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Densities, Viscosities and Adiabatic Compressibilities of Some Mineral Salts in Water at Different Temperatures

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The densities and viscosities of ammonium nitrate, lithium nitrate, sodium nitrate, potassium nitrate, magnesium nitrate, and calcium nitrate in water have been measured at the temperatures (303, 308, 313, 318, and 323) K. The apparent molar volumes (V_ϕ) and viscosity B coefficients of these salts are obtained from these data supplemented with their densities and viscosities, respectively. The limiting apparent molar volumes ($V_\phi°$) and experimental slopes (S_V*) derived from the Masson equation have been interpreted in terms of ion−solvent and ion−ion interactions, respectively. The viscosity data have been analyzed using the Jones−Dole equation, and the derived parameters B and A have also been interpreted in terms of ion−solvent and ion−ion interactions, respectively. The structure making/breaking capacities of these salts investigated have been discussed. The compressibility data also indicate the electrostriction of the solvent molecules around the metal ions.

Introduction

Studies on viscosities, densities, and ultrasonic velocities of ionic solutions assist in characterizing the structure and properties of solutions. Various types of interactions exist between the ions in solutions, and of these, ion−ion and ion−solvent interactions are of current interest in all branches of chemistry. These interactions help in better understanding the nature of solute and solvent, that is, whether the solute modifies or distorts the structure of the solvent. A survey of the literature[1−10] showed that although many studies have been carried out for various electrolytic solutions, few works have been done to discuss the behavior of mineral salts in water as reported earlier.[11,12] The present mineral salts have been selected for study because they are important constituents[13] of biofluids and soil fluids. The main ionic solutes in biofluids are the alkali cations, viz., Na^+ and K^+ with Mg^{2+} and Ca^{2+} in small amounts; the common anions are the small amounts of NO_3^-. The present investigation has been undertaken to provide better understanding of the nature of these mineral salts in water and to throw light on ion−solvent interactions.

Experimental Section

Ammonium nitrate, lithium nitrate, sodium nitrate, potassium nitrate, magnesium nitrate, and calcium nitrate (all A.R.) were used as such, only after drying over P_2O_5 in a desiccator for more than 48 h. Freshly distilled conductivity water was used. The aqueous solutions of nitrates were made by mass, and conversion of molality into molarity was done.[14]

The densities (ρ) were measured with an Ostwald−Sprengel type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at (303, 308, 313, 318, and 323) K with doubly distilled water and benzene. The pycnometer with the test solution was equilibrated in a water bath maintained at ±0.01 K of the desired temperature by means of a mercury in glass thermoregulator, and the temperature was determined with a calibrated thermometer and a Muller bridge. The pycnometer was then removed from the thermostatic bath, properly dried, and weighed. The evaporation losses remained insignificant during the time of actual measurements. Averages of triplicate measurements were taken into account. The density values were reproducible to $\pm 3 \times 10^{-5}$ g·cm^{-3}. Details have been described earlier.[15]

The viscosities were measured by means of a suspended-level Ubbelode[6] viscometer at the desired temperature (accuracy ±0.01 K). The precision of the viscosity measurements was 0.05%. Details have been described earlier.[7]

Sound velocities were determined with an accuracy of 0.3% using a single-crystal variable-path ultrasonic interferometer (Mittal Enterprises, New Delhi, India) working at 4 MHz which was calibrated with water, methanol, and benzene at each temperature. The temperature stability was maintained within ±0.01 K by circulating thermostated water around the cell with a circulating pump.

The experimental values of concentrations (c), densities (ρ_0), viscosities (η_0), and derived parameters of aqueous solutions of mineral salts at various temperatures are recorded in Table 1.

Results and Discussion

The apparent molar volumes (V_ϕ) were determined from the solution densities using the following equation,

$$V_\phi = M/\rho_0 - 1000(\rho - \rho_0)/c\rho_0 \qquad (1)$$

where M is the molecular weight of the solute, c is the molarity of the solution, and the other symbols have their usual significance.

