Density, surface tension and viscosity of liquid binary Al-Zn and ternary Al-Li-Zn alloys

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ABSTRACT

Three thermophysical properties: density, surface tension and viscosity of liquid binary Al-Zn and ternary Al-Li-Zn alloys have been investigated in this work, by means of the draining crucible method. Three Al-Li-Zn compositions corresponding to distinguished intermetallic phases, i.e. Al_5Li_3Zn, $Al_{35}Li_{32}Zn_{33}$ and $AlLiZn_3$, have been selected for investigation. Experimentally determined surface tension of ternaries has been compared to the modelled one, using the commonly known Butler's model and two sets of ternary interaction parameters given in the literature. Whereas, viscosity calculations for the ternary Al-Li-Zn alloys have been performed using three thermodynamics-based models, selected for their reliability, and confronted to the experimental data measured in this work. Both, measured and modelled surface tension decreased with increasing Li and Zn content, opposite to viscosities exhibiting an increase with Li and Zn content raise. Whereas measured densities of the investigated ternaries are decreasing with Li and Zn content growth in confrontation to the three respective Al-Zn binaries investigated in this work.

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1. Introduction

The knowledge of phase diagram and physicochemical properties is fundamental for designing new performance materials possessing improved mechanical properties and setting the conditions of technological processes. More importantly, thermophysical properties of ternary Al-Li-Zn alloys, still unknown, is of a great importance to optimize the technological processes such as melting or casting and extracting. Al-Li based ternary alloys, i.e. Al-Li-X (where X stands for Cu, Mg, Zn), are characterized by superior mechanical properties, these are low specific weight, high strength and high elasticity modulus. It has also been observed that ternary Al-X-Zn systems (where X stands for Mg, Li) show metastable quasicrystals existence in certain concentration ranges, which have recently been the subject of impressive experimental and theoretical contributions [1—3].

Although some systems, for instance the Al-Zn alloys, are almost fully recognized, however, it is still required to update their properties. Several interesting papers concerning solid materials' examinations have been reported in the literature in confrontation to smaller ones found for liquid properties of Al-Zn alloys [4—7].

Whereas, the Al-Li based alloys have recently received considerable attention as potential lightweight replacements for Al based alloys in light metal industry for aerospace applications. For instance, the addition of 1.8—2.1 at.% Li remarkably altered the precipitation behaviour of Al-Cu-Mg-Zn-Li alloys, which are the highest strength aluminium alloys known [8].

According to the previous experimental and theoretical reports, concerning thermodynamics of liquid Al-Zn alloys, positive deviations from ideal solution were observed, therefore signifying the phase segregation tendency occurring in liquid state [6]. In relation to the previously established thermophysical properties of liquid Al-Zn alloys, measured viscosity [9] and surface tension [4] exhibit significant negative deviation from their linear concentration dependence in comparison to density changing almost linearly with increasing Zn content [9]. Whereas thermodynamic studies for the two remaining binary systems, i.e. Al-Li and Li-Zn alloys, revealed negative deviations from ideal solution which were also confirmed and profoundly described in our last paper, concerning theoretical and experimental study of bulk and surface properties of those binaries [10].

Contrary to the records for limiting binaries mentioned above, any information on density, viscosity and surface tension for liquid ternary Al-Zn-Li alloys have not yet been found in the literature. Only one property has been given, the mixing enthalpy for three ratios of constant molar fraction of Al to Zn measured and modelled

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by Kim & Sommer [11]. Later, Guo et al. [12] devised the ternary interaction parameters for thermodynamic description of the liquid phase, and very recently we proposed proposed a new set of those [13], which allowed to better describe the thermodynamics of liquid Al-Zn-Li alloys including partial and mixing thermodynamic functions obtained from electromotive force measurement.

In correspondence to the solid state of the Al-Li-Zn system, it is important to mention a recent review of Bodak [14], compiling the full information on all works done for this system and containing important observations concerning intermetallic phases, i.e. $\tau(Al_5Li_3Zn)$, $\upsilon(Li_{26}Al_6(Al_{1-x}Zn_x)_{49})$ and $\gamma(AlLiZn_3)$, experimentally determined by Badeva & Sald'au [15]. Some interesting structural characteristics of these phases had been released and therefore, thermophysics knowledge of the three aforementioned Al-Li-Zn alloys' compositions is essential for their further investigation. Later Guo et al. applied this knowledge for phase diagram calculation [12].

