

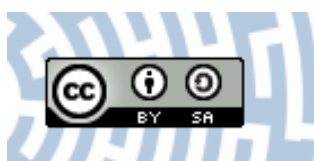


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**Title:** Acoustic nonlinearity parameter B/A, internal pressure, and acoustic impedance determined at pressures up to 100 MPa for 1-Ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide

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# Acoustic Nonlinearity Parameter $B/A$ , Internal Pressure, and Acoustic Impedance Determined at Pressures up to 100 MPa for 1-Ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide

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The nonlinearity parameter  $B/A$ , internal pressure, and acoustic impedance are calculated for a room temperature ionic liquid, i.e. for 1-ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl] imide for temperatures from (288.15 to 318.15) K and pressures up to 100 MPa. The  $B/A$  calculations are made by means of a thermodynamic method. The decrease of  $B/A$  values with the increasing pressure is observed. At the same time  $B/A$  is temperature independent in the range studied. The results are compared with corresponding data for organic molecular liquids. The isotherms of internal pressure cross at pressure in the vicinity of 70 MPa, i.e. in this range the internal pressure is temperature independent.

**Keywords:** nonlinearity parameter; speed of sound; high pressure; ionic liquids; internal pressure.

## 1. Introduction

The speed of sound measurements in fluids at frequencies well below the dispersion region offers a convenient and accurate route for determining important thermodynamic properties that are not easily measured directly (MATHESON, 1971; GOODWIN, TRUSLER, 2003; TAKAGI, WILHELM, 2010). This route is based on well-known Newton-Laplace relation which connected speed of sound with density and isentropic compressibility coefficient. Especially at high pressures, the reliability, relative low uncertainty and simplicity of the speed of sound measurements make it very attractive for indirect determination of the excellent quality data on related (to speed of sound) thermodynamic and thermophysical properties which would have been difficult to obtain otherwise (TAKAGI, WILHELM, 2010; GOODWIN, TRUSLER, 2003; DZIDA, 2004; 2007; ZOREŃBSKI, 2014). For example, in this way extremely rare reported values of internal pressure and  $B/A$  nonlinearity parameter can be obtained (LÓPEZ *et al.*, 2006; ZOREŃBSKI, ZOREŃBSKI, 2014).

Since the second-order nonlinearity parameter  $B/A$  (so-called Beyer nonlinearity parameter) (BEYER, 1960; 1998) characterizes the potential size of the nonlinearity and is a basic measure of acoustic nonlinearity properties of a liquid (generally of an each medium),  $B/A$  is very interesting and important both for the-

ory and praxis in many areas. This refers especially to underwater acoustics and modern medical applications of ultrasound (PRIEUR *et al.*, 2012; JACOB *et al.*, 2003; BJØRNØ, 2002; DUCK, 2002; LAW *et al.*, 1985; AVERKIOU, CLEVELAND, 1999). In the case of medical applications of ultrasound, knowledge of  $B/A$  is extremely important for accurate modelling and understanding of interactions between ultrasound wave and medium (DUCK, 2002; LAW *et al.*, 1985; AVERKIOU, CLEVELAND, 1999). In the case of liquids, the  $B/A$  values can be an important information's source about molecular structure (EMERY *et al.*, 1979; SARVAZIAN *et al.*, 1990; LISNYANSKII *et al.*, 1974) as well as can be treated as a complementary parameter in the general characterization of the liquids (LU *et al.*, 2001; LÓPEZ *et al.*, 2006). The  $B/A$  values are generally in the range of 8–12 for various classes of molecular organic liquids under atmospheric pressure and at room temperature. However, it should be noted that the clearly lower  $B/A$  value ( $B/A \approx 5$ ) shows water, whereas fluorocarbons show the highest  $B/A$  values ( $B/A \approx 13$ ) observed so far (BEYER, 1998). Generally,  $B/A$  depends on temperature and pressure. However, as far as the effect of temperature has been studied many times, studies of the behaviour of  $B/A$  as a function of pressure are very limited (LÓPEZ *et al.*, 2006; HAGELBERG *et al.*, 1967; HAGELBERG, 1970; PRAKASH *et al.*, 1972; NARAYAMA, SWAMY, 1980; 1981; HARTMANN, BAL-