The densities measured for the solutions of the salts in water at (303, 308, 313, 318, and 323) K have been used to calculate the apparent molar volume (V_ϕ) of the studied electrolytes. The plots of V_ϕ against square-root of molar concentration ($c^{1/2}$) were found to be linear with negative

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Table 1. Concentration (c), Density (ρ), Viscosity (η), Apparent Molar Volume (V_ϕ), and $(\eta/\eta_0 - 1)/\sqrt{c}$ of Some Mineral Salts in Water at Various Temperatures

c	$\sqrt{c}$	ρ	η	V_ϕ		c	$\sqrt{c}$	ρ	η	V_ϕ	
mol·dm^{-3}	(mol·dm^{-3})$^{1/2}$	g·cm^{-3}	cp	cm^3·mol^{-1}	$(\eta/\eta_0 - 1)/\sqrt{c}$	mol·dm^{-3}	(mol·dm^{-3})$^{1/2}$	g·cm^{-3}	cp	cm^3·mol^{-1}	$(\eta/\eta_0 - 1)/\sqrt{c}$
					T = 303.00 K						
		NH_4NO_3						KNO_3			
0.012 41	0.111 40	0.996 51	0.8291	12.087	0.318 76	0.012 05	0.109 77	0.996 25	0.8103	53.234	0.109 87
0.062 06	0.249 18	0.999 49	0.8590	18.548	0.292 54	0.060 26	0.245 48	0.998 77	0.8255	49.897	0.126 54
0.111 72	0.334 24	1.001 64	0.8780	26.675	0.288 86	0.108 47	0.329 35	1.001 59	0.8390	46.735	0.145 43
0.173 78	0.416 87	1.003 81	0.8941	33.343	0.279 99	0.168 74	0.410 78	1.005 39	0.8551	49.696	0.165 43
0.235 84	0.485 63	1.005 52	0.9035	38.453	0.264 53	0.228 99	0.478 53	1.009 09	0.8729	42.689	0.188 62
		$LiNO_3$						$Mg(NO_3)_2$			
0.121 48	0.110 22	0.996 12	0.8491	86.023	0.548 76	0.011 89	0.109 04	0.996 80	0.8106	162.045	0.113 67
0.060 74	0.246 45	0.998 19	0.9172	81.897	0.590 78	0.059 49	0.243 90	1.001 92	0.8293	151.999	0.146 54
0.109 33	0.330 65	1.000 83	0.9730	76.123	0.650 89	0.107 08	0.327 23	1.007 58	0.8454	145.789	0.170 98
0.170 08	0.412 41	1.004 72	1.0332	70.083	0.704 31	0.166 57	0.408 13	1.016 32	0.8685	132.978	0.207 54
0.230 82	0.480 44	1.008 91	1.0919	65.897	0.757 05	0.226 06	0.745 46	1.024 95	0.8903	127.456	0.235 43
		$NaNO_3$						$Ca(NO_3)_2$			
0.012 05	0.109 77	0.996 18	0.8130	42.907	0.140 98	0.012 04	0.109 73	0.997 31	0.8173	100.564	0.190 06
0.060 25	0.245 46	0.998 54	0.8323	37.453	0.160 98	0.060 18	0.245 31	1.004 32	0.8451	92.789	0.226 54
0.108 45	0.329 32	1.001 23	0.8483	33.869	0.180 87	0.108 32	0.329 12	1.012 36	0.8677	82.426	0.254 32
0.168 69	0.410 72	1.004 74	0.8693	31.564	0.208 76	0.168 49	0.410 47	1.023 23	0.8952	72.908	0.287 65
0.228 94	0.478 48	1.008 31	0.8885	29.908	0.229 22	0.228 67	0.478 19	1.034 67	0.9228	65.897	0.318 97
					T = 308.00 K						
		NH_4NO_3						KNO_3			
0.012 38	0.111 26	0.994 88	0.7362	13.543	0.170 80	0.012 03	0.109 68	0.994 55	0.7321	60.897	0.121 98
0.061 97	0.248 94	0.997 78	0.7438	19.986	0.118 70	0.060 09	0.245 13	0.996 67	0.7476	58.019	0.142 13
0.111 27	0.333 57	0.999 94	0.7504	27.341	0.116 14	0.108 19	0.328 92	0.999 11	0.7626	54.758	0.168 74
0.173 61	0.416 66	1.001 95	0.7573	34.781	0.115 64	0.168 29	0.410 23	1.002 76	0.7781	49.70O8	0.187 65
0.235 47	0.485 25	1.002 89	0.7629	42.795	0.115 43	0.228 39	0.477 90	1.006 25	0.7934	48.007	0.205 39
		$LiNO_3$						$Mg(NO_3)_2$			
0.012 12	0.110 09	0.994 29	0.7720	103.998	0.623 41	0.011 88	0.108 99	0.995 12	0.7327	167.890	0.130 78
0.060 62	0.246 21	0.995 46	0.8448	100.456	0.687 65	0.059 41	0.243 74	0.999 96	0.7510	157.987	0.161 89
0.108 94	0.330 06	0.997 23	0.9002	94.452	0.745 39	0.106 59	0.326 48	1.005 75	0.7688	147.567	0.196 54
0.169 42	0.411 61	1.000 80	0.9604	83.704	0.799 98	0.166 27	0.407 76	1.014 23	0.7895	135.897	0.227 65
0.230 10	0.479 69	1.002 93	1.0167	84.946	0.848 97	0.226 02	0.475 41	1.022 38	0.8101	131.897	0.255 29
		$NaNO_3$						$Ca(NO_3)_2$			
0.012 03	0.109 68	0.994 44	0.7343	53.089	0.150 09	0.011 99	0.109 49	0.995 49	0.7378	116.789	0.193 65