According to previous Trybula et al. [10] and Gancarz et al. [16,17] studies, the draining crucible method, applied in this work, is a promising experimental technique enabling to determine three thermophysical properties of dense liquids at one measurement, efficient for both light and heavy metals. Apart from the scientific reports mentioned above, related to methodology and data found, the proposition of this work is to show the capability of the draining crucible method to correctly measure the three physicochemical properties of the Al-Zn binary alloys. We chose Al-Zn alloys because complete thermophysical data existed in the literature for them and, therefore, it builds a correct background for further analysis of these properties in the liquid Al-Li-Zn alloys.

The primary aim of this work is to examine the influence of Li addition on density, viscosity and surface tension change measured in the 823–1023 K temperature range for three liquid binary Al-Zn alloys. Three different ratios of constant Al to Zn molar fraction have been taken into consideration which correspond to the compositions of three intermetallic phases mentioned above, occurring in the solid state of Al-Li-Zn alloys. In the first stage, three thermophysical properties of liquid Al-Zn alloys are discussed with regard to the available literature data. Further, these properties for liquid Al-Li-Zn alloys are determined and discussed with modelled data obtained in this work, using two assumptions in order to verify the existence of a ternary effect, which could correspond to an associative tendency previously observed in liquid Al-Li and Li-Zn alloys [10]. Finally, this work is addressed to build a complete database of thermophysical properties, including the three limiting binary alloys and Al-Li-Zn alloys, examined with use of the draining crucible (DC) method. The viscosities of Al-Zn-Li alloys are computed using the most representative thermodynamics-based models, as mentioned and used in Ref. [10], whereas, Butler's model [18] was employed to expand the discussion of experimental surface tension values.

2. Methodology

2.1. Experiment

Binary and ternary Al-Zn based alloys were prepared using high purity Al, Li and Zn metals (see details in Table 1), further melted in a molybdenum crucible which was placed in a furnace. To provide the best possible protective atmosphere, every experiment was conducted in a glove box filled with high purity argon. The level of oxygen, water vapour and nitrogen were kept constant and it was below 1 ppm as monitored by a solid-state analyser. Generally, three binaries: $Al_{75}Zn_{25}$, $Al_{51}Zn_{49}$, $Al_{83}Zn_{17}$ and ternaries: $\tau(Al_5Li_3Zn)$, $\upsilon(Al_{33}Li_{32}Zn_{33})$, $\gamma(AlLiZn_3)$ were the subject of presented and discussed herein experimental and theoretical

Table 1
Chemical compositions^a of Al-Zn binaries and Al-Li-Zn ternaries considered in this work.

Metals	Fraction purity		
Al, Zn − rods*	0.99999		
Li − rods*	0.99950		
	Al-Zn alloys		
Chemical formulae	$X_{Al}{}^b$		$X_{Zn}{}^b$
$Al_{83}Zn_{17}$	0.83		0.17
$Al_{51}Zn_{49}$	0.51		0.49
$Al_{25}Zn_{75}$	0.25		0.75
	Al-Li-Zn alloys		
	$X_{Al}{}^b$	$X_{Li}{}^b$	$X_{Zn}{}^b$
$Al_5Li_3Zn^\#$	0.56	0.33	0.11
$Al_{28}Li_{26}Zn_{27}^\#$	0.35	0.32	0.33
$AlLiZn_3^\#$	0.20	0.20	0.60

^{a,b} Standard uncertainties u are u(X) = 0.005 for Al and Zn, whereas u(X) = 0.01 for Li.
*Sigma Aldrich Distributor.
$^\#$ Al-Li-Zn alloy compositions and corresponding them signature used in this work: $\tau(Al_5Li_3Zn)$, $\upsilon(Al_{28}Li_{26}Zn_{27})$, $\gamma(AlLiZn_3)$.

contributions, which are plotted in Fig. 1, inscribed in a Gibbs triangle.

Appropriately prepared samples were subjected to simultaneous measurement of three thermophysical properties: density, surface tension and viscosity using the draining crucible (DC) method. In this work, we give only basic formulae which are used, in practise, for determination of the aforementioned properties, however, a reader interested in details of the DC method is referred to Refs. [10,19–21].

