J. Chem. Eng. Data **2006,** *51,* 1415−1423

Densities, Viscosities, and Sound Speeds of Some Acetate Salts in Binary Mixtures of Tetrahydrofuran and Methanol at (303.15, 313.15, and 323.15) K

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The densities and viscosities of ammonium acetate, potassium acetate, sodium acetate, and lithium acetate have been measured in 10, 20, and 30 mass % of tetrahydrofuran + methanol binary solvent mixtures at (303.15, 313.15, and 323.15) K. Apparent molar volumes (V_φ), partial molar expansibility (E_2), viscosity *B*-coefficients, and free energy of activation for viscous flow ($\Delta\mu^{0*}$) are obtained from these data. The limiting apparent molar volumes ($V_\varphi{}^0$) 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. The sound speeds measured at 303.15 K have been used to study the apparent molal isentropic compressibility ($K_{S,\varphi}$), intermolecular free length (L_f), relative association (R_A), relaxation strength (r'), and specific acoustic impedance (Z) of the solutions.

Introduction

Studies on densities, viscosities, and ultrasonic speeds of electrolytic solutions are of great use in characterizing their structure and properties. Various types of interactions exist between the ions in solutions, and these ion−ion and ion−solvent interactions are of current interest in all branches of chemistry. These interactions provide a better understanding of the nature of the solute and solvent (i.e., whether the solute modifies or distorts the structure of the solvent). The nature of ion−solvent interactions in nonaqueous solutions[1] has been successfully elucidated from the volumetric and viscometric behavior of the salts in solutions. A knowledge of this property is very important in many practical problems concerning energy transport, heat transport, mass transport, and fluid flow. Acoustic properties have been the subject of extensive research activity to study the intermolecular interactions in ion−solvent systems.[2] Besides finding applications in the engineering branch, the study is important from practical and theoretical points of view in understanding liquid theory. The nonaqueous systems have been of immense importance[1,3] to the technologist and theoretician as many chemical processes occur in these systems. In the present paper, we have chosen four acetate salts (i.e., ammonium acetate, potassium acetate, sodium acetate, and lithium acetate) and studied their volumetric and viscometric behavior in 10, 20, and 30 mass % of tetrahydrofuran + methanol binary solvent mixtures at (303.15, 313.15, and 323.15) K. The acoustic properties are studied at 303.15 K.

Experimental Section

THF (tetrahydrofuran, C_4H_8O) and MeOH (methanol, C_2H_5OH) were obtained from Merck, India. These were used after further purification by standard methods.[4] The purity of the liquids was checked by measuring their densities, viscosities, and sound speeds at 303.15 K, which was quite in agreement with the literature values.[5−9] The salts ammonium acetate (CH_3COONH_4), potassium acetate (CH_3COOK), sodium acetate ($CH_3COONa{\cdot}3H_2O$), and lithium acetate ($CH_3COOLi{\cdot}2H_2O$) of AR grade were used after purification.[4] The purity was detected by gas−liquid chromatography. The purity of the materials finally obtained was > 99.5 %.

Table 1. Comparison of Experimental Densities (ρ), Viscosities (η), and Ultrasonic Speeds (*u*) of the Solvents and Solvent Mixtures with Literature Values

solvents/ solvent mixtures	*T*/K	$\rho \times 10^{-3}$/kg·m^{-3}		$\eta \times 10^2$/ P		*u*/m·s^{-1}	
		expt	lit.	expt	lit.	expt	lit.
THF	303.15	0.8757	0.8759[6]	0.4452	0.4454[6]	1254.0	1252.1[8]
	313.15	0.8662	0.8663[6]	0.4088	0.4089[6]		
	323.15	0.8583		0.3716			
methanol	303.15	0.7824	0.7825[7]	0.5041	0.5080[7]	1088.5	1088.0[7]
	313.15	0.7718	0.7720[9]	0.4465	0.4470[9]		
	323.15	0.7621		0.4031			
10 % THF + MeOH	303.15	0.7951,[a] 0.7909[b]		0.5477,[a] 0.5166[b]		1177.6,[a] 1116.8[b]	
	313.15	0.7804,[a] 0.7831[b]		0.4701,[a] 0.4713[b]			
	323.15	0.7761,[a] 0.7742[b]		0.4192,[a] 0.4063[b]			
20 % THF + MeOH	303.15	0.8009		0.5016		1146.4	
	313.15	0.7921		0.4549			
	323.15	0.7816		0.3984			
30 % THF + MeOH	303.15	0.8106		0.4921		1144.4	
	313.15	0.8021		0.4413			
	323.15	0.7926		0.3927			

[a] Experimental values for $CH_3COONa{\cdot}3H_2O$ and CH_3COONH_4 solutions. [b] Experimental values for CH_3COOK and $CH_3COOLi{\cdot}2H_2O$ solutions.

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 1 mm. The pycnometer was calibrated at (303.15, 313.15, and 323.15) K with methanol and THF. The pycnometer with the test solution was equilibrated in a thermostatic 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.[10] The viscosities (η) were measured by means of a suspended Ubbelohde-type viscometer[11] that was calibrated at the desired temperatures. The ultrasonic speeds (*u*) were determined using a single-crystal variable path

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10.1021/je060113j CCC: $33.50

Table 2. Experimental Densities (ρ), Viscosities (η), Apparent Molar Volumes (V_φ) along with the Concentrations (in molarity) of Ammonium Acetate, Potassium Acetate, Sodium Acetate, and Lithium Acetate in Different Mass % of Tetrahydrofuran + Methanol Binary Solvent Mixtures at (303.15, 313.15, and 323.15) K