IZER, 1987; PLANTIER *et al.*, 2002a; 2002b; KHELLADI *et al.*, 2009; ZOREBSKI, ZOREBSKI, 2014; KIELCZYŃSKI *et al.*, 2014). What is more, it appears also that for some complete class of liquids, for example room temperature ionic liquids (RTILs), and generally all ionic liquids, the nonlinearity parameter has not been reported in the available literature in general.

RTILs are very interesting and promising liquids both for academia and industry (WILKES, 2002; PLECHKOVA, SEDDON, 2008). There are salts that have much lower melting points compared with the conventional molten salts, i.e. the melting points are lower than room temperatures. They are representatives of a broader class of ionic liquids (ILs), i.e. the salts with the melting points below 373.15 K (WILKES, 2002). RTILs, generally all ILs, are usually composed of a large organic cation with a rather low degree of symmetry, and an organic or inorganic anion. For more than two decades now, various properties of different families of ILs have been widely tested in order to find the new potential applications in chemical and industrial fields (PLECHKOVA, SEDDON, 2008) but very little effort was spent on the systematic study of acoustic properties in this class of compounds. Apart from the speed of sound, a literature survey shows that only very few experimental results have been reported for the ultrasound absorption coefficient in RTILs (ZOREBSKI *et al.*, 2013) and according to our best knowledge none for the  $B/A$  nonlinearity parameter.

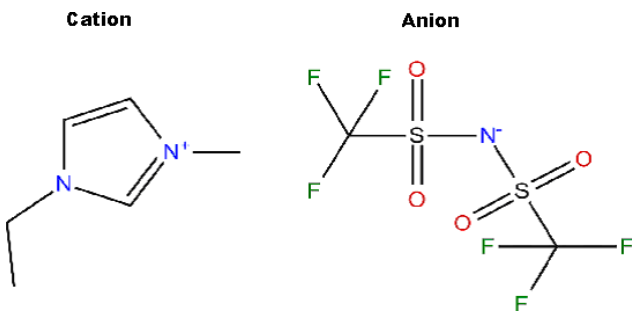


Fig. 1. Structures of cation (1-ethyl-3-methylimidazolium) and anion (bis[(trifluoromethyl)sulfonyl] imide) RTIL studied in this work.

Therefore the first and fundamental goal of this work is to determine the  $B/A$  parameter as function of pressure  $p$  (up to 100 MPa) and temperature  $T$  (from 288.15 K to 318.15 K) for one of a hydrophobic methylimidazolium based ionic liquids with a large anion which contains halogen, i.e. 1-ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide (Fig. 1 shows the structures of the cation and anion), which is the representative of homolog series of 1-alkyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imides ( $[C_n\text{MIm}][\text{NTf}_2]$ ). Generally, investigated liquid can be treated as a representative of a conventional aprotic RTILs, and more widely all ILs.

Thus, the second goal of this work is comparison of the obtained values for ionic liquid studied with the values for molecular organic liquids. The third goal is determination of the  $(p, T)$  data of internal pressure which is closely related to the liquid structure, i.e. describes macroscopic effect of molecular interactions and plays an important role in the physical chemistry of the liquid state (BARTON, 1971; DACK, 1975; MARCUS, 2013). Investigations are completed by determination of the acoustic impedance  $Z$  in the given above  $(p, T)$  range and all the present studies are based on the  $(p, T)$  speed of sound data reported recently (DZIDA *et al.*, 2013).

