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Apparent Molar Volumes and Expansivities of Ionic Liquids Based on *N*-Alkyl-*N*-methylmorpholinium Cations in Acetonitrile

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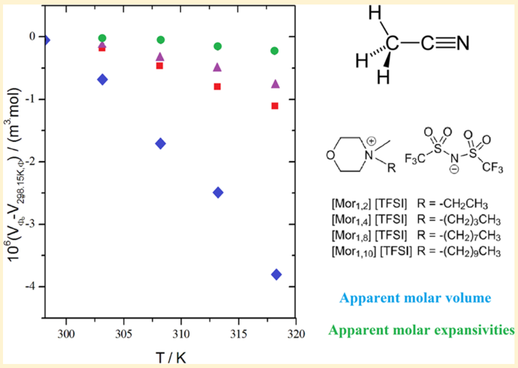
ABSTRACT: Densities of some acetonitrile solutions of ionic liquids based on *N*-alkyl-*N*-methyl-morpholinium cations, *N*-ethyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)imide, *N*-butyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)imide, *N*-methyl-*N*-octylmorpholinium bis(trifluoromethanesulfonyl)imide and *N*-decyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)imide were measured at T = (298.15–318.15) K and at atmospheric pressure. From density data the apparent molar volumes and partial molar volumes of the ILs at infinite dilution as well as the limiting apparent molar expansibilities and the Hepler's constant values have been evaluated. The results have been discussed in terms of the effect that alkyl chain length of the ILs and experimental temperature have on the ionic liquid−acetonitrile interactions occurring in the studied solutions.



1. INTRODUCTION

Over the past years ionic liquids have received much attention as potential green solvents or as materials for a wide range of applications in engineering. The main benefits of ionic liquids are their extremely low vapor pressure, nonflammability, high thermal and electrochemical stabilities, and wide liquid temperature range.[1−3] Nowadays ILs are widely used in organic synthesis, biocatalysis, nanotechnology, electrochemistry, and separation technologies, etc.[4−7]

Because of a growing interest in industrial applications of ionic liquids, various ILs have been subjected to studies of their structure−property relationships. Most of these studies concerned ionic liquids containing alkylimidazolium, alkyl pyrrolidinium, alkylpyridinium, phosphonium, and quaternary ammonium cations.[8−12] Recently, some work has been reported on the synthesis, thermal, electrochemical, and physicochemical characterization of morpholinium cation based ILs.[13−17] These ionic liquids can be conveniently synthesized because of their good product reproducibility, easy purification process, low cost, and short processing time. Morpholinium based ILs have been applied as catalysts, heat stabilizers, antioxidants for lubricating oils and as corrosion inhibitors.[18−20] Moreover, they have been considered as electrolytes for conventional lithium batteries.[21]

Despite its importance for process design, detailed knowledge of the thermodynamic and transport properties of mixtures of ionic liquids with other molecular solvents is limited. Existing studies mainly concern the density, viscosity, and speed of sound of mixtures of water or alcohols and ILs based on alkylimidazolium or alkylpyridinium cations.[22−26] However, in recent times data on the volumetric properties of systems involving ionic liquids with aprotic organic solvent have been published.[27−31] The results of density measurements have been used for the computation of excess molar volumes and interpreted in terms of ion−dipole interactions as well as the structural aspects of the ionic liquid and the investigated organic solvents. Only a few papers are focused on limiting molar quantities which may be determined by studying highly diluted solutions of ionic liquids.[32−35] Hence, in the present work we report the volumetric properties of some ionic liquids based on *N*-alkyl-*N*-methylmorpholinium cations in acetonitrile (AN) solutions. It is worth noting that so far the interactions of morpholinium cation-based ILs with nonpolar and dipolar solutes have been studied by Khara et al.[36,37] using the time-resolved fluorescence anisotropy measurements. Our interest in systems containing acetonitrile is due to the report of Chaban et al.[38] They found that acetonitrile decreases in an unprecedented way the viscosity of ILs and increases their ionic conductivity, which is not without significance for the application of IL/AN binary systems as advanced electrolyte solutions in electrochemistry. In our study, data on the densities of acetonitrile solutions of *N*-ethyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)imide, *N*-butyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)imide, *N*-methyl-*N*-octylmorpholinium bis(trifluoromethanesulfonyl)imide, and *N*-decyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)imide obtained at T = 298.15, 303.15, 308.15, 313.15, and 318.15 K are reported. From the experimental data, the apparent molar volumes and partial molar volumes of the ILs at infinite dilution as well as the limiting apparent molar expansibilities and the Hepler's constant values have been estimated. The results have been discussed in terms of the

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effect that alkyl chain length of the ILs and experimental temperature have on the ionic liquid−acetonitrile interactions occurring in the studied solutions.

2. EXPERIMENTAL SECTION

2.1. Chemicals. Acetonitrile (AN) (purity > 99.9 % and mass fraction of H_2O < 2.10^{-4}), *N*-methylmorpholine (ReagentPlus, 99 %), bromoethane (reagent grade, 98 %), 1-bromobutane (ReagentPlus, 99 %), 1-bromooctane (99 %), 1-bromodecane (98 %), lithium bis(trifluoromethylsulfonyl)-imide (99.95 % trace metals basis) were obtained from Sigma-Aldrich. Dichloromethane (>99.9 %) and acetone (>99.9 %) were purchased from POCH. All solvent and reagents were used without further purification.