0.060 16	0.245 27	0.996 37	0.7545	46.897	0.180 78	0.060 13	0.245 21	1.001 83	0.7634	107.570	0.231 26
0.108 07	0.328 74	0.998 79	0.7723	41.456	0.209 87	0.107 93	0.328 53	1.009 02	0.7854	98.078	0.265 41
0.168 13	0.410 04	1.001 99	0.7896	37.992	0.226 54	0.167 33	0.409 06	1.018 42	0.8092	91.089	0.293 42
0.228 25	0.477 75	1.005 74	0.8071	34.008	0.245 32	0.227 58	0.477 05	1.029 83	0.8343	79.456	0.324 56
					T = 313.00 K						
		NH_4NO_3						KNO_3			
0.012 37	0.111 22	0.993 05	0.6794	14.445	0.320 98	0.012 02	0.109 63	0.992 68	0.6647	64.786	0.122 09
0.061 91	0.248 82	0.995 96	0.7061	20.089	0.307 45	0.059 97	0.244 89	0.994 61	0.6790	62.009	0.143 27
0.111 16	0.333 41	0.998 04	0.7184	28.098	0.285 64	0.107 85	0.328 41	0.997 05	0.6924	56.894	0.169 08
0.173 25	0.416 23	1.000 07	0.7282	35.078	0.264 53	0.167 79	0.409 62	1.000 16	0.7065	54.342	0.188 09
0.235 19	0.484 96	1.000 85	0.7352	43.786	0.248 97	0.227 76	0.477 24	1.003 72	0.7207	41.103	0.206 89
		$LiNO_3$						$Mg(NO_3)_2$			
0.012 09	0.109 95	0.992 43	0.7013	104.045	0.628 76	0.011 87	0.108 95	0.993 25	0.6665	172.789	0.147 65
0.060 51	0.245 99	0.993 41	0.7674	104.453	0.690 87	0.059 39	0.243 70	0.997 81	0.6847	163.786	0.179 87
0.108 67	0.329 65	0.994 75	0.8183	100.674	0.750 89	0.106 57	0.326 45	1.003 18	0.7021	154.897	0.215 48
0.168 86	0.410 92	0.997 55	0.8734	92.259	0.806 75	0.166 00	0.407 43	1.011 08	0.7219	144.045	0.246 57
0.229 99	0.479 57	1.001 02	0.9244	85.453	0.853 47	0.225 91	0.475 29	1.019 90	0.7411	135.010	0.273 21
		$NaNO_3$						$Ca(NO_3)_2$			
0.012 02	0.109 64	0.992 59	0.6675	56.456	0.160 09	0.011 97	0.109 41	0.993 56	0.6703	126.023	0.199 99
0.060 12	0.245 19	0.994 35	0.6865	50.345	0.189 76	0.060 07	0.245 09	0.999 51	0.6945	115.997	0.239 91
0.107 91	0.328 49	0.996 89	0.7031	42.234	0.218 97	0.107 66	0.328 11	1.006 26	0.7150	106.750	0.234 32
0.167 72	0.409 54	0.999 73	0.7195	40.648	0.235 64	0.166 10	0.407 55	1.015 81	0.7378	95.001	0.306 32
0.227 79	0.477 27	1.003 27	0.7366	36.854	0.257 72	0.226 79	0.476 22	1.026 69	0.7597	84.911	0.332 11
					T = 318.00 K						
		NH_4NO_3						KNO_3			
0.012 35	0.111 13	0.991 05	0.6240	15.543	0.380 01	0.011 99	0.109 49	0.990 67	0.6073	66.458	0.130 07
0.061 78	0.248 55	0.993 86	0.6509	21.765	0.350 06	0.059 85	0.244 64	0.992 51	0.6214	63.973	0.154 32
0.110 89	0.333 00	0.995 94	0.6531	29.009	0.272 62	0.107 60	0.328 02	0.994 90	0.6334	58.546	0.176 54
0.172 66	0.415 52	0.997 87	0.6633	36.224	0.259 55	0.167 48	0.409 24	0.997 94	0.6472	55.737	0.197 86
0.234 43	0.484 18	0.998 44	0.6743	45.548	0.260 58	0.227 26	0.476 72	1.001 48	0.6614	52.204	0.219 33
		$LiNO_3$						$Mg(NO_3)_2$			
0.120 7	0.109 86	0.990 41	0.6408	110.678	0.639 87	0.011 82	0.108 72	0.991 21	0.6095	176.809	0.165 43
0.060 39	0.245 74	0.991 36	0.7076	105.564	0.739 98	0.059 14	0.243 19	0.995 55	0.6272	168.430	0.195 64
0.108 49	0.329 38	0.992 67	0.7519	101.675	0.776 54	0.106 38	0.326 16	1.000 89	0.6449	157.934	0.236 41
0.168 68	0.410 71	0.995 37	0.8054	93.564	0.840 09	0.165 37	0.406 66	1.008 45	0.6635	147.801	0.265 87
0.229 54	0.479 10	0.998 91	0.8540	86.089	0.889 67	0.225 02	0.474 36	1.017 15	0.6813	138.231	0.290 45
		$NaNO_3$						$Ca(NO_3)_2$			
0.012 00	0.109 54	0.990 57	0.6113	59.045	0.190 87	0.011 92	0.109 18	0.991 50	0.6137	132.564	0.212 87
0.060 04	0.245 03	0.992 21	0.6301	52.786	0.213 76	0.059 84	0.244 62	0.997 10	0.6347	122.870	0.245 32
0.107 77	0.328 28	0.994 46	0.6466	46.342	0.243 65	0.107 23	0.327 46	1.003 71	0.6545	111.700	0.284 53
0.167 29	0.409 01	0.997 22	0.6648	43.752	0.269 87	0.165 16	0.406 39	1.012 93	0.6763	99.823	0.318 75
0.227 31	0.476 77	1.001 15	0.6804	37.402	0.286 03	0.225 31	0.474 67	1.023 69	0.6970	88.589	0.345 63