T = 303.15 K				T = 313.15 K				T = 323.15 K			
concn	$\rho \times 10^{-3}$	$\eta \times 10^{2}$	$V_\varphi \times 10^{6}$	concn	$\rho \times 10^{-3}$	$\eta \times 10^{2}$	$V_\varphi \times 10^{6}$	concn	$\rho \times 10^{-3}$	$\eta \times 10^{2}$	$V_\varphi \times 10^{6}$
$mol \cdot L^{-1}$	$kg \cdot m^{-3}$	P	$m^3 \cdot mol^{-1}$	$mol \cdot L^{-1}$	$kg \cdot m^{-3}$	P	$m^3 \cdot mol^{-1}$	$mol \cdot L^{-1}$	$kg \cdot m^{-3}$	P	$m^3 \cdot mol^{-1}$
10 Mass % THF											
CH_3COONH_4											
0.0079	0.7954	0.556	38.7	0.0078	0.7809	0.480	24.7	0.0077	0.7766	0.431	15.8
0.0555	0.7972	0.579	48.8	0.0548	0.7831	0.502	36.0	0.0541	0.7790	0.450	28.8
0.1029	0.7986	0.597	54.2	0.1017	0.7849	0.519	42.7	0.1005	0.7810	0.462	36.0
0.1505	0.7997	0.615	58.2	0.1488	0.7864	0.534	47.6	0.1472	0.7827	0.472	41.6
0.1980	0.8006	0.631	61.8	0.1962	0.7876	0.548	51.9	0.1939	0.7839	0.480	46.8
0.2574	0.8015	0.651	65.5	0.2549	0.7889	0.564	56.1	0.2522	0.7854	0.489	51.5
CH_3COOK											
0.0079	0.7915	0.532	29.2	0.0078	0.7839	0.485	0.5	0.0077	0.7750	0.423	−5.2
0.0554	0.7946	0.566	41.2	0.0549	0.7881	0.514	10.8	0.0543	0.7793	0.453	5.7
0.1029	0.7971	0.593	48.8	0.1019	0.7918	0.535	16.5	0.1009	0.7832	0.473	11.9
0.1505	0.7992	0.614	54.7	0.1494	0.7953	0.553	21.1	0.1481	0.7868	0.489	17.2
0.1980	0.8010	0.635	59.7	0.1964	0.7986	0.571	25.1	0.1941	0.7901	0.503	21.2
0.2589	0.8029	0.659	65.4	0.2569	0.8025	0.591	29.3	0.2542	0.7939	0.519	26.4
$CH_3COONa \cdot 3H_2O$											
0.0080	0.7961	0.576	15.2	0.0079	0.7815	0.489	−1.7	0.0078	0.7772	0.442	−14.6
0.0561	0.8011	0.635	35.4	0.0553	0.7873	0.531	15.6	0.0548	0.7834	0.487	3.5
0.1042	0.8054	0.678	46.7	0.1028	0.7923	0.561	26.2	0.1017	0.7888	0.517	14.4
0.1522	0.8089	0.715	56.8	0.1499	0.7968	0.589	34.3	0.1489	0.7937	0.544	23.1
0.2003	0.8122	0.749	63.5	0.1978	0.8009	0.614	41.3	0.1961	0.7981	0.566	30.3
0.2203	0.8134	0.766	66.7	0.2172	0.8025	0.624	44.1	0.2158	0.7997	0.577	34.0
$CH_3COOLi \cdot 2H_2O$											
0.0079	0.7917	0.524	−0.6	0.0078	0.7840	0.481	−12.2	0.0077	0.7753	0.424	−42.3
0.0555	0.7957	0.554	20.8	0.0549	0.7883	0.509	11.3	0.0544	0.7805	0.461	−17.7
0.1031	0.7988	0.583	32.9	0.1019	0.7916	0.534	24.8	0.1009	0.7848	0.487	−2.8
0.1507	0.8014	0.611	41.5	0.1490	0.7941	0.558	36.0	0.1472	0.7883	0.511	8.4
0.1983	0.8033	0.641	50.0	0.1961	0.7963	0.580	44.9	0.1942	0.7914	0.533	17.3
0.2540	0.8051	0.675	58.4	0.2519	0.7983	0.606	53.3	0.2507	0.7945	0.556	27.5
20 Mass % THF											
CH_3COONH_4											
0.0080	0.8013	0.506	26.9	0.0079	0.7926	0.459	19.3	0.0078	0.7822	0.409	10.1
0.0562	0.8035	0.521	36.8	0.0555	0.7951	0.473	30.2	0.0550	0.7851	0.429	18.9
0.1043	0.8054	0.536	42.6	0.1031	0.7971	0.485	36.7	0.1020	0.7876	0.442	24.3
0.1524	0.8068	0.549	47.6	0.1507	0.7987	0.497	42.2	0.1492	0.7898	0.453	28.7
0.2006	0.8081	0.563	51.4	0.1988	0.8001	0.507	46.5	0.1966	0.7918	0.463	32.4
0.2647	0.8095	0.579	55.6	0.2619	0.8016	0.522	51.8	0.2595	0.7942	0.476	36.5
CH_3COOK											
0.0079	0.8016	0.509	10.7	0.0078	0.7929	0.465	−4.8	0.0077	0.7825	0.410	−14.6
0.0556	0.8053	0.531	23.0	0.0549	0.7969	0.490	11.9	0.0544	0.7869	0.433	−0.4
0.1032	0.8085	0.550	30.2	0.1021	0.8004	0.509	21.8	0.1012	0.7909	0.449	7.7
0.1509	0.8113	0.569	35.9	0.1491	0.8033	0.528	29.0	0.1476	0.7944	0.463	14.6
0.1985	0.8139	0.587	40.8	0.1965	0.8058	0.545	35.9	0.1946	0.7977	0.474	20.1
0.2462	0.8161	0.604	45.3	0.2438	0.8081	0.563	41.1	0.2415	0.8005	0.487	25.5
$CH_3COONa \cdot 3H_2O$											
0.0079	0.8019	0.517	−1.6	0.0078	0.7933	0.466	−23.5	0.0077	0.7829	0.415	−41.9
0.0554	0.8071	0.555	29.0	0.0548	0.7992	0.495	9.1	0.0541	0.7894	0.448	−9.7
0.1029	0.8109	0.586	47.5	0.1019	0.8036	0.519	29.4	0.1007	0.7945	0.471	11.0
0.1503	0.8139	0.615	62.1	0.1492	0.8072	0.542	44.0	0.1473	0.7988	0.491	25.2
0.1978	0.8160	0.642	74.3	0.1967	0.8099	0.563	57.4	0.1943	0.8020	0.509	40.0
0.2675	0.8178	0.681	91.1	0.2652	0.8124	0.595	75.4	0.2627	0.8057	0.537	56.9
$CH_3COOLi \cdot 2H_2O$											
0.0078	0.8018	0.511	−15.9	0.0077	0.7934	0.467	−74.5	0.0076	0.7832	0.416	−123.1
0.0544	0.8058	0.544	14.8	0.0539	0.7987	0.501	−25.8	0.0533	0.7896	0.455	−61.5
0.1011	0.8086	0.575	32.4	0.1001	0.8022	0.527	1.1	0.0989	0.7936	0.482	−24.5
0.1478	0.8105	0.606	46.2	0.1463	0.8044	0.554	22.8	0.1446	0.7958	0.507	5.5
0.1944	0.8116	0.633	58.6	0.1922	0.8055	0.578	40.8	0.1899	0.7968	0.529	28.3
0.2395	0.8122	0.664	68.6	0.2372	0.8056	0.601	56.9	0.2349	0.7962	0.554	51.1
30 Mass % THF											
CH_3COONH_4											
0.0080	0.8111	0.496	24.9	0.0079	0.8026	0.444	18.3	0.0078	0.7931	0.402	10.1
0.0561	0.8132	0.512	37.6	0.0555	0.8049	0.458	31.7	0.0549	0.7957	0.421	25.0
0.1042	0.8149	0.527	44.4	0.1031	0.8068	0.471	39.4	0.1020	0.7978	0.434	33.4
0.1523	0.8161	0.543	50.5	0.1507	0.8083	0.485	45.1	0.1492	0.7994	0.446	40.2
0.2004	0.8170	0.558	55.5	0.1984	0.8094	0.498	50.2	0.1966	0.8007	0.457	45.6
0.2485	0.8179	0.575	59.1	0.2462	0.8104	0.512	54.5	0.2436	0.8016	0.467	50.5
CH_3COOK											
0.0080	0.8114	0.495	3.7	0.0079	0.8029	0.444	−9.3	0.0078	0.7935	0.401	−20.3
0.0559	0.8152	0.514	19.3	0.0554	0.8073	0.459	6.0	0.0548	0.7980	0.421	−1.2
0.1038	0.8184	0.532	28.9	0.1028	0.8109	0.475	15.3	0.1017	0.8019	0.437	9.0
0.1517	0.8211	0.550	36.1	0.1502	0.8141	0.489	22.8	0.1482	0.8051	0.451	17.6
0.1997	0.8233	0.569	42.7	0.1974	0.8169	0.504	29.0	0.1952	0.8079	0.465	24.9
0.2476	0.8252	0.587	48.2	0.2449	0.8195	0.519	34.0	0.2422	0.8105	0.479	30.4

Table 2. (Continued)