Generally, a liquid alloy is flowing out through a hole at the bottom of a crucible under gravity and the cumulative weight of the liquid as a function of time is measured, and described by a polynomial:
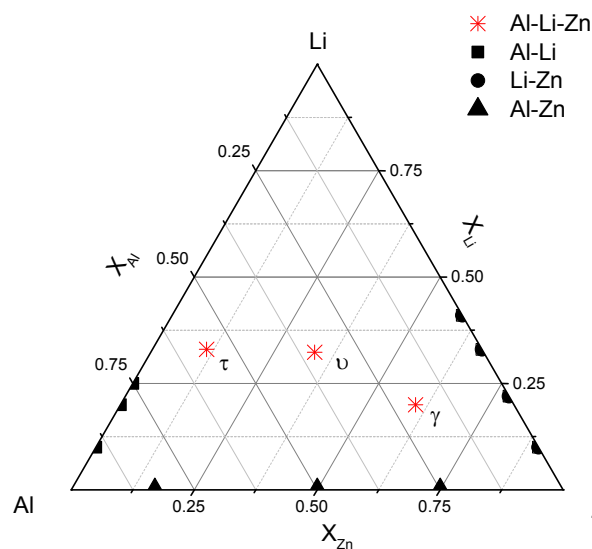
$$A_m = \sum_{i=1}^{n} A_i t^{i-1}, \tag{1}$$

Fig. 1. τ, υ and γ ternary Al-Li-Zn alloys depicted in Gibbs triangle (chemical compositions, see Table 1). ■, ● and ▲ closed triangle represent three reference binary systems, Al-Li, Li-Zn and Al-Zn, respectively.

where A_m are time dependent parameters used for calculation of a volumetric flow rate as follows:

$$Q = \frac{A_1 + A_2 t + A_3 t_2}{\rho}. \tag{2}$$

In practise, Eq. (3), describing the relationship between volumetric flow rate Q of a liquid flowing out the crucible through the orifice of fixed radius r_0 and head of the liquid h, is solved numerically by employing the Hooke-Jeeves algorithm.

$$h = \frac{1}{2g}\left(\frac{Q}{a_1 + a_2\left(\frac{2\rho Q}{\pi r_0 \eta}\right) + a_3\left(\frac{2\rho Q}{\pi r_0 \eta}\right)^2}\right) + \frac{\sigma}{\rho g r_0}. \tag{3}$$

Numerical solution of this equation allows to straightforwardly determine density, surface tension and viscosity of an alloy measured at a single experiment using the following formulae:

surface tension

$$\sigma = \rho \cdot g \cdot r \cdot \left[h - \frac{1}{2}\left(\frac{Q}{\left(a_2\left(\frac{2 \cdot r_0 \cdot Q}{\eta}\right) + a_1\right) \cdot \pi \cdot r_0^2}\right)^2\right], \tag{4}$$

density

$$\rho = \frac{\sigma}{g \cdot r_0 \cdot \left[h - \frac{1}{2g}\left(\frac{Q}{\left(a_2\left(\frac{2 \cdot r_0 \cdot Q}{\eta}\right) + a_1\right) \cdot \pi \cdot r_0^2}\right)^2\right]}, \tag{5}$$

viscosity

$$\eta = \frac{2 \cdot a_2 \cdot \rho \cdot r_0 \cdot Q}{\sqrt{2 \cdot g\left(h - \frac{\sigma}{\rho \cdot g \cdot r_0}\right) - \pi \cdot r_0^2 \cdot a_1}}. \tag{6}$$

Symbols in Eqs. (3) and (4-6) are: ρ, σ and η are density (kg·m^{-3}), surface tension (N·m^{-1}) and viscosity (Pa·s) of a liquid, including a reference system and measured one. r_0 and g are orifice radius of a crucible bottom and gravitational acceleration (m·s^{-2}), respectively. Whereas, a_1, a_2 and a_3 are constants describing the C_d vs. Re relationship (e.g. $C_d = a_1 + a_2(\text{Re}) + a_3(\text{Re})^2$, C_d − discharge coefficient, Re − Reynolds number), which is a fundamental for a calibration procedure, initially performed for a reference system, and described in detail in Ref. [10]. As a reference, in our experimental studies, available experimental data of thermophysics for the pure liquid Al metal were used and the orifice at the bottom of a crucible had radius analogous to that used in our previous work [10].

Measured thermophysical data expressed by linear temperature dependence (density and surface tension) and Arrhenius relation (viscosity) are gathered in Tables 2, 3 and 7, respectively, and discussed in the following Sections, whereas experimental data and their error analysis are compiled into Supporting Information.