Table 1. (Continued)

c mol·dm^{-3}	$\sqrt{c}$ (mol·dm^{-3})$^{1/2}$	ρ g·cm^{-3}	η cp	V_ϕ cm^3·mol^{-1}	$(\eta/\eta_0 - 1)\sqrt{c}$	c mol·dm^{-3}	$\sqrt{c}$ (mol·dm^{-3})$^{1/2}$	ρ g·cm^{-3}	η cp	V_ϕ cm^3·mol^{-1}	$(\eta/\eta_0 - 1)/\sqrt{c}$
T = 323.00 K											
NH_4NO_3						KNO_3					
0.012 30	0.110 90	0.988 85	0.5666	16.897	0.326 54	0.011 98	0.109 45	0.988 45	0.5551	70.345	0.140 02
0.061 56	0.248 11	0.991 64	0.5851	22.342	0.282 97	0.059 76	0.244 46	0.990 16	0.5683	66.897	0.161 23
0.110 53	0.332 46	0.993 43	0.5876	31.897	0.224 49	0.107 44	0.327 78	0.991 23	0.5800	64.086	0.185 43
0.171 97	0.041 469	0.994 64	0.5953	42.345	0.214 06	0.167 29	0.409 01	0.995 82	0.5934	55.456	0.208 76
0.233 52	0.483 24	0.995 90	0.5969	47.067	0.189 67	0.227 12	0.476 57	0.999 08	0.6064	53.234	0.228 76
$LiNO_3$						$Mg(NO_3)_2$					
0.012 05	0.109 77	0.988 21	0.5858	112.678	0.650 98	0.011 81	0.108 67	0.988 96	0.5575	182.908	0.180 92
0.060 30	0.245 56	0.989 11	0.6461	107.045	0.739 98	0.058 94	0.242 77	0.993 05	0.5773	173.897	0.229 99
0.108 31	0.329 10	0.990 38	0.6865	102.897	0.776 54	0.105 99	0.325 56	0.998 01	0.5927	164.567	0.258 12
0.168 32	0.410 27	0.993 08	0.7352	94.345	0.840 09	0.164 86	0.406 03	1.005 29	0.6106	153.809	0.287 65
0.229 40	0.478 96	0.996 34	0.7798	88.004	0.889 67	0.224 17	0.473 46	i.013 68	0.6276	143.897	0.312 34
$NaNO_3$						$Ca(NO_3)_2$					
0.011 96	0.109 36	0.988 35	0.5675	62.078	0.347 65	0.011 89	0.108 95	0.989 12	0.5602	149.620	0.226 54
0.059 80	0.244 54	0.989 89	0.5975	54.897	0.379 87	0.059 62	0.244 17	0.993 63	0.5835	144.678	0.275 61
0.107 42	0.327 75	0.991 74	0.6196	51.439	0.406 75	0.106 87	0.326 91	0.998 86	0.6017	136.820	0.307 34
0.167 26	0.408 97	0.994 45	0.6444	47.221	0.436 54	0.164 36	0.405 41	1.006 02	0.6205	128.543	0.332 65
0.226 73	0.476 16	0.998 57	0.6680	39.146	0.465 62	0.224 50	0.473 81	1.014 61	0.6421	119.345	0.367 89

