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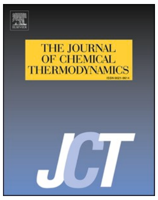

Influence of temperature and anion type on thermophysical properties of aqueous solutions of morpholine based amino acid ionic liquids

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ABSTRACT

Densities and sound velocities of aqueous solutions of N-butyl-N-methylmorpholine based amino acid ionic liquids (AAILs), including N-acetyl-L-alanine, N-acetyl-L-valinate, N-acetyl-L-leucinate, and *N*-acetyl-L-izoleucinate anions were measured at a temperature from 293.15 to 313.15 K at 5 K intervals and atmospheric pressure. These data were used to calculate the apparent molar volumes and the apparent molar compressibilities in the concentration range of (0.02 to 0.3) mol·kg^{-1}. Infinite dilution values for the volumetric and acoustic properties were evaluated by an extrapolation procedure based on Redlich – Meyer type equations. The limiting apparent molar expansibility coefficients were also obtained from the slopes of the apparent molar volume at infinite dilution versus temperature. Using the Passynski method, the hydration numbers for AAILs in an aqueous medium were calculated. The results indicate that in the studied solutions, the ion–solvent interactions are determined by the hydrophobic effect, which results in the decrease of the limiting apparent molar compressibilities and an increase of limiting apparent molar expansibility coefficients in the order: $[\text{Mor}_{1,4}]$[N-Ac-L-Ala], $[\text{Mor}_{1,4}]$[N-Ac-L-Val], $[\text{Mor}_{1,4}]$[N-Ac-L-Leu], $[\text{Mor}_{1,4}]$[N-Ac-L-Izoleu]. The empirical slopes in Redlich –Rosenfeld – Meyer equations show that the hydrophobicity of amino acid anions is also responsible for the ion-ion interactions.

1. Introduction

Ionic liquids (ILs) have drawn interest from both the industry and scientific community for several decades because of their unique physical and chemical characteristics, such as high thermal stability, negligible vapor pressure, and excellent chemical stability [1,2]. Ionic liquids are also referred to as “designer solvents” due to the wide variety of ion combinations that might cause distinct IL behavior. Combining various cations and anions and adding functional groups to the structure of the ions allows for the fine-tuning of the ILs’ properties. This idea is predicated on the fact that both chemical and physical qualities can be altered at will; yet, a focused design necessitates the availability of some level of predictability, which can be challenging given the wide range of possible combinations. The amino acid ionic liquids (AAILs) are an intriguing example in this regard. Fukumoto *et al.* were the first to introduce amino acid-based ionic liquids, which were made up of imidazolium cations and amino acid anions [3,4]. Amino acids are one of the most prevalent macromolecules in nature, making them inexpensive and readily available. AAILs are useful for dissolving biomaterials because of their inherent ability to create potent hydrogen bonds with amine and carboxyl groups [5,6]. These materials can be used in a variety of applications, including gas separation [7] and reaction medium [8], thanks to their excellent biodegradability [9] and low toxicity [10]. Noteworthy, as the crucial factor in the conformational stability of proteins is the interaction between amino acids and water, AAILs can be utilized as a medium for research on protein stability in aqueous solutions [11,12]. The multiple experimental parameters that may be determined from sound density and speed data provide important information about the presence of various intermolecular interactions in the binary AAILs-water system. Thermodynamic factors like temperature and pressure have an impact on proteins in aqueous media and are crucial in creating a comprehensive understanding of physical immutability [13].

The current paper reports the thermophysical properties obtained from measurements of the density and sound speed of N-butyl-N-methylmorpholine based amino acid ionic liquids with four different anions, namely: N-acetyl-L-alanine, N-acetyl-L-valinate, N-acetyl-L-leucinate, and *N*-acetyl-L-izoleucinate. The use of the morfpholinium cation results from its low toxicity, which causes it to be often used as a

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substitute for typical imidazolium or pyridinium cations [14]. The experimental results for investigated AAILS at 10 different concentrations (0.02 to 0.3 mol·kg^{-1}) and 5 temperatures (293.15 to 313.15 K) were collected. The apparent molar volumes and isentropic compressibility coefficients, as well as limiting apparent molar expansibility coefficients, have been determined based on experimental results. The nature of solute–solute and solute–solvent interactions occurring in the AAILs - water system have been derived and described.

2. Materials and methods

Synthesis and purification of *N*-butyl-*N*-methylmorpholinium *N*-acetyl-L-alaninate, *N*-butyl-*N*-methyl-morpholinium *N*-acetyl-L-valinate, *N*-butyl-*N*-methylmorpholinium *N*-acetyl-L-leucinate, and *N*-butyl-*N*-methylmorpholinium *N*-acetyl-L-izoleucinate was described in our previous paper [15]. ^{1}H NMR spectra of AAILs, presented in Supplementary material, were obtained by a Varian Unity 500 plus (500 MHz) in D_2O with TMS as internal lock and were used for IL's structure confirmation. Bromide content was measured via ion chromatography on Dionex ICS-3000 system with DionexIonPac® AS22 column, Dionex ASRS 300 suppressor, CD detection and eluted by 4.5 mmol/L Na_2CO_3, 1.4 mmol/L $NaHCO_3$ buffer solution. Before use, the samples of amino acid ionic liquids, the same as in Ref.[15], were dried under vacuum (0.1 Pa) at 323 K for 5 days. The ILs were analyzed by the Karl Fischer titration (831 KF Coulometer apparatus from Metrohm) and showed a mass fraction of water lower than 2000 ppm. Due to the fact that the relaxation time applied during NMR measurements did not allow the use of the obtained spectra for quantitative analysis, they were used mainly to confirm the structures of the ionic liquids. On the other hand, the integration of some peaks may suggest non-stoichiometric substrate ratios. This is evident in the singleton peaks for the methyl groups in the cation (NCH3) and the anion (CH3CO). However, it is difficult to assess to what extent this discrepancy is the result of the lack of a non-stoichiometric amount of substrates and to what extent it is the result of too short relaxation time during the measurements. Quantitative analysis of the ^{1}H NMR spectrum is possible in the case of an excess of anion substrate, which results from a different band shift for the CH3CO group in the substrate (~1.87) and the ionic liquid (~1.86) (see Figure S4), while in the case of NCH3 groups, both shifts are indistinguishable. Therefore, taking into consideration the lack of clear peaks from the substrates or other contaminants in the ^{1}H NMR spectra for ionic liquids with [N-Ac-L-Ala], [N-Ac-L-Val] and [N-Ac-L-Leu] anions, the purity of the AAILs was estimated to be greater than 0.99, while for ionic liquid with [N-Ac-L-Izoleu] anion greater than 0.95. That estimation is further supported by the summarized content of water and bromide not exceeding 0.003 mass fraction. Table 1 presents a characterization of the studied chemicals, and Figure 1 illustrates the structures of ions forming investigated ionic liquids.

Deionized, double distilled, degassed water with a specific conductance of 1.15×10^{-6} S·cm^{-1} was used for the preparation of solutions of AAILs.

Solutions for density and sound velocity measurements were prepared by mass, and the weighing was done by using an analytical balance (Mettler Toledo) with a precision of 0.1 mg. Moreover, the measured water content in the studied ILs was taken into account when preparing the solutions. Measurements of density and ultrasonic velocity were performed by using a digital vibration-tube analyzer (Anton Paar DSA 5000, Austria) with proportional temperature control that kept the samples at working temperature with an accuracy of 0.01 K. Experimental frequency for the measurements of the ultrasonic speed was equal to 3 MHz. The apparatus was calibrated according to the procedure described by Fortin *et al.*[16]. Before each series of density measurements, a two-point calibration was performed with freshly prepared water and dry air. Moreover, the calibration was verified by measurement with a certified reference fluid i.e. 0.09 abv (alcohol by voume) solution of ethanol in water (CRM) at 293.15 K. Taking into account the comparinig the obtained result to the reference value, the influence of errors at preparation of sample and its purity, the experimental uncertainty of density and ultrasonic velocity measurements was estimated as better than 0.035 kg·m^{-3} and 0.5 m·s^{-1}, respectively.

3. Results and discussion

3.1. Volumetric properties

The values of experimental density as a function of ionic liquid molality obtained for the aqueous solutions of AAILs based on the *N*-butyl-*N*-methylmorpholinium cation and *N*-acetyl-L-alaninate, *N*-acetyl-L-valinate, *N*-acetyl-L-leucinate and *N*-acetyl-L-izoleucinate anions at temperatures between 293.15 and 313.15 K are reported in Table 2. These data were used to calculate the apparent molar volumes V_Φ, using the following equation:

$$V_\Phi = (d_0 - d)/(mdd_0) + M_2/d \quad (1)$$

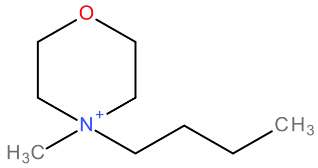
where m denotes the number of moles of the solute per kilogram of solvent (molality); d and d_0 are the densities of solution and solvent, respectively; and M_2 is the molar mass of the solute. Table 2 shows the apparent molar volume values of the studied aqueous solutions of amino acid ionic liquids at all temperatures. Figure 2 presents the concentration dependence of the apparent molar volume at 298.15 K.

As is seen from Table 2 and Figure 2, the apparent molar volume is more or less constant in the lower concentration range and decreases

Table 1
Provenance and mass fraction purity of the studied compounds.

Chemical name	Source	Mass fraction purity[b]	Water content in mass fraction [c]	Bromide content in mass fraction[d]	Method of purification
N-butyl-*N*-methylmorpholinium *N*-acetyl-L-alaninate [$Mor_{1,4}$][N-Ac-L-Ala]	Previous work [a]	>0.99	0.0019	0.00081	extraction evaporation and drying under vacuum
N-butyl-*N*-methyl-morpholinium *N*-acetyl-L-valinate [$Mor_{1,4}$][N-Ac-L-Val]	Previous work [a]	>0.99	0.0011	0.00085	extraction evaporation and drying under vacuum
N-butyl-*N*-methylmorpholinium *N*-acetyl-L-leucinate [$Mor_{1,4}$][N-Ac-L-Leu]	Previous work [a]	>0.99	0.0020	0.00077	extraction evaporation and drying under vacuum
N-butyl-*N*-methylmorpholinium *N*-acetyl-L-izoleucinate [$Mor_{1,4}$][N-Ac-L-Izoleu]	Previous work [a]	>0.95	0.0019	0.00067	extraction evaporation and drying under vacuum

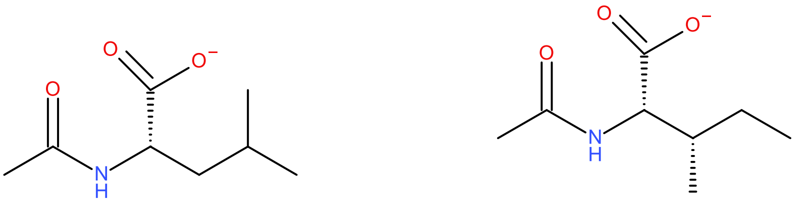
[a] synthesized in our laboratory (the corresponding characterization information is provided in Ref. [15]).
[b] estimated by the purities of reagents combined with Karl Fischer titration and ion chromatography analysis.
[c] Karl-Fischer titration method.
[d] from ion chromatography analysis.