2.2. Modelling

Thermophysical properties, including viscosity and surface tension, of the investigated ternaries were modelled using well-known thermodynamics-based models. To be coherent with our previous studies performed for Al-Li and Li-Zn as well as Al-Zn binaries, the present discussion is limited to three previously selected viscosity models [10], and principally Butler's model was applied to surface tension. Modelling studies of three

thermophysical properties of liquid Al-Zn binary are not presented hereafter, because such studies were already performed [5] and therefore they will not be repeated.

2.3. Viscosity

Various propositions for viscosity estimation have been recently reported in the literature, as shown Gasior [5]. In this work, three best ones: Kozlov-Romanov-Petrov (KRP, η^{KRP}) [22], Kaptay (Kap, η^{Kap}) [23] and Gasior (Gas, η^{Gas}) [5] are employed. Mathematical representations of the aforementioned models, originally formulated for binary systems, are as follows:

$$\eta^{KRP} = \sum_i X_i \ln(\eta_i) \cdot \exp(-H_M/3RT), \tag{7}$$

$$\eta^{Kap} = \frac{M}{\rho}\exp\left(\frac{\sum_i X_i \Delta G_i^* - \alpha H_M}{R \cdot T}\right), \tag{8}$$

$$\eta^{Gas} = \left(\eta_i X_i + \eta_j X_j\right) \cdot \left(1 - 2\frac{S^{xc}}{R}\right). \tag{9}$$

Parameters in Eqs. (7)–(9) i.e. $X_i, \eta_i, (i = A, B)$ are mole fraction and viscosity of i-th species, respectively. α parameter is equalled to 0.155±0.055. G^*, H_M, S^{xc} are activation Gibbs energy, mixing enthalpy and excess entropy of binary and ternary systems, correspondingly. M, R, T are molar mass (g·mol^{-1}), gas constant (8.314 J·mol^{-1}·K^{-1}) and absolute temperature (K). Each thermodynamic function, employed in the aforementioned formulae, is expressed in the form of a Redlich-Kister polynomial [24] according to the recipe given for a ternary system, Eq. (10):

$$\Delta G^{xc} = \sum_{i,j} \sum_k \left(X_i \cdot X_j \cdot \sum_m {}^m L_{i,j}(X_k - X_j)^m\right) \\ + X_i \cdot X_j \cdot X_k \cdot ({}^0 L_{123} \cdot X_i + {}^1 L_{123} \cdot X_j + {}^2 L_{123} \cdot X_k). \tag{10}$$

ΔG^{xc} is the excess Gibbs free energy, whereas X_i, X_j, X_k denote the Al, Li and Zn concentrations corresponding to these attached in Table 1 for three Al-Li-Zn alloys' compositions presented in this work, correspondingly. $^m L$ s are an interaction parameters of Redlich-Kister (RK) polynomial defined as

$${}^m L = {}^m M + {}^m N \cdot T + {}^m O \cdot T \ln T + \dots., \tag{10a}$$

where $^m M$, $^m N$ and $^m O$ are temperature-independent coefficients. Therefore, $^m L$ s' parameters, concerning the first term in Eq. (10) − $^m L_{i,j}$ (for m = 0, 1, 2, 3, 4) represent binary systems, i.e. Al-Li, Li-Zn and Al-Zn, whereas the three remaining ones, i.e. $^0 L_{123}$, $^1 L_{123}$, $^2 L_{123}$, describe ternary interactions embedded into Eq. (10).

2.4. Surface tension

Surface tension of a liquid binary metallic system, σ, formulated within Butler's formalism is given as follows [18]:

$$\sigma = \sigma_i + \frac{RT}{S_i}\ln\frac{X_i^s}{X_i} + \frac{1}{S_i}\left[G_i^{xc,s} - G_i^{xc,b}\right] \tag{11a}$$

$$\sigma = \sigma_j + \frac{RT}{S_j}\ln\frac{X_j^s}{X_j} + \frac{1}{S_j}\left[G_j^{xc,s} - G_j^{xc,b}\right], \tag{11b}$$

where $G_{i,j}^{xc,b}$ are the partial excess Gibbs free energy of i and j-th component in the bulk phase. Whereas, partial excess Gibbs energy of i-th component in the surface is reduced by adjustable parameter β and given as:

$$G_i^{xc,s} = \beta \cdot G_i^{xc,b}. \tag{12}$$

Employed adjustable parameter β results from the assumption that atomic coordination numbers in the surface layer are lower than those in the bulk phase and was taken as Tanaka et al. suggested [25], namely $\beta = 0.83$.

