Volumetric and Viscometric Studies of Some Metal Acetates in Aqueous Solutions at $T = (288.15 \text{ to } 318.15)$ K

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Precise density and viscosity measurements on aqueous solutions of lithium acetate, sodium acetate, potassium acetate, magnesium acetate, and calcium acetate have been carried out in the temperature range of $T = (288.15 \text{ to } 318.15)$ K using a vibrating-tube digital densimeter and Micro-Ubbelohde type capillary viscometer, respectively. The data have been used to obtain partial molar volumes at infinite dilution, V_2^{o}, and viscosity B-coefficients for these salts. The effect of temperature on these thermodynamic properties has been studied by determining the partial molar expansibilities $(\partial V_2^{\text{o}}/\partial T)_{\text{P}}$ and $(\partial^2 V_2^{\text{o}}/\partial T^2)_{\text{P}}$ and $(\partial B/\partial T)$ coefficients. The activation free energies, $\Delta\mu_2^{0,\ddagger}$, for the viscous flow of solutions have also been obtained by application of transition state theory to the viscosity B-coefficient data. The results have been rationalized in terms of various interactions taking place in these solutions.

Introduction

Various biomolecules, e.g., proteins, nucleic acids, lipids, and complex carbohydrates, function as a result of their interactions with their aqueous environment.[1] Electrolytes are known to influence the stability of biologically important molecules[2,3] and also play an important role in many areas of solution chemistry[4] as well as in living cells,[5] seawater,[6] and soils.[7] Therefore, the thermodynamic properties[8,9] (apparent molar volumes, partial molar volumes, adiabatic compressibilities, heat capacities) and transport properties (viscosities and electrical conductivities)[10] of aqueous electrolyte solutions in a wide range of concentrations and solution temperatures are of fundamental importance for understanding various physiochemical processes. The apparent and partial molar volumes of electrolyte solutions have proven to be a very useful tool in elucidating structural interactions (i.e., ion—ion, ion—solvent, and solvent—solvent) occurring in solution.[11] The viscosity of electrolyte solutions is another important parameter to study their solution behavior. The temperature and concentration dependence of viscosity of aqueous electrolyte solutions help to understand ion—solvent (solvation) and long-range ion—ion electrostatic interactions. The Jones—Dole viscosity B-coefficient is important in the description and understanding of ionic processes, for example, solvation effects of cations and anions.[12] Further, the temperature dependence of partial molar volumes and viscosity B-coefficients provides the information regarding the structure making and breaking effect of the electrolytes. A literature survey shows that there are limited data on the physicochemical properties of metal acetates.[12,13] Therefore, in the present paper, we report systematically experimental data on the density and viscosity of lithium acetate (LA), sodium acetate (SA), potassium acetate (PA), magnesium acetate (MA), and calcium acetate (CA) in aqueous solutions at $T = (288.15, 298.15, 308.15, \text{ and } 318.15)$ K. Partial molar volumes, viscosity B-coefficients, activation free energy for viscous flow, and other related parameters have been derived and discussed in terms of various interactions occurring in solutions.

Experimental

Analytical grade lithium acetate dihydrate (99 %), sodium acetate trihydrate (99 %), and magnesium acetate tetrahydrate (99 %) were obtained from the SISCO Research Laboratory, India, and calcium acetate (99 %) from Loba Chemie, India, and potassium acetate (99 %) from S. D. Fine-Chem. Ltd., India. These salts were used without any further purification, but they were dried in a vacuum desiccator before use. All the solutions were prepared in deionized, doubly distilled, and degassed water of specific conductance less than $1.3 \cdot 10^{-6}\ \Omega^{-1} \cdot \text{cm}^{-1}$, on the basis of weight using a Mettler balance having a precision of $\pm\ 1.0 \cdot 10^{-8}$ kg. The densities of solutions were measured using a vibrating-tube digital densimeter (DMA 60/602) with precision of $\pm\ 1 \cdot 10^{-3}\ \text{kg} \cdot \text{m}^{-3}$ and accuracy of $\pm\ 3 \cdot 10^{-3}\ \text{kg} \cdot \text{m}^{-3}$. The temperature of water around the cell was controlled using a thermostatic water bath having a precision of ± 0.01 K. The densimeter was calibrated with dry air and pure water. The working of the densimeter was checked by the method described elsewhere.[14] Viscosity measurements were carried out with a Micro-Ubbelohde viscometer. The viscometer was calibrated with double distilled deionized water with flow time data collected at four different temperatures, (288.15, 298.15, 308.15, and 318.15) K, and by using the viscosity data from the literature.[15] Flow time measurements were performed using an automatic viscosity (time) measurement unit (SCHOTT AVS 350) with a resolution of 0.01 s. The temperature around the viscometer was maintained within ± 0.01 K using a constant-temperature bath (model: MC 31A Julabo/Germany). The average of at least six readings reproducible within 0.01 s was used as the final efflux time. The calculated viscosities have an uncertainty within $\pm\ 0.001\ \text{mPa} \cdot \text{s}$.

Results and Discussion

The apparent molar volumes, $V_{2,\phi}$, of the metal acetates were calculated by using the equation

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$$V_{2,\phi} = M_2/\rho - (\rho - \rho_o)/m\rho\rho_o \qquad (1)$$

where M_2 is the solute molar mass; m is molality; and ρ_o and ρ are densities of water and the solution, respectively. The ρ_o values were taken from the literature,[16] and these values are (999.098, 997.047, 994.033, and 990.244) kg·m^{-3} at (288.15, 298.15, 308.15, and 318.15) K, respectively. The densities and calculated $V_{2,\phi}$ values are summarized in Table 1. The uncertainties in the $V_{2,\phi}$ values resulting from various experimentally measured quantities have been calculated, and it comes out to be $0.01 \cdot 10^{-6}$ m^3·mol^{-1} at high and $0.04 \cdot 10^{-6}$ m^3·mol^{-1} at low (m < 0.02581 mol·kg^{-1}) concentration of monovalent metal acetates (LA, SA, and PA) and $0.02 \cdot 10^{-6}$ m^3·mol^{-1} at high and $0.09 \cdot 10^{-6}$ m^3·mol^{-1} at low (m < 0.01371 mol·kg^{-1}) concentration of divalent metal acetates (MA and CA). The