N-butyl-*N*-methylmorpholinium cation

N-acetyl-L-alaninate

N-acetyl-L-valinate



N-acetyl-L-leucinate

N-acetyl-L-izoleucinate

Figure 1. Chemical structures of ions forming the investigated ionic liquids.

vary slightly at higher concentrations. According to Dagade et al., the decrease in the apparent molar volumes with concentration occurs as a result of the ion-ion association which dominates over ionic hydration [17]. Thus, it can be said that in more concentrated AAILs solutions, the interactions between ions become stronger and begin to determine the system.

Since the direct measure of the ion–solvent interactions is the limiting apparent molar volume, this property was determined using the apparent molar volume data, which was treated according to the Redlich, Rosenfeld and Meyer (RRM) equation as [18]:

$$V_{\Phi} = V_{\Phi}^{0} + S_{V}^{DH}\sqrt{m} + b_{V}\cdot m \qquad (2)$$

where V_{Φ}^{0} is the apparent molar volume at infinite dilution, S_{V}^{DH} is the Pitzer-Debye-Hückel limiting slope (1.7922; 1.8743; 1.9616; 2.0547 and 2.1540 $\text{cm}^3\text{kg}^{1/2}\text{mol}^{-3/2}$ for 1:1 electrolytes in water at 293.15; 298.15; 303.15; 308.15 and 313.15 K, respectively) and b_v is the deviation parameter, which indicates the deviation from limiting law due to non-electrostatic solute – solute interactions [19]. In this treatment, the difference $(V_{\Phi} - S_{V}^{DH}\sqrt{m})$ against molality were regressed linearly to determine the limiting apparent molar volume and b_v parameters. Typical plots for *N*-butyl-*N*-methylmorpholinium *N*-acetyl-L-alaninate in water are given in Figure 3. The parameters of equation 2 and the standard deviations σ are shown in Table 3.

Inspection of Table 3 and Figure 3 shows that the experimental slopes b_V of Redlich, Rosenfeld and Meyer equation are negative and magnitude of the slope decreases with increase in temperature. According to the literature, the sign and magnitude of deviation parameter b_V in the RRM equation indicate the nature of ion-ion interactions. The relatively high and negative value of b_V is the result of the hydrophobicity of ions and indicates dominance of hydrophobic interactions over electrostatic ones [17]. Therefore, the obtained negative values of the experimental slope for N-butyl-N-methylmorpholine based amino acid ionic liquids in water show that the hydrophobic interactions between cation and anion of AAIL are the main factor controlling the properties of the studied systems. This conclusion is supported by the fact that b_V values become more negative in the order $[\text{Mor}_{1,4}]$[N-Ac-L-Ala] > $[\text{Mor}_{1,4}]$[N-Ac-L-Val] > $[\text{Mor}_{1,4}]$[N-Ac-L-Leu] ≈ $[\text{Mor}_{1,4}]$[N-Ac-L-Izoleu], which is consistent with the hydrophobicity of the amino acids involved [20,21]. A similar trend in b_V values for aqueous solutions of nitrate based amino acid ionic liquids was reported by Patil *et al.* [22].

For all studied N-butyl-N-methylmorpholine based amino acid ionic liquids, the experimental values of b_V increase with increasing temperature. Thus, the obtained results suggest the domination of hydrophobic association at lower temperatures and the advantage of ionic hydration at higher temperatures.

As can be seen from Table 3, regardless of the temperature, the limiting apparent molar volume of the studied AAILs changes in the order: $[\text{Mor}_{1,4}]$[N-Ac-L-Ala] < $[\text{Mor}_{1,4}]$[N-Ac-L-Val] < $[\text{Mor}_{1,4}]$[N-Ac-L-Leu] > $[\text{Mor}_{1,4}]$[N-Ac-L-Izoleu], which was also observed by Dagade et al. for respective 1-butyl-3-methylimidazolium based amino acid ionic liquids in water [17]. Since the cation is the same in all studied AAILs, the change in the apparent molar volume at infinite dilution depends obviously on the anion of ionic liquid i.e., its size and interactions with water. Table 4 presents the limiting apparent molar volume differences for pair of amino acid ionic liquids from this study with the corresponding literature differences for amino acids and AAILs based on an imidazolium cation in aqueous solutions at 298.15 K [17].

Inspection of the table shows that, despite the fact that *N*-acetylated amino acid ionic liquids have been now studied, the respective differences are similar in magnitude. This suggests that the behavior of amino acids is more or less similar, whether they are present in a neutral form in aqueous solutions or in ionic form as components of morpholine and imidazole-based ionic liquids. The main factor determining the value of limiting the apparent molar volume of AAILs seems to be the hydrophobicity of the amino acid anion, which increases with the increasing length of its alkyl chain or with the presence of a methyl group. This phenomenon causes hydrophobic hydration to dominate hydrogen / electrostatic bonding interactions and leads to higher values of V_{Φ}^{0}.

Figure 4 presents temperature dependence of the limiting values of the apparent molar volumes obtained for AAILs based on the *N*-butyl-*N*-methylmorpholinium cation and *N*-acetyl-L-alaninate, *N*-acetyl-L-valinate, *N*-acetyl-L-leucinate and *N*-acetyl-L-izoleucinate anions in water.

Table 2

Densities, *d* and apparent molar volumes, V_Φ, for the binary mixtures (ionic liquid + water), as a function of the molality of AAIL, *m*, at temperatures T = (293.15 to 313.15) K and experimental pressure, P = 101.3 kPa.

m / (mol·kg^{-1})	T = 293.15 K d / (kg·m^{-3})	 $10^6\ V_\Phi$ / (m^3·mol^{-1})	T = 298.15 K d / (kg·m^{-3})	 $10^6\ V_\Phi$ / (m^3·mol^{-1})	T = 303.15 K d / (kg·m^{-3})	 $10^6\ V_\Phi$ / (m^3·mol^{-1})	T = 308.15 K d / (kg·m^{-3})	 $10^6\ V_\Phi$ / (m^3·mol^{-1})	T = 313.15 K d / (kg·m^{-3})	 $10^6\ V_\Phi$ / (m^3·mol^{-1})
[Mor$_{1,4}$][N-Ac-L-Ala]										
0.0000	998.206	–	997.048	–	995.648	–	994.034	–	992.214	–
0.0191	998.817	256.85	997.645	257.84	996.233	258.79	994.608	259.75	992.780	260.59
0.0432	999.570	256.85	998.379	257.89	996.955	258.78	995.314	259.78	993.473	260.70
0.0523	999.854	256.84	998.658	257.84	997.225	258.80	995.579	259.80	993.730	260.71
0.0677	1000.332	256.85	999.126	257.83	997.683	258.80	996.030	259.76	994.180	260.69
0.0906	1001.046	256.71	999.821	257.73	998.363	258.70	996.696	259.68	994.830	260.62
0.1197	1001.939	256.65	1000.693	257.67	999.217	258.65	997.531	259.64	995.650	260.58
0.1525	1002.937	256.55	1001.670	257.55	1000.172	258.54	998.468	259.53	996.570	260.48
0.1851	1003.930	256.40	1002.637	257.42	1001.117	258.42	999.392	259.42	997.479	260.37
0.2298	1005.262	256.28	1003.937	257.31	1002.389	258.31	1000.636	259.33	998.694	260.31
0.2908	1007.065	256.06	1005.685	257.14	1004.094	258.16	1002.300	259.20	1000.323	260.20
[Mor$_{1,4}$][N-Ac-L-Val]										
0.0000	998.206	–	997.048	–	995.648	–	994.034	–	992.216	–
0.0171	998.835	279.91	997.662	281.08	996.250	282.13	994.625	283.19	992.796	284.30
0.0251	999.126	279.98	997.947	281.11	996.530	282.14	994.900	283.19	993.066	284.30
0.0415	999.723	279.92	998.532	281.01	997.103	282.06	995.460	283.18	993.615	284.30
0.0589	1000.349	279.89	999.143	281.01	997.702	282.06	996.049	283.14	994.197	284.19
0.0827	1001.207	279.76	999.974	280.97	998.520	281.98	996.849	283.09	994.980	284.19
0.1078	1002.100	279.66	1000.853	280.80	999.378	281.86	997.688	282.99	995.804	284.08
0.1359	1003.091	279.56	1001.819	280.72	1000.322	281.80	998.615	282.92	996.717	283.99
0.1723	1004.360	279.44	1003.058	280.59	1001.532	281.70	999.800	282.83	997.879	283.91
0.2095	1005.653	279.26	1004.320	280.42	1002.764	281.55	1001.005	282.69	999.062	283.78
0.2620	1007.444	279.04	1006.063	280.23	1004.468	281.37	1002.671	282.52	1000.692	283.64
[Mor$_{1,4}$][N-Ac-L-leu]										
0.0000	998.205	–	997.046	–	995.646	–	994.031	–	992.221	–
0.0160	998.734	297.82	997.561	298.95	996.148	300.08	994.522	301.28	992.700	302.54
0.0240	998.997	297.83	997.817	298.99	996.397	300.08	994.765	301.28	992.936	302.54
0.0386	999.476	297.77	998.281	298.98	996.850	300.12	995.206	301.32	993.366	302.53
0.0560	1000.039	297.64	998.830	298.86	997.388	300.09	995.731	301.26	993.877	302.51
0.0762	1000.690	297.61	999.465	298.87	998.003	300.01	996.327	301.23	994.460	302.47
0.1085	1001.728	297.42	1000.471	298.66	998.983	299.88	997.287	301.09	995.393	302.39
0.1302	1002.422	297.29	1001.144	298.55	999.636	299.79	997.921	301.03	996.014	302.30
0.1609	1003.398	297.13	1002.090	298.41	1000.555	299.66	998.815	300.92	996.884	302.20
0.1948	1004.468	296.94	1003.119	298.28	1001.548	299.58	999.783	300.78	997.827	302.07
0.2460	1006.065	296.67	1004.672	297.99	1003.053	299.28	1001.246	300.55	999.250	301.86
[Mor$_{1,4}$][N-Ac-L-izoleu]										
0.0000	998.207	–	997.054	–	995.650	–	994.036	–	992.225	–
0.0200	998.916	295.20	997.746	296.31	996.326	297.55	994.698	298.69	992.872	299.94
0.0307	999.295	295.20	998.115	296.36	996.688	297.52	995.050	298.74	993.219	299.89
0.0391	999.589	295.19	998.402	296.34	996.968	297.52	995.326	298.68	993.488	299.87
0.0493	999.946	295.12	998.749	296.31	997.307	297.49	995.657	298.66	993.812	299.86
0.0711	1000.708	295.01	999.492	296.20	998.030	297.42	996.366	298.57	994.505	299.78
0.0980	1001.642	294.88	1000.399	296.12	998.917	297.32	997.231	298.51	995.350	299.73
0.1272	1002.641	294.77	1001.370	296.03	999.869	297.20	998.162	298.39	996.260	299.62
0.1624	1003.834	294.62	1002.530	295.89	1001.000	297.08	999.258	298.33	997.335	299.55
0.2031	1005.200	294.45	1003.858	295.73	1002.287	296.97	1000.511	298.25	998.561	299.46
0.2497	1006.746	294.22	1005.360	295.52	1003.753	296.76	1001.951	298.00	999.967	299.23
0.3157	1008.929	293.83	1007.469	295.18	1005.808	296.44	1003.951	297.70	1001.915	298.97

Standard uncertainties u are $u(T)$ = 0.01 K and $u(P)$ = 0.5 kPa and standard combined uncertainties are: $u(d)$ = 0.035 kg·m^{-}3, $u(m)$ = 0.0015 mol·kg^{-1} and $u(V_\Phi)$ = (0.13 ÷ 1.8)·10^{-6} m^3·mol^{-1} for high and low concentration range of AAILs, respectively.