Table 2. Molality (m), Density (ρ), Sound Velocity (u), Adiabatic Compressibility (β), Apparent Molal Adiabatic Compressibility (ϕ_k), Limiting Apparent Molal Adiabatic Compressibility ($\phi_k°$), and Experimental Slope (S_k*) of Some Mineral Salts at 303.00 K

m mol·kg^{-1}	$\sqrt{m}$ (mol·kg^{-1})$^{1/2}$	$10^3\rho$ kg·m^3	u m·s^{-1}	$10^{10}\beta$ Pa^{-1}	$10^7\phi_k$ m^3·mol^{-1}·Pa^{-1}	$10^7\phi_k°$ m^3·mol^{-1}·Pa^{-1}	$10^7 S_k$ m^3·mol$^{-3/2}$·Pa^{-1}·kg^{-1}
NH_4NO_3							
0.012 45	0.111 58	0.997 62	1519.951 68	4.338 86	−1.307 63		
0.062 45	0.249 89	0.998 71	1523.652 31	4.313 09	−1.179 80		
0.112 52	0.335 44	1.001 87	1533.467 31	4.244 63	−1.007 86	−1.580	1.851
0.175 55	0.418 99	1.003 81	1536.074 42	4.222 06	−0.845 20		
0.239 29	0.489 17	1.004 46	1537.714 70	4.210 33	−0.590 78		
$LiNO_3$							
0.012 21	0.110 49	0.996 59	1525.426 38	4.312 22	−1.543 28		
0.061 37	0.247 73	0.997 27	1529.906 65	4.284 08	−1.396 59		
0.110 73	0.332 76	1.000 83	1535.000 30	4.240 56	−1.074 21	−1.900	2.505
0.172 88	0.415 79	1.004 72	1540.693 98	4.192 97	−0.874 48		
0.236 09	0.485 89	1.006 05	1543.840 84	4.170 38	0.622 94		
$NaNO_3$							
0.012 11	0.110 04	0.995 81	1533.426 87	4.270 68	−2.999 67		
0.060 70	0.246 37	0.997 69	1540.573 97	4.223 18	−2.621 96		
0.109 32	0.330 63	1.001 23	1548.574 46	4.164 87	−1.970 13	−3.559	4.505
0.170 19.	0.412 54	0.005 49	1558.761 75	4.093 20	1.666 83		
0.231 52	0.481 16	1.008 31	1566.762 23	4.040 17	−1.413 60		
KNO_3							
0.012 11	0.110 04	0.996 02	1526.759 79	4.307 16	−2.567 52		
0.060 67	0.247 73	0.999 40	1532.453 47	4.260 75	−2.051 00		
0.109 49	0.330 89	1.001 59	1540.693 98	4.206 08	−1.532 78	−2.895	3.530
0.170 73	0.413 19	1.005 39	1554.388 15	4.116 67	−1.452 70		
0.232 25	0.481 92	1.009 09	1586.030 08	3.939 56	−1.287 62		
$Mg(NO_3)$							
0.011 97	0.109 41	0.996 47	1519.104 87	4.340 71	−1.306 76		
0.060 32	0.245 60	1.001 54	1525.105 89	4.292 71	−1.014 60		
0.109 05	0.330 23	1.009 35	1531.046 90	4.226 50	−0.707 86	−1.648	2.841
0.172 02	0.414 75	1.011 01	1534.380 80	4.201 25	−0.420 77		
0.235 72	0.485 51	1.016 98	1539.048 26	4.015 129	−0.286 75		
$Ca(NO_3)_2$							
0.012 06	0.109 82	1.000 66	1545.289 32	4.184 98	−4.012 35		
0.060 88	0.246 74	1.002 72	1548.383 18	4.159 71	−3.375 54		
0.109 77	0.331 32	1.012 36	1553.110 65	4.095 06	−2.389 68	−4.894	7.124
0.171 15	0.413 70	1.024 25	1561.052 00	4.006 45	−1.985 19		
0.235 25	0.485 02	1.026 01	1568.326 57	3.962 56	−1.406 13		

slopes for the nitrates of lithium, sodium, potassium, magnesium, and calcium and positive slopes for the nitrate of ammonium.