Table 1. Densities, ρ, and Apparent Molar Volumes, $V_{2,\phi}$, of Aqueous LA, SA, PA, MA, and CA Solutions at T = (288.15 to 318.15) K

$^a m$ mol·kg^{-1}	$\rho \cdot 10^{-3}$ kg·m^{-3}	$V_{2,\phi} \cdot 10^6$ m^3·mol^{-1}	m mol·kg^{-1}	$\rho \cdot 10^{-3}$ kg·m^{-3}	$V_{2,\phi} \cdot 10^6$ m^3·mol^{-1}
LA					
T/K = 288.15					
0.09432	1.002659	64.08	0.38826	1.013267	64.64
0.17429	1.005618	64.23	0.43693	1.014960	64.72
0.19005	1.006181	64.33	0.49131	1.016864	64.74
0.27939	1.009429	64.41	0.75367	1.025828	64.85
0.33169	1.011283	64.53			
T/K = 298.15					
0.03696	0.998437	64.35	0.18195	1.003767	64.72
0.05940	0.999272	64.47	0.20995	1.004778	64.77
0.09149	1.000457	64.59	0.30313	1.008132	64.81
0.15642	1.002843	64.66	0.30386	1.008152	64.83
T/K = 308.15					
0.06615	0.996502	64.70	0.35446	1.006787	65.38
0.10635	0.997960	65.01	0.38337	1.007809	65.36
0.13989	0.999184	65.03	0.52436	1.012616	65.54
0.18388	1.000776	65.08	0.57492	1.014321	65.58
0.28213	1.004275	65.22	0.66152	1.017193	65.67
0.31253	1.005323	65.33			
T/K = 318.15					
0.06623	0.992771	64.87	0.41347	1.005093	65.42
0.12654	0.994925	64.99	0.52336	1.008839	65.56
0.20639	0.997815	65.12	0.65429	1.013232	65.67
0.35432	1.003044	65.34			
SA					
T/K = 288.15					
0.10004	1.003438	92.33	0.50010	1.019341	93.75
0.19846	1.007544	92.78	0.74286	1.028343	94.01
0.25001	1.009612	93.09	0.89621	1.033707	94.25
0.39801	1.015476	93.45	1.00009	1.037222	94.41
T/K = 298.15					
0.10004	1.001299	93.33	0.50010	1.017052	94.35
0.19846	1.005332	93.71	0.74286	1.025937	94.62
0.25001	1.007393	93.88	0.89621	1.031275	94.81
0.39806	1.013191	94.16	1.00009	1.034758	94.96
T/K = 308.15					
0.10004	0.998223	94.11	0.50010	1.013899	94.80
0.19846	1.002224	94.35	0.74286	1.022693	95.11
0.25001	1.004269	94.49	0.89621	1.028037	95.24
0.39806	1.010038	94.68	1.00009	1.031563	95.32
T/K = 318.15					
0.10004	0.994376	94.90	0.50010	1.009844	95.56
0.19846	0.998321	95.14	0.74286	1.018559	95.81
0.25001	1.000351	95.22	0.89621	1.023795	95.99
0.39806	1.006044	95.42	1.00009	1.027235	96.11
PA					
T/K = 288.15					
0.12326	1.004980	50.14	0.25951	1.011203	50.89
0.13335	1.005436	50.31	0.35723	1.015604	51.10
0.18317	1.007736	50.56	0.71988	1.031400	51.61
0.20149	1.008579	50.62			
T/K = 298.15					
0.02581	0.99825	51.42	0.19631	1.005965	52.18
0.11382	1.002278	51.91	0.24809	1.008277	52.31
0.14352	1.003619	52.01	0.32895	1.011760	52.40
0.15359	1.004074	52.03			
T/K = 308.15					
0.02581	0.995208	52.54	0.19361	1.002698	52.97
0.06931	0.997178	52.63	0.19631	1.002815	52.98
0.14352	1.000499	52.78	0.32895	1.008578	53.20
T/K = 318.15					
0.04864	0.992421	52.70	0.20479	0.999409	52.80
0.01857	0.991057	52.71	0.30991	1.004040	52.86
0.09370	0.994454	52.72	0.34382	1.005516	52.90
0.12357	0.995795	52.74	0.39542	1.007747	52.95
0.18534	0.998552	52.78	0.43513	1.009451	52.99
MA					
T/K = 288.15					
0.05044	1.003158	133.41	0.27282	1.019854	135.56
0.11332	1.008044	134.30	0.31295	1.022694	135.85
0.14323	1.010331	134.51	0.40685	1.029181	136.41
0.23005	1.016762	135.28	0.53568	1.037780	136.95
0.24324	1.017718	135.38			
T/K = 298.15					
0.01442	0.998216	133.33	0.20616	1.012865	135.70
0.02261	0.998872	133.60	0.26305	1.017001	136.01
0.04257	1.000455	134.05	0.39161	1.025918	136.91
0.08718	1.003926	134.73	0.57282	1.037792	137.85
0.15133	1.008817	135.20			
T/K = 308.15					
0.02622	0.996136	134.18	0.51362	1.030914	137.90
0.07392	0.999881	134.85	0.64378	1.039191	138.41
0.20424	1.009661	136.11	0.97512	1.058335	139.90
0.37292	1.021507	137.33			
T/K = 318.15					
0.02744	0.992438	134.68	0.24980	1.009162	136.67
0.09153	0.997435	135.41	0.31579	1.013778	137.25
0.14069	1.001171	135.81	0.35420	1.016468	137.37
0.18089	1.004131	136.31	0.56782	1.030591	138.41
CA					
T/K = 288.15					
0.01371	1.000272	72.41	0.15278	1.011628	75.21
0.03399	1.001979	73.15	0.24636	1.01894	76.11
0.06666	1.004705	73.62	0.39845	1.030466	77.02
0.08915	1.006529	74.25	0.60746	1.045206	78.64
0.12568	1.009492	74.68			
T/K = 298.15					
0.04540	1.000837	74.39	0.24039	1.016193	77.05
0.09847	1.005162	75.14	0.25851	1.017603	77.06
0.11651	1.006609	75.37	0.40042	1.028087	78.22
0.18065	1.011675	76.08	0.46552	1.032821	78.51
0.21071	1.013967	76.56			
T/K = 308.15					
0.05575	0.998626	75.39	0.23404	1.012495	77.84
0.10026	1.002189	76.17	0.26836	1.015160	77.79
0.13839	1.005209	76.53	0.34645	1.020876	78.58
0.22552	1.011902	77.53	0.58903	1.037990	80.06
T/K = 318.15					
0.06321	0.995380	75.97	0.34741	1.017171	78.46
0.11358	0.999391	76.61	0.48132	1.026852	79.17
0.21598	1.007335	77.54	0.56103	1.032274	79.88
0.29341	1.013192	78.05			

[a] Molality of metal acetate solutions.