For better visualization, plots of the differences $\left[V^0_\Phi - V^0_{\Phi,298.15K}\right]$, calculated for the ionic liquids against temperature are shown.

As seen in Figure 4, the limiting apparent molar volumes increase with increasing temperature for all systems studied. The plots are linear and the best description of the temperature dependence of V^0_Φ was obtained using the equation:

$$V^0_\Phi = A_T + B_T(\mathrm{T}/K\text{-}298.15) \qquad (3)$$

where the first coefficient, A_T, is equal to the value of the limiting molar volume at T = 298.15 K, while the second one, B_T, can be treated as the limiting apparent molar isobaric expansibility, $E^0_\Phi = \left(\mathrm{d}V^0_\Phi/\mathrm{d}T\right)_P$.

The volume expansibility coefficients for the limiting values of the apparent molar volumes of the ionic liquids studied were calculated using Eq. 4:

$$\alpha^0_V = \left(\mathrm{d}V^0_\Phi/\mathrm{d}T\right)_P/V^0_\Phi \qquad (4)$$

The coefficients of Eq.4, along with the respective values of their standard deviations and the volume expansibility coefficients at 298.15 K calculated from Eq. 4, are listed in Table 5.

As the temperature effect can be better understood using the expansibility parameter for solutions with finite concentrations, also the apparent molar expansibility of the ionic liquids in aqueous solutions, E_Φ, over the entire molality range were calculated from the equation [23]:

$$E_\Phi = (\alpha d_0 - \alpha_0 d)/(m d d_0) + M_2\alpha/d \qquad (5)$$

where α and α $_0$ are the coefficient of thermal expansion of solution

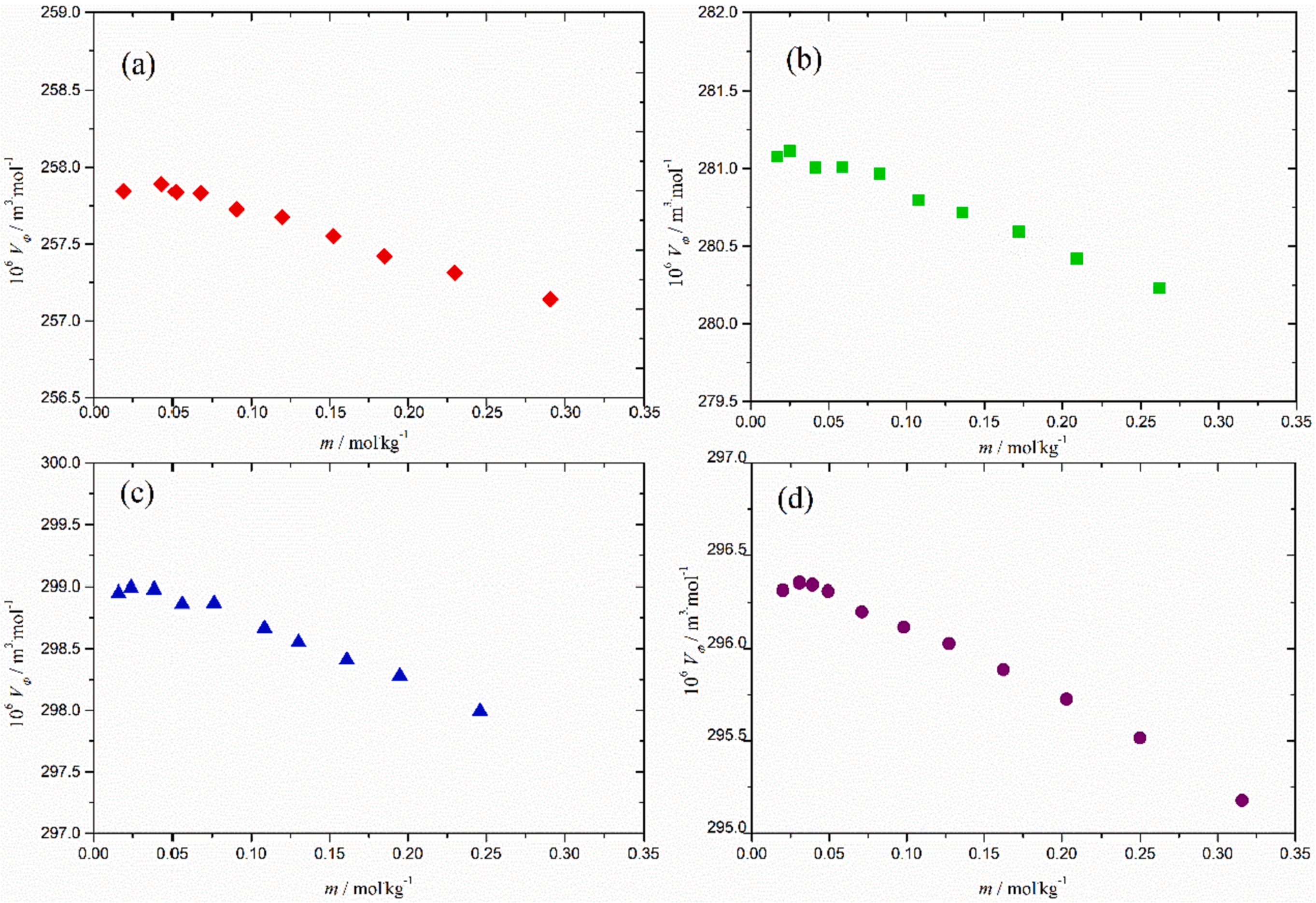


Figure 2. The concentration dependencies of the apparent molar volume for the studied amino acid ionic liquids in water solutions at $T = 298.15$ K: (◆) [$Mor_{1,4}$][N-Ac-L-Ala], (■) [$Mor_{1,4}$][N-Ac-L-Val], (▲) [$Mor_{1,4}$][N-Ac-L-Leu], and (●) [$Mor_{1,4}$][N-Ac-L-Izoleu].

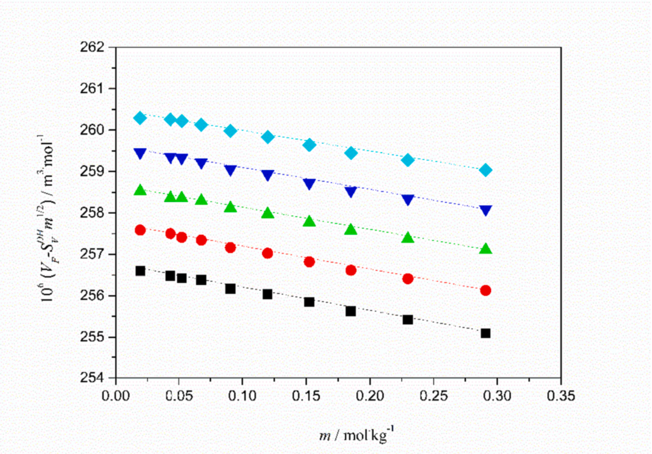


Figure 3. The concentration dependencies of the difference $(V_\Phi - S_V^{DH}\sqrt{m})$ for [$Mor_{1,4}$][N-Ac-L-Ala] in water solutions at $T = (293.15–313.15)$: 293.15 K (■), 298.15 K (●), 303.15 K (▲), 308.15 K (▼) and 313.15 K (◆). The dashed lines show the linear, least-squares fit of the individual data series.

and solvent, respectively.

Table 6 presents the obtained values of E_Φ and α ($\alpha = -(\partial d/\partial T)_p/d$) as a function of ionic liquid molality at temperatures between 298.15 and 308.15 K. The expansibility parameter cannot be studied at the lowest and highest temperature studied as there are no reference points

Table 3
Coefficients of Redlich, Rosenfeld and Meyer equation, V_Φ^0 and b_V, for apparent molar volume of [$Mor_{1,4}$][N-Ac-L-Ala], [$Mor_{1,4}$][N-Ac-L-Val], [$Mor_{1,4}$][N-Ac-L-Leu] and [$Mor_{1,4}$][N-Ac-L- Izoleu] in water at temperatures T = (293.15 to 313.15) K. (P_{atm} = 101325 Pa).

T / K	$10^6\ V_\Phi^0$ / (m^3 mol^{-1})	$10^6 b_V$ / (m^3 kg mol^{-2})	$10^6\sigma$ / (m^3 mol^{-1})
[$Mor_{1,4}$][N-Ac-L-Ala]			
293.15	256.71 ± 0.021	−5.6 ± 0.16	0.029
298.15	257.70 ± 0.024	−5.5 ± 0.20	0.036
303.15	258.61 ± 0.021	−5.3 ± 0.24	0.032
308.15	259.56 ± 0.027	−5.3 ± 0.18	0.038
313.15	260.43 ± 0.028	−5.0 ± 0.20	0.044
[$Mor_{1,4}$][N-Ac-L-Val]			
293.15	279.81 ± 0.021	−6.6 ± 0.18	0.031
298.15	280.93 ± 0.020	−6.5 ± 0.18	0.035
303.15	281.94 ± 0.021	−6.2 ± 0.19	0.036
308.15	283.00 ± 0.014	−6.0 ± 0.10	0.023
313.15	284.08 ± 0.024	−6.1 ± 0.17	0.042
[$Mor_{1,4}$][N-Ac-L-Leu]			
293.15	297.71 ± 0.018	−8.0 ± 0.21	0.028
298.15	298.86 ± 0.018	−7.3 ± 0.17	0.032
303.15	299.96 ± 0.022	−6.6 ± 0.19	0.030
308.15	301.14 ± 0.010	−6.5 ± 0.10	0.018
313.15	302.36 ± 0.010	−6.4 ± 0.10	0.010
[$Mor_{1,4}$][N-Ac-L-Izoleu]			
293.15	295.07 ± 0.019	−7.1 ± 0.15	0.034
298.15	296.20 ± 0.013	−6.6 ± 0.13	0.024
303.15	297.36 ± 0.019	−6.4 ± 0.12	0.029
308.15	298.51 ± 0.023	−6.2 ± 0.17	0.044
313.15	299.69 ± 0.024	−6.1 ± 0.17	0.039

Table 4
Comparison of limiting apparent molar volume difference, ΔV_{Φ}^{o}, for pair of AAILs with corresponding amino acids in aqueous solutions at 298.15 K.

morpholinium based amino acid ionic liquids	$10^6\Delta V_{\Phi}^{o}$/ (m^3 mol^{-1})	imidazioum based amino acid ionic liquids[a]	$10^6\Delta V_{\Phi}^{o}$/ (m^3 mol^{-1})	amino acids[a]	$10^6\Delta V_{\Phi}^{o}$/ (m^3 mol^{-1})
$[Mor_{1,4}]$[N-Ac-L-Val]-$[Mor_{1,4}]$[N-Ac-L-Ala]	23.23 ± 0.044	[bmim][Val] - [bmim][Ala]	30.76 ± 0.68	Val - Ala	29.54 ± 0.09
$[Mor_{1,4}]$[N-Ac-L-Leu]-$[Mor_{1,4}]$[N-Ac-L-Val]	17.93 ± 0.042	[bmim][Leu] - [bmim][Val]	14.23 ± 0.69	Leu - Val	17.54 ± 0.09
$[Mor_{1,4}]$[N-Ac-L-Izoleu]-$[Mor_{1,4}]$[N-Ac-L-Leu]	−2.66 ± 0.041	[bmim][Ile] - [bmim][Leu]	−0.37 ± 0.78	Ile - Leu	−1.88 ± 0.03

[a]from ref. 16.

to take slopes.