2.2. Synthesis of Ionic Liquid. Figure 1 presents the molecular structures of the studied ionic liquids. All of them were prepared according to the procedure described for the first time by Kim et al., which was modified in terms of the reaction length and workup.[39] The sequence of reactions leading to the formation of the required ionic liquid is shown in Scheme 1. In the synthesis, commercially available *N*-methylmorpholine was used as a starting substrate which, upon treatment with bromoethane, 1-bromobutane, 1-bromooctane, or 1-bromodecane in acetonitrile, gives the resepective quaternary morpholinium salts. In the next step the obtained bromide salts were converted into the corresponding [TFSI] products by treatment with lithium bis(trifluoromethylsulfonyl)imide in dichloromethane in an anion exchange reaction. It is noteworthy that one of the synthesized ionic liquids, namely $[Mor_{1,10}]$[TFSI], is a new compound which has been synthesized for the first time. The prepared ionic liquids were characterized using ^1H and ^{13}C NMR (Varian Unity Plus spectrometer operating at 500 and 125 MHz, respectively).

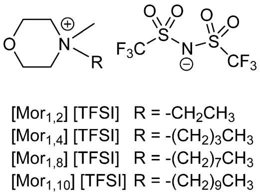
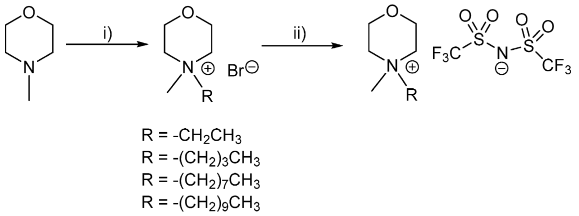


Figure 1. Molecular structures of the studied ionic liquids.

Scheme 1. The Sequence of Reactions Leading to the Formation of Required Ionic Liquid[a]



[a]Reagents and conditions: (i) RBr, CH_3CN, 65 °C, 48 h; (ii) $(CF_3SO_2)_2NLi$, CH_2Cl_2, 48 h, room temp.

N-Ethyl-N-methylmorpholinium Bis(trifluoromethanesulfonyl)imide $[Mor_{1,2}]$[TFSI]. ^1H NMR ($CDCl_3$, δ/ppm relative to TMS): δ 3.92 (t, J = 4.7 Hz, 4H), 3.45 (q, J = 7.2 Hz, 2H), 3.34 (m, 4H), 3.06 (s, 3H), 1,35 (t, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 119.72 (q, J_{CF} = 321.0 Hz), 61.23, 60.23, 59.35, 45.77, 6.62.

N-Butyl-N-methylmorpholinium Bis(trifluoromethanesulfonyl)imide $[Mor_{1,4}]$[TFSI]. ^1H NMR (DMSO-d_6, δ/ppm relative to TMS): δ 3.89 (brs, 4H), 3.38 (m, 6H), 3.09 (s, 3H), 1.64 (m, 2H), 1.30 (m, 2H), 0.93 (t, J = 7.4, Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 119.99 (q, J_{CF} = 321.1 Hz), 66.29, 60.60, 60.09, 46.54, 23.40, 19.46, 13.32.

N-Methyl-N-octylmorpholinium Bis(trifluoromethanesulfonyl)imide $[Mor_{1,8}]$[TFSI]. ^1H NMR ($CDCl_3$, δ/ppm relative to TMS): δ 3.96 (dd, J = 6.6 and 3.3 Hz, 4H), 3.41 (m, 4H), 3.34 (m, 2H), 3.15 (s, 3H), 1.72 (m, 2H), 1.34 (m, 4H), 1.27 (m, 5H), 0.87 (t, J = 6.8 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 119.95 (q, J_{CF} = 321.1 Hz), 66.79, 60.73, 60.18, 46.76, 31.75, 29.10, 29.07, 26.19, 22.72, 21.69, 14.20.

N-Decyl-N-methylmorpholinium Bis(trifluoromethanesulfonyl)imide $[Mor_{1,10}]$[TFSI]. ^1H NMR ($CDCl_3$ δ/ppm relative to TMS): δ 3.96 (t, J = 4.8 Hz, 4H), 3.42 (m, 4H), 3.35 (m, 2H), 3.16 (s, 3H), 1.75 (m, 2H), 1.34 (m, 4H), 1.27 (m, 9H), 0.87 (t, J = 6.9 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 119.99 (q, J_{CF} = 321.2 Hz), 66.82, 60.75, 60.20, 46.79, 32.02, 29.54, 29.48, 29.40, 29.15, 26.23, 22.84, 21.73, 14.28.