Table 2. Partial Molar Volumes, V_2^o, for Some Metal Acetates in Aqueous Solutions at T = (288.15 to 318.15) K[a]

	$V_2^o \cdot 10^6$ m$^3\cdot$mol^{-1}			
compound	T/K = 288.15	T/K = 298.15	T/K = 308.15	T/K = 318.15
LA	27.54 ± 0.06	28.07 ± 0.03	28.14 ± 0.05	28.07 ± 0.04
	(1.549)	(1.152)	(1.600)	(1.492)
	[b]63.66 ± 0.06	64.17 ± 0.04	64.41 ± 0.05	64.47 ± 0.02
	(1.490)	(1.292)	(1.567)	(1.485)
SA	37.39 ± 0.09	38.44 ± 0.05	39.17 ± 0.02	39.75 ± 0.03
	(3.045)	(2.367)	(1.830)	(1.790)
	[b]91.52 ± 0.10	92.69 ± 0.05	93.57 ± 0.02	94.35 ± 0.02
	(2.939)	(2.278)	(1.703)	(1.727)
PA	49.31 ± 0.10	51.07 ± 0.04	52.23 ± 0.05	52.57 ± 0.04
	(2.828)	(2.441)	(1.677)	(0.556)
MA	59.69 ± 0.04	60.23 ± 0.08	60.46 ± 0.12	60.67 ± 0.09
	(7.205)	(7.085)	(7.110)	(6.662)
	[b]131.89 ± 0.05	132.56 ± 0.07	133.02 ± 0.09	133.50 ± 0.09
	(7.028)	(6.932)	(6.877)	(6.493)
CA	71.40 ± 0.14	72.32 ± 0.13	73.34 ± 0.12	74.02 ± 0.10
	(9.241)	(9.218)	(8.817)	(7.586)

[a] Values in parenthesis are of standard deviation of the fitting of eq 2. [b] Partial molar volumes of hydrated metal acetates.

Table 3. Fitting Parameters of Equation 6 along with Standard Deviations

compound	a	b	c	[a]SD	[b]R^2
parameters of V_2^o values					
LA	−114.74	0.9260	−0.0015	0.07	0.9786
	[c](−47.16)	(0.7087)	(−0.0011)	(0.02)	(0.9990)
SA	−92.82	0.7905	−0.0012	0.03	0.9993
	(−24.85)	(0.6848)	($-9.75\cdot10^{-4}$)	(0.04)	(0.9996)
PA	−307.67	2.2618	−0.0035	0.05	0.9996
MA	−25.06	0.5319	$-8.25\cdot14^{-4}$	0.06	0.9921
	(73.11)	(0.3409)	($-4.75\cdot10^{-4}$)	(0.05)	(0.9981)
CA	−9.21	0.4525	$-6.0\cdot10^{-4}$	0.09	0.9997
parameters of S_v values					
LA	–	–	–	–	–
SA	161.79	−1.0182	0.0016	0.08	0.9938
	(157.92)	(−0.9873)	(0.0056)	(0.07)	(0.9943)
PA	−139.44	1.0098	−0.0018	0.02	0.9999
MA	−62.1078	0.4727	$-8.1\cdot10^{-4}$	0.14	0.8910
	(−54.28)	(0.4204)	($-7.2\cdot10^{-4}$)	(0.08)	(0.9592)
CA	−252.15	1.7772	−0.0030	0.10	0.9944

[a] SD = standard deviation. [b] R^2 = coefficients of determination. [c] Values of parameter for hydrated salts.

values of partial molar volumes at infinite dilution, V_2^o, were obtained by least-squares fitting of the data to a Masson equation[17,18] of the form

$$V_{2,\phi} = V_2^o + S_v m^{0.5} \tag{2}$$

In this equation, S_v is the experimental slope. The V_2^o and S_v values along with their standard deviations are listed in Table 2.

At infinite dilution, each ion is surrounded only by the solvent molecules and is infinitely distant with other ions. It follows that V_2^o is unaffected by ion−ion interactions and is a measure of only ion−solvent interaction.[19,20] It can be seen that the apparent molar volume of metal acetates in water increases with an increase in salt concentration. At low concentration, the small values of apparent molar volume is attributed to the strong attractive interaction within the hydration sphere (solute−solvent interactions). The positive slope of $V_{2,\phi}$ against $m^{0.5}$ is indicative of ion−ion interactions with an increase in concentration. This is attributed to the phenomenon described in terms of destructive overlap of cospheres[21] resulting in the net decrease of solvation, thereby increasing the solute volume.

From Table 2, it is observed that the S_v values for monovalent anhydrous metal acetates (LA, SA, and PA) increase with the size of the metal ion (Li^+ to Na^+) at all temperatures and decrease from Na^+ to K^+ at all temperatures except 298.15 K. For the divalent metal acetates (MA and CA), the values of S_v increase with an increase in size of the cation at all temperatures. Moreover, the values of S_v are greater for divalent metal acetates as compared to monovalent metal acetates, which indicate stronger solute−solute interactions in the case of divalent metal acetates. Moreover, the S_v values increase with an increase in the size of divalent metal acetates. The slopes (S_v) of plots of $V_{2,\phi}$ vs $m^{0.5}$ decrease with temperature for all studied metal acetates (Table 2) because at higher temperature the ion−solvent interactions are weakened.

