.09 ± 0.06
0.19844	1.109352	101.46 ± 0.12	1.107603	102.54 ± 0.18	1.105681	103.52 ± 0.12	1.103607	104.46 ± 0.13	1.099035	105.46 ± 0.13
0.29744	1.116015	101.96 ± 0.14	1.114209	103.04 ± 0.16	1.112245	104.02 ± 0.11	1.110358	104.97 ± 0.16	1.105723	105.86 ± 0.14
0.39611	1.121731	102.46 ± 0.06	1.119883	103.54 ± 0.09	1.117889	104.51 ± 0.05	1.115741	105.46 ± 0.19	1.111055	106.36 ± 0.19
0.49498	1.127856	102.91 ± 0.21	1.125972	103.99 ± 0.12	1.123749	104.97 ± 0.22	1.121563	105.91 ± 0.24	1.117017	106.51 ± 0.21
m_{BaCl_2} = 0.61882 mol kg^{-1}										
0.09970	1.138209	101.19 ± 0.23	1.136329	102.18 ± 0.25	1.134298	103.16 ± 0.28	1.132123	104.02 ± 0.15	1.127421	105.54 ± 0.19
0.19903	1.144248	101.90 ± 0.21	1.142324	103.05 ± 0.32	1.139847	104.07 ± 0.16	1.137783	105.06 ± 0.37	1.132991	105.95 ± 0.11
0.29762	1.149951	102.40 ± 0.16	1.149950	103.55 ± 0.04	1.145898	104.57 ± 0.13	1.143665	105.56 ± 0.13	1.138656	106.25 ± 0.05
0.39697	1.155774	102.90 ± 0.18	1.153772	104.05 ± 0.11	1.151633	105.06 ± 0.21	1.149363	106.06 ± 0.25	1.144459	106.65 ± 0.13
0.49573	1.161533	103.35 ± 0.09	1.160336	104.50 ± 0.20	1.158176	105.52 ± 0.28	1.155657	106.51 ± 0.19	1.150268	107.30 ± 0.20
m_{BaCl_2} = 0.89137 mol kg^{-1}										
0.09957	1.195283	101.50 ± 0.20	1.193785	102.51 ± 0.39	1.192301	103.41 ± 0.35	1.191883	104.32 ± 0.28	1.185489	105.88 ± 0.11
0.19831	1.200582	102.30 ± 0.14	1.198866	103.42 ± 0.12	1.197745	104.47 ± 0.19	1.194375	105.42 ± 0.16	1.190845	106.31 ± 0.19
0.29764	1.205293	102.81 ± 0.22	1.204150	103.92 ± 0.15	1.203081	104.97 ± 0.22	1.203395	105.92 ± 0.13	1.197241	106.81 ± 0.20
0.39587	1.210292	103.30 ± 0.13	1.207902	104.41 ± 0.20	1.206765	105.47 ± 0.18	1.205298	106.42 ± 0.20	1.200379	107.31 ± 0.15
0.49540	1.215672	103.75 ± 0.19	1.213415	104.87 ± 0.26	1.213043	105.92 ± 0.13	1.210572	106.87 ± 0.09	1.206643	107.76 ± 0.29

Table 2
Partial molar volumes (V_φ^0) and transfer partial molar volumes ($\Delta_{trs}V_\varphi^0$) of MI in aqueous MCl_2 solutions at different temperatures.