The possible presence of residual of Br^- in the prepared ionic liquids was examined by ionic chromatography measurements (ICS 3000 ion-exchange chromatography apparatus from Dionex, equipped in electrochemical detector operated in the conductivity mode). Determinations were performed using Dionex AS22 IonPac column. Ionic liquid samples were prepared by dissolution of the 0.10 g of the given IL in 10 mL of the 40% acetonitrile in water solutions. Thus the final concentrations of the samples were equal 1% w/v. Chromatographic system was calibrated using standard solutions prepared using analytical grade potassium bromide (concentrations varied from 1 $\mu g \cdot g^{-1}$ to 50 $\mu g \cdot g^{-1}$). All samples, as well as chromatographic eluent were prepared using deionized water (Milli-Q water system, Bedford, MA, USA). Eluent contained 4.5 mM Na_2CO_3 and 1.4 mM $NaHCO_3$ was delivered in the 0,3 $mL \cdot min^{-1}$ rate. The Br^- content for [Mor1,2] [TFSI], [Mor1,4] [TFSI], [Mor1,8] [TFSI] and [Mor1,10] [TFSI] was found to be equal 65, 190, 55, and 530 $\mu g \cdot g^{-1}$, respectively.).

Taking in to account low content of water and bromide, as well as the high purity of the reagents used for synthesis, we assumed that overall purity of investigated ionic liquids was higher than 99 %. Before measurements the ionic liquids were dried by purging them with a neutral gas (N_2) at 323 K for more than 72 h. The water content in the ILs, measured by the Karl Fischer titration method (831 KF Coulometer apparatus from Metrohm), for [Mor1,2] [TFSI], [Mor1,4] [TFSI], [Mor1,8] [TFSI], and [Mor1,10] [TFSI] was found to be equal to (192, 187, 204, and 210) $\mu g \cdot g^{-1}$ mass fraction, respectively.

2.3. Apparatus and Procedure. Stock solutions of the ILs were prepared by mass and then diluted by acetonitrile to get the test samples. All the preparations and manipulations involving anhydrous materials were performed in a drybox.

Densities of the solutions were measured using an Anton Paar DMA 5000 density meter with a thermostat system based on a Peltier unit with a repeatability of $5.0 \cdot 10^{-3}$ kg m^{-3} and an standard uncertainty equal $1.0 \cdot 10^{-2}$ kg m^{-3}. The temperature was kept constant between 298.15 K and 318.15 K with an accuracy of 0.01 K. Before each measurement series, the accuracy of the density measurements and solvent purity were verified by measuring the density of pure acetonitrile at T =

Table 1. Densities, *d* and Apparent Molar Volumes, $V\varphi$ of Solutions of Ionic Liquids in Acetonitrile at T = (298.15 to 318.15) K (Pressure p = 0.1 MPa)