The $V_{2,\phi}$ values for anhydrous LA, SA, and MA have also been calculated by using the molalities of anhydrous salts obtained by applying correction to the molalities of corresponding hydrated salts at 298.15 K. These data were used to obtain partial molar volumes, V_2^o, using eq 2 for anhydrous salts. The V_2^o values for the anhydrous salts are also given in Table 2 along with the values for hydrated salts. These values agree very well with the V_2^o values obtained by subtracting the molar volume of water at 298.15 K ($V_1^o = 18.07\cdot10^{-6}$ m$^3\cdot$mol^{-1}) from the V_2^o values of hydrated salts and the errors lies between $(0.04$ to $0.05)\cdot10^{-6}$ m$^3\cdot$mol^{-1}, and these errors are almost within the uncertainty range. Thus, the calculations have been restricted to only one temperature, i.e., 298.15 K. The partial molar volumes obtained by applying molality correction at 298.15 K for LA, SA, and MA are $(28.03\cdot10^{-6}$, $38.48\cdot10^{-6}$, and $60.28\cdot10^{-6})$ m$^3\cdot$mol^{-1}, respectively. To the best of our knowledge, no data are available for comparison. The V_2^o values of anhydrous salts have been further used to calculate the contributions of ions toward partial molar volumes of metal acetates.

By the additivity scheme,[22] the partial molar volume of monovalent V_2^o(MA) and divalent metal acetates $V_2^o(MA_2)$ can be written as

$$V_2^o(MA) = V_2^o(M^+) + V_2^o(A^-) \tag{3}$$

$$V_2^o(MA_2) = V_2^o(M^{+2}) + 2V_2^o(A^-) \tag{4}$$

By considering $V_2^o(CH_3COO^-) = 40.46\cdot10^{-6}$ m$^3\cdot$mol^{-1} as reported by Millero,[19] the contributions of other ions (as acetate ions are common in these solutes) toward partial molar volumes have been calculated at 298.15 K from the volumes of anhydrous metal acetates obtained after subtracting the partial molar volume of water from hydrated salts (LA, SA, and MA). The $V_{2\,\mathrm{ion}}^o$ values in the case of the Na^+, K^+, and Mg^{2+} ions agree very well with the values reported in the literature,[19] but $V_{2\,\mathrm{ion}}^o$ values

Table 4. Parameters $V_2{}^{o}{}_{ion}$, B_{ion}, B_{size}, and B_{solv} of Li^+, Na^+, K^+, Mg^{2+}, and Ca^{2+} Ions in Water at 298.15 K

ion	$V_2{}^{o}{}_{ion} \cdot 10^6$ $m^3 \cdot mol^{-1}$	$B_{ion} \cdot 10^3$ $m^3 \cdot mol^{-1}$	$B_{size} \cdot 10^3$ $m^3 \cdot mol^{-1}$	$B_{solv} \cdot 10^3$ $m^3 \cdot mol^{-1}$
Li^+	−12.39 (−0.88)[a]	0.2188 (0.150)[b]	−0.0312	0.2500
Na^+	−2.02 (−1.21)	0.1273 (0.086)	−0.0048	0.1312
K^+	10.61 (9.02)	−0.0045 (−0.007)	0.0246	−0.0291
Mg^{2+}	−20.69 (−21.17)	0.5363 (0.385)	0.0574	0.4759
Ca^{2+}	−8.60 (−17.85)	0.2877 (0.284)	0.0203	0.2674

[a] Ref 29. [b] Ref 10.

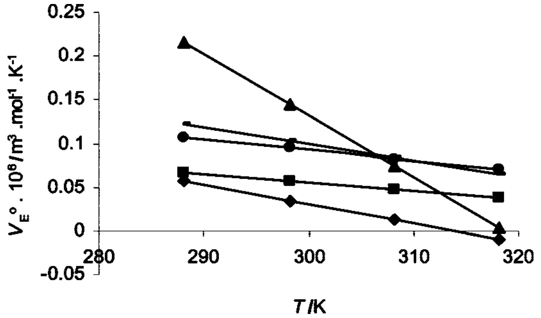

Figure 1. Partial molar expansibilities, $V_E{}^{o}$, of metal acetates vs temperature: ◆, LA; —, SA; ▲, PA; ■, MA; ●, CA.

for the Li^+ and Ca^{2+} ions differ from other reported values (Table 4). We have not been able to explain these discrepancies. Due to nonavailability of data on $V_2{}^{o}(CH_3COO^-)$ values at other temperatures, the calculations have been carried out only at one temperature, i.e., 298.15 K.

The partial molar volume of ions $V_2{}^{o}{}_{ion}$ can be expressed as follows[22]

$$V_2{}^{o}{}_{ion} = V_2{}^{o}(\text{int}) + V_2{}^{o}(\text{elect}) \tag{5}$$

where $V_2{}^{o}$(int) is the intrinsic apparent molar volume related to the size of the ion and packing effect, and $V_2{}^{o}$(elect) is the electrostriction apparent molar volume results from the ion−solvent interactions. The $V_2{}^{o}$(int) further consists of two terms, $V_2{}^{o}$(cryst) and $V_2{}^{o}$(disord). $V_2{}^{o}$(cryst) remains almost constant with temperature; however, $V_2{}^{o}$(disord) slightly increases with temperature.[19] Thus, the change in partial molar volume with temperature results from the change in both $V_2{}^{o}$(disord) and $V_2{}^{o}$(elect).

The temperature dependence of function, X ($V_2{}^{o}$ and S_v), has been expressed in polynomial form with T/K as the variable,[11] as follows

$$X(V_2{}^{o} \text{ or } S_v) = a + bT + cT^2 \tag{6}$$

The coefficients of these equations and the corresponding standard deviations at each temperature are given in Table 3. To study the effect of temperature on the volumetric properties, the partial molar expansibilities, $V_E{}^{o} = (\partial V_2{}^{o}/\partial T)_P$, and $(\partial^2 V_2{}^{o}/\partial T^2)_P$ coefficients have been calculated from eq 6. The $V_E{}^{o}$ values as a function of temperature are illustrated in Figure 1. The $V_E{}^{o}$ values decrease with an increase in temperature, and the decrease is sharp in the case of PA. Further, the partial molar expansibilities of SA, PA, MA, and CA are positive at all temperatures (288.15 to 318.15) K, and for LA, these are positive up to 308.15 K and become slightly negative at 318.15 K. It is also very interesting to note that partial molar expansibilities increase with an increase in size of monovalent metal ions up to 306 K, and above this temperature, no definite trend has been observed. This shows that the $V_E{}^{o}$ values are highly temperature specific.