The limiting apparent molar expansibility values at 298.15, 303.15 and 308.15 K were estimated by the linear regression of E_{Φ} against the square root of molality: $E_{\Phi} = E_{\Phi}^{0} + S_{E}\sqrt{m}$, and are collected in Table 7.

The temperature dependences of the limiting apparent molar isobaric expansibility E_{Φ}^{0} for the studied AAILs in aqueous solutions are shown in Figure 5.

Inspection of Tables 5 and 7 shows that the values of the limiting apparent molar isobaric expansibility calculated using equation 3, that is, assuming they are independent of temperature, reveal the same outcome as the values of E_{Φ}^{0} estimated by linear regression of E_{Φ} against the square root of molality. As seen, the values of limiting apparent molar isobaric expansibility, as well as the volume expansibility coefficients, are positive and change according to the sequence: $[Mor_{1,4}]$[N-Ac-L-Ala] < $[Mor_{1,4}]$[N-Ac-L-Val] < $[Mor_{1,4}]$[N-Ac-L-Leu] indicating that V_{Φ}^{0} becomes more sensitive to temperature with the increase in side alkyl chain length or methyl group of amino acid. Moreover, E_{Φ}^{0} and α_{V}^{0} for leucine and isoleucine based ionic liquids are very similar in their magnitude. Due to the heating, some water molecules are released from the IL hydration layers, resulting in a greater increase in the volume of the solution than with pure water and positive values for the limiting apparent molar isobaric expansibility, and the effect is stronger with the more hydrophobic AAILs. Similar types of trends were also reported for other classes of Ils in aqueous solutions [24] and amino acid ionic liquids based on the *N*-acetyl-L-alaninate ([N-Ac-L-Ala]) anion and the *N*-alkyl-*N*-methylmorpholinium cation ($[Mor_{1,R}]$, R = 2, 3, 6, 8) with different length of the alkyl chain than that considered in the present study [25].

The values of limiting apparent molar isobaric expansibility for $[Mor_{1,4}]$[N-Ac-L-Ala] are within the range of these values observed for $[Mor_{1,3}]$[N-Ac-L-Ala] and $[Mor_{1,6}]$[N-Ac-L-Ala] regardless of the temperature[25]. Similarly, the limiting volume expansibility coefficient at 298.15 K for this IL fits perfectly into this relationship.

An examination of Figure 5 reveals the temperature dependences of the limiting apparent molar isobaric expansibility for the studied ILs are different. The values of E_{Φ}^{0} decrease with increasing temperature for

Table 5
The coefficients of Eq. 3, A_T and B_T, with the corresponding standard deviations, σ, and limiting expansibility coefficients, α_V^0, for $[Mor_{1,4}]$[N-Ac-L-Ala], $[Mor_{1,4}]$[N-Ac-L-Val], $[Mor_{1,4}]$[N-Ac-L-Leu] and $[Mor_{1,4}]$[N-Ac-L-Izoleu] in water.

ionic liquid	$10^6 A_T$ / ($m^3 \cdot mol^{-1}$)	$10^6 B_T$ (E_{Φ}^{0}) / ($m^3 \cdot mol^{-1}$)	10^6 σ/ ($m^3 \cdot mol^{-1}$)	10^4 $\alpha_V^0/(K^{-1})$ (298.15 K)
$[Mor_{1,4}]$[N-Ac-L-Ala]	257.70 ± 0.024	0.1841 ± 0.0024	0.040	7.145 ± 0.080
$[Mor_{1,4}]$[N-Ac-L-Val]	280.93 ± 0.020	0.2096 ± 0.0023	0.043	7.461 ± 0.079
$[Mor_{1,4}]$[N-Ac-L-Leu]	298.86 ± 0.018	0.2308 ± 0.0019	0.036	7.723 ± 0.063
$[Mor_{1,4}]$[N-Ac-L-Ile]	296.20 ± 0.013	0.2317 ± 0.0010	0.017	7.824 ± 0.030

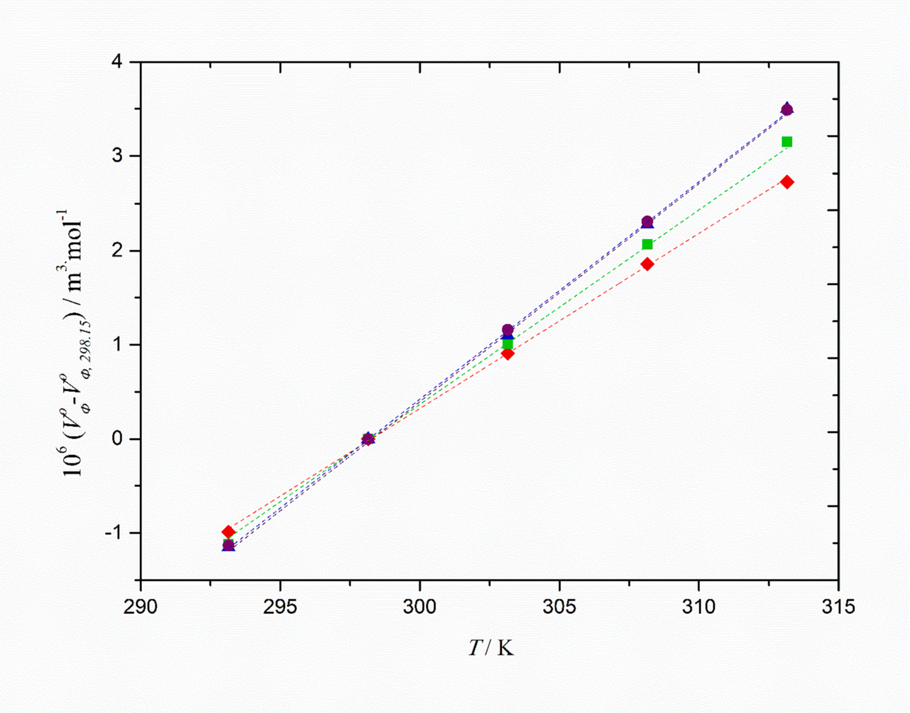


Figure 4. The difference $\left[V_{\Phi}^{0} - V_{\Phi,298.15K}^{0}\right]$ calculated for: (◆) $[Mor_{1,4}]$[N-Ac-L-Ala], (■) $[Mor_{1,4}]$[N-Ac-L-Val], (▲) $[Mor_{1,4}]$[N-Ac-L-Leu], and (●) $[Mor_{1,4}]$[N-Ac-L-Izoleu] against temperature in aqueous solutions. The dashed lines show the linear, least-squares fit of the individual data series.

Table 6
Isobaric expansibility coefficient, α, and apparent molar expansibility, E_Φ, for the binary mixtures (ionic liquid + water), as a function of the molality of IL, m, at temperatures T = (298.15 to 308.15) K and experimental pressure, P = 101.3 kPa.

m / (mol·kg^{-1})	T = 298.15 K		T = 303.15 K		T = 308.15 K	
	10^4 α / (K^{-1})	10^6 E_Φ / (m^3·mol^{-1}·K^{-1})	10^4 α / (K^{-1})	10^6 E_Φ / (m^3·mol^{-1}·K^{-1})	10^4 α / (K^{-1})	10^6 E_Φ / (m^3·mol^{-1}·K^{-1})
[$Mor_{1,4}$][N-Ac-L-Ala]						
0.0000	2.568	–	3.013	–	3.460	–
0.0191	2.593	0.196	3.034	0.188	3.477	0.179
0.0432	2.623	0.195	3.061	0.192	3.502	0.189
0.0523	2.636	0.198	3.072	0.194	3.511	0.190
0.0677	2.654	0.196	3.088	0.192	3.525	0.188
0.0906	2.686	0.200	3.116	0.196	3.549	0.192
0.1197	2.724	0.201	3.150	0.196	3.578	0.192
0.1525	2.763	0.200	3.187	0.197	3.612	0.194
0.1851	2.809	0.203	3.226	0.199	3.644	0.195
0.2298	2.865	0.203	3.280	0.201	3.696	0.199
0.2908	2.958	0.211	3.360	0.207	3.764	0.203
[$Mor_{1,4}$][N-Ac-L-Val]						
0.0000	2.568	–	3.012	–	3.458	–
0.0171	2.593	0.221	3.034	0.217	3.477	0.214
0.0251	2.604	0.215	3.044	0.214	3.486	0.214
0.0415	2.627	0.215	3.066	0.219	3.508	0.222
0.0589	2.652	0.218	3.087	0.215	3.523	0.212
0.0827	2.690	0.223	3.120	0.220	3.552	0.216
0.1078	2.724	0.221	3.153	0.221	3.585	0.220
0.1359	2.768	0.225	3.189	0.221	3.613	0.217
0.1723	2.823	0.227	3.239	0.224	3.657	0.220
0.2095	2.880	0.230	3.290	0.226	3.702	0.222
0.2620	2.962	0.234	3.364	0.230	3.769	0.226
[$Mor_{1,4}$][N-Ac-L-Leu]						
0.0000	2.571	–	3.010	–	3.451	
0.0160	2.594	0.226	3.033	0.235	3.473	0.245
0.0240	2.606	0.225	3.044	0.234	3.484	0.243
0.0386	2.631	0.235	3.065	0.237	3.502	0.239
0.0560	2.662	0.243	3.093	0.243	3.527	0.243
0.0762	2.693	0.241	3.122	0.242	3.554	0.243
0.1085	2.746	0.244	3.174	0.247	3.604	0.251
0.1302	2.786	0.249	3.209	0.250	3.634	0.251
0.1609	2.840	0.253	3.259	0.253	3.680	0.254
0.1948	2.909	0.261	3.312	0.255	3.718	0.250
0.2460	2.990	0.260	3.395	0.259	3.802	0.258
[$Mor_{1,4}$][N-Ac-L-Ile]						
0.0000	2.567	–	3.011	–	3.456	
0.0200	2.599	0.235	3.038	0.229	3.480	0.223
0.0307	2.616	0.236	3.054	0.230	3.493	0.224
0.0391	2.628	0.234	3.065	0.230	3.503	0.226
0.0493	2.646	0.238	3.080	0.233	3.517	0.229
0.0711	2.681	0.240	3.113	0.236	3.546	0.232
0.0980	2.726	0.244	3.154	0.240	3.583	0.237
0.1272	2.771	0.242	3.194	0.240	3.620	0.237
0.1624	2.833	0.248	3.251	0.245	3.671	0.242
0.2031	2.908	0.254	3.317	0.250	3.729	0.246
0.2497	2.980	0.254	3.381	0.249	3.783	0.245
0.3157	3.101	0.261	3.489	0.255	3.879	0.250

Standard uncertainties u are $u(T)$ = 0.01 K, $u(P)$ = 0.5 kPa and standard combined uncertainties are: $u(m)$ = 0.0015 mol·kg^{-1}, u(α) = (0.04 ÷ 0.084)·10^{-4} K^{-1} and $u(E_\Phi)$ = (0.052 ÷ 0.65)·10^{-6} m^3·mol^{-1} for high and low concentration range of AAILs, respectively.