		T = 298.15 K		T = 303.15 K		T = 308.15 K		T = 313.15 K		T = 318.15 K	
m_S	m	$10^{-3}d$	10^6V_Φ	$10^{-3}d$	10^6V_Φ	$10^{-3}d$	10^6V_Φ	$10^{-3}d$	10^6V_Φ	$10^{-3}d$	10^6V_Φ
$mol \cdot kg^{-1}$	$mol \cdot kg^{-1}$	$kg \cdot m^{-3}$	$m^3 \cdot mol^{-1}$	$kg \cdot m^{-3}$	$m^3 \cdot mol^{-1}$	$kg \cdot m^{-3}$	$m^3 \cdot mol^{-1}$	$kg \cdot m^{-3}$	$m^3 \cdot mol^{-1}$	$kg \cdot m^{-3}$	$m^3 \cdot mol^{-1}$
$[Mor_{1,2}][TFSI]$											
0.00940	0.009434	0.778145	248.26	0.772716	247.85	0.767263	246.85	0.761774	246.17	0.756247	245.44
0.01643	0.01654	0.779333	248.98	0.773905	248.56	0.768452	247.89	0.762964	247.28	0.75744	246.41
0.02623	0.02652	0.780985	249.89	0.77556	249.37	0.770110	248.68	0.764619	248.39	0.759113	247.23
0.03729	0.03788	0.782850	250.74	0.777429	250.15	0.771974	249.84	0.766483	249.58	0.760976	248.26
0.05146	0.05256	0.785240	251.62	0.779815	251.26	0.774365	250.86	0.768876	250.55	0.763372	249.44
0.06670	0.06858	0.787810	252.58	0.782385	252.31	0.776944	251.73	0.771442	251.79	0.765945	250.72
0.08395	0.08695	0.790740	253.25	0.785318	252.96	0.779877	252.48	0.774373	252.54	0.768855	252.09
0.1032	0.1078	0.794037	253.70	0.788611	253.52	0.783146	253.50	0.777657	253.29	0.772158	252.59
0.1249	0.1316	0.797714	254.83	0.792286	254.71	0.786836	254.50	0.781334	254.49	0.775832	253.95
0.1531	0.1634	0.802540	256.14	0.797108	256.10	0.791661	255.90	0.786155	255.94	0.780648	255.55
$[Mor_{1,4}][TFSI]$											
0.00876	0.00879	0.778005	290.27	0.772575	290.37	0.767120	290.06	0.761631	289.71	0.756103	289.52
0.01641	0.01653	0.779272	290.92	0.773845	290.73	0.768390	290.61	0.762901	290.46	0.757375	290.16
0.02727	0.02761	0.781074	291.33	0.775647	291.28	0.770192	291.25	0.764703	291.19	0.759178	290.98
0.0374	0.03802	0.782759	291.61	0.777331	291.66	0.771873	291.81	0.766385	291.76	0.760862	291.53
0.05109	0.05226	0.785036	292.23	0.779607	292.35	0.774153	292.37	0.768667	292.30	0.763147	292.06
0.06543	0.06737	0.787436	292.58	0.781999	292.92	0.776549	292.88	0.771064	292.83	0.765551	292.49
0.08326	0.08642	0.790427	293.11	0.784994	293.34	0.779543	293.37	0.774057	293.39	0.768552	293.00
0.1051	0.1101	0.794115	293.54	0.788679	293.82	0.783226	293.92	0.777740	293.98	0.772235	293.72
0.1229	0.1300	0.797144	294.013	0.791717	294.18	0.786253	294.45	0.780771	294.48	0.775257	294.41
0.1515	0.1623	0.802019	294.75	0.796577	295.09	0.791135	295.14	0.785644	295.32	0.780136	295.24
$[Mor_{1,8}][TFSI]$											
0.00860	0.00864	0.778032	352.47	0.772604	352.55	0.767150	352.40	0.761661	352.42	0.756135	352.19
0.01582	0.01594	0.779270	353.04	0.773845	353.00	0.768392	353.02	0.762906	352.91	0.757382	352.75
0.02493	0.02524	0.780834	353.64	0.775414	353.47	0.769962	353.59	0.764479	353.49	0.758957	353.41
0.03657	0.03724	0.782840	354.04	0.777423	353.96	0.771972	354.16	0.766490	354.19	0.760974	354.00
0.04938	0.05062	0.785053	354.50	0.779637	354.55	0.774191	354.67	0.768712	354.72	0.763200	354.57
0.06357	0.06563	0.787516	354.82	0.782098	355.04	0.776655	355.18	0.771180	355.23	0.765666	355.29
0.08323	0.08680	0.790942	355.34	0.785532	355.50	0.780089	355.74	0.774615	355.90	0.769109	355.90
0.09874	0.1038	0.793660	355.72	0.788255	355.87	0.782815	356.12	0.777346	356.26	0.771842	356.33
0.1214	0.1292	0.797655	356.22	0.792260	356.34	0.786817	356.70	0.781350	356.91	0.775861	356.86
0.1462	0.1576	0.802048	356.79	0.796655	356.98	0.791206	357.46	0.785752	357.60	0.780271	357.59
$[Mor_{1,10}][TFSI]$											
0.00834	0.00838	0.777974	391.20	0.772547	391.35	0.767094	391.28	0.761606	391.37	0.756080	391.43
0.01551	0.01564	0.779195	391.57	0.773770	391.80	0.768318	392.00	0.762833	392.06	0.757311	391.98
0.02440	0.02472	0.780710	392.02	0.775289	392.19	0.769839	392.46	0.764357	392.56	0.758838	392.57
0.03643	0.03714	0.782766	392.40	0.777348	392.65	0.771899	393.05	0.766421	393.19	0.760906	393.26
0.04973	0.05106	0.785044	392.92	0.779630	393.19	0.774185	393.57	0.768710	393.79	0.763198	393.95
0.06430	0.06653	0.787549	393.32	0.782140	393.60	0.776698	394.01	0.771222	394.39	0.765716	394.54
0.08140	0.08502	0.790507	393.71	0.785101	394.06	0.779664	394.46	0.774189	394.93	0.768695	394.97
0.09973	0.1052	0.793696	394.05	0.788290	394.50	0.782856	394.95	0.777385	395.42	0.771901	395.45
0.1212	0.1294	0.797448	394.45	0.792039	395.03	0.786610	395.50	0.781149	395.92	0.775667	396.08
0.1484	0.1609	0.802250	395.08	0.796850	395.63	0.791423	396.17	0.785970	396.60	0.780493	396.86

Standard uncertainties u are $u(T)$ = 0.01 K, $u(d)$ = 0.08 $kg \cdot m^{-3}$, standard uncertainty of molinity $u(m_S)$ = 0.001 $mol \cdot kg^{-1}$ and standard uncertainty of molality $u(m)$ = 0.001 $mol \cdot kg^{-1}$

298.15 K. A density of 776.554 $kg \cdot m^{-3}$ with standard uncertainty 0.08 $kg \cdot m^{-3}$ was found, whereas the literature values vary from 775.9 $kg \cdot m^{-3}$ to 776.93 $kg \cdot m^{-3}$.[40,41]

3. RESULTS AND DISCUSSION

The apparent molar volume V_Φ is defined as the difference between the volume of the solution and the volume of pure solvent per mole of solute and is given by the equation:

$$V_\Phi = (V - n_1 V_1^0) n_2 \qquad (1)$$

where V is the volume of the solution, n_1 and n_2 denote the number of moles of the solvent and solute, respectively, and V_1^0 is the molar volume of the solvent.