m_{MCl_2}/mol kg^{-1}	V_φ^0/cm^3 mol^{-1}	$\Delta_{trs}V_\varphi^0$/cm^3 mol^{-1}	V_φ^0/cm^3 mol^{-1}	$\Delta_{trs}V_\varphi^0$/cm^3 mol^{-1}	V_φ^0/cm^3 mol^{-1}	$\Delta_{trs}V_\varphi^0$/cm^3 mol^{-1}	V_φ^0/cm^3 mol^{-1}	$\Delta_{trs}V_\varphi^0$/cm^3 mol^{-1}	V_φ^0/cm^3 mol^{-1}	$\Delta_{trs}V_\varphi^0$/cm^3 mol^{-1}
	293.15 K		298.15 K		303.15 K		308.15 K		318.15 K	
H_2O										
0	99.04 ± 0.22	0	100.13 ± 0.26	0	101.17 ± 0.31	0	102.13 ± 0.18	0	103.67 ± 0.11	0
$MgCl_2$										
0.09953	99.60 ± 0.16	0.56 ± 0.10	100.63 ± 0.22	0.50 ± 01	101.62 ± 0.28	0.45 ± 0.03	102.51 ± 0.09	0.38 ± 0.09	103.94 ± 0.05	0.27 ± 0.06
0.29436	100.09 ± 0.24	1.05 ± 0.06	101.10 ± 0.18	0.97 ± 0.08	102.11 ± 0.21	0.94 ± 0.10	103.03 ± 0.17	0.90 ± 0.01	104.451 ± 0.09	0.78 ± 0.02
0.48305	100.45 ± 0.17	1.41 ± 0.09	101.51 ± 0.20	1.38 ± 0.06	102.47 ± 0.23	1.30 ± 0.08	103.38 ± 0.08	1.25 ± 0.10	104.83 ± 0.10	1.16 ± 0.01
0.66604	100.89 ± 0.22	1.85 ± 0.06	101.88 ± 0.19	1.75 ± 0.07	102.87 ± 0.26	1.70 ± 0.05	103.75 ± 0.21	1.62 ± 0.03	105.20 ± 0.17	1.53 ± 0.06
0.93300	101.22 ± 0.23	2.18 ± 0.03	102.22 ± 0.25	2.09 ± 0.09	103.17 ± 0.24	2.00 ± 0.07	104.05 ± 0.16	1.92 ± 0.02	105.46 ± 0.21	1.79 ± 0.10
$CaCl_2$										
0.09955	99.56 ± 0.18	0.52 ± 0.04	100.58 ± 0.22	0.45 ± 0.04	101.58 ± 0.23	0.41 ± 0.08	102.46 ± 0.21	0.33 ± 0.0	103.89 ± 0.20	0.22 ± 0.09
0.29303	99.98 ± 0.20	0.94 ± 0.02	101.03 ± 0.18	0.90 ± 0.08	102.03 ± 0.25	0.86 ± 006.	102.97 ± 0.16	0.83 ± 0.02	104.38 ± 0.05	0.71 ± 0.06
0.48148	100.41 ± 0.21	1.37 ± 0.01	101.44 ± 0.20	1.31 ± 0.06	102.45 ± 0.29	1.28 ± 0.02	103.31 ± 0.23	1.18 ± 0.05	104.79 ± 0.12	1.12 ± 0.01