Hepler[23] used a mathematical relation that correlates the change in heat capacity with pressure to the second-order derivative of volume with respect to temperature, to draw inference about the structure-breaking and -making property of solutes. He postulated that the second-order derivatives (curvature) of partial molar volume of solute at infinite dilution with respect to temperature, $(\partial^2 V_2{}^{o}/\partial T^2)_P$, should be negative for structure breakers and positive for structure makers. The hydrophilic compounds are characterized by large values of partial molar expansibilities $(\partial V_2{}^{o}/\partial T)_P$ and negative curvature,[19] $(\partial^2 V_2{}^{o}/\partial T^2)_P$. Presently observed $(\partial^2 V_2{}^{o}/\partial T^2)_P$ values are negative for all metal acetates ((LA $= -0.0023 \cdot 10^{-6}$, SA $= -0.0020 \cdot 10^{-6}$, PA $= -0.0710 \cdot 10^{-6}$, MA $= -0.0010 \cdot 10^{-6}$, and CA $= -0.0012 \cdot 10^{-6}$) $m^3 \cdot mol^{-1} \cdot K^{-2}$) which suggest that the studied metal acetates behave as structure breakers which is characteristic of ionic interactions.

The viscosities, η, of solutions were calculated by using the expression

$$\eta/\rho = at - b/t \tag{7}$$

where ρ is the density of solution; t is the flow time; and a and b are the viscometer constants ($a = 3.13127 \cdot 10^{-5}$ $mPa \cdot m^3 \cdot kg^{-1}$ and $b = 1.08820 \cdot 10^{-2}$ $mPa \cdot s^2 \cdot m^3 \cdot kg^{-1}$). The relative viscosities η_r ($\eta_r = \eta/\eta_o$, where η_o and η are the viscosities of solvent and solution, respectively) are given in Table 5. The viscosity data have been fitted using the Jones−Dole empirical equation,[24] which describes the relative viscosities of electrolyte solutions as a function of the concentration.

$$\eta/\eta_o = 1 + AC^{1/2} + BC \tag{8}$$

Where C is molarity (calculated from molality); A is the constant arising from the interactions between the ions; and B is the viscosity B-coefficient. The above equation upon rearrangement becomes

$$(\eta/\eta_o - 1)/C^{1/2} = A + BC^{1/2} \tag{9}$$

The plots of $(\eta/\eta_o - 1)/C^{1/2}$ vs $C^{1/2}$ have been found to be linear (not shown) at all temperatures in accordance with the Jones−Dole equation. The values of the A- and B-coefficients obtained from the intercept and slope of the straight line, respectively, along with their standard deviations are summarized in Table 6. The values of the viscosity A- and B-coefficients have also been calculated for anhydrous LA, SA, and MA by applying eq 9 at 298.15 K to the corrected values C. However, the values come out to be exactly the same as for the hydrated salts. The value of the viscosity A-coefficient of the Jones−Dole equation is a measure of long-range ion−ion interactions (Coulombic forces), while the B-coefficient is a manifestation of ion−solvent interactions. At a given concentration, the B-coefficient can be interpreted in terms of competition between specialized viscosity effects (Coulombic interaction, size and shape effects, or Einstein effect, alignment or orientation of polar molecules by the ionic field, and distortion of the solvent structure). These effects govern the viscosity behavior of the aqueous electrolyte solutions.[9]

A perusal of Table 6 shows that the values of the A-coefficients are either negative or positive but very small for all metal acetates over the studied temperature and concentration range thereby showing the presence of very weak ion−ion interactions. In other words, these results indicate that the metal acetates dissolve almost ideally, and solvation of these salts results in weak ion−ion interactions. It is also evident from Table 6 that the B-coefficients for all the metal acetates are positive and fairly large, thereby suggesting the presence of

Table 5. Relative Viscosities, η_r, of Aqueous LA, SA, PA, MA, and CA Solutions as a Function of Concentration of Metal Acetates at T = (288.15 to 318.15) K