## 2. Determination of the nonlinearity parameter and internal pressure

For determination of the acoustic nonlinearity parameter  $B/A$  various methods have been proposed (BEYER, 1998). One of them is so-called classical thermodynamic method proposed by BEYER (1960; 1998). As known, the  $B/A$  nonlinearity parameter is connected with relation between the pressure and density during the speed of sound propagation that is a substantially isentropic process, and  $B/A$  can be expressed as:

$$B/A = 2 \cdot \rho_0 \cdot u_0 \cdot (\partial u / \partial p)_S, \quad (1)$$

where  $u_0$  is the infinitesimal amplitude speed of sound,  $\rho_0$  is the equilibrium density, and  $S$  is the entropy. On this expression are based the pressure-jump methods (variations of the thermodynamic method) where the speed of sound is measured during a sufficiently rapid and smooth pressure change (the system is considered thermodynamically reversible).

The classical thermodynamic method is based on the expression proposed by BEYER (1960):

$$B/A = 2 \cdot \rho_0 \cdot u_0 \cdot (\partial u / \partial p)_T + 2 \cdot u_0 \cdot T \cdot \alpha_p \cdot c_p^{-1} \cdot (\partial u / \partial T)_p, \quad (2)$$

where  $T$  is the temperature,  $c_p$  is the isobaric specific heat capacity,  $\alpha_p$  is the isobaric thermal expansion coefficient, and  $(\partial u / \partial p)_T$  and  $(\partial u / \partial T)_p$  are, respectively, the change of the speed of sound with pressure at constant temperature and the change of the speed of sound with temperature at constant pressure. The expression (2) can be rewritten in the form:

$$B/A = (B'/A) + (B''/A), \quad (3)$$

i.e. as the sum of two terms: a pressure derivative term  $(B'/A)$  and a temperature derivative term  $(B''/A)$ . For molecular liquids, the dominant part of the expression is the pressure derivative term which is very sensitive to pressure, at least at relatively low pressures

(BEYER, 1960; HAGELBERG, 1970; ZORĘBSKI, ZORĘBSKI, 2014). At the same time the variation of  $(B'/A)$  with temperature at a given pressure is usually small and close to experimental error.

The speed of sound can be also used for indirect determination of the internal pressure  $P_{\text{int}}$  by the use of relation:

$$P_{\text{int}} = T \cdot \alpha_p \cdot [(\rho^{-1} \cdot u^{-2}) + \alpha_p^2 \cdot T \cdot (\rho \cdot c_p)^{-1}]^{-1} - p, \quad (4)$$

where  $(\rho^{-1} \cdot u^{-2})$  is the isentropic compressibility coefficient  $\kappa_S$  (according to mentioned in introduction Newton-Laplace relation) and  $[(\rho^{-1} \cdot u^{-2}) + \alpha_p^2 \cdot T \cdot (\rho \cdot c_p)^{-1}]$  equals the isothermal compressibility coefficient  $\kappa_T$ . Above relation is in principle so-called first thermodynamic equation of state:

$$(\partial U/\partial V)_T = (\partial F/\partial V)_T + T \cdot (\partial S/\partial V)_T, \quad (5)$$

where the partial derivative  $(\partial U/\partial V)_T$  defines  $P_{\text{int}}$ ,  $(\partial S/\partial V)_T = (\partial p/\partial T)_V$  is called the isochoric thermal pressure coefficient which may be calculated as the ratio  $\alpha_p \cdot \kappa_T^{-1}$  and  $(\partial F/\partial V)_T = -p$ . Symbols  $U$  and  $F$  denote internal energy and Helmholtz energy, respectively.

### 3. Calculations and results

Fundamental acoustic properties at  $T = 298.15$  K and atmospheric pressure as well as the purity of the investigated RTIL are summarized in Table 1. The sample (CAS 174899-82-2) was purchased from Io-LiTec GmbH, Germany. Apart from the placing under vacuum for ca. 48 h (DZIDA *et al.*, 2013), the liquid was used as supplied by the manufacturer and stored all the time under argon.