$X_{i,j}$, $X_{i,j}^s$ correspond to atomic concentration in the bulk and surface phase of i- and j-th component of a binary alloy, respectively. Detailed description of Butler's surface tension formulation for a binary system can be found elsewhere [10,18,26]. While S_i represents the surface layer area given as follows:

$$S_i = LV_i^{2/3} / N^{1/3}, \tag{13}$$

where L, V_i and N are geometric factor, which recalculates the surface layer area referred to a close packed structure (L = 1.091), the molar volume of i-th component and Avogadro number, respectively.

Extension of the aforementioned formulae (11 (a − b)) on ternary alloy is given as:

$$\sigma = \sigma_i + \frac{RT}{S_i}\ln\frac{X_i^s}{X_i} + \frac{1}{S_i}\left[G_i^{xc,s} - G_i^{xc,b}\right] \tag{14a}$$

$$\sigma = \sigma_j + \frac{RT}{S_j}\ln\frac{X_j^s}{X_j} + \frac{1}{S_j}\left[G_j^{xc,s} - G_j^{xc,b}\right] \tag{14b}$$

$$\sigma = \sigma_k + \frac{RT}{S_k}\ln\frac{X_k^s}{X_k} + \frac{1}{S_k}\left[G_k^{xc,s} - G_k^{xc,b}\right]. \tag{14c}$$

Meaning of the symbols used in Eq. (14 (a − c)) is analogous to those in Eq. (11(a − b)).

3. Results and discussion

Draining crucible experiments for density, viscosity and surface tension measurement of three liquid Al-Zn and respective Al-Li-Zn alloys (Fig. 1) were conducted in the 823−1023 K temperature range. Viscosity and surface tension isotherms measured and computed at 973 K for liquid Al-Zn alloys are discussed with available experimental and theoretical contributions reported in the literature [4−6,9].

Chemical compositions of three liquid Al-Zn and three Al-Li-Zn alloys investigated in this work are given in Table 1. Measured thermophysical properties are described as linear temperature functions − density and surface tension, while viscosity is expressed in the form of the Arrhenius equation (given later in the text (Eq. (15)). Coefficients of appropriate equations together with their error values are gathered in Tables 2, 3 and 7 corresponding to density, viscosity and surface tension, respectively.

3.1. Density

Densities measured for binary Al-Zn and ternary Al-Li-Zn alloys' compositions, listed in Table 1 and described by a linear equation ($\rho = A + B \cdot T$, kg·m^{-3}) are drawn in Fig. 2. Upper and bottom panels in Fig. 2 correspond to three binary Al-Zn and Al-Li-Zn alloys investigated in this work, whereas lines relate to densities fitted. Coefficients of linear temperature dependence with their errors are included in Table 2 as well as density values computed at 973 K.

Therefore, density increase with increasing Zn content (decreasing X_{Al}/X_{Zn} molar ratio) has been found in the liquid Al-Zn alloys investigated. Density measured for the three liquid Al-Li-Zn alloys also demonstrates linear compositional dependence, moving from τ ternary alloy composition through υ to γ, correspondingly. With reference to temperature dependence of density, a linear decrease with temperature increase has been observed. Density isotherm of binary Al-Zn alloys at 973 K determined in this work and that one found in the literature, given by Gebhardt et al. [9], are pictured in Fig. 3, also including density data for pure metals. An excellent agreement between our results presented in this work results and those given by Gebhardt has been found that also confirms the error bars plotted in Fig. 3 which are not large enough to be visible. Principally, densities of liquid Al-Zn alloys increase with increasing Zn content that results from higher density value for pure Zn compared to pure Al, and therefore, it can be concluded that the observed changes are correct.