[$Mor_{1,4}$][N-Ac-L-izoleu] and [$Mor_{1,4}$][N-Ac-L-Ala], for [$Mor_{1,4}$][N-Ac-L-Val] are almost constant, and for [$Mor_{1,4}$][N-Ac-L-leu] they increase with grow of the temperature. According to the literature, in the case of the electrolytes, the value of the limiting apparent molar isobaric expansibility consists mainly of electrostriction and structure factors which are temperature dependent. At higher temperatures, the electrostriction factor dominates, while at lower temperatures, about the value of E_Φ^0 decides the structure effect [26]. Looking at Figure 5, it can be concluded that these factors and their temperature dependences must be distinctly different for the studied ILs. Moreover, since the slope values can be taken as indicators of whether the solutes act as a structure maker or breaker in solvents, [$Mor_{1,4}$][N-Ac-L-leu] seems to act as a structure maker in water, while [$Mor_{1,4}$][N-Ac-L-Ala] and [$Mor_{1,4}$][N-Ac-L-izoleu] behave as a structure breaker, and [$Mor_{1,4}$][N-Ac-L-Val] has no effect on the structure of water.

3.2. *Acoustic properties*

The speed of sound values obtained for the aqueous solutions of [$Mor_{1,4}$][N-Ac-L-Ala], [$Mor_{1,4}$][N-Ac-L-Val], [$Mor_{1,4}$][N-Ac-L-Leu] and [$Mor_{1,4}$][N-Ac-L-Izoleu] over the composition range studied, together with the values of the apparent molar isentropic compressibility and the hydration numbers at all temperatures, are collected in Table 8. As observed from Table 8, the speed of sound increases with increasing concentration for all electrolyte solutions and all temperatures studied. Moreover, with increasing temperature, the speed of sound increases regardless of the system.

The isentropic compressibility of water and aqueous AAIL solutions was obtained using the Laplace-Newton equation:

$$\kappa_S = 1/du^2 \tag{6}$$

and was used to calculate the apparent molar compressibility from the relation:

Table 7

Limiting apparent molar expansibility, E^0_Φ, and limiting slope, S_E, with the corresponding standard deviations for [$Mor_{1,4}$][N-Ac-L-Ala], [$Mor_{1,4}$][N-Ac-L-Val], [$Mor_{1,4}$][N-Ac-L-Leu] and [$Mor_{1,4}$][N-Ac-L-Izoleu] in water at varied temperatures, T, (293.15 to 308.15) K (P_{atm} = 101325 Pa).

T / K	$10^6\ E^0_\Phi$ / ($m^3 \cdot mol^{-1} \cdot K^{-1}$)	$10^6\ S_E$/ ($m^3 \cdot kg^{-1/2} \cdot mol^{-1/2} \cdot K^{-1}$)	$10^6\ \sigma$ / ($m^3 \cdot mol^{-1} \cdot K^{-1}$)
[$Mor_{1,4}$][N-Ac-L-Ala]			
298.15	0.190 ± 0.0025	0.033 ± 0.0059	0.0021
303.15	0.183 ± 0.0017	0.041 ± 0.0043	0.0015
308.15	0.176 ± 0.0026	0.048 ± 0.0061	0.0022
[$Mor_{1,4}$][N-Ac-L-Val]			
298.15	0.209 ± 0.0028	0.044 ± 0.0075	0.0028
303.15	0.210 ± 0.0022	0.035 ± 0.0055	0.0021
308.15	0.210 ± 0.0032	0.026 ± 0.0092	0.0034
[$Mor_{1,4}$][N-Ac-L-Leu]			
298.15	0.214 ± 0.0030	0.098 ± 0.0089	0.0032
303.15	0.225 ± 0.0017	0.069 ± 0.0037	0.0014
308.15	0.235 ± 0.0032	0.040 ± 0.0088	0.0032
[$Mor_{1,4}$][N-Ac-L-Ile]			
298.15	0.225 ± 0.0020	0.058 ± 0.0055	0.0020
303.15	0.219 ± 0.0014	0.064 ± 0.0042	0.0015
308.15	0.213 ± 0.0018	0.071 ± 0.0049	0.0018

$$K_{S,\Phi} = (\kappa_s d_0 - \kappa_{S0} d)/(m d d_0) + M_2 \kappa_S / d \tag{7}$$

where κ_S and κ_{S0} are the isentropic compressibility of solution and solvent, respectively.

Figure 6 presents the concentration dependence of the isentropic compressibility for all systems at 298.15 K. As seen, the highest values of isentropic compressibility are observed for aqueous solutions of [Mor1,4][N-Ac-L-Ala] in which the electrostriction effect is most effective. In the case of the solutions of [$Mor_{1,4}$][N-Ac-L-Val], [$Mor_{1,4}$][N-Ac-L-Leu] and [$Mor_{1,4}$][N-Ac-L-Izoleu], i.e. AAILs with a longer anion alkyl chain, electrostriction screening may occur, leading to a reduction in the compressibility of the solution because electrostricted water is less compressible than bulk water.

Inspection of Table 8 reveals that the values of apparent molar compressibilities are negative at low temperatures and they strongly increase with growing temperature achieving positive values at 313.15 K for [$Mor_{1,4}$][N-Ac-L-Val] while for the other AAILs, the positive values are observed already at 308.15 K. It can therefore be said that the effect of AAIL on the ordering of a solution depends on the temperature and hydrophobicity of the ionic liquid.

At low temperatures, all the studied ILs behave as structure makers, but at high temperatures, they behave as structure breakers.

Moreover, the apparent molar compressibilities become more positive with the increase in concentration. This behavior is obviously a result of increasing ionic association and decreasing ion–solvent interactions which both lead to the loss of hydrated water that is less compressible than the bulk solvent.

Since at all studied temperatures, the values of the theoretical Debye-Hückel slope for the compressibilities are available, and they are equal to $-34.173 \cdot 10^{-14}$, $-37.784 \cdot 10^{-14}$, $-41.573 \cdot 10^{-14}$, $-45.589 \cdot 10^{-14}$ and $-49.882 \cdot 10^{-14}$ $m^3 \cdot kg^{1/2} \cdot mol^{-3/2} \cdot Pa^{-1}$ for 1:1 type electrolytes in water at 293.15; 298.15; 303.15; 308.15 and 313.15 K, respectively [19], to obtain the limiting apparent molar compressibilities, the extrapolation of the experimental apparent molar compressibilities based on the Redlich, Rosenfeld and Meyer equation in the dilute region was applied [18]:

$$K_{S,\phi} = K^0_{S,\phi} + S^{DH}_k \sqrt{m} + b_k \cdot m \tag{8}$$

where S^{DH}_k denotes the theoretical Debye-Hückel slope for compressibilities and b_K is an empirical parameter. The obtained parameters of the RRM-type equations, i.e., the values of the limiting apparent molar compressibilities and corresponding slopes, are collected in Table 9. Typical plots of the difference $(K_\Phi - S^{DH}_K \sqrt{m})$ against molality for N-butyl-N-methylmorpholinium N-acetyl-L-alaninate in water are presented in Figure 7.

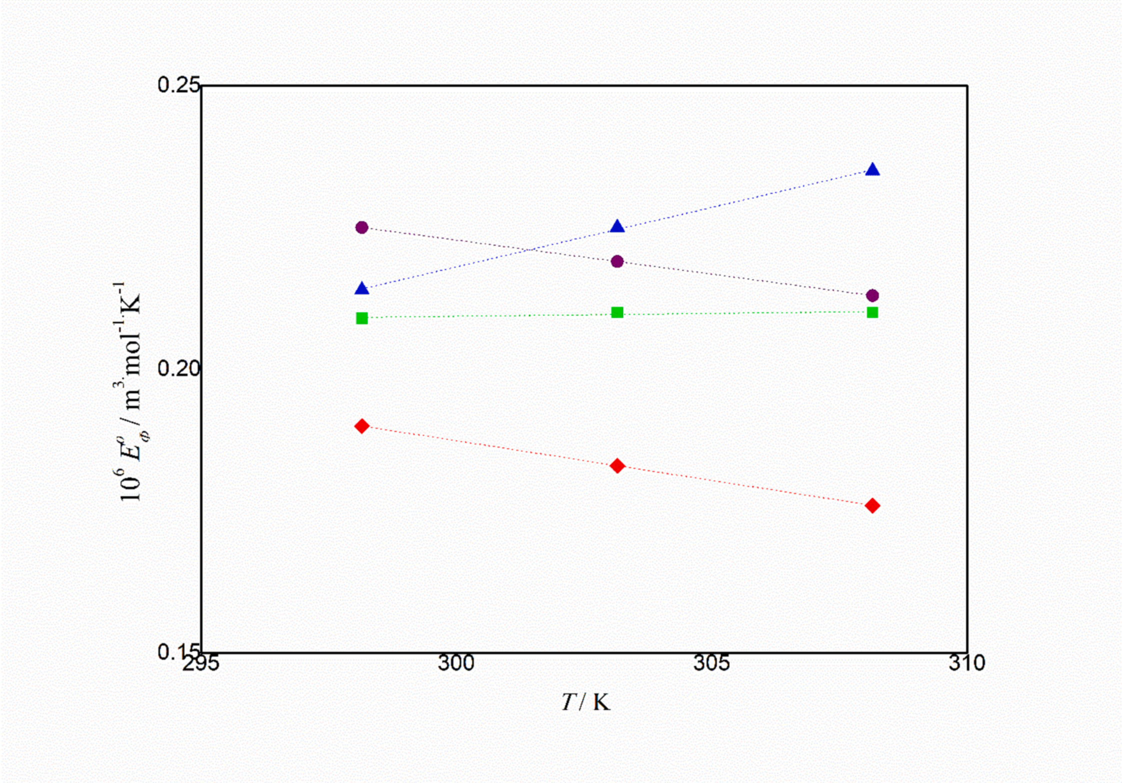


Figure 5. The temperature dependences of the limiting apparent molar isobaric expansibility E^0_Φ for (◆) [$Mor_{1,4}$][N-Ac-L-Ala], (■) [$Mor_{1,4}$][N-Ac-L-Val], (▲) [$Mor_{1,4}$][N-Ac-L-Leu], and (●) [$Mor_{1,4}$][N-Ac-L-Izoleu] in aqueous solutions.