The limiting apparent molar volumes ($V_\phi°$) were calculated using the least-squares treatment of the plots of V_ϕ versus $c^{1/2}$ using the Masson equation,[6]

$$V_\phi = V_\phi° + S_V{*}c^{1/2} \qquad (2)$$

where $V_\phi°$ is the partial molar volume at infinite dilution and S_V* the experimental slope. The values of $V_\phi°$ and S_V* along with standard errors are given in Table 3. It is evident from the data that S_V* is positive and large for ammonium nitrate in water at different temperatures. Since S_V* is a measure of solute−solute/ion−ion interactions, the results indicate the presence of very strong ion−ion interactions. These interactions, however, increase with

Table 3. Limiting Apparent Molar Volume ($V_\phi°$/cm^3·mol^{-1}), Experimental Slope (S_V/cm^3·dm$^{1/2}$·mol$^{-3/2}$), and Values of the Parameters A/dm$^{3/2}$·mol$^{-1/2}$ and B/dm^3·mol^{-1} of the Jones–Dole Equation for Some Mineral Salts in Water at Various Temperatures

T/K	$V_\phi°$/cm^3·mol^{-1}	S_V/cm^3·dm$^{1/2}$·mol$^{-3/2}$	B/dm^3·mol^{-1}	A/dm$^{3/2}$·mol$^{-1/2}$
		NH_4NO_3		
303.00	2.619 (±0.05)	72.626 (±0.09)	−0.133 (±0.40)	0.331 (±0.20)
308.00	2.752 (±0.20)	78.139 (±0.02)	−0.137 (±0.20)	0.171 (±0.06)
313.00	3.319 (±0.30)	78.324 (±0.20)	−0.199 (±0.19)	0.349 (±0.12)
318.00	4.357 (±0.21)	79.316 (±0.09)	−0.364 (±0.06)	0.420 (±0.20)
323.00	4.724 (±0.43)	86.148 (±0.03)	−0.377 (±0.05)	0.367 (±0.04)
		$LiNO_3$		
303.00	93.754 (±0.52)	−56.163 (±0.50)	0.571 (±0.20)	0.469 (±0.20)
308.00	112.316 (±0.22)	−59.597 (±0.52)	0.615 (±0.06)	0.547 (±0.17)
313.00	117.405 (±0.32)	−60.999 (±0.42)	0.617 (±0.09)	0.531 (±0.11)
318.00	120.154 (±0.33)	−65.532 (±0.40)	0.627 (±0.10)	0.561 (±0.11)
323.00	122.031 (±0.44)	−66.843 (±0.38)	0.636 (±0.19)	0.579 (±0.10)
		$NaNO_3$		
303.00	46.399 (±0.31)	−35.771 (±0.32)	0.242 (±0.06)	0.107 (±0.16)
308.00	59.044 (±0.25)	−52.039 (±0.40)	0.261 (±0.04)	0.120 (±0.07)
313.00	62.418 (±0.20)	−54.488 (±0.39)	0.267 (±0.02)	0.128 (±0.09)
318.00	65.941 (±0.42)	−57.615 (±0.44)	0.270 (0.12)	0.156 (±0.17)
323.00	69.301 (±0.37)	−58.537 (±0.28)	0.320 (±0.15)	0.306 (±0.12)
		KNO_3		
303.00	56.745 (±0.40)	−30.163 (±0.51)	0.218 (±0.09)	0.080 (±0.13)
308.00	65.930 (±0.50)	−37.067 (±0.46)	0.232 (±0.14)	0.092 (±0.10)
313.00	69.829 (±0.38)	−38.229 (±0.38)	0.232 (±0.10)	0.092 (±0.15)
318.00	71.904 (±0.36)	−39.982 (±0.30)	0.243 (±0.20)	0.099 (±0.10)
323.00	77.484 (±0.28)	−49.387 (±0.53)	0.245 (0.08)	0.107 (±0.14)
		$Mg(NO_3)_2$		
303.00	174.344 (±0.56)	−96.853 (±0.32)	0.333 (±0.08)	0.070 (±0.02)
308.00	180.720 (±0.40)	−103.922 (±0.41)	0.345 (±0.09)	0.086 (±0.03)
313.00	186.617 (±0.37)	−104.083 (±0.39)	0.349 (±0.10)	0.103 (±0.01)
318.00	191.161 (±0.42)	−106.858 (±0.40)	0.353 (±0.07)	0.121 (±0.03)
323.00	197.260 (±0.51)	−107.435 (±0.33)	0.358 (±0.05)	0.142 (±0.07)
		$Ca(NO_3)_2$		
303.00	113.451 (±0.33)	−97.067 (±0.50)	0.348 (±0.07)	0.146 (±0.10)
308.00	129.758 (±0.41)	−99.284 (±0.27)	0.355 (±0.04)	0.150 (±0.20)
313.00	141.039 (±0.48)	−112.690 (±0.29)	0.365 (±0.06)	0.156 (±0.06)
318.00	149.025 (±0.52)	−121.344 (±0.42)	0.373 (±0.08)	0.164 (±0.08)
323.00	161.753 (±0.36)	−83.276 (±0.39)	0.379 (±0.09)	0.184 (±0.05)