Density isotherm obtained for pure Al, Li and Zn elements, binaries including Al-Li, Li-Zn (taken from Ref. [10]) and Al-Zn, as well as ternaries Al-Li-Zn alloys at 973 K is presented in Fig. 4. The trend in density change, observed for the liquid binary alloys examined, i.e. Al$_{83}$Zn$_{17}$, Al$_{51}$Zn$_{49}$ and Al$_{25}$Zn$_{75}$ is adequate to that measured for the investigated ternary alloys. Basically, the density of liquid binaries and ternaries increases with Zn content growth, (through γ ternary alloy composition). Whereas, its decrease with Li addition to Al-Zn alloys was found and the most prominent density lowering

Table 2
Coefficients and their errors[a] of linear temperature dependence of density ($\rho = A + B \cdot T$) for three liquid binary Al-Zn alloys and ternary Al-Li-Zn alloys. The last two columns represent density and its errors[b] computed at 973 K.[c]

T − range/K	Density of liquid Al-Zn alloys						
	X_{Zn}	A/kgm^{-3}	u(A)	B/kg·m^{-3} T^{-1}	u(B)	ρ(973)/kg m^{-3}	U(ρ)
923−1023	0.17	4490	62.0	−1.90	0.64	2641	47.5
873−1023	0.49	5390	12.0	−1.35	0.12	4076	14.5
873−1023	0.75	6290	70.0	−1.24	0.08	5083	19.9

T − range/K	Density of liquid Al-Li-Zn alloys						
	X_{Li}	X_{Zn}	A/kgm^{-3}	u(A)	B/kg·m^{-3}·T^{-1}	u(B)	ρ(973)/kg m^{-3}	U(ρ)
923−1023	0.33	0.11	5570	3.9	−4.03	0.40	1652	28.5
823−1023	0.32	0.33	6150	3.6	−3.40	0.40	2846	27.3
853−1023	0.20	0.60	7050	3.6	−2.91	0.14	4224	65.1

[a] Estimated from linear regression error as implemented in Grapher Softaware Package.
[b] Estimated from difference computed between experimental and calculated from linear density fit, $u(m) = \frac{1}{N}\sum_{i=1}^{N}|m^{exp} - m^{fit}|$, where N is number of experimental points (i.e. for Al-Zn alloys N = 3, whereas for ternary Al-Li-Zn alloys N = 4) and the combined expanded uncertainty U(ρ) (0.95 level of confidence with k = 2).
[c] Standard uncertainties u are u(T) = 1 K, u(p) = 0.1 kPa at atmospheric pressure p = 0.1 MPa, u(X) = 0.005 for Al and Zn, whereas u(X) = 0.01 for Li.

demonstrates liquid $Al_{83}Zn_{17}$ alloy compared to two remaining binaries investigated. The last point of the present discussion on density, which deserves to be mentioned, is related to the complete isotherm drawn in Fig. 4. Namely, density lowering with Li-content growth is observed for the two Li-containing binary systems (Al-Li, Li-Zn) [10]. An important observation emerging from Fig. 4 concerns the density increase, starting from the Al-Li limiting binary through three ternaries towards the Li-Zn edge of Gibbs triangle. An adequate density change has also been recorded, starting from pure Al through limiting Al-Zn alloys and moving towards pure Zn.

3.2. Viscosity

Measured viscosities of liquid binaries and ternaries Al-Zn based alloys have been described by the Arrhenius equation:

$$\eta = A_r \cdot exp(-E_a/RT). \qquad (15)$$

A_r is the pre-exponential parameter (Pa·s) and E_a is the activation energy (J·mol^{-1}) which are gathered in Table 3 with respective error values, and temperature dependence of viscosity is drawn in Fig. 5, upper panel for binaries and bottom one represents ternaries. Points correspond to the measured values, and the solid lines represent the viscosities computed using Eq. (15). As a consequence, nonlinear temperature dependence of viscosity, demonstrated in Fig. 5 (η decreases with increasing temperature) and a good relationship between measured and fitted viscosity are observed.