Table 8

Sound velocities, u, apparent molar compressibilities, $K_{s,\Phi}$, and the hydration numbers, n_H, of solutions of AAILs in water as a function of the molality of AAIL, m, at temperatures $T = (293.15 \text{ to } 313.15)$ K and experimental pressure, $P = 101.3$ kPa.

m / (mol·kg^{-1})	T = 293.15 K			T = 298.15 K			T = 303.15 K			T = 308.15 K			T = 313.15 K		
	u / (m·s^{-1})	10^{14} $K_{s,\Phi}$ / (m^3·mol^{-1}·Pa^{-1})	n_H	u / (m·s^{-1})	10^{14} $K_{s,\Phi}$ / (m^3·mol^{-1}·Pa^{-1})	n_H	u / (m·s^{-1})	10^{14} $K_{s,\Phi}$ / (m^3·mol^{-1}·Pa^{-1})	n_H	u / (m·s^{-1})	10^{14} $K_{s,\Phi}$ / (m^3·mol^{-1}·Pa^{-1})	n_H	u / (m·s^{-1})	10^{14} $K_{s,\Phi}$ / (m^3· mol^{-1}· Pa^{-1})	n_H
[Mor$_{1,4}$][N-Ac-L-Ala]															
0.0000	1482.77	–	–	1497.01	–	–	1509.35	–	–	1520.11	–	–	1529.11	–	–
0.0191	1486.69	−2.318	16.97	1500.70	−1.385	15.90	1512.83	−0.583	14.96	1523.34	0.292	13.89	1532.14	0.968	13.05
0.0432	1491.57	−2.313	16.86	1505.29	−1.375	15.80	1517.14	−0.557	14.84	1527.35	0.303	13.80	1535.90	0.985	12.96
0.0523	1493.39	−2.279	16.78	1506.99	−1.335	15.71	1518.75	−0.527	14.76	1528.85	0.325	13.74	1537.33	0.978	12.93
0.0677	1496.48	−2.238	16.66	1509.91	−1.316	15.63	1521.48	−0.494	14.67	1531.39	0.349	13.65	1539.72	0.999	12.86
0.0906	1501.04	−2.208	16.53	1514.15	−1.257	15.46	1525.48	−0.451	14.52	1535.16	0.354	13.56	1543.30	0.981	12.80
0.1197	1506.74	−2.127	16.31	1519.51	−1.194	15.27	1530.53	−0.400	14.35	1539.90	0.385	13.42	1547.72	1.029	12.65
0.1525	1513.05	−2.047	16.08	1525.42	−1.123	15.05	1536.07	−0.330	14.15	1545.08	0.443	13.24	1552.54	1.100	12.45
0.1851	1519.35	−2.010	15.90	1531.34	−1.096	14.89	1541.57	−0.288	13.98	1550.30	0.453	13.11	1557.38	1.123	12.32
0.2298	1527.72	−1.905	15.60	1539.14	−0.994	14.61	1548.92	−0.207	13.72	1557.14	0.535	12.87	1563.86	1.178	12.11
0.2908	1538.89	−1.784	15.23	1549.59	−0.885	14.26	1558.73	−0.112	13.41	1566.36	0.609	12.59	1572.56	1.234	11.86
[Mor$_{1,4}$][N-Ac-L-Val]															
0.0000	1482.77	–	–	1497.01	–	–	1509.40	–	–	1520.10	–	–	1529.16	–	–
0.0171	1486.68	−3.020	19.09	1500.70	−1.994	17.94	1512.86	−1.018	16.79	1523.35	−0.167	15.76	1532.18	0.713	14.68
0.0251	1488.50	−2.982	19.01	1502.42	−1.970	17.87	1514.48	−1.016	16.75	1524.87	−0.162	15.72	1533.60	0.698	14.66
0.0415	1492.24	−2.983	18.92	1505.93	−1.948	17.75	1517.78	−1.003	16.65	1527.98	−0.164	15.65	1536.49	0.702	14.59
0.0589	1496.20	−2.983	18.83	1509.64	−1.929	17.65	1521.26	−0.983	16.55	1531.26	−0.159	15.57	1539.53	0.708	14.51
0.0827	1501.49	−2.895	18.59	1514.64	−1.865	17.45	1526.01	−0.970	16.42	1535.72	−0.141	15.44	1543.71	0.700	14.42
0.1078	1507.07	−2.853	18.41	1519.88	−1.829	17.28	1530.91	−0.919	16.24	1540.36	−0.114	15.30	1548.04	0.717	14.30
0.1359	1513.27	−2.805	18.21	1525.74	−1.801	17.11	1536.38	−0.879	16.06	1545.48	−0.069	15.12	1552.92	0.707	14.19
0.1723	1521.17	−2.728	17.94	1533.21	−1.747	16.88	1543.42	−0.842	15.86	1552.01	−0.010	14.90	1559.06	0.749	14.00
0.2095	1528.96	−2.604	17.61	1540.50	−1.625	16.56	1550.35	−0.757	15.59	1558.63	0.032	14.69	1565.28	0.779	13.82
0.2620	1539.69	−2.444	17.18	1550.54	−1.472	16.15	1559.84	−0.631	15.22	1567.72	0.108	14.39	1573.85	0.834	13.56
[Mor$_{1,4}$][N-Ac-L-Leu]															
0.0000	1482.77	–	–	1497.01	–	–	1509.35	–	–	1520.00	–	–	1529.01	–	–
0.0160	1486.72	−3.163	20.25	1500.73	−2.039	18.98	1512.87	−1.105	17.88	1523.31	−0.186	16.78	1532.11	0.691	15.70
0.0240	1488.69	−3.154	20.19	1502.58	−2.017	18.91	1514.60	−1.039	17.76	1524.95	−0.159	16.71	1533.67	0.658	15.71
0.0386	1492.25	−3.075	20.01	1505.92	−1.930	18.72	1517.75	−0.961	17.59	1527.93	−0.103	16.57	1536.47	0.712	15.57
0.0560	1496.42	−2.983	19.79	1509.85	−1.860	18.53	1521.49	−0.929	17.46	1531.40	−0.017	16.37	1539.72	0.806	15.37
0.0762	1501.28	−2.931	19.61	1514.41	−1.805	18.36	1525.72	−0.827	17.23	1535.38	0.071	16.16	1543.46	0.883	15.18
0.1085	1508.84	−2.802	19.27	1521.57	−1.726	18.08	1532.40	−0.726	16.94	1541.60	0.187	15.86	1549.30	0.992	14.90
0.1302	1513.78	−2.695	19.02	1526.14	−1.594	17.80	1536.76	−0.639	16.72	1545.69	0.263	15.67	1553.03	1.106	14.66
0.1609	1520.75	−2.584	18.71	1532.66	−1.489	17.52	1542.84	−0.527	16.43	1551.39	0.361	15.40	1558.29	1.217	14.40
0.1948	1528.51	−2.533	18.47	1539.88	−1.427	17.27	1549.58	−0.461	16.19	1557.53	0.463	15.13	1564.12	1.276	14.18
0.2460	1539.44	−2.310	17.94	1549.94	−1.193	16.74	1558.93	−0.236	15.69	1566.09	0.704	14.62	1572.42	1.426	13.79
[Mor$_{1,4}$][N-Ac-L-Izoleu]															
0.0000	1482.77	–	–	1497.01	–	–	1509.35	–	–	1520.11	–	–	1529.11	–	–
0.0200	1487.52	−2.840	19.69	1501.43	−1.600	18.27	1513.52	−0.668	17.18	1523.98	0.201	16.13	1532.76	1.093	15.03
0.0307	1490.05	−2.781	19.56	1503.80	−1.576	18.19	1515.73	−0.657	17.04	1526.08	0.223	16.05	1534.73	1.077	15.00
0.0391	1492.06	−2.819	19.56	1505.65	−1.576	18.14	1517.51	−0.667	17.08	1527.70	0.246	15.98	1536.25	0.958	15.27
0.0493	1494.41	−2.750	19.42	1507.86	−1.543	18.04	1519.60	−0.642	17.00	1529.65	0.276	15.90	1538.10	1.088	14.95
0.0711	1499.45	−2.668	19.19	1512.54	−1.459	17.82	1524.05	−0.589	16.82	1533.80	0.330	15.72	1542.03	1.083	14.91
0.0980	1505.59	−2.571	18.92	1518.29	−1.395	17.60	1529.40	−0.481	16.55	1538.94	0.346	15.58	1546.76	1.099	14.79
0.1272	1512.09	−2.449	18.61	1524.40	−1.312	17.35	1535.13	−0.400	16.31	1544.31	0.427	15.34	1551.75	1.171	14.59
0.1624	1519.79	−2.324	18.28	1531.67	−1.233	17.08	1541.93	−0.318	16.05	1550.58	0.547	15.04	1557.71	1.255	14.36
0.2031	1528.52	−2.185	17.90	1539.84	−1.114	16.74	1549.59	−0.205	15.73	1557.77	0.642	14.76	1564.45	1.322	14.13
0.2497	1538.31	−2.054	17.52	1549.00	−1.002	16.39	1558.17	−0.105	15.40	1565.81	0.723	14.46	1571.98	1.403	13.86
0.3157	1551.83	−1.890	17.01	1561.83	−0.894	15.96	1570.07	0.096	14.98	1576.93	0.827	14.06	1582.51	1.544	13.25

Standard uncertainties u are u(T) = 0.01 K, u(P) = 0.5 kPa, u(u) = 0.5 m s^{-1} and standard combined uncertainties are: $u(m) = 0.0015$ mol·kg^{-1}, $u(K_{S,\Phi}) = (0.14 \div 2.4)\cdot 10^{-14}$ m^3·mol^{-1}·Pa^{-1} and $u(n_H) = 0.16 \div 2.7$ for high and low concentration range of AAILs, respectively.

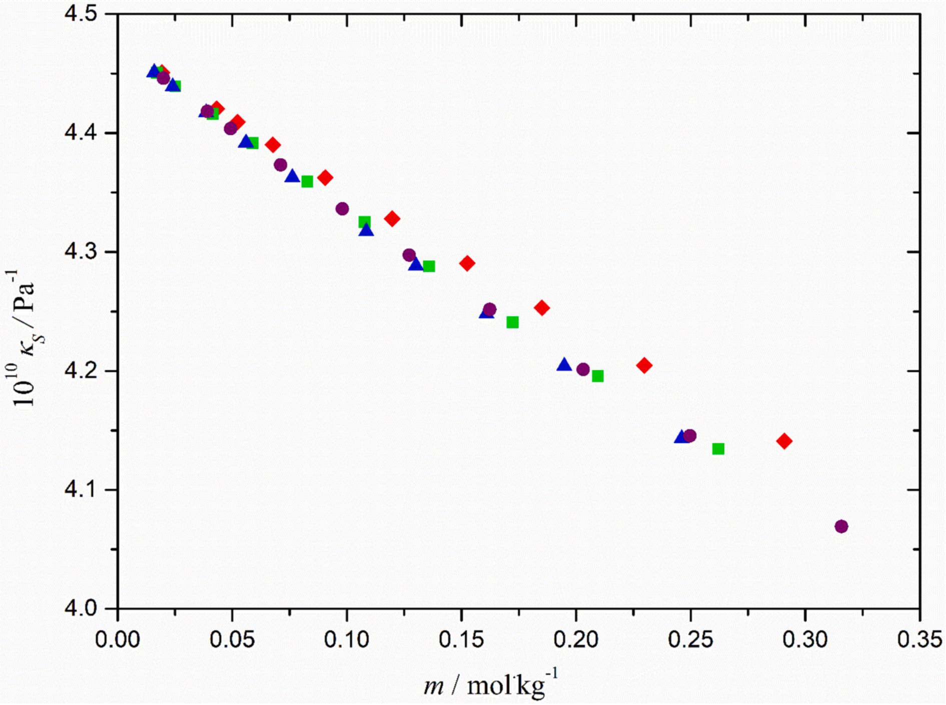


Figure 6. The concentration dependencies of the isentropic compressibility for: (◆) $[\mathrm{Mor}_{1,4}]$[N-Ac-L-Ala], (■) $[\mathrm{Mor}_{1,4}]$[N-Ac-L-Val], (▲) $[\mathrm{Mor}_{1,4}]$[N-Ac-L-Leu], and (●) $[\mathrm{Mor}_{1,4}]$[N-Ac-L-Izoleu] in water solutions at T = 298.15 K.