For our calculations of the  $B/A$  ( $p, T$ ),  $P_{\text{int}}$  ( $p, T$ ) and  $Z$  ( $p, T$ ), the speed of sound  $u$  ( $p, T$ ), density  $\rho$  ( $p, T$ ) and isentropic compressibility coefficient  $\kappa_S$  ( $p, T$ ) data reported very recently were used (DZIDA *et al.*, 2013). Needed for calculations but not reported previously the values of  $\alpha_p$  ( $p, T$ ) and  $c_p$  ( $p, T$ ) are calculated by means of the acoustic method similarly as in our previous works (ZORĘBSKI, DZIDA, 2012; DZIDA, 2004; ZORĘBSKI, 2014). Generally, this method is based on

appropriate integration procedure in the range of  $p$  and  $T$  in which the experimental speeds of sound data are available. The procedure gives the isobars of density and isobaric heat capacity covering  $p$  and  $T$  range for the speed of sound measurements. As initial values of integration procedure, the values of the density and isobaric heat capacity measured as functions of  $T$  at atmospheric pressure are used (such values are easily available and the procedure of integration is very stable if the initial values are specified at the lowest pressure of the range).

For reliable results, apart from the appropriate integration procedure, the uncertainties of the  $u$  ( $p, T$ ),  $\rho$  (0.1 MPa,  $T$ ) and  $c_p$  (0.1 MPa,  $T$ ) data are crucial. In the case of  $u$ , two measuring methods with constant acoustic pathlength were used, i.e. the sing-around method at atmospheric pressure and the pulse-echo-overlap method at elevated pressures (the basic advantages and disadvantages of these methods were discussed previously (ZORĘBSKI *et al.*, 2005)). In both cases, a home-made measuring setups were used. In the case of sing-around set-up, a measuring cell with two piezoceramic transducers was used, whereas in the case of pulse-echo-overlap set-up, a cell with one piezoceramic transmitting-receiving transducer and an acoustic reflector was used. In both cases transducers operating at 2 MHz and cells made of stainless steel (1H18N9T) were applied. The speed of sound was determined by direct measurement of the repetition frequency of the sing-around loop. In turn, in the case of the pulse-echo-overlap set-up, the speed of sound was determined by measurement of the frequency of the appropriate synchronization pulse (adjustable with high accuracy and precision), which enables the overlap of the first echo (acoustic pulse travelling acoustic way twice) and second echo (acoustic pulse travelling acoustic way four times) on the oscilloscope screen. The estimated speed of sound uncertainties were  $(\pm 0.5$  and  $\pm 1)$  m·s<sup>-1</sup> at atmospheric and elevated pressure, respectively. In the case of  $\rho$ , the uncertainty was  $\pm 5 \cdot 10^{-2}$  kg·m<sup>-3</sup>, whereas the uncertainty of  $c_p$  was  $\pm 1\%$ . More details can be found elsewhere (DZIDA *et al.*, 2013).

Table 1. Purity, density,  $\rho$ , speed of sound,  $u$ , acoustic impedance,  $Z$ , partial derivatives  $(\partial u/\partial T)_p$  and  $(\partial u/\partial p)_T$ , as well as ultrasound absorption coefficient  $\alpha$  per squared frequency  $f$ ,  $(\alpha \cdot f^{-2})_0$  at  $T = 298.15$  K and atmospheric pressure.

Acronym	Mass fraction purity	$\rho$ [kg·m <sup>-3</sup> ]	$u$ [m·s <sup>-1</sup> ]	$Z \cdot 10^{-6}$ [kg·m <sup>-2</sup> ·s <sup>-1</sup> ]	$(\partial u/\partial T)_p$ [m·s <sup>-1</sup> ·K <sup>-1</sup> ]	$(\partial u/\partial p)_T$ [m·s <sup>-1</sup> ·MPa <sup>-1</sup> ]	$(\alpha \cdot f^{-2})_0 \cdot 10^{15}$ [m <sup>-1</sup> ·s <sup>2</sup> ]
[C <sub>2</sub> MIm][NTf <sub>2</sub> ] <sup>a</sup>	0.990	1518.38 <sup>b</sup>	1240.44 <sup>b</sup>	1.8835 <sup>c</sup>	-2.238	3.269	483 <sup>d</sup>

<sup>a</sup> [C<sub>2</sub>MIm][NTf<sub>2</sub>] = 1-ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl] imide.