0.69410	100.84 ± 0.16	1.80 ± 006	101.85 ± 0.18	1.72 ± 0.08	102.84 ± 0.26	1.67 ± 0.05	103.72 ± 0.20	1.59 ± 0.02	105.14 ± 0.15	1.47 ± 0.04
0.93763	101.16 ± 0.14	2.12 ± 008	102.19 ± 0.17	2.06 ± 0.09	103.1 ± 0.24	1.93 ± 0.07	104.02 ± 0.09	1.89 ± 0.09	105.43 ± 0.19	1.76 ± 0.08
$SrCl_2$										
0.09897	99.48 ± 0.31	0.44 ± 0.09	100.53 ± 0.23	0.38 ± 0.03	101.51 ± 0.28	0.34 ± 0.03	102.42 ± 0.09	0.29 ± 0.09	103.85 ± 0.20	0.18 ± 0.09
0.28887	99.96 ± 0.20	0.92 ± 0.02	100.99 ± 0.31	0.86 ± 0.05	102.00 ± 0.26	0.83 ± 0.05	102.90 ± 0.16	0.77 ± 0.02	104.32 ± 0.13	0.65 ± 0.02
0.46906	100.39 ± 0.19	1.35 ± 0.03	101.41 ± 0.19	1.28 ± 0.07	102.41 ± 0.35	1.24 ± 0.04	103.28 ± 0.13	1.15 ± 0.05	104.76 ± 0.19	1.09 ± 0.08
0.64118	100.78 ± 0.26	1.74 ± 0.04	101.79 ± 0.24	1.66 ± 0.02	102.79 ± 0.30	1.62 ± 0.01	103.69 ± 0.21	1.56 ± 0.03	105.10 ± 0.08	1.43 ± 0.03
0.91565	101.13 ± 0.19	2.09 ± 0.03	102.15 ± 0.34	2.02 ± 0.08	103.09 ± 0.19	1.92 ± 0.12	103.99 ± 0.23	1.86 ± 0.05	105.42 ± 0.07	1.75 ± 0.04
$BaCl_2$										
0.09824	99.42 ± 0.19	0.38 ± 0.03	100.47 ± 0.23	0.32 ± 0.03	101.49 ± 0.36	0.28 ± 0.05	102.40 ± 0.20	0.25 ± 0.02	103.82 ± 0.05	0.15 ± 0.06
0.28388	99.94 ± 0.26	0.90 ± 0.04	100.94 ± 0.19	0.83 ± 0.07	101.95 ± 0.28	0.80 ± 0.03	102.85 ± 0.13	0.74 ± 0.05	104.35 ± 0.16	0.68 ± 0.05
0.45658	100.35 ± 0.30	1.31 ± 0.08	101.38 ± 0.30	1.25 ± 0.04	102.38 ± 0.40	1.21 ± 0.09	103.30 ± 0.09	1.11 ± 0.09	104.72 ± 0.20	1.05 ± 0.09
0.61882	100.75 ± 0.22	1.71 ± 0.00	101.78 ± 0.25	1.65 ± 0.01	102.76 ± 0.22	1.59 ± 0.09	103.65 ± 0.16	1.52 ± 0.02	105.08 ± 0.19	1.41 ± 0.02
0.89137	101.08 ± 0.16	2.04 ± 0.06	102.11 ± 0.18	1.99 ± 0.08	103.04 ± 0.19	1.87 ± 0.12	103.96 ± 0.22	1.81 ± 0.04	105.39 ± 0.23	1.72 ± 0.12