As it can be seen from Table 9, the values of empirical slopes b_K are positive and they generally decrease with growing temperature as well as with the increase in side alkyl chain length or methyl group of the amino acid cation. The decrease of b_K values with increasing temperature indicates that the increase in temperature causes a decrease in ion-ion interactions, obviously both hydrophobic and electrostatic ones.

Inspection of Table 9 also shows that, regardless of the temperature, the limiting apparent molar compressibility of the studied AAILs changes in the order: $[\mathrm{Mor}_{1,4}]$[N-Ac-L-Ala] > $[\mathrm{Mor}_{1,4}]$[N-Ac-L-Val] > $[\mathrm{Mor}_{1,4}]$[N-Ac-L-Leu] < $[\mathrm{Mor}_{1,4}]$[N-Ac-L-Izoleu] which is inversed to the order of the limiting apparent molar volumes for this solutes. Thus, the limiting apparent molar compressibility becomes more negative with the increase of hydrophobicity of AAIL, which has already been observed for amino acids by Kharzakoz *et al.* and for imidazolium-based amino acid ionic liquids by Dagade *et al.* [27,17].

Table 9
Coefficients of Redlich, Rosenfeld and Meyer equation for apparent molar compressibility, $K^0_{S,\varphi}$ and b_K, of $[\mathrm{Mor}_{1,4}]$[N-Ac-L-Ala], $[\mathrm{Mor}_{1,4}]$[N-Ac-L-Val], $[\mathrm{Mor}_{1,4}]$[N-Ac-L-Leu] and $[\mathrm{Mor}_{1,4}]$[N-Ac-L- Izoleu] in water at various temperatures (293.15 to 313.15) K. (P_{atm} = 101325 Pa).

T / K	$10^{14}\,K^0_{S,\varphi}$ ($\mathrm{m^3{\cdot}mol^{-1}{\cdot}Pa^{-1}}$)	$10^{14}b_K$/ /($\mathrm{m^3{\cdot}kg{\cdot}mol^{-2}{\cdot}Pa^{-1}}$)	$10^{14}\,\sigma$ / ($\mathrm{m^3{\cdot}mol^{-1}{\cdot}Pa^{-1}}$)
$[\mathrm{Mor}_{1,4}]$[N-Ac-L-Ala]			
293.15	−2.30 ± 0.010	2.54 ± 0.057	0.016
298.15	−1.40 ± 0.010	2.45 ± 0.066	0.018
303.15	−0.55 ± 0.010	2.37 ± 0.064	0.017
308.15	0.33 ± 0.010	1.82 ± 0.042	0.011
313.15	1.00 ± 0.010	1.77 ± 0.062	0.017
$[\mathrm{Mor}_{1,4}]$[N-Ac-L-Val]			
293.15	−3.03 ± 0.018	2.78 ± 0.11	0.026
298.15	−1.98 ± 0.020	2.56 ± 0.10	0.024
303.15	−1.01 ± 0.010	2.16 ± 0.074	0.017
308.15	−0.15 ± 0.010	1.86 ± 0.043	0.011
313.15	0.75 ± 0.010	1.24 ± 0.048	0.012
$[\mathrm{Mor}_{1,4}]$[N-Ac-Leu]			
293.15	−3.17 ± 0.018	4.2 ± 0.19	0.032
298.15	−2.03 ± 0.018	4.2 ± 0.16	0.028
303.15	−1.07 ± 0.017	4.3 ± 0.17	0.031
308.15	−0.18 ± 0.017	4.5 ± 0.11	0.024
313.15	0.68 ± 0.023	4.3 ± 0.21	0.040
$[\mathrm{Mor}_{1,4}]$[N-Ac-L-Izoleu]			
293.15	−2.85 ± 0.020	3.8 ± 0.16	0.036
298.15	−1.59 ± 0.016	3.0 ± 0.10	0.028
303.15	−0.68 ± 0.016	3.1 ± 0.10	0.031
308.15	0.23 ± 0.014	2.8 ± 0.10	0.028
313.15	1.10 ± 0.015	2.4 ± 0.10	0.029

Moreover, as can be seen from Table 9, the values of the limiting apparent molar compressibility for all systems studied increase with temperature. This is obviously due to the less organized structure of the solution at higher temperatures. The increase of thermal agitation at higher temperatures causes the release of solvent molecules from the solute layers and the increase in the solution volume and thus making it more compressible.

The hydration numbers of the studied AAILs were estimated using an equation developed by Passynski [28] for aqueous electrolyte solutions:

$$n_H = \frac{n_1}{n_2}\left(1-\frac{\kappa_s}{\kappa_s^0}\right) \tag{8}$$

where n_1 is the number of moles of water, n_2 is the number of moles of solute, κ_s is the isentropic compressibility of solution and κ_s^o is the isentropic compressibility of pure water. Concentration dependence hydration numbers for studied AALs in aqueous solutions are given in Table 8 and presented in Figure 8 at 298.15 K. As seen, at all investigated temperatures, the hydration number changes according to the order: $[\mathrm{Mor}_{1,4}]$[N-Ac-L-Ala] < $[\mathrm{Mor}_{1,4}]$[N-Ac-L-Val] < $[\mathrm{Mor}_{1,4}]$[N-Ac-L-Leu] > $[\mathrm{Mor}_{1,4}]$[N-Ac-L-Izoleu], confirming the increasing strength of hydrophobic hydration with an elongation of the alkyl chain of IL. Moreover, the hydration number decreases with the increase in the concentration of ILs, showing ionic association at higher concentrations.

4. Conclusions

In the present study, experimental data of the density and sound velocity for AAILs based on the *N*-butyl-*N*-methylmorpholinium cation and *N*-acetyl-L-alaninate, *N*-acetyl-L-valinate, *N*-acetyl-L-leucinate and

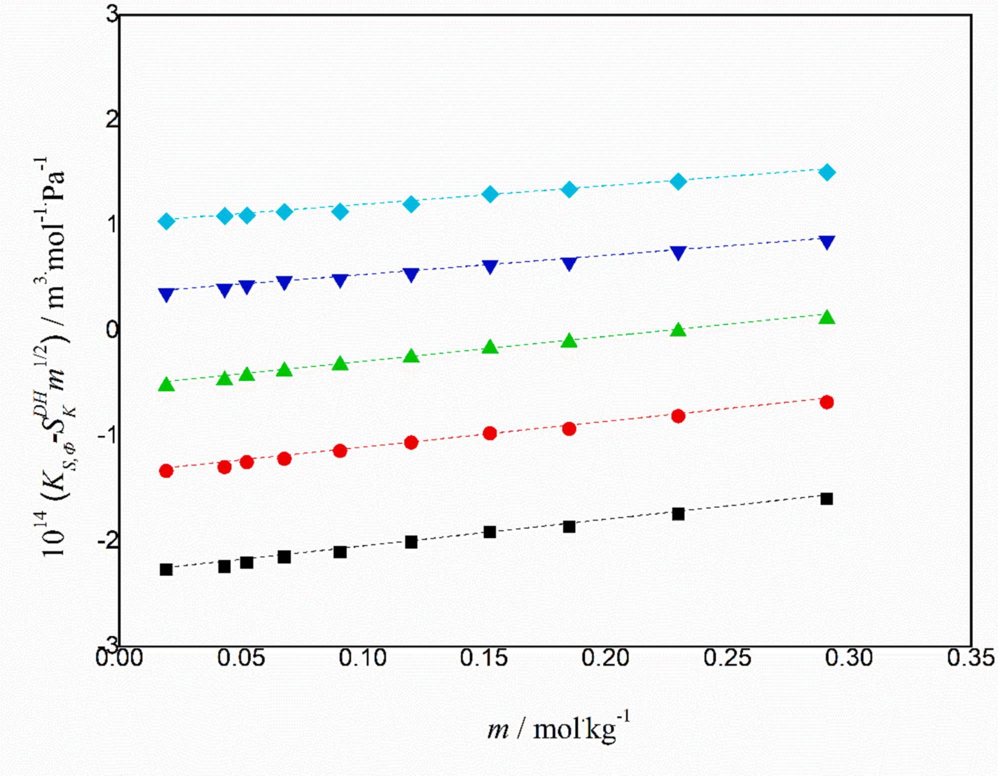


Figure 7. The concentration dependencies of the difference ($K_{S,\Phi} - S_K^{DH}\sqrt{m}$) for [Mor$_{1,4}$][N-Ac-L-Ala] in water solutions at T = (293.15–313.15): 293.15 K (■), 298.15 K (●), 303.15 K (▲), 308.15 K (▼) and 313.15 K (◆). The dashed lines show the linear, least-squares fit of the individual data series.

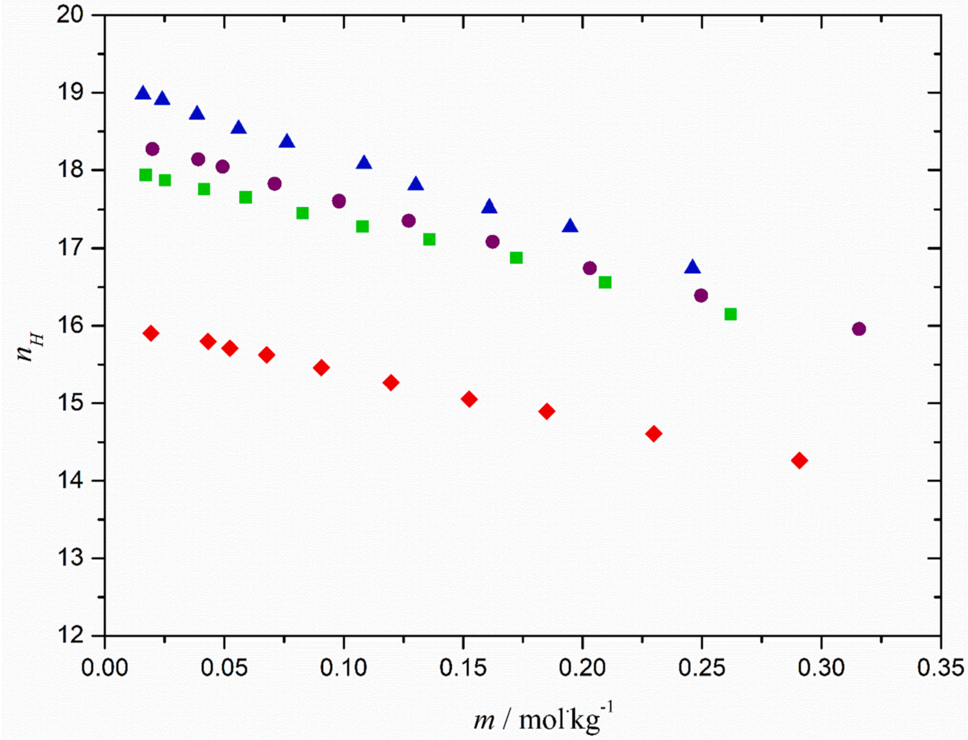


Figure 8. The concentration dependencies of the hydration number for aqueous solutions of [Mor$_{1,4}$][N-Ac-L-Ala] (◆), [Mor$_{1,4}$][N-Ac-L-Val] (■), [Mor$_{1,4}$][N-Ac-L-Leu] (▲) and [Mor$_{1,4}$][N-Ac-L-Izoleu] (●) at temperature T = 298.15 K.