$T = 303.15$ K				$T = 313.15$ K				$T = 323.15$ K			
concn	$\rho \times 10^{-3}$	$\eta \times 10^2$	$V_\varphi \times 10^6$	concn	$\rho \times 10^{-3}$	$\eta \times 10^2$	$V_\varphi \times 10^6$	concn	$\rho \times 10^{-3}$	$\eta \times 10^2$	$V_\varphi \times 10^6$
$mol \cdot L^{-1}$	$kg \cdot m^{-3}$	P	$m^3 \cdot mol^{-1}$	$mol \cdot L^{-1}$	$kg \cdot m^{-3}$	P	$m^3 \cdot mol^{-1}$	$mol \cdot L^{-1}$	$kg \cdot m^{-3}$	P	$m^3 \cdot mol^{-1}$
30 mass % THF											
$CH_3COONa \cdot 3H_2O$											
0.0079	0.8118	0.501	−15.6	0.0078	0.8036	0.449	−65.3	0.0077	0.7942	0.404	−96.0
0.0553	0.8173	0.531	19.5	0.0548	0.8102	0.474	−14.3	0.0542	0.8015	0.432	−36.0
0.1028	0.8213	0.557	39.4	0.1018	0.8148	0.496	14.5	0.1008	0.8065	0.454	−2.8
0.1502	0.8244	0.583	54.8	0.1486	0.8179	0.518	36.7	0.1472	0.8096	0.473	26.1
0.1977	0.8267	0.608	67.7	0.1961	0.8200	0.539	56.0	0.1939	0.8115	0.491	48.6
0.2530	0.8284	0.639	81.3	0.2507	0.8213	0.561	74.4	0.2480	0.8124	0.513	70.9
$CH_3COOLi \cdot 2H_2O$											
0.0080	0.8118	0.498	−60.3	0.0079	0.8036	0.447	−102.1	0.0078	0.7945	0.399	−177.1
0.0561	0.8171	0.526	−16.0	0.0555	0.8098	0.473	−45.5	0.0550	0.8022	0.421	−92.1
0.1041	0.8205	0.555	8.6	0.1029	0.8135	0.496	−10.8	0.1021	0.8066	0.439	−44.1
0.1522	0.8227	0.583	27.5	0.1507	0.8157	0.520	14.9	0.1492	0.8084	0.459	−4.7
0.2003	0.8239	0.612	44.0	0.1981	0.8163	0.542	38.0	0.1964	0.8087	0.475	25.2
0.2483	0.8242	0.642	58.6	0.2456	0.8158	0.564	57.9	0.2432	0.8068	0.491	55.1

Table 3. Limiting Apparent Molar Volume ($V_\varphi{}^0$) and Experimental Slope (S_V^*) for the Acetate Salts in Different Mass % of THF + MeOH Mixtures along with Standard Errors at (303.15, 313.15 and 323.15) K

		CH_3COONH_4		CH_3COOK		$CH_3COONa \cdot 3H_2O$		$CH_3COOLi \cdot 2H_2O$	
mass % of THF	T	$V_\varphi{}^0 \times 10^6$	$S_V^* \times 10^6$	$V_\varphi{}^0 \times 10^6$	$S_V^* \times 10^6$	$V_\varphi{}^0 \times 10^6$	$S_V^* \times 10^6$	$V_\varphi{}^0 \times 10^6$	$S_V^* \times 10^6$
	K	$m^3 \cdot mol^{-1}$	$(m^9 \cdot mol^{-3})^{1/2}$	$m^3 \cdot mol^{-1}$	$(m^9 \cdot mol^{-3})^{1/2}$	$m^3 \cdot mol^{-1}$	$(m^9 \cdot mol^{-3})^{1/2}$	$m^3 \cdot mol^{-1}$	$(m^9 \cdot mol^{-3})^{1/2}$
10	303.15	33.4 ± 0.02	63.8 ± 0.01	21.2 ± 0.01	86.5 ± 0.04	3.2 ± 0.03	135.6 ± 0.07	−12.9 ± 0.01	141.4 ± 0.01
	313.15	18.2 ± 0.05	75.8 ± 0.02	−5.5 ± 0.02	68.8 ± 0.02	−12.7 ± 0.06	121.4 ± 0.04	−26.2 ± 0.02	159.7 ± 0.02
	323.15	8.4 ± 0.01	86.5 ± 0.03	−11.9 ± 0.07	75.6 ± 0.04	−26.2 ± 0.04	128.3 ± 0.07	−57.1 ± 0.02	169.5 ± 0.02
20	303.15	20.8 ± 0.02	68.1 ± 0.03	3.0 ± 0.09	84.9 ± 0.07	−21.4 ± 0.02	215.9 ± 0.01	−34.5 ± 0.02	210.7 ± 0.01
	313.15	12.2 ± 0.04	76.9 ± 0.01	−14.7 ± 0.02	113.6 ± 0.09	−44.4 ± 0.08	230.8 ± 0.02	−102.8 ± 0.05	328.2 ± 0.02
	323.15	4.3 ± 0.04	63.1 ± 0.02	−23.5 ± 0.03	99.0 ± 0.03	−63.2 ± 0.05	233.1 ± 0.02	−161.9 ± 0.01	438.2 ± 0.04
30	303.15	17.5 ± 0.02	84.2 ± 0.06	−6.3 ± 0.01	109.3 ± 0.09	−35.9 ± 0.02	233.5 ± 0.08	−85.5 ± 0.02	289.9 ± 0.02
	313.15	10.6 ± 0.08	88.9 ± 0.06	−19.0 ± 0.07	107.5 ± 0.02	−94.4 ± 0.02	339.3 ± 0.08	−137.6 ± 0.02	394.1 ± 0.07
	323.15	1.5 ± 0.03	99.6 ± 0.03	−31.2 ± 0.02	126.1 ± 0.06	−131.6 ± 0.02	408.4 ± 0.04	−227.1 ± 0.03	572.4 ± 0.02

ultrasonic interferometer[12] (Mittal Enterprises, New Delhi) working at 4 MHz. The instrument was calibrated, and the temperature stability was maintained within ± 0.01 K by circulating thermostatic water around the cell with a circulating pump. The solutions were prepared with an accuracy of 1×10^{-4} in airtight stoppered bottles at 303.15 K. The weights were taken on a Mettler electronic analytical balance (AG285, Switzerland). The uncertainties in the density, viscosity, and speed of sound measurements were estimated to be 0.003 $kg \cdot m^{-3}$, 0.002 P, and 0.2 $m \cdot s^{-1}$, respectively.

Results

The physical properties of the solvents along with the solvent mixtures are given in Table 1. (It should be mentioned here that in carrying out the experimental work there was loss of the solvent mixture due to personal error for 10 % THF + MeOH solvent mixture, so we have performed the work in two sets.)

Table 2 contains the experimental densities (ρ), viscosities (η), and apparent molar volumes (V_φ) along with the molar concentrations of ammonium acetate, potassium acetate, sodium acetate, and lithium acetate in 10, 20, and 30 mass % of tetrahydrofuran + methanol binary mixtures at (303.15, 313.15, and 323.15) K.

The apparent molar volumes (V_φ) are determined from the solution densities using the following equation:[13]

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

where M is the molar mass of the salt, c is the molarity of the solution, and ρ_0 and ρ are the densities of the solvent mixtures and solution, respectively. The uncertainty in the measurement of V_φ values was found to be ± 0.002 %.

The limiting apparent molar volumes ($V_\varphi{}^0$) are calculated using a least-squares treatment to the plots of V_φ versus $c^{1/2}$ using the following Masson equation:[14]

$$V_\varphi = V_\varphi{}^0 + S_V{}^* \sqrt{c} \qquad (2)$$

where $V_\varphi{}^0$ is the partial molar volume at infinite dilution and S_V^* is the experimental slope. The plots of V_φ against square root of molar concentration ($c^{1/2}$) are found to be linear. The values of $V_\varphi{}^0$ and S_V^* are reported in Table 3.