Viscosity isotherm of binary Al-Zn alloys at 973 K determined in this work and that given by Gebhardt et al. [9], are pictured in Fig. 6 also including data for pure metals (circle − Al and triangle − Zn). A significant quantitative inconsistency between data determined in this work and those measured by Gebhardt et al. [9] is found, including also pure elements. Consequently, the present values are higher than Gebhardt's viscosity of pure Al and Zn as well as binary Al-Zn alloys, however trend in viscosity changes is retained. Errors associated with measured viscosities (black squares), marked in Fig. 6, are small and, therefore, we could assume the correctness of determined viscosities. One note can be made concerning the discrepancy observed for pure Al, namely eliminating the difference in viscosity of pure liquid Al will allow to be closer of viscosities determined in this work for liquid Al-Zn alloys to literature data (stars in Fig. 6). Keeping in mind the volatility of Zn and vulnerability of viscosity measurements to even negligible amounts of impurities, which may result in significant decreases [29], hence such a remarkable scatter can be explained by these factors. One note
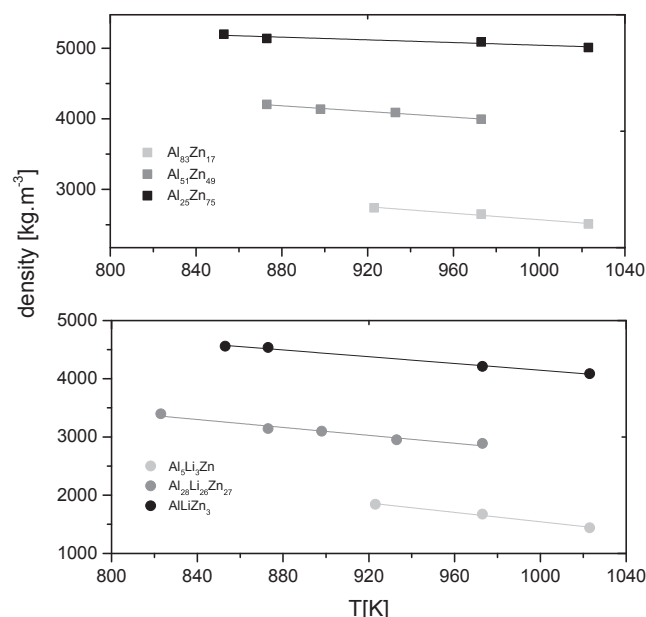

Fig. 2. Density measured and computed using linear temperature dependence of liquid binary Al-Zn (upper panel) and ternary Al-Li-Zn alloys (bottom panel). Coloured squares and balls represent binaries and ternaries investigated, respectively.

can be mentioned that the draining crucible method uses large amount of the investigated alloy compared to the method Gebhardt used and, therefore, it is less sensitized on composition change caused by Zn evaporation or impurities.

Compositional dependence of viscosity (three-dimensional viscosity isotherm) at 973 K is pictured in Fig. 7 and, its analysis is presented in two ways, the first one is that performed along a line starting from the liquid Al-Zn limiting binary and moving towards the ternaries, whereas the second one concerns the complete viscosity isotherm (global trend analysis). Like for density, the viscosity isotherm presented as a 3-dimensional representation in Fig. 7 also includes our previously determined viscosities for liquid Al-Li and Li-Zn alloys [10] as well as those for pure metals, taken from literature.

In relation to the first way of present discussion, a remarkable viscosity increase with Li addition to the three respective binary Al-Zn alloys (see Table 1), has been recorded. It could mean that liquid ternaries are more viscous and thereby such remarkable increase could simultaneously suggest to liquid Al_5Li_3Zn,

Table 3
Coefficients (A_r, E_a) and their errors[a] in Arrhenius relation (Eq. (15)) of viscosities measured for liquid binary Al-Zn and ternary Al-Li-Zn alloys as a function of temperature. The last two columns present viscosity values and its errors[b] computed at 973 K.[c]

T − range/K		Viscosity of liquid Al-Zn alloys					
	X_{Zn}	A_r/Pa·s	$u_{(A_r)}$	E_a/J·mol^{-1}	$u(E_a)$	$\eta(973)$/Pa·s	$U(\eta)$
923−1023	0.17	0.000461	0.000051	−8249.5	903	0.001280	0.000062
873−1023	0.49	0.000564	0.000038	−7704	539	0.001462	0.000014
873−1023	0.75	0.000652	0.000049	−7799	592	0.001709	0.000022

T − range/K			Viscosity of liquid Al-Li-Zn alloys				
	X_{Li}	X_{Zn}	A_r/Pa·s	$u_{(A_r)}$	E_a/J·mol^{-1}	$u(E_a)$	$\eta(973)$/Pa·s	$U(\eta)$
923−1023	0.33	0.11	0.000531	0.000076	−9130	1180	0.001642	0.000018
823−1023	0.32	0.33	0.000749	0.000150	−7445	261	0.001881	0.000013
853−1023	0.20	0.60	0.001013	0.000059	−5798	449	0.002074	0.000025