C^a / $\mathrm{mol \cdot L^{-1}}$	η_r	C / $\mathrm{mol \cdot L^{-1}}$	η_r	C / $\mathrm{mol \cdot L^{-1}}$	η_r
LA					
T/K = 288.15					
0.05042	1.0229	0.18568	1.0817	0.60301	1.2857
0.09317	1.0411	0.29267	1.1307		
T/K = 298.15					
0.05032	1.0193	0.18528	1.0753	0.60159	1.2661
0.09297	1.0370	0.29202	1.1212		
T/K = 308.15					
0.06409	1.0262	0.14062	1.0560	0.27373	1.1100
0.10553	1.0424	0.21374	1.0852	0.35051	1.1416
T/K = 318.15					
0.06385	1.0274	0.14008	1.0557	0.27373	1.1072
0.10553	1.0433	0.21293	1.0832	0.34920	1.1366
SA					
T/K = 288.15					
0.04971	1.0190	0.15961	1.0591	0.38634	1.1480
0.10362	1.0405	0.30695	1.1170		
T/K = 298.15					
0.04960	1.0175	0.15927	1.0558	0.38547	1.1411
0.10340	1.0377	0.30626	1.1120		
T/K = 308.15					
0.06114	1.0212	0.17361	1.0612	0.37823	1.1348
0.11110	1.0389	0.26161	1.0922	0.49674	1.1779
T/K = 318.15					
0.06090	1.0220	0.18347	1.0648	0.36805	1.1293
0.11067	1.0391	0.26058	1.0909	0.49476	1.1740
PA					
T/K = 288.15					
0.03642	1.0094	0.17963	1.0407	0.26467	1.0605
0.09167	1.0209	0.22983	1.0523		
T/K = 298.15					
0.03634	1.0071	0.17922	1.0394	0.26407	1.0592
0.09146	1.0193	0.22931	1.0510		
T/K = 308.15					
0.03581	1.0089	0.11941	1.0280	0.21882	1.0506
0.08035	1.0187	0.16602	1.0383	0.28569	1.0656
T/K = 318.15					
0.03567	1.0110	0.11788	1.0298	0.22827	1.0545
0.08004	1.0204	0.16539	1.0396	0.28459	1.0679
MA					
T/K = 288.15					
0.02073	1.0225	0.08431	1.0839	0.30462	1.3338
0.03748	1.0379	0.13767	1.1379		
T/K = 298.15					
0.02068	1.0184	0.08414	1.0769	0.30401	1.3020
0.03740	1.0339	0.13739	1.1284		
T/K = 308.15					
0.01923	1.0189	0.06531	1.0591	0.14146	1.1273
0.04809	1.0431	0.09111	1.0814	0.20133	1.1838
T/K = 318.15					
0.01916	1.0198	0.06581	1.0601	0.13927	1.1145
0.04791	1.0433	0.09077	1.0798	0.20059	1.1771
CA					
T/K = 288.15					
0.03150	1.0256	0.14049	1.1114	0.18042	1.1465
0.08571	1.0690	0.18518	1.1483		
T/K = 298.15					
0.03144	1.0231	0.14018	1.1050	0.18002	1.1375
0.08553	1.0635	0.18477	1.1400		
T/K = 308.15					
0.04618	1.0348	0.10050	1.0746	0.21212	1.1591
0.06623	1.0494	0.16315	1.1203	0.25860	1.1957
T/K = 318.15					
0.04600	1.0353	0.10008	1.0740	0.20677	1.1507
0.07449	1.0557	0.16246	1.1170	0.25745	1.1885

[a] Molarity of metal acetate solutions.

strong ion–solvent interactions, which reinforce the above observations. The *B*-coefficients of monovalent metal acetates (LA, SA, and PA) are less than those divalent metal acetates (MA and CA) at all temperatures (Figure 2). In the case of LA and SA, the values of the *B*-coefficients continuously decrease with an increase in temperature; however, for PA, the value first increases at 298.15 K, and thereafter the values continuously decrease with a rise in temperature. Generally, the *B*-coefficients increase with an increase in the size of solute molecules,[25] but it is interesting to note that the values of the *B*-coefficients of the studied metal acetates decrease with an increase in ionic radii of the anhydrous metal ion (Li^+ = 86, Na^+ = 112, and K^+ = 144 pm). The small size Li^+ ion gets heavily hydrated as compared to the Na^+ and K^+ ions as the ionic radii of hydrated ions are as follows ($Li^+_{(aq)}$ = 340 pm, $Na^+_{(aq)}$ = 276 pm, and $K^+_{(aq)}$ = 232 pm).[26] From comparison of the *B*-coefficients of metal acetates with the size of monovalent metal ions (both anhydrous and hydrated), it is found that the *B*-coefficients also increase with an increase in the size of the hydrated but not the anhydrous metal ion. Figure 3 suggests that the *B*-coefficient is highly sensitive toward temperature for the largely hydrated ion (Li^+) but less sensitive for the less hydrated ions (Na^+ and K^+). Due to nonavailability of data on radii of the hydrated Mg^{2+} and Ca^{2+} ions, the comparison has been carried out only for monovalent metal acetates.

The higher *B*-coefficient values of divalent metal acetates arise from the higher charge density as well as the ionic strength of divalent metal acetates. Moreover, the *B*-coefficients of MA are greater than CA at all temperatures. Therefore, the *B*-coefficients for various studied metal acetates follow the order: MA > CA > LA > SA > PA.

The values of d*B*/d*T* are negative for all metal acetates ((LA = −0.00421, SA = −0.00111, PA = −0.00199, MA = −0.00975, and CA = −0.00315) $m^3 \cdot mol^{-1} \cdot K^{-1}$), thereby showing that these salts act as structure makers. Unlike this, the volumetric results suggest these salts act as structure breakers. Therefore, it may be noted that this information is model dependent.

The value of the viscosity *B*-coefficient is a highly specific property of the solute and can be determined by adding individual contributions of ions of the solute.[10]

$$B = Z^+B^- + Z^-B^+ \tag{10}$$

where Z^+/Z^- and B^+/B^- refer to the ionic valence and ionic (cationic and anionic) viscosity *B*-coefficients. By taking $B(CH_3COO^-)$ = $0.246 \cdot 10^{-3}$ $m^3 \cdot mol^{-1}$ as reported in the literature,[10] the B_{ion} values of different metal ions have been calculated and listed in Table 4. It has been observed that the B_{ion} values of all metal ions agree well with literature[10] values

Table 6. Viscosity *A*- and *B*-Coefficients of Aqueous LA, SA, PA, MA, and CA Solutions at T = (288.15 to 318.15) K

T/K	$A\cdot10^{3/2}$/$\mathrm{m^{3/2}\cdot mol^{-1/2}}$	$B\cdot10^{3}$/$\mathrm{m^{3}\cdot mol^{-1}}$	[a]SD	[b]R^2
		LA		
288.15	−0.0127	0.4825	0.0071	0.9983
298.15	−0.0216	0.4648	0.0048	0.9991
308.15	−0.0003	0.4024	0.0013	0.9997
318.15	0.0162	0.3604	0.0021	0.9991
		SA		
288.15	0.0003	0.3804	0.0032	0.9990
298.15	−0.0051	0.3733	0.0028	0.9992
308.15	−0.0048	0.3641	0.0010	0.9999
318.15	0.0029	0.3464	0.0011	0.9999
		PA		
288.15	0.0070	0.2124	0.0020	0.9981
298.15	−0.0091	0.2415	0.0002	0.9999
308.15	0.0046	0.2213	0.0011	0.9993
318.15	0.0176	0.2017	0.0024	0.9964
		MA		
288.15	−0.0180	1.1012	0.0183	0.9960
298.15	−0.0262	1.0283	0.0084	0.9990
308.15	0.0041	0.8891	0.0070	0.9980
318.15	0.0224	0.8225	0.0054	0.9984
		CA		
288.15	0.0021	0.7978	0.0039	0.9994
298.15	−0.0094	0.7797	0.0023	0.9997
308.15	−0.0025	0.7553	0.0031	0.9995
318.15	0.0126	0.7011	0.0031	0.9994

[a] SD = standard deviation for the fitting of eq 9. [b] R^2 = Coefficients of determination.