The partial molar expansibility (E_2) has been calculated from the equation:[15]

$$E_2 = E_\varphi + [(1000 - cE_\varphi)(2000 + S_E c^{3/2})^{-1}]S_E c^{1/2} \qquad (3)$$

The uncertainty in the measurement of E_2 values was found to be ± 0.004 %. Here E_φ is the apparent molar expansibility, and its value is determined from

$$E_\varphi = \alpha_0 V_\phi + (\alpha - \alpha_0)1000c^{-1} \qquad (4)$$

S_E is the slope of the plot of E_φ versus $c^{1/2}$:

$$E_\varphi = E_\varphi{}^0 + S_E\sqrt{c} \qquad (5)$$

In eq 4, α_0 and α are the coefficients of thermal expansion of the solvent mixture and solution, respectively, and are obtained by the usual relation as follows:

$$\alpha_0 = -1/\rho_0(\delta\rho_0/\delta T) \text{ and } \alpha = -1/\rho(\delta\rho/\delta T) \qquad (6)$$

The values of $E_\varphi{}^0$ and S_E are given in Table 4 along with the standard errors.

Table 4. Limiting Apparent Molar Expansibility (E_φ^0) and Experimental Slope (S_E) for the Acetate Salts in Different Mass % of THF + MeOH Mixtures along with Standard Errors at (303.15, 313.15, and 323.15) K

mass % of THF	T / K	CH_3COONH_4 $E_\varphi^0 \times 10^6$ / $m^3 \cdot mol^{-1}K^{-1}$	CH_3COONH_4 $S_E \times 10^6$ / $(m^9 \cdot mol^{-3})^{1/2} \cdot K^{-1}$	CH_3COOK $E_\varphi^0 \times 10^6$ / $m^3 \cdot mol^{-1}K^{-1}$	CH_3COOK $S_E \times 10^6$ / $(m^9 \cdot mol^{-3})^{1/2} \cdot K^{-1}$	$CH_3COONa \cdot 3H_2O$ $E_\varphi^0 \times 10^6$ / $m^3 \cdot mol^{-1}K^{-1}$	$CH_3COONa \cdot 3H_2O$ $S_E \times 10^6$ / $(m^9 \cdot mol^{-3})^{1/2} \cdot K^{-1}$	$CH_3COOLi \cdot 2H_2O$ $E_\varphi^0 \times 10^6$ / $m^3 \cdot mol^{-1}K^{-1}$	$CH_3COOLi \cdot 2H_2O$ $S_E \times 10^6$ / $(m^9 \cdot mol^{-3})^{1/2} \cdot K^{-1}$
10	303.15	−1.15 ± 0.01	0.95 ± 0.02	−1.61 ± 0.03	−0.48 ± 0.06	−1.47 ± 0.04	−0.20 ± 0.01	−2.16 ± 0.01	1.40 ± 0.01
	313.15	−1.23 ± 0.04	1.02 ± 0.01	−1.71 ± 0.02	−0.48 ± 0.02	−1.57 ± 0.05	−0.21 ± 0.04	−2.23 ± 0.02	1.49 ± 0.02
	323.15	−1.28 ± 0.02	1.09 ± 0.04	−1.76 ± 0.09	−0.47 ± 0.03	−1.63 ± 0.04	−0.16 ± 0.03	−2.35 ± 0.02	1.57 ± 0.02
20	303.15	−0.75 ± 0.01	−0.35 ± 0.03	−1.28 ± 0.05	0.66 ± 0.07	−2.02 ± 0.03	0.78 ± 0.01	−6.12 ± 0.09	10.77 ± 0.01
	313.15	−0.78 ± 0.03	−0.36 ± 0.01	−1.35 ± 0.02	0.74 ± 0.07	−2.11 ± 0.04	0.85 ± 0.04	−6.41 ± 0.05	11.33 ± 0.02
	323.15	−0.83 ± 0.05	−0.39 ± 0.02	−1.41 ± 0.01	0.75 ± 0.03	−2.23 ± 0.05	0.93 ± 0.02	−6.71 ± 0.07	11.93 ± 0.04
30	303.15	−0.73 ± 0.01	0.62 ± 0.06	−1.19 ± 0.01	0.76 ± 0.04	−4.54 ± 0.02	8.09 ± 0.07	−6.77 ± 0.02	13.24 ± 0.02
	313.15	−0.76 ± 0.07	0.64 ± 0.05	−1.23 ± 0.07	0.75 ± 0.01	−4.76 ± 0.02	8.53 ± 0.08	−7.01 ± 0.01	13.79 ± 0.07
	323.15	−0.80 ± 0.04	0.67 ± 0.03	−1.28 ± 0.04	0.81 ± 0.06	−4.95 ± 0.02	8.91 ± 0.04	−7.37 ± 0.03	14.58 ± 0.02

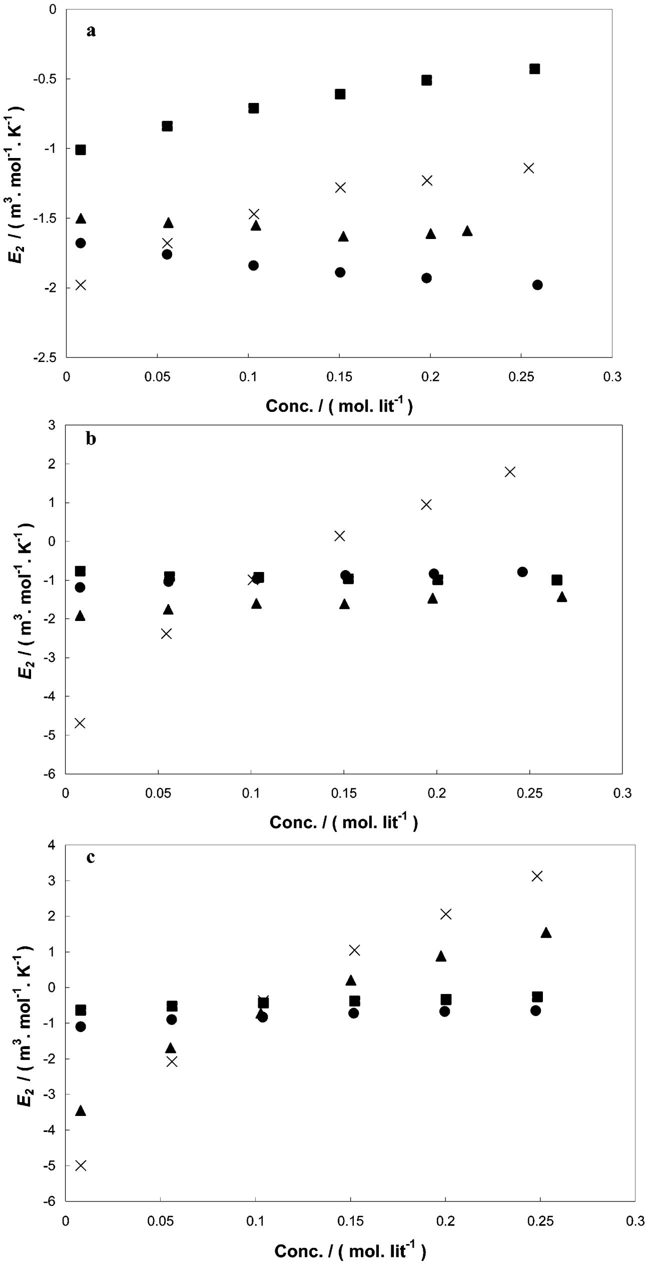

Figure 1. (a) Variation of E_2 with concentration of ■, CH_3COONH_4; ●, CH_3COOK; ▲, $CH_3COONa \cdot 3H_2O$; and ×, $CH_3COOLi \cdot 2H_2O$ in 10 mass % THF at 303.15 K. (b) Variation of E_2 with concentration of ■, CH_3COONH_4; ●, CH_3COOK; ▲, $CH_3COONa \cdot 3H_2O$; and ×, $CH_3COOLi \cdot 2H_2O$ in 20 mass % THF at 303.15 K. (c) Variation of E_2 with concentration of ■, CH_3COONH_4; ●, CH_3COOK; ▲, $CH_3COONa \cdot 3H_2O$; and ×, $CH_3COOLi \cdot 2H_2O$ in 30 mass % THF at 303.15 K.