<sup>b</sup> Ref. (DZIDA *et al.*, 2013).

<sup>c</sup>  $Z$  is calculated as product of speed of sound and density (to be precise, such product is the specific acoustic impedance); data taken from Ref. (DZIDA *et al.*, 2013).

<sup>d</sup> Ref. (ZORĘBSKI *et al.*, 2013), below relaxation region.

Table 2. The nonlinearity parameter  $B/A$  as function of pressure  $p$  and temperature  $T$  for  $[\text{C}_2\text{MIm}][\text{NTf}_2]$ .

$p$ [MPa]	$B/A$ at various $T$ [K]						
	288.15	293.15	298.15	303.15	308.15	313.15	318.15
0.1	11.4	11.5	11.5	11.5	11.5	11.5	11.6
10	11.0	11.0	11.0	11.0	11.0	11.0	11.0
20	10.6	10.6	10.6	10.6	10.6	10.6	10.6
30	10.3	10.3	10.3	10.3	10.3	10.3	10.3
40	10.1	10.1	10.0	10.0	10.0	10.0	10.0
50	9.87	9.86	9.84	9.83	9.82	9.81	9.80
60	9.70	9.69	9.67	9.66	9.65	9.64	9.63
70	9.56	9.54	9.53	9.52	9.51	9.50	9.49
80	9.44	9.42	9.41	9.39	9.39	9.38	9.37
90	9.33	9.32	9.30	9.29	9.28	9.28	9.27
100	9.24	9.22	9.21	9.20	9.20	9.19	9.19

The pressure and temperature derivative of the speed of sound were obtained directly by differentiation of the equation used for smoothing out the  $u$ ,  $p$  and  $T$  values

$$p - p_{0.1} \text{ (MPa)} = \sum_{i=1}^m \sum_{j=0}^n a_{ij} (u - u_{0.1})^i T^j, \quad (6)$$

where  $u$  is the speed of sound at  $p > 0.1$  MPa,  $u_{0.1}$  is the speed of sound at atmospheric pressure  $p_{0.1}$ . The corresponding statistically significant coefficients  $a_{ij}$  are taken from (DZIDA *et al.*, 2013). Since only statistically significant coefficients  $a_{ij}$  in smoothing equations of  $u(p, T)$  are used, it introduces some error in calculations. However, as has been shown (ZOREBSKI, ZOREBSKI, 2014), this error not exceed  $\pm 1.5\%$ . Generally, the values of  $B/A$  are estimated roughly to be uncertain to within about  $\pm 3\%$ . As has also been shown recently, the correctness and reliability of the calculation procedure is very satisfying (ZOREBSKI, ZOREBSKI, 2014). The calculated for  $[\text{C}_2\text{MIm}][\text{NTf}_2]$  values of  $B/A(p, T)$  are summarized in Table 2.

Figure 2 shows the pressure dependence on  $u$  and  $(\partial u / \partial p)_T$  for  $[\text{C}_2\text{MIm}][\text{NTf}_2]$  at  $T = 298.15$  K. In both cases, the dependencies are typical and similar to those for organic molecular liquids. Obviously the acoustic impedance  $Z (Z = \rho \cdot u)$  shows the same trends as  $u$  (and  $\rho$ ), *i.e.*  $Z$  increases with the pressure and decreases with the temperature. The lowest value of the  $Z$  ( $1.7934 \cdot 10^6 \text{ kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ ) corresponds to the highest temperature and the lowest pressure (318.15 K, 0.1 MPa). Conversely, the highest value of the  $Z$  ( $2.4006 \cdot 10^6 \text{ kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ ) corresponds to the lowest temperature and the highest pressure (288.15 K, 100 MPa).