[a] Standard errors are given in parentheses.

Table 4. Values of Various Coefficients of Eq 3 for Different Salts

salt	a cm^3·mol^{-1}	b cm^3·mol^{-1}·K^{-1}	c cm^3·mol^{-1}·K^{-2}
NH_4NO_3	315.716	−2.101	0.003
$LiNO_3$	−9644.430	60.962	−0.095
$NaNO_3$	−4771.222	29.740	−0.045
KNO_3	−2914.104	18.029	−0.027
$Mg(NO_3)_2$	−970.465	6.247	−0.008
$Ca(NO_3)_2$	−3982.081	23.930	−0.034

the increase in temperature in the case of ammonium nitrate, which may be attributed to the decrease in solvation of ions; that is, more and more solute is accommodated in the void space left in the packing of large associated solvent molecules with the rise in temperature. In the cases of lithium nitrate, sodium nitrate, potassium nitrate, magnesium nitrate, and calcium nitrate, the interactions decrease with the rise in temperature, which is attributed to more violent thermal agitation at higher temperature resulting in diminishing the force of ion–ion interactions (ionic dissociations).[17]

Since $V_\phi°$ is a measure of ion–solvent interactions (as ionic interactions vanish at infinite dilution), therefore, it is evident from Table 3 that the values of $V_\phi°$ are positive and large for all mineral salts studied here in water at different temperatures, indicating the presence of strong ion–solvent interactions. These interactions are further strengthened with the rise in temperature, indicating that solvent molecules are loosely attached to solute, which expands with increase of temperature. Similar results are reported for some 1:1 electrolytes in aqueous DMF.[6,18]

Since the nitrate ion is common in the cases of the studied mineral salts, so from the values of $V_\phi°$ at a particular temperature, it may be concluded that the solvation of cations in water follows the order $Mg^{2+} > Ca^{2+} > Li^+ > K^+ > Na^+ > NH_4^+$. The same results are observed for some metal sulfates in water.[19]

The temperature dependence of $V_\phi°$ for various mineral salts, studied here in water, can be expressed by the general equation as follows:

$$V_\phi° = a + bT + cT^2 \tag{3}$$

Values of various coefficients of the above equation for various salts are recorded in Table 4.

The partial molar (limiting apparent molar) expansibilities, $\phi_E° = (\delta V_\phi°/\delta T)_\rho$, calculated from the general equation are given in Table 5. It is found from Table 5 that $\phi_E°$ decreases in magnitude with increase in temperature for lithium nitrate, sodium nitrate, potassium nitrate, magnesium nitrate, and calcium nitrate in water, indicating thereby that the behavior of these salts is just like that of common salts, because in the case of common salts the molar expansibility should decrease with rise in temperature.[17,20] It is also evident from Table 5 that the value of $\phi_E°$ increases in magnitude with increase in temperature for ammonium nitrate in water, suggesting that the behavior of this salt is similar to that of symmetrical tetraalkylammonium salts.[17]

During the past few years it has been emphasized by different workers that S_V* is not the sole criterion for determining the structure making or structure breaking nature of any solute. Hepler[21] developed a technique of examining the sign of $(\delta^2 V_\phi°/\delta T^2)_\rho$ for various solutes in terms of long-range structure making and breaking capac-

Table 5. Limiting Apparent Molar Expansibility $\phi_E°/cm^3·mol^{-1}·K^{-1}$ for Some Mineral Salts in Water at Different Temperatures