Figure 1, panels a to c, depicts the plots of E_2 against c for 10, 20, and 30 mass % THF + MeOH for the four salts at 303.15 K. Similar curves are obtained at higher temperatures. The viscosity data for acetates in 10, 20, and 30 mass % of THF + MeOH mixtures have been analyzed using the Jones−Dole equation:[16]

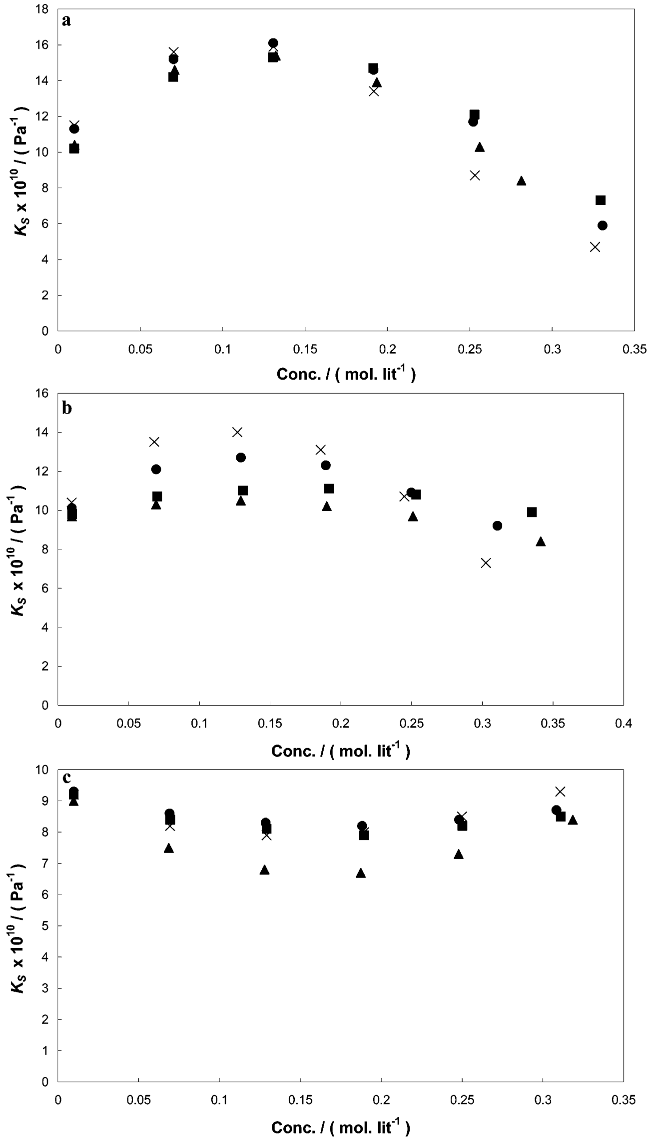

Figure 2. (a) Variation of K_S with concentration of ■, CH_3COONH_4; ●, CH_3COOK; ▲, $CH_3COONa \cdot 3H_2O$; and ×, $CH_3COOLi \cdot 2H_2O$ in 10 mass % THF at 303.15 K. (b) Variation of K_S with concentration of ■, CH_3COONH_4; ●, CH_3COOK; ▲, $CH_3COONa \cdot 3H_2O$; and ×, $CH_3COOLi \cdot 2H_2O$ in 20 mass % THF at 303.15 K. (c) Variation of K_S with concentration of ■, CH_3COONH_4; ●, CH_3COOK; ▲, $CH_3COONa \cdot 3H_2O$; and ×, $CH_3COOLi \cdot 2H_2O$ in 30 mass % THF at 303.15 K.

$$(\eta/\eta_0 - 1)/c^{1/2} = A + Bc^{1/2} \qquad (7)$$

Table 5. Jones−Dole Coefficients *A* and *B* with Standard Errors along with the Free Energy of Activation for Viscous Flow of Solvent Mixture ($\Delta\mu^{0}*_1$) and Solution ($\Delta\mu^{0}*_2$) for the Acetate Salts in Different Mass % of THF + MeOH at (303.15, 313.15, and 323.15) K

$T = 303.15$ K				$T = 313.15$ K				$T = 323.15$ K			
A	*B*	$\Delta\mu^{0}*_1$	$\Delta\mu^{0}*_2 \times 10^{-3}$	*A*	*B*	$\Delta\mu^{0}*_1$	$\Delta\mu^{0}*_2 \times 10^{-3}$	*A*	*B*	$\Delta\mu^{0}*_1$	$\Delta\mu^{0}*_2 \times 10^{-3}$
$m^{3/2}\cdot mol^{-1/2}$	$m^3\cdot mol^{-1}$	$kJ\cdot mol^{-1}$	$kJ\cdot mol^{-1}$	$m^{3/2}\cdot mol^{-1/2}$	$m^3\cdot mol^{-1}$	$kJ\cdot mol^{-1}$	$kJ\cdot mol^{-1}$	$m^{3/2}\cdot mol^{-1/2}$	$m^3\cdot mol^{-1}$	$kJ\cdot mol^{-1}$	$kJ\cdot mol^{-1}$
10 Mass % THF											
CH_3COONH_4											
0.14 ± 0.01	0.46 ± 0.03	33.48	27.19	0.21 ± 0.06	0.37 ± 0.01	34.23	21.48	0.31 ± 0.02	0.06 ± 0.03	35.03	3.49
CH_3COOK											
0.29 ± 0.03	0.50 ± 0.06	33.34	29.41	0.28 ± 0.01	0.43 ± 0.01	34.23	25.05	0.45 ± 0.02	0.19 ± 0.05	34.96	10.96
$CH_3COONa\cdot 3H_2O$											
0.51 ± 0.04	0.71 ± 0.01	33.48	41.96	0.41 ± 0.07	0.62 ± 0.02	34.23	35.97	0.58 ± 0.03	0.49 ± 0.04	35.03	28.28
$CH_3COOLi\cdot 2H_2O$											
0.06 ± 0.11	1.08± 0.01	33.34	63.49	0.15 ± 0.08	0.84 ± 0.03	34.23	48.89	0.44 ± 0.02	0.60± 0.02	34.96	34.54
20 Mass % THF											
CH_3COONH_4											
0.05 ± 0.01	0.50± 0.06	33.39	28.03	0.07 ± 0.02	0.42 ± 0.12	34.27	23.29	0.30 ± 0.09	0.15 ± 0.01	35.04	8.23
CH_3COOK											
0.11 ± 0.01	0.60 ± 0.04	33.39	33.63	0.19 ± 0.05	0.57 ± 0.02	34.27	31.6	0.31 ± 0.02	0.29 ± 0.07	35.04	15.88
$CH_3COONa\cdot 3H_2O$											
0.26 ± 0.01	0.82 ± 0.07	33.39	45.95	0.20 ± 0.03	0.76 ± 0.03	34.27	42.12	0.41 ± 0.04	0.51 ± 0.01	35.04	27.91
$CH_3COOLi\cdot 2H_2O$											
0.11 ± 0.03	1.12 ± 0.04	33.39	62.75	0.23 ± 0.03	0.88 ± 0.01	34.27	48.77	0.44 ± 0.08	0.72 ± 0.02	35.04	39.38
30 Mass % THF											
CH_3COONH_4											
0.03 ± 0.04	0.62 ± 0.02	33.47	32.98	0.02 ± 0.01	0.59 ± 0.06	34.32	31.05	0.25 ± 0.06	0.27 ± 0.04	35.14	14.06
CH_3COOK											
0.01 ± 0.01	0.76 ± 0.05	33.47	40.42	0.02 ± 0.10	0.68 ± 0.01	34.32	35.78	0.19 ± 0.04	0.49 ± 0.05	35.14	25.49
$CH_3COONa\cdot 3H_2O$											
0.11 ± 0.01	0.94 ± 0.01	33.47	49.98	0.12 ± 0.04	0.86 ± 0.07	34.32	45.25	0.27 ± 0.04	0.68 ± 0.02	35.14	35.37
$CH_3COOLi\cdot 2H_2O$											
0.02 ± 0.05	1.17 ± 0.11	33.47	62.21	0.06 ± 0.03	1.01 ± 0.01	34.32	53.13	0.12 ± 0.04	0.79 ± 0.05	35.14	41.08

where η_0 and η are the viscosities of solvent mixtures and solution, respectively. *A* is the constant characteristic of the salt, and *B* is the Jones−Dole coefficient; both are obtained from the plot of $(\eta/\eta_0 - 1)/c^{1/2}$ versus $c^{1/2}$. The corresponding data for *A* and *B* are reported in Table 5.