to better than ±0.001 °C. The precision of the densimeter was $\pm 1 \times 10^{-6}$ g cm^{-3}. The densimeter was calibrated with twice distilled water and dried air. The average of triplicate measurements was as the final result.

3. Results and discussions

3.1. The apparent molar volume

Apparent molar volumes (V_φ) of MI in pure water were calculated from the density values using the equation [14]:

$$V_\varphi = M_b/\rho - 1000(\rho - \rho^0)/(m_b \rho \rho^0) \quad (1)$$

where M_b is the molar mass of the solute (MI), m_b is the molality of MI in solution; ρ^0 and ρ are the densities of the pure water and solution.

In ternary systems MI + MCl_2 + water, the apparent molar volumes of MI can be calculated by using

$$V_\varphi = M_b/\rho - (1000 + M_a m_a)(\rho - \rho^{0'})/(m_b \rho \rho^{0'}) \quad (2)$$

where m_a and m_b are the molalities defined per kilogram of pure water respectively for MCl_2 and MI in an aqueous solution; ρ is the densities of the ternary aqueous solution and $\rho^{0'}$ is the density of MCl_2 + water binary solution. The densities and apparent molar volumes of MI are presented in Table 1.

3.2. The partial molar volume and transfer partial molar volume

Table 1 shows the apparent molar volumes of MI (V_φ) were a good linear function of molality of MI over the concentration range studied, so partial molar volumes at infinite dilutions (V_φ^0) were obtained by least squares fitting to the equation:

$$V_\varphi = V_\varphi^0 + S_v m_b \quad (3)$$

where S_v is the experimental slope, and m_b is the molality of the solute (MI) in mixtures. From Table 2 we could found that the V_φ^0 (100.13 ± 0.26) cm^3 mol^{-1} (298.15 K), (102.13 ± 0.18) cm^3 mol^{-1} (308.15 K), (103.67 ± 0.11) cm^3 mol^{-1} (318.15 K) are close to the Ref. [15] (101.8 ± 1.0) cm^3 mol^{-1} (298.15 K), (103.3 ± 1.1) cm^3 mol^{-1} (308.15 K), (104.5 ± 1.2) cm^3 mol^{-1} (318.15 K). Then the corresponding transfer parameters can be calculated as defined by

$$\Delta_{trs} V_\varphi^0\{\text{water to } MCl_2(aq)\} = V_\varphi^0\{\text{in } MCl_2(aq)\} - V_\varphi^0\{\text{in water}\} \quad (4)$$

The partial molar volumes and the transfer partial molar volumes of MI at infinite dilutions with the literature method [16] were calculated and summarized in Table 2.

3.3. The voluminal interaction coefficient

Friedman and Krishnan [17] considered that the thermodynamic transfer properties of solutes from solutions of pure water as solvent to aqueous electrolytic solutions could be explained in terms of the cosolutes interaction. At infinite dilutions, the interactions between molecules of the diluted solutes can be neglected, and then the transfer partial molar volume of the diluted nonelectrolyte can be expressed as

$$\Delta_{trs} V_\varphi^0\{\text{water to } MCl_2(aq)\} = 2V_{ab} m_a + 3V_{aab} m_a^2 + 4V_{aaab} m_a^3 + \cdots \quad (5)$$

where V_{ab} is the volumetric pair interaction coefficient and V_{aab}, and V_{aaab} are the ternary and quaternary interaction coefficients, respectively. m_a is the molalities of MCl_2. The data in Table 2 were fitted to Eq. (5) using a multiple regression procedure and the interaction coefficients of MI with MCl_2 in the aqueous solutions were obtained (Table 3).

3.4. The partial molar volume at infinite dilution and the transfer partial molar volume

Table 2 clearly demonstrates that both infinite dilutions V_φ^0 and $\Delta_{trs} V_\varphi^0$ are positive and become more positive with the increase of MCl_2 molality, which can be verified by the variation tendency of V_φ^0 and $\Delta_{trs} V_\varphi^0$ from Figs. 1 and 2. This tendency can be explained using the cosphere overlap model [18]. For apolar species, the hydrophobic hydration gives a positive volume contribution. Thus, the overlap of two hydrophobic hydration cospheres releases some water molecules from the solvation sphere to the bulk, which gives rise to a negative change in volume. In contrast, for polar species, the volume of water molecules is smaller in the solvate sphere due to (i) the effect of electrostriction and (ii) the decrease of hydrogen-bonded network with water molecules in the sol-

Table 3
The voluminal interaction coefficients of MI in aqueous MCl_2 solutions at different temperatures.

T/K	M	V_{ab}/cm^3 mol^{-2} kg^{-1}	V_{aab}/cm^3 mol^{-2} kg^{-1}	V_{aaab}/cm^3 mol^{-2} kg^{-1}	R^2	S.D.
293.15 K	$MgCl_2$	1.0412	0.3314	−0.3003	0.9991	0.0531
	$CaCl_2$	1.6638	−0.7902	0.1787	0.9998	0.0646
	$SrCl_2$	1.0617	0.4825	−0.4188	0.9995	0.0143
	$BaCl_2$	1.2782	0.2689	−0.3380	0.9992	0.0303
298.15 K	$MgCl_2$	1.1438	0.1714	−0.2342	0.9996	0.0124
	$CaCl_2$	1.7877	−0.9466	0.2348	0.9993	0.0515
	$SrCl_2$	1.1264	0.3396	−0.3407	0.9995	0.0139
	$BaCl_2$	1.2143	0.3659	−0.3792	0.9991	0.0237
303.15 K	$MgCl_2$	1.1524	0.1479	−0.2328	0.9994	0.0423
	$CaCl_2$	1.7911	−0.9228	0.2113	0.9991	0.0563
	$SrCl_2$	1.1244	0.3881	−0.3986	0.9992	0.0226
	$BaCl_2$	1.2787	0.3017	−0.3966	0.9996	0.0269
308.15 K	$MgCl_2$	1.4416	−0.2844	−0.0404	0.9995	0.0441
	$CaCl_2$	1.8536	−1.0241	0.2538	0.9998	0.0089
	$SrCl_2$	1.1205	0.3989	−0.4083	0.9999	0.0065
	$BaCl_2$	1.1995	0.3717	−0.4210	0.9999	0.0042
318.15 K	$MgCl_2$	1.2998	0.0106	−0.2083	0.9993	0.0343
	$CaCl_2$	2.0049	−1.1778	0.30011	0.9993	0.0491
	$SrCl_2$	1.1538	0.3126	−0.3558	0.9999	0.0070
	$BaCl_2$	1.5525	−0.2837	−0.0606	0.9992	0.0328