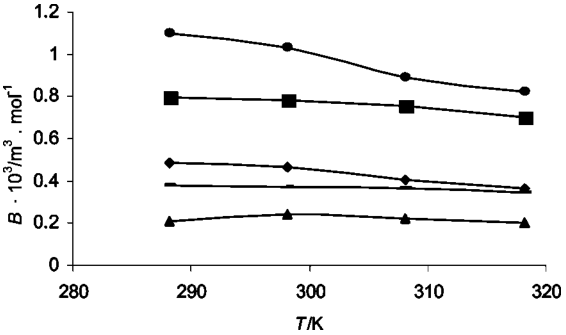

Figure 2. Viscosity *B*-coefficients of metal acetates vs temperature: ◆, LA; −, SA; ▲, PA; ●, MA; ■, CA.

except for the $\mathrm{Mg^{2+}}$ ion (Table 4). The viscosity B_{ion}-coefficient is usually interpreted as consisting of two terms:[27] the first is the effect of the ionic size, B_{size}, and the second is the contribution arising from the ion−solvent interactions, B_{solv}.

$$B_{\mathrm{ion}} = B_{\mathrm{size}} + B_{\mathrm{solv}} \tag{11}$$

If we assume that the Einstein equation derived for the case of spherical colloids may be applied approximately to the aqueous electrolyte solutions, B_{size} may be obtained from the equation

$$B_{\mathrm{size}} = 2.5V_{2\ \mathrm{ion}}^{\mathrm{o}} \tag{12}$$

where $V_{2\ \mathrm{ion}}^{\mathrm{o}}$ is the ionic partial molar volume expressed in $\mathrm{m^3\cdot mol^{-1}}$. Thus, B_{solv} can be obtained by the use of the equation[28]

$$B_{\mathrm{solv}} = B_{\mathrm{ion}} - 2.5V_{2\ \mathrm{ion}}^{\mathrm{o}} \tag{13}$$

B_{ion} values of both monovalent as well as divalent metal ions decrease with an increase in the size of the anhydrous metal ion (Table 4), and moreover the values are higher for divalent metal ions. B_{ion} of the $\mathrm{Li^+}$ and $\mathrm{Na^+}$ ions are positive, whereas that of the $\mathrm{K^+}$ ion is negative. B_{ion} values of all metal ions except $\mathrm{Mg^{2+}}$ are very close to the values reported in the literature.[29] To study the solvation effect of the metal ion, the B_{solv} values have also been calculated (Table 4) by using eq 13. It may be noted that B_{solv} values also follow the same trend as that of B_{ion} values and are negative for the $\mathrm{K^+}$ ion only, whereas the rest of the ions have positive values of B_{solv}.

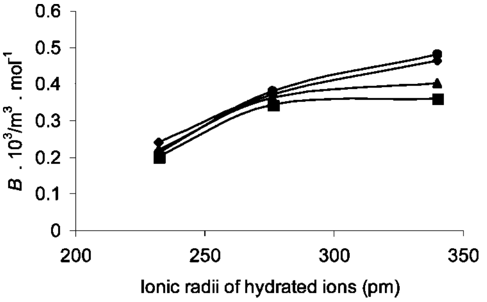

Figure 3. Viscosity *B*-coefficients of LA, SA, and PA vs ionic radii of hydrated ions: ●, 288.15 K; ◆, 298.15 K; ▲, 308.15 K; ■, 318.15 K.

According to Eyring's simple model,[30] the average activation free energy of a single solute in a pure solvent can be calculated from the following equation

$$\eta_{\mathrm{o}} = [hN_{\mathrm{A}}/V_1^{\mathrm{o}}]\exp(\Delta\mu_1^{\mathrm{o},\ddagger}/RT) \tag{14}$$

where h, N_{A}, T, and R are Planck's constant, Avogadro's number, temperature, and the universal gas constant, respectively, and V_1^{o} is the average molar volume of water at various temperatures, calculated from density data. The $\Delta\mu_1^{\mathrm{o},\ddagger}$ and V_1^{o} values are given in Table 7. The activation free energy, $\Delta\mu_2^{\mathrm{o},\ddagger}$, for viscous flow of metal acetates in aqueous solution is related to the *B*-coefficient as reported by Feakins et al.[31,32]

$$B = [(V_1^{\mathrm{o}} - V_2^{\mathrm{o}})/1000] + V_1^{\mathrm{o}}[(\mu_2^{\mathrm{o},\ddagger} - \mu_1^{\mathrm{o},\ddagger})/(1000RT)] \tag{15}$$

which upon rearrangement gives the equation

$$\Delta\mu_2^{\mathrm{o},\ddagger} = \Delta\mu_1^{\mathrm{o},\ddagger} + [RT/V_1^{\mathrm{o}}][1000B - (V_1^{\mathrm{o}} - V_2^{\mathrm{o}})] \tag{16}$$

The $\Delta\mu_2^{\mathrm{o},\ddagger}$ values (Table 6) contain the change in the free energy of activation of solvent molecules in the presence of solutes and have also the contribution from the movement of solutes.