The obtained value of  $B/A = 11.5$  at  $T = 298.15$  K and atmospheric pressure lies in the range typical for mostly molecular organic liquids. Moreover, the values

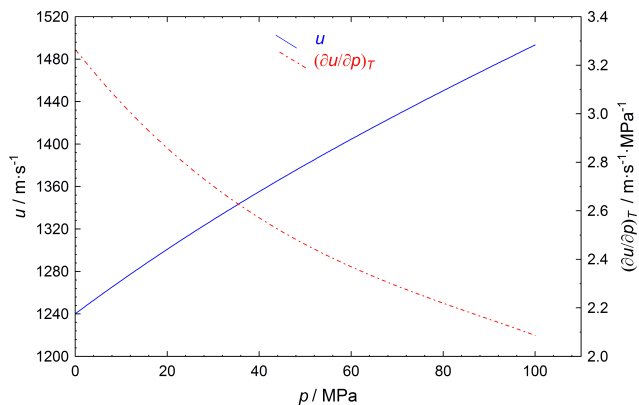


Fig. 2. Dependence of the speed of sound  $u$  (continuous line) and the pressure derivative of the speed of sound  $(\partial u / \partial p)_T$  (dashed line) on pressure  $p$  for  $[\text{C}_2\text{MIm}][\text{NTf}_2]$  at temperature 298.15 K. Lines are obtained from smoothing equation  $u = u(p, T)$  reported in (DZIDA *et al.*, 2013) and from derivation of this smoothing equation.

of  $B/A$  obtained in this work (Table 2) show clearly that this ratio is in practice temperature independent in the studied range. It is in accordance with previous results for akanedioles (ZOREBSKI, ZOREBSKI, 2014) and other reports which show to be sure very slightly temperature dependence but in the broader temperature range (BEYER, 1960; KHELLADI *et al.*, 2009).

Also the contribution to  $B/A$  from temperature changes is much smaller than that due to pressure changes. In other words,  $(B''/A)$  represents only a small negative correction to the  $(B'/A)$  ( $(B''/A)$  is from 5% (high pressure) to 7% (atmospheric pressure) as large as  $(B'/A)$ ). Thus, the result that  $B/A$  is insensitive to temperature is not surprising, and in the case of RTIL studied can be also related to very small values of the  $\alpha_p$  (in practice  $\alpha_p \approx 0$ ) reported previously (ZOREBSKI *et al.*, 2013). On the other hand, the pres-

sure dependence of  $B/A$  is evident, *i.e.* the  $B/A$  decreases nonlinearly with increasing pressure (Table 2, Fig. 3). Moreover, as can be seen from Fig. 3, the  $B/A$  is more sensitive to pressure at lower pressures similarly as for alkanediols.

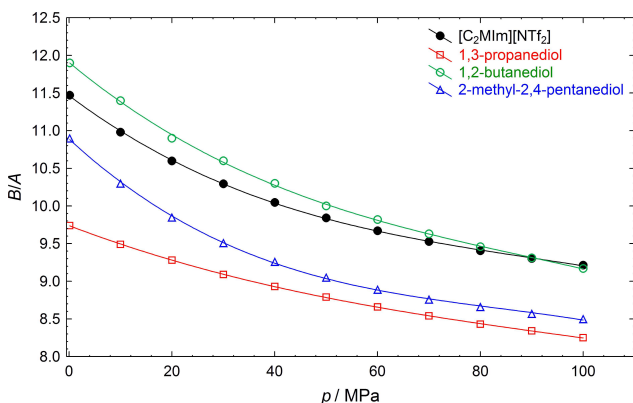


Fig. 3. Dependence of the nonlinear parameter  $B/A$  on pressure  $p$  at temperature 298.15 K for: •  $[C_2MIm][NTf_2]$ , this work; □ 1,3-propanediol (ZORĘBSKI, ZORĘBSKI, 2014); ○ 1,2-butanediol (ZORĘBSKI, ZORĘBSKI, 2014); and △ 2-methyl-2,4-pentanediol (ZORĘBSKI, ZORĘBSKI, 2014). Lines – arbitrary, to aid the eye.