The values of the apparent molar volumes V_Φ of the studied solutions of ionic liquids were calculated from experimental density data using the following equation:

$$V_\Phi = (d_0 - d)/(m_S d d_0) + M_2/d_0 \qquad (2)$$

where m_s denotes the number of moles of the solute per kilogram of solution (molinity); d and d_0 are the densities of solution and solvent, respectively; and M_2 is the molar mass of the solute. Equations based on molarity, c, or molality, m, have somewhat different forms. Equation 2 was preferred because the value m_s is a direct experimental quantity characterizing the solution. It obvious that the calculation of molar concentration is possible using the equation:

$$c = m_S d \tag{3}$$

The density data and apparent molar volumes obtained for the solutions of [Mor$_{1,2}$][TFSI], [Mor$_{1,4}$][TFSI], [Mor$_{1,8}$][TFSI], and [Mor$_{1,10}$][TFSI] in acetonitrile at temperatures between 298.15 K and 318.15 K are collected in Table 1. As seen, the apparent molar volume of all the studied ionic liquids is found to be increasing with concentration at all temperatures investigated. At low molarities of IL, the ions are surrounded by the solvent molecules, indicating strong ion−solvent interaction, an increase in the IL molarity increases the ion−ion interactions resulting in greater V_Φ values.

To provide a more complete discussion of the effect of alkyl chain length of the ILs and experimental temperature on the ionic liquid−acetonitrile interactions, the apparent molar volumes at infinite dilution were estimated. At this limit, each ion is surrounded only by the solvent molecules and therefore V_Φ^0 is unaffected by ion−ion interactions and is a measure only of the ion−solvent interactions.

The extrapolation of the experimental apparent molar volumes to infinite dilution to obtain the limiting apparent molar volumes at 298.15 K was based on the Redlich, Rosenfeld, and Meyer (RRM) equation:[42]

$$V_\Phi = V_\Phi^0 + S_V^{\mathrm{DH}}\sqrt{c} + b_V c \tag{4}$$

where S_V^{DH} denotes the theoretical Debye−Hückel slope for the volumes and b_V is an empirical term. For the ionic liquids studied, that is, type 1−1 electrolytes, the slope equal in acetonitrile to 13.17 cm^3 dm$^{3/2}$ mol$^{-3/2}$ was calculated from the expression:

$$S_V^{\mathrm{DH}} = 6RTA_\Phi[(\partial \ln \varepsilon/\partial P)_T - \kappa_T/3] \tag{5}$$

where R is the gas constant, T is the temperature, κ_T is the isothermal compressibility of acetonitrile,[43] ε is its dielectric constant[44] and $(\partial \ln \varepsilon/\partial P)_T$ is its pressure dependence[43] The Debye−Hückel slope for molarity-based osmotic coefficients A_Φ was obtained by

$$A_\Phi = (1/3)(2\pi N_A)^{1/2}[e^2/4\pi\varepsilon\varepsilon_0 kT]^{3/2} \tag{6}$$

where N_A is Avogadro's number, e is the unit charge, ε_0 is the permittivity of free space, and k is the Boltzmann constant.

To estimate the apparent molar volumes of ionic liquids at infinite dilution in acetonitrile the appropriate RRM equation was rearranged into a linear form:

$$V_\Phi - S_V^{\mathrm{DH}}\sqrt{c} = V_\Phi^0 + b_V c \tag{7}$$

The parameters of eq 7 and the standard deviations σ are given in Table 2.

Because of the lack or poor quality of data required for calculating the theoretical Debye−Hückel slopes S_V^{DH}, (i.e., dielectric constant, isothermal compressibility, and the pressure derivative of solvent permittivity) at temperatures different than 298.15 K, the purely empirical Masson-type equation was used to obtain the V_Φ^0 over the temperature range studied:[45]

$$V_\Phi = V_\Phi^0 + S_V\sqrt{c} \tag{8}$$

Table 2. The Coefficients of the Redlich, Rosenfeld, and Meyer (RRM) Equation, the Corresponding Standard Deviations σ and the Limiting Apparent Molar Volumes for Ionic Liquids in Acetonitrile Obtained by Using Masson Equation at 298.15 K

	Redlich, Rosenfeld, and Meyer (RRM) equation			Masson equation
	$10^6V_\Phi^0$	10^9b_v	$10^6\sigma$	$10^6V_\Phi^0$
ionic liquid	m^3·mol^{-1}	m^6·mol^{-2}	m^3·mol^{-1}	m^3·mol^{-1}
[Mor$_{1,2}$][TFSI]	247.26 ± 0.36	35.6 ± 5.5	0.28	245.75
[Mor$_{1,4}$][TFSI]	289.05 ± 0.11	3.1 ± 1.4	0.085	288.95
[Mor$_{1,8}$][TFSI]	351.55 ± 0.13	6.4 ± 2.1	0.10	351.282
[Mor$_{1,10}$][TFSI]	390.14 ± 0.10	2.87 ± 0.98	0.049	390.019

Moreover, analysis at 298.15 K on the basis of eq 8 has been attempted. The obtained values of empirical slopes S_V, the apparent molar volumes of ionic liquids at infinite dilution at experimental temperatures, and their standard deviations σ are collected in Table 3. As seen from Table 2, the values of the limiting apparent molar volumes obtained using RRM and Masson equation agree generally. Moreover, standard deviations of the empirical slope S_V of the Masson equation are significantly smaller than those obtained for the RRM equation. Thus, we based further calculations and the discussion on the values of V_Φ^0 obtained from the Massson equation. Figure 2