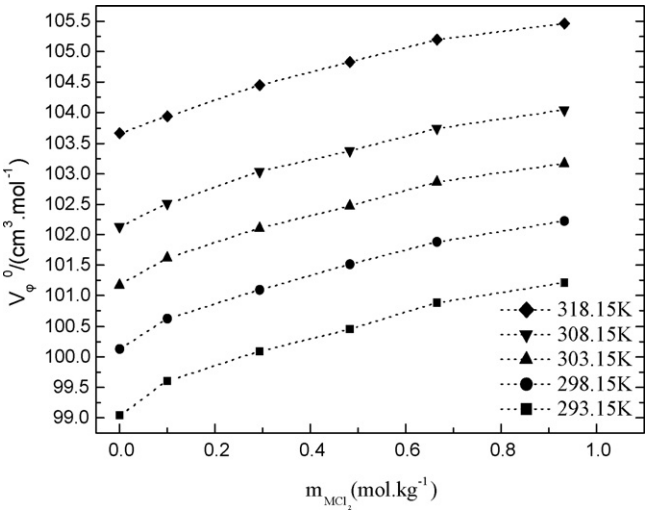

Fig. 1. The variation tendency of MI's partial molar volumes V_φ^0 in aqueous MCl_2 (M = Mg, Ca, Sr, Ba) solution at different temperatures.

vate sphere transferring to the bulk [19]. So the overlap of two hydrophilic hydration cospheres releases some water molecules to the bulk giving rise to a positive change in volume. The influence of hydrophilic species on the hydrophobic hydration sphere of apolar species gives a negative volume effect. The changes in volume due to various types of abovementioned interactions were demonstrated in cosphere overlap model.

3.5. Size effect of cation

For different cosolutes, under the same positive charge concentrations of MCl_2, the value of V_φ^0 at infinite dilution and that of $\Delta_{trs}V_\varphi^0$ increase following the order $MgCl_2 > CaCl_2 > SrCl_2 > BaCl_2$. This phenomenon might be explained as follows: bivalent alkaline earth metal ions can partly destroy the secondary hydration layer and affect the primary hydration layer through the relatively strong interaction between the salt and MI molecule due to their electric charge. This makes it easier to partly break the hydration layer around each polylol molecule. For the different aqueous MCl_2 solutions with the same anion Cl^-, the differences arise from the influences of cations. Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} have the same charge, but Ba^{2+} has the longest ionic radius, and Mg^{2+} has the shortest ionic radius. The longer the radius (of naked cation), the weaker the interaction between the cation and the dipolar bonds of MI molecule. Therefore, the ability to destroy the hydration layer of the polylol molecule should vary as $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$, which lead to V_φ^0 and $\Delta_{trs}V_\varphi^0$ of MI are the biggest for aqueous $MgCl_2$ solution, and the corresponding ones in aqueous $BaCl_2$ solution are the smallest. Therefore, it can speculated that the positive values of V_φ^0 and $\Delta_{trs}V_\varphi^0$ are mainly the result of interaction between the ions (M^{2+}, Cl^-) and the dipolar bonds of MI molecule.