It is interesting that generally the  $B/A$  values over the whole range ( $p, T$ ) studied in this work for the investigated RTIL, are similar to those obtained for molecular organic liquids. This refers also to pressure and temperature dependence. Thus, in this aspect (nonlinear properties related to the propagation of the ultrasonic waves), the behaviour of the studied RTIL does not run away from behaviour of molecular liquids both associated (LÓPEZ *et al.*, 2006; NARAYAMA, SWAMY, 1980; PLANTIER *et al.*, 2002a; 2002b; KHELLADI *et al.*, 2009; ZORĘBSKI, ZORĘBSKI, 2014) and non-associated (NARAYAMA, SWAMY, 1981;

HARTMANN, BALIZER, 1987). Moreover, because studied RTIL can be treated as a some model substance for all RTILs, it seems that above conclusion can be extended on all RTILs. However, it is necessary to remember, that  $[C_2MIm][NTf_2]$  shows rather low ultrasound absorption in comparison to other examined till now RTILs (ZORĘBSKI *et al.*, 2013).

The calculated according to Eq. (4) values of  $P_{int}(p, T)$ , are summarized in Table 3. It should be pointed out that the uncertainty of  $P_{int}$  obtained by the indirect method used in this work was estimated to be  $\pm 1\%$ . As known, this property is a measure of cohesive forces, *i.e.* the sum of attractive and repulsive forces acting in the liquid. Since according to a definition,  $P_{int}$  is the change of the internal energy per mole when the liquid undergoes a very small isothermal expansion,  $P_{int}$  is mainly affected by weak intermolecular forces (dispersive and weakly dipolar) which are strongly affected by the intermolecular distance. Simultaneously, although the strong intermolecular forces (strong dipole-dipole and hydrogen bonding) are also distance dependent they most probably do not markedly affect the internal pressure of liquid (DACK, 1975; IVANOV, ABROSIMOV, 2005) since very small isothermal expansion does not necessarily disrupt such intermolecular forces. Generally, however, the interpretation of the  $P_{int}$  is difficult and an open question because the  $P_{int}$  can be surely partially affected by the strong intermolecular forces. According to some authors (APARICIO, ALCALDE, 2009), such contribution can be of 30% of  $P_{int}$ . Unfortunately, this problem is closely related to RTIL under investigation because of presence of such strong intermolecular forces, and generally, the balance between Coulomb forces, hydrogen bonds, and dispersion forces is one of the crucial problem for the understanding of ionic liquids (FUMINO, LUDWIG, 2014).

Table 3. The internal pressure  $P_{int}$  as function of pressure  $p$  and temperature  $T$  for  $[C_2MIm][NTf_2]$ .

$p$ [MPa]	$P_{int}$ [MPa] at various $T$ [K]						
	288.15	293.15	298.15	303.15	308.15	313.15	318.15
0.1	404.1	402.7	401.2	399.7	398.1	396.5	394.9
10	404.3	403.2	401.9	400.7	399.4	398.1	396.7
20	403.8	402.9	401.9	400.9	399.9	398.8	397.7
30	402.8	402.1	401.3	400.5	399.7	398.9	398.0
40	401.2	400.8	400.2	399.6	399.0	398.4	397.8
50	399.3	399.0	398.7	398.3	397.9	397.5	397.1
60	397.0	396.9	396.8	396.6	396.4	396.2	396.0
70	394.4	394.5	394.5	394.6	394.6	394.6	394.6
80	391.5	391.8	392.1	392.3	392.5	392.7	392.9
90	388.4	388.9	389.3	389.8	390.2	390.6	390.9
100	385.0	385.7	386.4	387.0	387.6	388.2	388.8