Table 3. The Coefficients of Masson Equation and the Corresponding Standard Deviations σ for [Mor$_{1,2}$][TFSI], [Mor$_{1,4}$][TFSI], [Mor$_{1,8}$][TFSI], and [Mor$_{1,10}$][TFSI] in Acetonitrile from (298.15 to 318.15) K

	Masson equation		
T	$10^6V_\Phi^0$	10^6S_V	$10^6\sigma$
K	m^3·mol^{-1}	(m^9·mol^{-3})$^{1/2}$	m^3·mol^{-1}
	[Mor$_{1,2}$][TFSI]		
298.15	245.75 ± 0.15	0.92 ± 0.020	0.17
303.15	245.06 ± 0.17	0.98 ± 0.028	0.19
308.15	244.03 ± 0.11	1.06 ± 0.015	0.12
313.15	243.25 ± 0.15	1.15 ± 0.021	0.18
318.15	241.95 ± 0.20	1.22 ± 0.028	0.23
	[Mor$_{1,4}$][TFSI]		
298.15	288.95 ± 0.10	0.51 ± 0.015	0.10
303.15	288.77 ± 0.11	0.56 ± 0.017	0.12
308.15	288.51 ± 0.10	0.61 ± 0.011	0.10
313.15	288.15 ± 0.10	0.65 ± 0.010	0.10
318.15	287.84 ± 0.11	0.67 ± 0.017	0.12
	[Mor$_{1,8}$][TFSI]		
298.15	351.282 ± 0.066	0.506 ± 0.0096	0.076
303.15	351.142 ± 0.052	0.538 ± 0.0073	0.060
308.15	350.923 ± 0.055	0.599 ± 0.0077	0.063
313.15	350.764 ± 0.046	0.635 ± 0.0065	0.053
318.15	350.506 ± 0.061	0.666 ± 0.0086	0.070
	[Mor$_{1,10}$][TFSI]		
298.15	390.019 ± 0.036	0.460 ± 0.0057	0.042
303.15	389.989 ± 0.042	0.513 ± 0.0059	0.049
308.15	389.967 ± 0.060	0.570 ± 0.0084	0.069
313.15	389.871 ± 0.054	0.629 ± 0.0076	0.063
318.15	389.793 ± 0.071	0.655 ± 0.0099	0.082

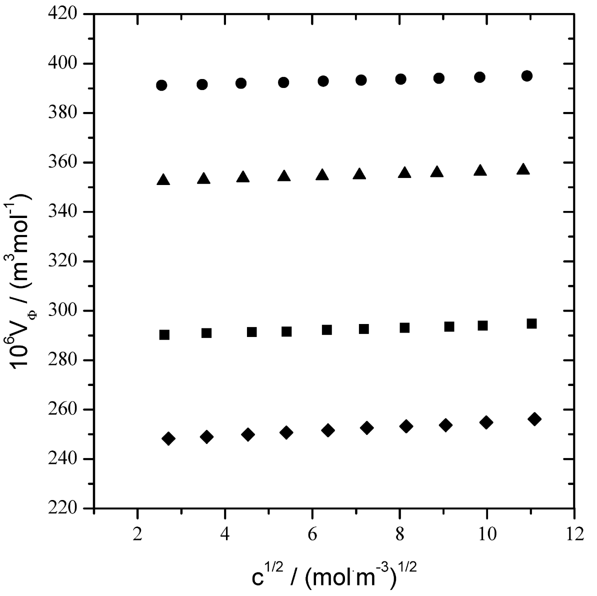


Figure 2. The concentration dependencies of the apparent molar volume for $[Mor_{1,2}][TFSI]$ (◆), $[Mor_{1,4}][TFSI]$ (■), $[Mor_{1,8}][TFSI]$ (▲), and $[Mor_{1,10}][TFSI]$ (●) in acetonitrile solutions at T = 298.15 K.

shows the apparent molar volumes against the square root of molarities for $[Mor_{1,2}][TFSI]$, $[Mor_{1,4}][TFSI]$, $[Mor_{1,8}][TFSI]$, and $[Mor_{1,10}][TFSI]$ in acetonitrile at T = 298.15 K.

Figure 2, as well as the data collected in Table 3, show that the values of empirical slope S_V are positive, suggesting that ion−ion interactions are one of the factors controlling the properties of the studied systems. Furthermore, Figure 2 shows that the values of slope decrease with the increase in the alkyl chain length of the cation constituent of the ionic liquid and increase with growing temperature. It should be noted that highest values of S_V were observed for acetonitrile solution of $[Mor_{1,2}][TFSI]$ while the lowest values for $[Mor_{1,10}][TFSI]$ solutions. Apparently, this variation is related to the increasing size of the cation which seems to be the most important factor controlling ion−ion as well as ion−solvent interactions. The latter are quantified by the apparent molar volume at infinite dilution.