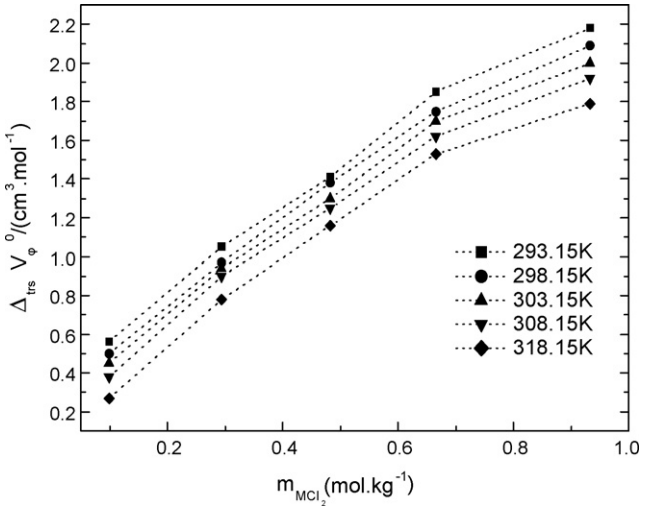

Fig. 2. The variation tendency of MI's transfer partial molar volumes $\Delta_{trs}V_\varphi^0$ in aqueous MCl_2 (M = Mg, Ca, Sr, Ba) solution at different temperatures.

3.6. Temperature effect

Earlier reports clarified that group contributions of–OH [20] in volume increase with ascent of temperature. On the other hand, an increase in temperature weakens the electrostriction. The both factors make the V_φ^0 increase with temperature increasing.

Table 2 also demonstrates that V_φ^0 of MI increase with the ascent of temperature, however, anomalies that $\Delta_{trs}V_\varphi^0$ slightly decrease with increase of temperature was also observed. The reason is that V_φ of MI is increase in both water and the aqueous solutions of MCl_2 with the increasing temperature, but in the aqueous solutions of MCl_2 the hydrophobic hydration gives more negative volume contribution to the whole system than in the water, so it induces both V_φ and V_φ^0 of MI increase more in water than that do in the aqueous solutions of MCl_2, and makes the increase more in water than that do in the aqueous solutions of MCl_2, At last, it leads the $\Delta_{trs}V_\varphi^0$ decrease a little with the temperature increasing.

3.7. The voluminal interaction coefficient

The V_{ab}, V_{aab}, V_{aaab} are volumetric interaction coefficients [21] which determine the volume changes caused by the interaction modes of MI with MCl_2 in the molecular ratio 1:1, 1:2, 1:3, respectively. By observing the data in Table 3, it can be seen that the values of V_{ab} are always obviously larger than those of V_{aab} and V_{aaab} in aqueous MCl_2 solution at the experimental temperatures. So value of V_φ^0 is in direct ratio with m_a in low concentration range of MCl_2 and the primary interaction mode of MI molecules with MCl_2 is approximately 1:1. If the concentration of MCl_2 is not very low, the multiple interactions, i.e. one MI molecule simultaneously interacts with two or more MCl_2 units become evident.

4. Conclusions

Apparent molar volumes (V_φ) of MI in aqueous solutions of MCl_2 have been obtained from densities at different temperatures (range from 293.15 K to 318.15 K) measured with a vibrating-tube densimeter. These data have been used to deduce partial molar volumes (V_φ^0) at infinite dilution and transfer partial molar volumes ($\Delta_{trs}V_\varphi^0$) of MI from water to different salt solutions at different concentrations. The results indicate that the longer the radius of naked cation (M^{2+}), the larger the contribution of MCl_2 made to the partial volume (V_φ^0) of MI, and enhancement of temperature can enlarge V_φ^0 and slightly reduce $\Delta_{trs}V_\varphi^0$. The change tendency of volume property of MI can be explained in the light of interaction between the charged centers of MI and ions as well as solvent effect.

Acknowledgements

The authors are grateful to the National Natural Science Foundation of China for support (No. 20773059).

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