Inspection of Table 3 and Fig. 4 shows that at pressures from 0.1 MPa to 60 MPa  $P_{\text{int}}$  decreases with the increasing temperature (the temperature coefficients of internal pressure  $(\partial P_{\text{int}}/\partial T)_p$  are negative), at pressure in the vicinity of 70 MPa  $P_{\text{int}}$  is temperature independent  $((\partial P_{\text{int}}/\partial T)_p \approx 0)$ , and for higher pressures  $P_{\text{int}}$  increases with the increasing temperature  $((\partial P_{\text{int}}/\partial T)_p$  are positive). In other words,  $P_{\text{int}}(p)$  isotherms show a maxima which are shifted towards higher pressures with increasing temperature and clear crossing point of  $P_{\text{int}}(p)$  isotherms is observed (Fig. 4). Previously, similar crossing point was observed only for associated molecular organic liquids. For example, the existence of such unique crossing point is typical in the case of primary linear alkanols (ZORĘBSKI, 2007; DZIDA, 2007) but such crossing point was observed also in the case of 2-methyl-2,4-pentanediol (CEMPA *et al.*, 2008). Unfortunately, published data of the internal pressures for RTILs are not plentiful and thus, comparison with the available literature data is very limited. According to our best knowledge, the crossing point of  $P_{\text{int}}(p)$  isotherms has not been reported till now. Contrary to our results, reported before by SAFAROV *et al.* (2011)  $P_{\text{int}}(p, T)$  data for  $[\text{C}_2\text{MIm}][\text{NTf}_2]$  are monotonic and the crossing point is not observed. This different behaviour of the data of SAFAROV *et al.* (2011) is probably connected with the used differentiation procedure of the correlated  $(p\rho T)$  data which were obtained from density measurements (by means of a vibrating-tube densimeter) as function of  $p$  and  $T$ . Also in the case of 1-butyl-3-methylimidazolium octylsulfate  $([\text{C}_4\text{MIm}][\text{OS}])$  (DÁVILA *et al.*, 2007), *i.e.* for non-halogenated RTIL with similar cation,  $P_{\text{int}}(p)$  isotherms are monotonic in the investigated range (up to 60 MPa) and crossing point is not observed. For 1-butyl-4-methylpyridinium tetrafluoroborate (halogenated RTIL with spherical anion) (SAFAROV *et al.*, 2012) such crossing point is not observed in the range up to 100 MPa as well.

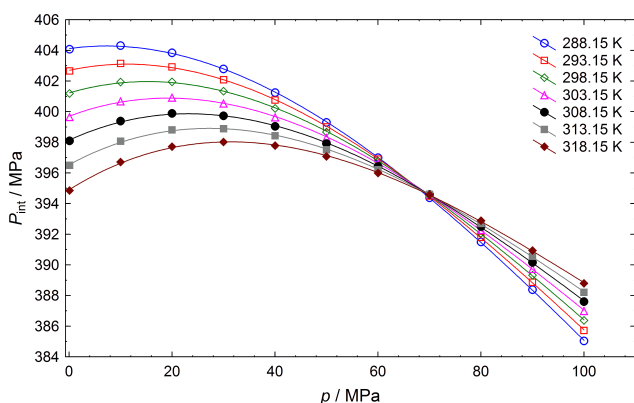


Fig. 4. Isotherms of the dependence of the internal pressure  $P_{\text{int}}$  on pressure  $p$  at temperatures in the range 288.15–318.5 K with the 5 K step for  $[\text{C}_2\text{MIm}][\text{NTf}_2]$ . Lines – third order polynomials.

## 4. Conclusions

The consistent data on Beyer's nonlinearity parameter  $B/A$  and internal pressure for one of the standard RTILs, namely  $[\text{C}_2\text{MIm}][\text{NTf}_2]$  as a function of pressure and temperature are reported. The obtained by means of thermodynamic method  $B/A$  values are similar to those reported for many molecular organic liquids, whether associated or non-associated. As for molecular liquids,  $B/A$  decreases as the pressure increases and is in practice temperature independent in the studied range. Thus, no essential differences between RTIL studied in this work and molecular organic liquids in relation to nonlinear properties are observed. However, it would be of interest and desirable to study  $B/A$  also in other types of ILs which are materials of great current interest. In the case of internal pressure, the unique crossing point of  $P_{\text{int}}(p)$  isotherms is observed for the studied RTIL.

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