As seen from Table 3, the apparent molar volumes at infinite dilution for the morpholinium based ionic liquids in acetonitrile increase with the increase in the cation size at all temperatures investigated. This effect is presented in Figure 3 as plots of the limiting values of V_φ against the alkyl chain length of the cation. Similar results were reported for some ionic liquids based on imidazolium cations in dimethylsulfoxide and water.[32,33]

The limiting values of the apparent molar volumes of a solute V_Φ^0 can be expressed as the sum of the three contributions:

$$V_\Phi^0(\mathrm{IL}) = V_{\mathrm{int}}^0 + V_{\mathrm{elec}}^0 + V_{\mathrm{str}}^0 \qquad (10)$$

where V_{int}^0 represents the intrinsic volume of solute molecules, V_{elec}^0 denotes the volume change related to electrostriction (decrease of the solution volume due to electrostatic attraction between solute and surrounding solvent molecules), and V_{str}^0 is the volume contribution reflecting all the structural volume changes in the surrounding solvent (negative effect). The electrostriction volume is the most significant factor controlling the volumetric properties of smaller cations while the structural contribution is the factor determining the partial molar volume of larger cations. Thus, the apparent molar volumes at infinite dilution of ionic liquids based on morpholinium cations in acetonitrile result mainly from the cation size which determines not only the intrinsic volume but also the volume of electrostriction and the structural contribution to the volume.

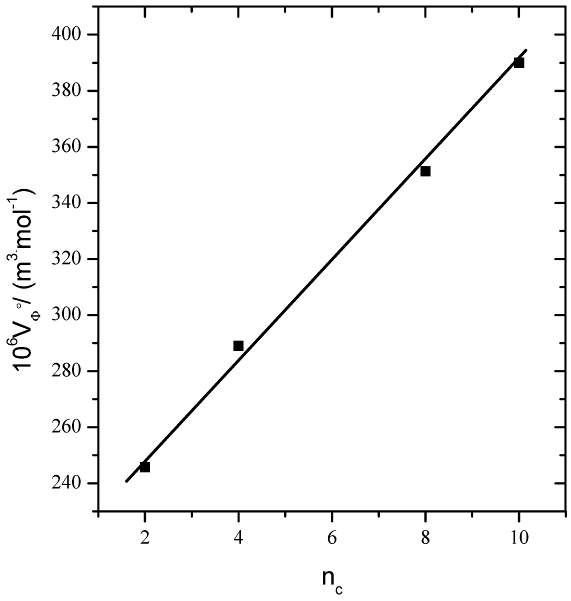


Figure 3. The limiting values of V_φ against the alkyl chain length of the cation of ionic liquid at T = 298.15 K.

Figure 4 presents the influence of temperature on the obtained limiting molar volumes of ILs. For better visualization, plots of the difference $[V_\Phi^0(\mathrm{IL}) - V_{\Phi,298.15\mathrm{K}}^0(\mathrm{IL})]$ calculated for the ionic liquids against temperature are shown. The temperature dependence of V_Φ^0 is not linear, and the best curve description is obtained using the second-order polynomial:

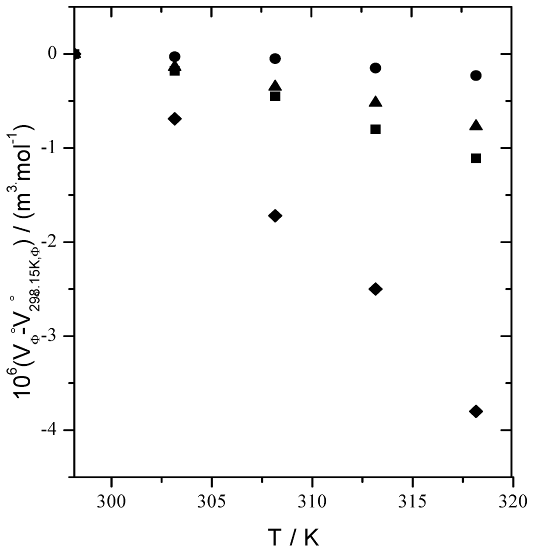


Figure 4. The difference $[V_\Phi^0(IL) - V_{\Phi,298.15K}^0(IL)]$ calculated for $[Mor_{1,2}][TFSI]$ (◆), $[Mor_{1,4}][TFSI]$ (■), $[Mor_{1,8}][TFSI]$ (▲), and $[Mor_{1,10}][TFSI]$ (●) in acetonitrile solutions against temperature.

$$V_\Phi^0 = A + B(T/\mathrm{K}) + C(T/\mathrm{K})^2 \qquad (11)$$

where A, B, and C are empirical parameters whose values obtained by regression analysis along with the respective values

Table 4. The Coefficients of eq 11 and the Corresponding Standard Deviations σ for $[Mor_{1,2}][TFSI]$, $[Mor_{1,4}][TFSI]$, $[Mor_{1,8}][TFSI]$, and $[Mor_{1,10}][TFSI]$ in Acetonitrile

	10^6A	10^6B	10^6C	$10^6\sigma$
ionic liquid	$m^3 \cdot mol^{-1}$	$m^3 \cdot mol^{-1}$	$m^3 \cdot mol^{-1}$	$m^3 \cdot mol^{-1}$
$[Mor_{1,2}][TFSI]$	247.3 ± 1.3	0.006 ± 0.075	−0.0028 ± 0.0011	0.099
$[Mor_{1,4}][TFSI]$	289.29 ± 0.32	0.011 ± 0.019	−0.00097 ± 0.00028	0.025
$[Mor_{1,8}][TFSI]$	351.66 ± 0.21	−0.002 ± 0.012	−0.00051 ± 0.00018	0.016
$[Mor_{1,10}][TFSI]$	389.73 ± 0.17	0.024 ± 0.011	−0.00051 ± 0.00015	0.014