According to transition state theory, every solvent molecule in one mole of solution must pass through the transition state and also interact more or less strongly with solute molecules. Thus, $\Delta\mu_2^{\mathrm{o},\ddagger}$ includes the free energy of transfer of solute from the ground-state to transition state solvents, $\Delta G_2^{\mathrm{o}}(1\rightarrow1')$, and the free energy of solute through its own viscous transition state, $\Delta G_2^{\mathrm{o}}(2\rightarrow2')$. The $\Delta G_2^{\mathrm{o}}(1\rightarrow1')$ values have been obtained from the $\Delta\mu_2^{\mathrm{o},\ddagger}$ values and $\Delta G_2^{\mathrm{o}}(2\rightarrow2')$ which is equal to $\Delta\mu_1^{\mathrm{o},\ddagger}$ by the method reported elsewhere.[33]

$\Delta\mu_2^{\mathrm{o},\ddagger}$ values of LA and MA decrease with temperature, whereas for SA and CA, they almost remain constant up to 308.15 K and decrease slightly at 318.15 K. In the case of PA, the $\Delta\mu_2^{\mathrm{o},\ddagger}$ values increase up to 298.15 K and thereafter show a continuous decrease over the studied temperature range. The positive $\Delta\mu_2^{\mathrm{o},\ddagger}$ and $\Delta G_2^{\mathrm{o}}(1\rightarrow1')$ values are much larger in comparison to $\Delta\mu_1^{\mathrm{o},\ddagger}$ and suggest that the formation of the transition state is less favored in the presence of metal acetates. This may be because of the breaking and distortion of intermolecular bonds. The decrease in $\Delta\mu_2^{\mathrm{o},\ddagger}$ values with

Table 7. Average Molar Volume, V_1°, and Activation Free Energy, $\Delta\mu_1^{\circ,\ddagger}$, of Water and Thermodynamic Activation Parameters of Viscous Flow of Metal Acetates

property	compound	temperature			
		288.15 K	298.15 K	308.15 K	318.15 K
$V_1^{\circ}\cdot 10^6/\mathrm{m}^3\cdot\mathrm{mol}^{-1}$	Water	18.016	18.053	18.108	18.177
$\Delta\mu_1^{\circ,\ddagger}/\mathrm{kJ}\cdot\mathrm{mol}^{-1}$	Water	9.437	9.161	8.930	8.733
$\Delta\mu_2^{\circ,\ddagger}/\mathrm{kJ}\cdot\mathrm{mol}^{-1}$	LA	74.86	74.36	67.28	62.28
	SA	62.51	63.22	63.42	62.28
	PA	41.84	46.85	45.07	43.08
	MA	161.41	156.14	140.06	134.60
	CA	122.62	123.67	123.61	118.92
$\Delta G_2^{\circ}(1-1')/\mathrm{kJ}\cdot\mathrm{mol}^{-1}$	LA	65.42	65.70	58.35	53.89
	SA	53.16	54.06	54.49	53.55
	PA	32.40	37.61	36.14	34.36
	MA	151.91	146.98	131.78	128.87
	CA	113.16	114.51	114.68	110.14
$\Delta H_2^{\circ,\ddagger}/\mathrm{kJ}\cdot\mathrm{mol}^{-1}$	LA	201.07	204.95	202.25	201.97
	SA	64.79	65.49	65.76	64.70
	PA	33.05	37.75	35.67	33.39
	MA	437.63	442.48	435.56	439.58
	CA	154.58	156.76	157.81	154.23
$T\Delta S_2^{\circ,\ddagger}/\mathrm{kJ}\cdot\mathrm{mol}^{-1}$	LA	126.21	130.59	134.97	139.35
	SA	2.19	2.27	2.34	2.41
	PA	−8.79	−9.09	−9.39	−9.70
	MA	276.22	285.81	295.39	304.98
	CA	31.98	33.09	34.20	35.31

temperature for LA and MA along with negative values of d*B*/d*T* suggest the structure making nature of these solutes. As far as SA, PA, and CA are concerned, $\Delta\mu_2^{\circ,\ddagger}$ almost remains the same for SA at all temperatures and after an initial increase shows a slight decrease in their values at higher temperatures for PA and CA.

The values of $\Delta S_2^{\circ,\ddagger}$ have been calculated from the slopes of $\Delta\mu_2^{\circ,\ddagger}$ vs *T*. The values of $T\Delta S_2^{\circ,\ddagger}$ at different temperatures are listed in Table 7. The activation enthalpies, $\Delta H_2^{\circ,\ddagger}$, have been calculated by using the relation

$$\Delta H_2^{\circ,\ddagger} = \Delta\mu_1^{\circ,\ddagger} + T\Delta S_2^{\circ,\ddagger} \tag{17}$$

and the values are reported in Table 7. Both enthalpies and entropies of activation are positive in the case of LA, MA, and CA, and moreover $\Delta H_2^{\circ,\ddagger} > T\Delta S_2^{\circ,\ddagger}$ thereby suggesting that ion−solvent interactions for the above metal acetates are nearly complete in the ground state. Further, the positive values of activation enthalpies and entropies suggest that the formation of the transition state is associated with bond breaking and a decrease in order. In the case of SA and PA, the activation enthalpies are positive and entropies are negative. Also, $\Delta H_2^{\circ,\ddagger} > T\Delta S_2^{\circ,\ddagger}$ which suggests that the ion−solvent interactions are also complete in the ground-state and the formation of the transition state is accompanied by bond breaking along with a slight increase in the order.

Conclusions

In present work, partial molar volumes, partial molar expansibilities, relative viscosities, *B*-coefficients, and related thermodynamic parameters of some metal acetates have been obtained from density and viscosity measurements at (288.15, 298.15, 308.15, and 318.15) K. Partial molar volumes of metal acetates increase with an increase of temperature, and partial molar expansibilities come out to be positive and their magnitude further decreases with temperature. All metal acetates have negative values of second-order derivative (curvature) of partial molar volume with respect to temperature, which suggests that the metal acetates behave as structure breakers in water.

Viscosity *B*-coefficients of metal acetates are positive, and their magnitude decreases with an increase in temperature and thus has a negative value of d*B*/d*T*, which indicates the structure-making nature of studied metal acetates. Thus, both volumetric and viscometric studies give opposite behavior of metal acetates, and these controversial observations arise due to the specificity of the model applied. The positive values of thermodynamic parameters $\Delta H_2^{\circ,\ddagger}$, $\Delta\mu_2^{\circ,\ddagger}$, and $\Delta G_2^{\circ}(1 \rightarrow 1')$ suggest that the formation of the transition state is less favored in the presence of metal acetates. $T\Delta S_2^{\circ,\ddagger}$ values are positive for LA, MA, and CA and negative for SA and PA, which suggest that formation of the transition state is accompanied by a decrease in order, whereas in SA and PA, it is accompanied by an increase in order.

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