N-acetyl-L-izoleucinate anions were measured in aqueous solutions at T = (293.15–313.15) K. The apparent molar volumes and the apparent molar compressibilities as a function of molality, together with their limited values for solutions at infinite dilution and limiting apparent molar expansibility coefficients, have been calculated.

The results show that the limiting apparent molar volume of the studied AAILs changes in the order: [Mor$_{1,4}$][N-Ac-L-Ala] < [Mor$_{1,4}$][N-Ac-L-Val] < [Mor$_{1,4}$][N-Ac-L-Leu] > [Mor$_{1,4}$][N-Ac-L-Izoleu], while the reverse order is observed for the limiting apparent molar compressibility. Thus, the main factor determining the ion–solvent interactions in aqueous solutions of *N*-butyl-*N*-methylmorpholinium based amino acid ionic liquids is the hydrophobicity of the amino acid anion, which increases with the increasing length of its alkyl chain or with the presence of methyl group. This conclusion is supported by the values of the hydration number, which at all investigated temperatures change in the same order as for the limiting apparent molar volume, confirming the increasing strength of hydrophobic hydration with an elongation of the alkyl chain of IL. The values of limiting apparent molar isobaric expansion, as well as the volume expansibility coefficients, are positive and vary according to the sequence: [Mor$_{1,4}$][N-Ac-L-Ala] < [Mor$_{1,4}$][N-Ac-L-Val] < [Mor$_{1,4}$][N-Ac-L-Leu] ≈ [Mor$_{1,4}$][N-Ac-L-Izoleu], which indicates that V_Φ^0 becomes more sensitive to temperature also with the increase in side alkyl chain length or methyl group of amino acid.

The negative values of the experimental slope b_v in the RRM equation for apparent molar volumes obtained for N-butyl-N-methylmorpholine based amino acid ionic liquids in water indicate that the ion-ion interactions, like the ion–solvent interactions in the studied solutions, are also dominated by the hydrophobic effect that weakens with temperature rise.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jct.2023.107148.

References

[1] A. J. Greer, J. Jacquemin, and C. Hardacre, “Industrial Applications of Ionic Liquids,” *Molecules*, vol. 25, no. 21, 2020, 10.3390/molecules25215207.

[2] R. D. Rogers and K. R. Seddon, “Ionic Liquids - Solvents of the Future?,” *Science (80-.).*, vol. 302, no. 5646, pp. 792–793, 2003, 10.1126/science.1090313.

[3] K. Fukumoto, M. Yoshizawa, H. Ohno, Room temperature ionic liquids from 20 natural amino acids, J. Am. Chem. Soc. 127 (8) (2005) 2398–2399, https://doi.org/10.1021/ja043451i.

[4] G.H. Tao, L. He, N. Sun, Y. Kou, New generation ionic liquids: Cations derived from amino acids, Chem. Commun. 28 (2005) 3562–3564, https://doi.org/10.1039/b504256a.

[5] M. Bisht, I. Jha, P. Venkatesu, Comprehensive Evaluation of Biomolecular Interactions between Protein and Amino Acid Based-Ionic Liquids: A Comparable Study between [Bmim][Br] and [Bmim][Gly] Ionic Liquids, ChemistrySelect 1 (13) (2016) 3510–3519, https://doi.org/10.1002/slct.201600524.

[6] Q.P. Liu, X.D. Hou, N. Li, M.H. Zong, Ionic liquids from renewable biomaterials: Synthesis, characterization and application in the pretreatment of biomass, Green Chem. 14 (2) (2012) 304–307, https://doi.org/10.1039/c2gc16128a.

[7] J. Zhang, S. Zhang, K. Dong, Y. Zhang, Y. Shen, X. Lv, Supported absorption of CO2 by tetrabutylphosphonium amino acid ionic liquids, Chem. - A Eur. J. 12 (15) (2006) 4021–4026, https://doi.org/10.1002/chem.200501015.

[8] F. Shi, Y. Gu, Q. Zhang, Y. Deng, Development of ionic liquids as green reaction media and catalysts, Catal. Surv. from Asia 8 (3) (2004) 179–186, https://doi.org/10.1023/B:CATS.0000038536.55980.f3.

[9] N. Gathergood, M.T. Garcia, P.J. Scammells, Biodegradable ionic liquids: Part I. Concept, preliminary targets and evaluation, Green Chem. 6 (3) (2004) 166–175, https://doi.org/10.1039/b315270g.

[10] S. Wu, F. Li, L. Zeng, C. Wang, Y. Yang, Z. Tan, Assessment of the toxicity and biodegradation of amino acid-based ionic liquids, RSC Adv. 9 (18) (2019) 10100–10108, https://doi.org/10.1039/c8ra06929h.

[11] C. Schröder, Proteins in Ionic Liquids: Current Status of Experiments and Simulations, Top Curr Chem (Z) 375 (2) (2017).

[12] A. Sindhu, S. Kumar, P. Venkatesu, Contemporary Advancement of Cholinium-Based Ionic Liquids for Protein Stability and Long-Term Storage: Past, Present, and Future Outlook, ACS Sustain. Chem. Eng. 10 (14) (2022) 4323–4344, https://doi.org/10.1021/acssuschemeng.1c08595.

[13] G.R. Hedwig, H. Høiland, Thermodynamic properties of peptide solutions 20. Partial molar volumes and isothermal compressions for some tripeptides of sequence gly-X-gly (X = gly, ala, leu, asn, thr, and tyr) in aqueous solution at T = 298.15 K and p = (10–120) MPa, J. Chem. Thermodyn. 99 (2016) 30–39, https://doi.org/10.1016/j.jct.2016.03.032.

[14] C. Pretti, M. Renzi, S. Ettore Focardi, A. Giovani, G. Monni, B. Melai, S. Rajamani, C. Chiappe, Acute toxicity and biodegradability of N-alkyl-N-methylmorpholinium and N-alkyl-DABCO based ionic liquids, Ecotoxicol. Environ. Saf. 74 (4) (2011) 748–753.

[15] Ł. Marcinkowski, E. Szepiński, M.J. Milewska, A. Kloskowski, Density, sound velocity, viscosity, and refractive index of new morpholinium ionic liquids with amino acid-based anions: Effect of temperature, alkyl chain length, and anion, J. Mol. Liq. 284 (2019) 557–568, https://doi.org/10.1016/j.molliq.2019.04.026.

[16] T.J. Fortin, A. Laesecke, M. Freund, S. Outcalt, Advanced calibration, adjustment, and operation of a density and sound speed analyzer, J. Chem. Thermodyn. 57 (2013) 276–285, https://doi.org/10.1016/j.jct.2012.09.009.

[17] D.H. Dagade, S.P. Shinde, K.R. Madkar, S.S. Barge, Density and sound speed study of hydration of 1-butyl-3-methylimidazolium based amino acid ionic liquids in aqueous solutions, J. Chem. Thermodyn. 79 (2014) 192–204, https://doi.org/10.1016/j.jct.2014.07.026.

[18] O. Redlich, D.M. Meyer, The molal volumes of electrolytes, Chem. Rev. 64 (3) (1964) 221–227, https://doi.org/10.1021/cr60229a001.

[19] J. Ananthaswamy, G. Atkinson, Thermodynamics of concentrated electrolyte mixtures. 4. Pitzer-Debye-Hueckel limiting slopes for water from 0 to 100.degree.C and from 1 atm to 1 kbar, J. Chem. Eng. Data 29 (1) (Jan. 1984) 81–87, https://doi.org/10.1021/je00035a027.

[20] L.H. Kapcha, P.J. Rossky, A simple atomic-level hydrophobicity scale reveals protein interfacial structure, J. Mol. Biol. 426 (2) (2014) 484–498, https://doi.org/10.1016/j.jmb.2013.09.039.

[21] D. Eisenberg, R.M. Weiss, T.C. Terwilliger, W. Wilcox, Hydrophobic Moments and Protein Structure, Faraday Symp. Chem. Soc. 17 (1982) 109.

[22] K.R. Patil, A.D. Surwade, P.J. Rajput, V.R. Shaikh, Investigations of solute–solvent interactions in aqueous solutions of amino acids ionic liquids having the common nitrate as anion at different temperatures, J. Mol. Liq. 329 (2021) 115546.

[23] H. S. Harned and B. . Owen, *The Physical Chemistry of Electrolyte Solutions*, Third edit., no. July. New York: American Chemical Society Monograph Series: Reinhold Publishing Corp., 1958.

[24] D. Singh, R.L. Gardas, Influence of N-1 alkyl substituent on apparent molar properties of 1,2,4-triazolium based ionic liquids in aqueous solutions, J. Mol. Liq. 250 (2018) 477–484, https://doi.org/10.1016/j.molliq.2017.12.024.

[25] D. Warmińska, M. Śmiechowski, Understanding ion–ion and ion–solvent interactions in aqueous solutions of morpholinium ionic liquids with N-acetyl-L-alaninate anion through partial molar properties and molecular dynamics simulations, J. Mol. Liq. (2022), 118876, https://doi.org/10.1016/j.molliq.2022.118876.

[26] A. Jain, V.S. Shende, D.V. Kawadkar, U.R. Pratap, A.V. Wankhade, S.P. Zodape, Studies of solute–solvent interactions of imidazolium-based ionic liquid in water and aqueous L-alanine solution via volumetric and compressibility properties at T = (293.15–313.15) K, J. Chem. Thermodyn. 162 (2021), https://doi.org/10.1016/j.jct.2021.106561.

[27] D.P. Kharakoz, Volumetric properties of proteins and their analogues in diluted water solutions. 2. Partial adlabatic compressibilities of amino acids at 15–70 °C, J. Phys. Chem. 95 (14) (1991) 5634–5642, https://doi.org/10.1021/j100167a049.

[28] A. Passynski, “Compressibility and solvation of solutions of electrolytes. [Ambient pressure, 20/sup 0/C, experimental data],” *Acta Physicochim. URSS*, vol. 8, no. 385–418, 1938.