	$\phi_E°/cm^3·mol^{-1}·K^{-1}$					
salt	303.00 K	308.00 K	313.00 K	318.00 K	323.00 K	$(\delta\phi_E°/\delta T)_p$
NH_4NO_3	0.347	0.070	0.105	0.140	0.175	positive
$LiNO_3$	3.316	2.365	1.413	0.462	−0.488	negative
$NaNO_3$	2.058	1.601	1.145	0.688	0.231	negative
KNO_3	1.395	1.120	0.846	0.571	0.297	negative
$Mg(NO_3)_2$	1.308	1.227	1.145	1.064	0.982	negative
$Ca(NO_3)_2$	3.102	2.758	2.415	2.071	1.727	negative

ity of the solutes in aqueous solutions using the general thermodynamic expression

$$(\delta c_p/\delta p)_T = -(\delta^2 V_\phi°/\delta T^2)_\rho \qquad (4)$$

On the basis of this expression it has been deduced that structure making solutes should have positive values, whereas structure breaking solutes should have negative values. In the present system, it is evident from Table 5 that $(\delta^2 V_\phi°/\delta T^2)_\rho$ is negative for lithium nitrate, sodium nitrate, potassium nitrate, magnesium nitrate, and calcium nitrate in water, which means that these mineral salts behave as structure breakers. On the other hand, the value of $(\delta^2 V_\phi°/\delta T^2)_\rho$ is positive for ammonium nitrate, suggesting thereby that this mineral salt acts as a structure maker in water.

The viscosity data of solutions for various electrolytes studied here in water have been analyzed using the Jones−Dole equation.

$$\eta/\eta_0 = 1 + A\sqrt{c} + Bc$$

$$(\eta/\eta_0 - 1)/\sqrt{c} = A + B\sqrt{c} \qquad (5)$$

$$\text{where} \quad \eta = (Kt - L/t)\rho$$

where η_0 and η are the viscosities of water and solution, respectively. *A* and *B* are constants, ρ is the density of the solution, and *K* and *L* are constants for a particular viscometer. The values of *A* and *B* are estimated by a computerized least-squares method and recorded in Table 3.

A perusal of Table 3 shows that the values of the *A* coefficient are very small for all the mineral salts studied in water at different temperatures, thereby showing the presence of very weak solute−solute interactions. In other words, these results indicate that all the mineral salts mix really with water and there is a perfect solvation of these ions resulting in either no or weak solute−solute interactions.

It is also found from Table 3 that the *B* coefficients for all mineral salts studied here in water at various temperatures are positive and fairly large (except for ammonium nitrate), thereby suggesting the presence of strong ion−solvent interactions. The values of the *B* coefficient also increase with the increase in temperature for the solutions of lithium nitrate, sodium nitrate, potassium nitrate, magnesium nitrate, and calcium nitrate, thereby showing the ion−solvent interactions further improve with the increase in temperature, which results in the improvement of ionic solvation. On the other hand, the value of the *B* coefficient for the solutions of ammonium nitrate decreases with the rise in temperature, thereby showing that ion−solvent interactions are further weakened with the increase in temperature, which may be attributed to the decrease in solvation of ions by water. A similar result was reported by some workers[22] in the case of the viscosity of perchlorate of lithium and sodium propionic acid + ethanol mixtures.

The positive temperature coefficient of *B*, that is, d*B*/d*T*, which is a better criterion[23,24] in the case of the solutions of the nitrates of lithium, sodium, potassium, magnesium, and calcium in water, suggests that these mineral salts behave as structure breakers. On the other hand, a negative temperature coefficient of *B*, that is, d*B*/d*T* in the case of solutions of ammonium nitrate in water, indicates that this salt behaves as a structure maker/promoter. These conclusions are in excellent agreement with that drawn from $(\delta^2 V_\phi°/6T^2)_\rho$ explained earlier.

Adiabatic compressibility coefficients *B* were derived from the relation

$$B = 1/u^2\rho \qquad (6)$$

where ρ is the solution density and *u* is the sound velocity in the solution. The apparent molal adiabatic compressibility ($\phi_k°$) of the liquid solutions was calculated from the relation

$$\phi_k = M/\rho_0 B + 1000(B\rho_0 - B_0\rho)/m\rho\rho_0 \qquad (7)$$

The limiting apparent molal adiabatic compressibilities ($\phi_k°$) were obtained by extrapolating the plots of ϕ_k versus the square root of molal concentration of the solute to zero concentration by the computerized least-squares method.

$$\phi_k = \phi_k° + S_k{}^* m^{1/2} \qquad (8)$$

The values of *u*, *B*, ϕ_k, $\phi_k°$, and $S_k{}^*$ are reported in Table 2.

It is evident from Table 2 that all the mineral salts investigated here have negative apparent molar adiabiatic compressibilities ($\phi_k°$) and positive limiting experimental slopes ($S_k°$). These results can be interpreted in terms of the loss of compressibility of water due to electrostrictive forces in the vicinity of the ions. The same conclusion was obtained by us[25] in the case of studies on sound velocities of some alkali metal halides in THF + H_2O mixtures.

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