The viscosity data are also analyzed on the basis of transition state theory for relative viscosity of the acetate solutions as suggested by Feakins et al.[17] using eq 8:

$$\Delta\mu^{0}*_2 = \Delta\mu^{0}*_1 + (RT/V^{0}_1)1000B - (V^{0}_1 - V^{0}_2) \qquad (8)$$

where $\Delta\mu^{0}*_2$ is the contribution per mole of the salt to free energy of activation for viscous flow of solution and $\Delta\mu^{0}*_1$ is the free energy of activation per mole of the solvent mixture. The values are reported in Table 5. V^{0}_1 ($= M/\rho$) is the partial molar volume of the solvent mixture, V^{0}_2 ($= V_{\varphi}{}^{0}$) is the partial molar volume of the solute. $\Delta\mu^{0}*_1$ is calculated from

$$\Delta\mu^{0}*_1 = 2.303RT\log(\eta_0 V^{0}_1/hN) \qquad (9)$$

where *h* is Planck's constant and *N* is Avogadro's number.

The isentropic compressibility (K_S) of the solution is calculated from the Laplace's equation:[18]

$$K_S = 1/(u^2\rho) \qquad (10)$$

where ρ is the solution density and *u* is the ultrasonic speed in the solution. The variation of K_S with *m* is shown graphically in Figure 2, panels a to c, at 303.15 K. The apparent molal isentropic compressibility ($K_{S,\varphi}$) of the solutions is determined from the relation

$$K_{S,\varphi} = M_2K_S/\rho_0 + 1000(K_S\rho_0 - K_S{}^{0}\rho)/(m\rho\rho_0) \qquad (11)$$

M_2 is the molar mass of the salt and $K_S{}^0$ is the isentropic compressibility of the solvent mixture. The limiting apparent molal isentropic compressibility ($K_{S,\varphi}{}^0$) was obtained by extrapolating the plots of $K_{S,\varphi}$ versus the square root of molal concentration of the solute to zero concentration by a least-squares method:

$$K_{S,\varphi} = K_{S,\varphi}{}^{0} + S^*_K m^{1/2} \qquad (12)$$

where S^*_K is the experimental slope. The values of *u*, $K_{S,\varphi}$, $K_{S,\varphi}{}^0$ and S^*_K are reported in Table 6.

Various acoustical parameters such as specific acoustic impedance *Z*, intermolecular free length L_f, van der Waals constant *b*, molecular radius *r*, geometrical volume *B*, molar surface area *Y*, available volume V_a, molar speed of sound R',

Table 6. Ultrasonic Speed (u), Apparent Molal Isentropic Compressibility ($K_{S,\varphi}$), Limiting Apparent Molal Isentropic Compressibility ($K^0_{S,\varphi}$), and Experimental Slope (S^*_K) against the Respective Molalities of the Solutions along with Standard Errors at 303.15 K

concn mol·kg^{-1}	u m·s^{-1}	$K_{S,\varphi}\times 10^{10}$ $\text{m}^3\text{·mol}^{-1}\text{·Pa}^{-1}$	$K_{S,\varphi}{}^0\times 10^{10}$ $\text{m}^3\text{·mol}^{-1}\text{·Pa}^{-1}$	S^*_K/ $\text{m}^{9/2}\text{·mol}^{-3/2}\text{·Pa}^{-1}$	concn mol·kg^{-1}	u m·s^{-1}	$K_{S,\varphi}\times 10^{10}$ $\text{m}^3\text{·mol}^{-1}\text{·Pa}^{-1}$	$K_{S,\varphi}{}^0\times 10^{10}$ $\text{m}^3\text{·mol}^{-1}\text{·Pa}^{-1}$	S^*_K/ $\text{m}^{9/2}\text{·mol}^{-3/2}\text{·Pa}^{-1}$
10 Mass % THF									
CH_3COONH_4									
0.0099	1108.3	147.4			0.1913	920.8	38.2		
0.0700	941.5	92.0			0.2528	1014.6	16.0		
0.1305	904.4	61.0	0.55 ± 0.03	−0.003 ± 0.002	0.3294	1310.2	−6.4		
CH_3COOK									
0.0100	1055.2	153.0			0.1916	924.7	30.5		
0.0702	909.6	92.0			0.2521	1033.4	8.5		
0.1307	882.9	58.4	0.53 ± 0.01	−0.003 ± 0.005	0.3306	1458.9	−16.0		
$CH_3COONa·3H_2O$									
0.0101	1098.6	167.0			0.1936	941.1	32.6		
0.0709	923.1	99.6			0.2559	1094.8	6.6		
0.1322	897.8	61.0	0.52 ± 0.02	−0.003 ± 0.003	0.2813	1211.4	−2.5		
$CH_3COOLi·2H_2O$									
0.0100	1048.7	170.0			0.1917	963.4	22.4		
0.0703	897.8	98.5			0.2531	1194.4	−6.6		
0.1308	888.3	55.9	0.49 ± 0.03	−0.002 ± 0.001	0.3259	1619.8	−20.7		
20 Mass % THF									
CH_3COONH_4									
0.0100	1130.9	32.3			0.1918	1055.6	11.1		
0.0703	1078.4	21.7			0.2533	1070.1	7.0		
0.1308	1057.9	15.7	0.61± 0.02	−0.016 ± 0.003	0.3352	1113.3	2.3		
CH_3COOK									
0.0099	1111.2	76.3			0.1895	1000.5	19.0		
0.0695	1011.4	47.7			0.2499	1061.3	7.5		
0.1294	985.1	31.7	0.55 ± 0.01	−0.006 ± 0.005	0.3109	1153.4	−0.7		
$CH_3COONa·3H_2O$									
0.0099	1133.7	25.4			0.1901	1097.2	5.3		
0.0694	1094.4	15.5			0.2510	1125.6	1.6		
0.1293	1085.7	9.8	0.53 ± 0.03	−0.017 ± 0.006	0.3414	1205.9	−3.2		
$CH_3COOLi·2H_2O$									
0.0097	1092.9	120.7			0.1859	972.2	24.5		
0.0682	959.1	73.3			0.2449	1074.6	6.6		
0.1269	939.7	44.8	0.52 ± 0.04	−0.003 ± 0.004	0.3026	1295.1	−8.4		
30 Mass % THF									
CH_3COONH_4									
0.0099	1157.0	−25.9			0.1895	1239.6	−9.0		
0.0695	1209.1	−17.6			0.2503	1224.1	−5.7		
0.1292	1233.7	−12.6	0.62 ± 0.01	0.020 ± 0.001	0.3111	1200.0	−3.2		
CH_3COOK									
0.0099	1154.3	−21.2			0.1883	1212.2	−7.1		
0.0691	1193.9	−14.4			0.2483	1202.3	−4.7		
0.1286	1211.7	−10.2	0.61 ± 0.02	0.024 ± 0.008	0.3084	1177.3	−2.3		
$CH_3COONa·3H_2O$									
0.0098	1169.8	−52.9			0.1874	1340.8	−17.2		
0.0686	1280.4	−35.0			0.2479	1286.8	−10.0		
0.1279	1335.3	−24.7	0.59 ± 0.05	0.009 ± 0.001	0.3185	1201.4	−3.4		
$CH_3COOLi·2H_2O$									
0.0099	1159.8	−33.3			0.1894	1229.0	−8.7		
0.0693	1219.9	−21.4			0.2499	1195.7	−4.2		
0.1291	1240.1	−14.2	0.56 ± 0.02	0.014 ± 0.007	0.3108	1140.5	0.2		