Table 5. The Infinite Dilution Apparent Molar Expansibility, $10^6E_\Phi^0$ /($m^3 \cdot mol^{-1} \cdot K$) Values Derived from eq 12 at Different Temperatures

ionic liquid	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15
$[Mor_{1,2}][TFSI]$	−0.1328	−0.1605	−0.1882	−0.2159	−0.2436
$[Mor_{1,4}][TFSI]$	−0.0374	−0.0471	−0.0568	−0.0665	−0.0762
$[Mor_{1,8}][TFSI]$	−0.0281	−0.0333	−0.0384	−0.0435	−0.0487
$[Mor_{1,10}][TFSI]$	−0.0013	−0.0064	−0.0116	−0.0167	−0.0219

of the residual variance are listed in Table 4. In general, an increase in temperature causes a decrease in the values of the apparent molar volumes of all the investigated ionic liquids. A significantly higher decrease in the limiting apparent molar volume with temperature is observed for $[Mor_{1,2}][TFSI]$, for example, the ionic liquid with the shortest alkyl chain. In the case of the other ionic liquids the influence of temperature on V_Φ^0 is relatively small, and it changes according to the sequence: $[Mor_{1,4}][TFSI] > [Mor_{1,8}][TFSI] > [Mor_{1,10}][TFSI]$. One might suspect that the observed result is the effect of electrostriction and the ability of the alkyl chains of the *N*-alkyl-*N*-methylmorpholinium cations to penetrate the solvent. It is well-known that the increase of temperature weakens the solvent structure, thereby increasing the electrostriction and penetration effects. As these two different effects lead to decreasing the limiting molar volume, the obtained sequence of the influence of temperature on V_Φ^0 indicates that the most significant factor controlling the volumetric properties of the studied ILs is electrostriction. When considering ionic liquids, one should keep in mind that the longer is the alkyl chain, the weaker is the electrostatic ion−solvent interactions because of the increasing masking of the cation positive charge and stronger "solvofobic" interactions between the solvent molecules and the $-CH_2$ units of the cations. The particularly strong temperature effect observed for $[Mor_{1,2}][TFSI]$ and the weak temperature effect observed for the other ILs indicates that the penetration effect is much less important than the electrostriction effect. This conclusion is supported by the almost constant values of limiting molar volumes for solutions of $[Mor_{1,10}][TFSI]$ across the temperature range investigated.

Limiting apparent molar expansibility is a quantitative measure of the variation of limiting apparent molar volume with temperature. Its temperature dependence can be described by the equation:

$$E_\Phi^0 = (\partial V_\Phi^0/\partial T)_P = B + 2CT \tag{12}$$

The values of limiting apparent molar expansibility for the studied ILs are listed in Table 5 as a function of experimental temperature. In the light of the discussion presented above, it is not surprising that at each temperature E_Φ^0 values for ionic liquids based on morpholinium cations in acetonitrile are negative and decrease with rising temperature. As the temperature increases the effects connected with the weakening of the solvent structure are enhanced.

It has been shown that the sign of $(\partial^2 V_\Phi^0/\partial^2 T)_P$ is a better criterion in characterizing the long-range structure making and breaking capacity of electrolytes in solution.[46] The values of the second derivative obtained for $[Mor_{1,2}][TFSI]$ (−0.0056), $[Mor_{1,4}][TFSI]$ (−0.002), $[Mor_{1,8}][TFSI]$ (−0.0012), and $[Mor_{1,10}][TFSI]$ (−0.0012) in acetonitrile are small and negative for all the studied systems. Therefore, the ionic liquids under study act as structure breakers in acetonitrile. It is worth noting that similar results for the acetonitrile solution of 1,3-dimethylimidazolium methyl sulfate were reported by Shekaari et al.[47]

4. CONCLUSIONS

Densities of acetonitrile solutions of *N*-ethyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)imide, *N*-butyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)imide, *N*-methyl-*N*-octylmorpholinium bis(trifluoromethanesulfonyl)imide and *N*-decyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)imide have been measured at several temperatures. Because of solute−solvent interactions, the apparent molar volumes of all the studied ionic liquids increase with increasing concentration at all investigated temperatures. The values of the apparent molar volumes at infinite dilution obtained using Redlich, Rosenfeld, and Meyer (RRM) and Masson equations were found to be in good agreement, and they increase with increasing cation size at all temperatures investigated. The values of the limiting apparent molar expansibilities as well as the sequence of the influence of temperature on the limiting molar volumes ($[Mor_{1,2}][TFSI] \gg [Mor_{1,4}][TFSI] > [Mor_{1,8}][TFSI] > [Mor_{1,10}][TFSI]$) indicate that the most significant factor controlling the volumetric properties of the studied ILs is electrostriction. The obtained sign of $(\partial^2 V_\Phi^0/\partial^2 T)_P$ for the ionic liquids investigated indicates that ionic liquids based on morpholinium cations act as structure breakers in acetonitrile.

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Notes

The authors declare no competing financial interest.

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