Table 7. Derived Values of Specific Acoustic Impedance (Z), Intermolecular Free Length (L_f), van der Waals Constant (b), Molecular Radius (r), Geometrical Volume (B), Molar Surface Area (Y), Available Volume (V_a), Volume at Absolute Zero (V_0), Molar Speed of Sound (R'), Collision Factor (S), Relaxation Strength (r'), and Space Filling Factor (r_f) of the Solvent Mixtures at 303.15 K

mass % of THF	$b\times 10^3$ m^3	r nm	$B\times 10^3$ $\text{m}^3\text{·mol}^{-1}$	S	$R'\times 10^4$ $\text{m}^3\text{·mol}^{-1}\text{·(ms}^{-1})^{1/3}$	$V_a\times 10^3$ $\text{m}^3\text{· mol}^{-1}$	$V_0\times 10^3$ $\text{m}^3\text{·mol}^{-1}$	L_f nm	r'	r_f	$Y\times 10^{-6}$ $\text{m}^2\text{·mol}^{-1}$	$Z\times 10^{-3}$ $\text{m}^3\text{·mol}^{-1}$
10[a]	42.49	1.615	10.62	2.96	4506.6	11.27	31.41	0.0625	0.458	0.249	19.72	936.26
10[b]	42.71	1.618	10.68	2.80	4450.9	12.95	29.94	0.0661	0.513	0.249	19.80	883.29
20	44.83	1.644	11.21	2.88	4711.1	12.76	32.25	0.0639	0.487	0.249	20.45	918.12
30	47.24	1.673	11.81	2.87	4961.5	13.51	33.92	0.0637	0.488	0.249	21.18	927.66

[a] Experimental values of 10 mass % THF that was used for $CH_3COONa·3H_2O$ and CH_3COONH_4 solutions. [b] Experimental values of 10 mass % THF that has been used for CH_3COOK and $CH_3COOLi·2H_2O$ solutions.

Table 8. Derived Values of Specific Acoustic Impedance (Z), Intermolecular Free Length (L_f), Relaxation Strength (r'), and Relative Association (R_A) for the Acetate Salts in Different Mass % of THF + MeOH Mixtures at 303.15 K

CH_3COONH_4				CH_3COOK				$CH_3COONa{\cdot}3H_2O$				$CH_3COOLi{\cdot}2H_2O$			
$Z \times 10^{-3}$	L_f			$Z \times 10^{-3}$	L_f			$Z \times 10^{-3}$	L_f			$Z \times 10^{-3}$	L_f		
$m^3{\cdot}mol^{-1}$	nm	r'	R_A	$m^3{\cdot}mol^{-1}$	nm	r'	R_A	$m^3{\cdot}mol^{-1}$	nm	r'	R_A	$m^3{\cdot}mol^{-1}$	nm	r'	R_A
10 Mass % THF															
881.58	0.066	0.52	1.02	835.20	0.069	0.57	1.02	874.54	0.067	0.53	1.02	830.29	0.070	0.57	1.02
750.54	0.078	0.65	1.08	722.72	0.081	0.68	1.08	739.50	0.079	0.67	1.09	714.35	0.082	0.68	1.08
722.22	0.081	0.68	1.10	703.72	0.083	0.69	1.09	723.06	0.081	0.69	1.11	709.53	0.083	0.69	1.09
736.35	0.079	0.67	1.09	739.00	0.079	0.67	1.07	761.26	0.078	0.65	1.10	772.02	0.076	0.64	1.06
812.28	0.072	0.59	1.06	827.75	0.071	0.58	1.04	889.19	0.067	0.53	1.05	959.47	0.061	0.44	0.99
1050.13	0.056	0.33	0.97	1171.41	0.050	0.17	0.93	985.30	0.060	0.43	1.01	1304.12	0.045	0.12	0.89
20 Mass % THF															
906.21	0.065	0.50	1.01	890.72	0.066	0.52	1.01	909.18	0.065	0.49	1.01	876.24	0.067	0.53	1.02
866.54	0.068	0.55	1.02	814.48	0.072	0.60	1.05	883.31	0.066	0.53	1.02	772.82	0.076	0.64	1.07
851.98	0.069	0.56	1.03	796.46	0.074	0.62	1.07	880.46	0.067	0.54	1.03	759.80	0.078	0.66	1.08
851.67	0.070	0.57	1.04	811.75	0.073	0.61	1.06	892.96	0.066	0.53	1.03	787.95	0.075	0.63	1.07
864.72	0.068	0.55	1.03	863.75	0.069	0.56	1.04	918.51	0.065	0.51	1.02	872.12	0.068	0.55	1.04
901.19	0.066	0.52	1.02	941.28	0.063	0.48	1.02	986.14	0.060	0.43	1.00	1051.82	0.056	0.34	0.97
30 Mass % THF															
938.41	0.063	0.48	1.00	936.56	0.063	0.48	1.00	949.63	0.062	0.47	0.99	941.55	0.063	0.47	1.00
983.26	0.060	0.43	0.99	973.29	0.061	0.44	0.99	1046.43	0.057	0.36	0.97	996.73	0.060	0.42	0.99
1005.33	0.059	0.41	0.98	991.62	0.060	0.43	0.99	1096.69	0.054	0.30	0.96	1017.51	0.058	0.40	0.98
1011.65	0.058	0.40	0.98	995.29	0.059	0.43	0.99	1105.33	0.054	0.29	0.96	1011.15	0.059	0.41	0.99
1000.14	0.059	0.41	0.99	989.84	0.060	0.44	1.00	1063.75	0.056	0.35	0.98	985.13	0.060	0.44	1.00
981.44	0.060	0.44	0.99	971.54	0.061	0.46	1.01	995.20	0.060	0.44	1.01	939.94	0.063	0.49	1.02

collision factor S, relaxation strength r', and space filling factor r_f has been calculated from the speeds of sound and densitydata of the solvent mixtures using the following relations:[19]

$$Z = u\rho \tag{13}$$

$$b = (M/\rho) - (RT/\rho u^2)\{[1 + (Mu^2/3RT)]^{1/2} - 1\} \tag{14}$$

$$r = (3b/16\pi N)^{1/3} \tag{15}$$

$$L_f = K/(u\rho^{1/2}) \tag{16}$$

$$B = (4/3)\pi r^3 N \tag{17}$$

$$Y = (36\pi NB^2)^{1/3} \tag{18}$$

$$V_a = V - V_0 = V(1 - u/u_\infty) \tag{19}$$

$$R' = Mu^{1/3}/\rho \tag{20}$$

$$S = uV/u_\infty B \tag{21}$$

$$r' = 1 - (u/u_\infty)^2 \tag{22}$$

$$r_f = B/V \tag{23}$$

where K is a temperature-dependent Jacobson's constant (= $(93.875 + 0.375\ T) \times 10^{-8}$), V_0 is volume at absolute zero, V is the molecular volume, and u_∞ is taken as 1600 ms^{-1}. These parameters are listed in Table 7 for the solvent mixtures whereas Table 8 gives the Z, L_f, and r' values along with the relative association R_A for the salt solutions at (303.15, 313.15, and 323.15) K:

$$R_A = \rho_S/\rho_0(u_0/u_S)^{1/3} \tag{24}$$

Discussions

The limiting apparent molar volumes ($V_\varphi{}^0$) shown in Table 3 are a mixture of positive and negative values. $V_\varphi{}^0$ is found to decrease for all the acetate salts as mass % of THF increases in the THF + MeOH binary solvent mixtures. Furthermore, $V_\varphi{}^0$ decreases with the decrease in the size of the cations of the acetate salts (i.e., from NH_4^+ to Li^+) as well as with increase in temperature (from 303.15 to 323.15 K). $V_\varphi{}^0$ is the measure of the ion−solvent interactions as it is the apparent molar volume at infinite dilution, by definition, and is independent of ion−ion interactions. The positive values indicate the presence of strong ion−solvent interactions between NH_4^+ ion and THF + MeOH molecules. These interactions are weakened with the decrease in the size of the cations and also with rise in temperature. The negative values indicate that electrostriction occurs in these solutions and that this electrostrictive solvation is greater for smaller cations and at higher temperature along with the increase in amount of THF in the solution. A similar type of results has been reported for some metal sulfates in DMF + H_2O mixtures at different temperatures.[20]

The positive values of S_V^*, which is the experimental slope, indicates the presence of ion−ion interactions in the system. The slope increases as we move from NH_4^+ to Li^+, indicating the highest amount of ion−ion interactions between Li^+ ion and THF + MeOH molecules. The smaller ions show a stronger affinity toward the ionic association while the larger ions seems to be responsible for the inability to ion-pair formation. S_V^* values are found to increase as mass % of THF increases along with the rise in temperature. This is reflected to accommodate more and more solute molecules in the empty space left in the packing of associated solvent molecules resulting in an increased ion-pairing.[21] However, the decrease in S_V^* with rise in temperature is attributed to violent thermal agitation, resulting in diminishing the force of ion−ion interactions.

The limiting apparent molar expansibility ($E_\varphi{}^0$) is found to be negative throughout as shown in Table 4. It is found to decrease with the decrease in ionic size and increase in temperature but increases as mass % of THF increases in the systems. Whereas the slope (S_E) is greater for smaller ions at higher temperature and for greater amount of THF in the solvent mixtures. These results are in excellent agreement with that of $V_\varphi{}^0$ and S_V^* values. The behavior of these salts is similar to that of common salts whose molar expansibility should decrease with rise in temperature.[22]

In Figure 1, panels a to c, variation of the partial molar expansibility (E_2) is shown against a concentration of the acetates at 303.15 K in 10, 20, and 30 mass % of THF, respectively. Figure 1a shows negative values for all the salts, which increases with concentration of CH_3COONH_4 and $CH_3COOLi{\cdot}2H_2O$ and decreases with increasing concentration of CH_3COOK and $CH_3COONa{\cdot}3H_2O$. Figure 1b depicts negative values for all the salts having similar curves except $CH_3COOLi{\cdot}2H_2O$, which has positive values at higher concentration. For 30 mass % of THF + MeOH mixture, E_2 increases with concentration. The salts CH_3COONH_4 and CH_3COOK behave similarly whereas Na and Li salts are positive at higher concentration. Similar curves are obtained at higher temperatures.

Table 5 contains the viscosity parameters, *A* and *B* from the Jones-Dole equation. *A* is the measure of long-range Coulombic forces between the ions whereas *B* reflects the effect of ion−solvent interactions. Positive values of *B* coefficients indicate the large size of moving particles (i.e., increase in the viscosity of the solution), decreasing with increasing temperature. This phenomenon can be attributed to the breakup of the solvation shell due to the thermal motion. *A* and *B* are constants at a given temperature and are characteristics of the solution. *A* coefficients are the measure of the ion−atmosphere effects whereas *B* coefficients can provide information concerning the solvation of the ions and their effects on the structure of the solvent in the near environment of the solute particles. The small *A* values in Table 5 indicate weak ion−ion interactions, and positive *B* values suggest the presence of strong ion−solvent interactions. The *B* coefficients increase from NH_4^+ to Li^+ as mass % of THF increases but decrease with rise in temperature, thus, indicating the weakest ionic solvation for Li^+ salt. A similar type of work was done by Quickenden and Zamir.[23]

In Table 5, variation of $\Delta\mu^{0*}_2$ (i.e., the contribution per mole of the solute to free energy of activation for viscous flow of solution) is given for the acetates in 10, 20, and 30 mass % of THF at (303.15, 313.15, and 323.15) K, respectively. The order it follows is

$$CH_3COOLi{\cdot}2H_2O > CH_3COONa{\cdot}3H_2O > CH_3COOK > CH_3COONH_4$$

where $\Delta\mu^{0*}_2$ is found to be maximum in 30 mass % of THF + MeOH mixture. Furthermore, the $\Delta\mu^{0*}_2$ values are positive and much larger than $\Delta\mu^{0*}_1$, indicating stronger ion−solvent interactions, suggesting that the formation of transition state is accompanied by the rupture and distortion of the intermolecular forces in solvent structure.[24]

In Figure 2, panels a to c, variation of isentropic compressibility (K_S) of the solution is shown against a concentration of the acetates at 303.15 K in 10, 20, and 30 mass % of THF, respectively. The figure indicates that K_S increases to a maximum and then decreases in the solvent mixtures with maximum for 10 mass % THF, giving the highest values for the Li salts. The increase in K_S is an indication of the strengthening of intermolecular forces. The formation of molecular aggregates reduces the compressibility of the medium. A similar type of work was performed by Naidu and John.[25]

It is evident from Table 6 that all the acetate salts investigated here have positive $K_{S,\varphi}^0$. S^*_K are negative for 10 and 20 mass % of THF but positive in 30 mass % of THF. $K_{S,\varphi}^0$ and S^*_K are measures of the ion−solvent and ion−ion interactions, respectively. The results are in good agreement with conclusions drawn here from density and viscosity data as explained earlier.

Table 8 shows the specific acoustic impedance *Z*, intermolecular free length L_f, relaxation strength r', and relative association R_A for the solutions. L_f, r', and R_A are observed to decrease, but *Z* increases with increasing amount of THF in the mixture. The change observed in *Z* with concentration is attributed to a change of ultrasonic speed with concentration (Table 6). This behavior is due to association of molecules and formation of molecular aggregates.[26] The increase in L_f implies an increase in number of free ions showing the occurrence of ionic dissociation.[27] The change of r' with concentration may be interpreted in terms of an increase in intermolecular forces due to increase in concentration and subsequent decrease in the relaxation of the molecules. R_A is used to understand the interaction influenced by the breaking of the solvent structure on addition of solute and the solvation of the solute simultaneously produced.

Conclusion

The extensive study of the densities, viscosities, and sound speeds of ammonium acetate, potassium acetate, sodium acetate, and lithium acetate in various mass % of the solvent mixture of tetrahydrofuran and methanol at different temperatures reveals the characteristics and structural properties prevalent in the solutions. It also indicates the presence of strong ion−solvent interaction between NH_4^+ ion and THF + MeOH molecules and the highest ion−ion interaction between Li^+ ion and THF + MeOH molecules. In other words, the weakest ionic solvation is observed for the Li^+ salt.

Acknowledgment

The authors are grateful to the Head, Department of Chemistry, University of North Bengal, Darjeeling, India, for providing various facilities.

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Received for review March 10, 2006. Accepted May 2, 2006. A.S. is grateful to the University of North Bengal for awarding a Senior Research Fellowship (SRF) and granting full financial support in this research work.

JE060113J