[a] Estimated from nonlinear regression error as implemented in Grapher Software Package.
[b] Estimated from difference computed between experimental and calculated from Arrhenius equation fit, $u\ (m) = \frac{1}{N}\sum_{i=1}^{N}|m^{exp} - m^{fit}|$, where N is number of experimental points (i.e. for Al-Zn alloys N = 3, whereas for ternary Al-Li-Zn alloys N = 4) and the combined expanded uncertainty $U(\eta)$ (0.95 level of confidence with k = 2).
[c] Standard uncertainties u are $u(T) = 1$ K, $u(p) = 0.1$ kPa at atmospheric pressure p = 0.1 MPa, u(X) = 0.005 for Al and Zn, whereas u(X) = 0.01 for Li.
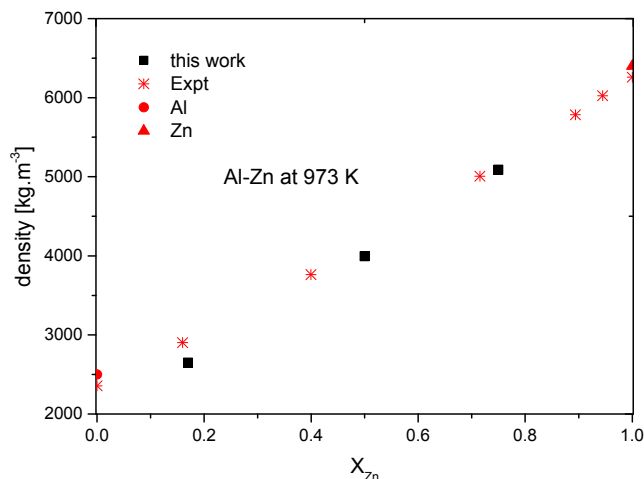
Fig. 3. Density isotherm at 973 K, measured in this work (black squares, ■) and determined by Gebhardt et al. [9] (Expt, ✳). ● and ▲ correspond to pure Al and Zn taken from Refs. [27] and [21], respectively. Error bars for present data are also included but they are smaller than size of symbol.

Al$_{28}$Li$_{26}$Zn$_{27}$, and AlLiZn$_3$ alloys be more densely-packed compared to the binary Al-Zn alloys. To our best knowledge, an adequate observation, was very recently recorded by Gancarz & Gasior for liquid Sn-Zn-Na alloys, namely, the viscosity increase with Na content growth [17]. Apart from this fact, it should be mentioned that the thermodynamics of liquid Sn-Zn and Al-Zn informs about positive deviations from Raoult's law signifying phase separation [30,31]. It is important to mention that Gancarz, very recently has studied the liquid (Al-Zn)$_{eut}$ − 8 at.% Li addition thermophysical properties and he observed an adequate trend in viscosity change with Li addition as it is found in this work, namely its increase (results to be published). Considering the phase segregation behaviour manifested by liquid Al-Zn alloys [6,30] and significant difference in viscosity for pure metals, in particular, between Li and Zn, Li addition should rather lower the viscosity than increase it in
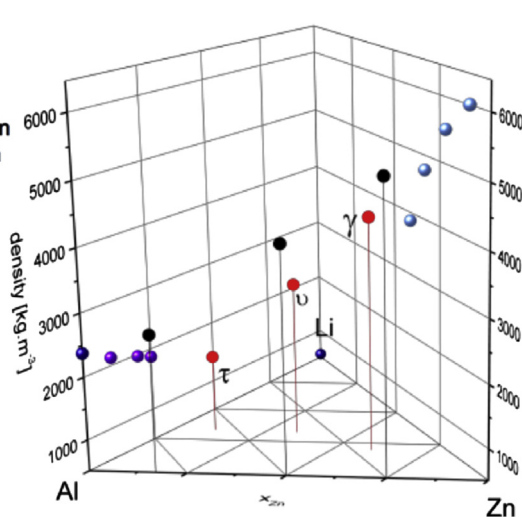

Fig. 4. Three-dimensional representation of density isotherm at 973 K: black balls (●) − Al-Zn alloys. Dark blue balls (●) − pure liquid metals (Al [27], Li [28] and Zn [21]), violet (●) and blue (●) balls correspond to densities of Al-Li and Li-Zn alloys, taken from Refs. [10], respectively. Red balls (●) − represent τ(Al$_5$Li$_3$Zn), υ(Al$_{28}$Li$_{26}$Zn$_{27}$) and γ(AlLiZn$_3$) ternary alloys investigated in this work. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
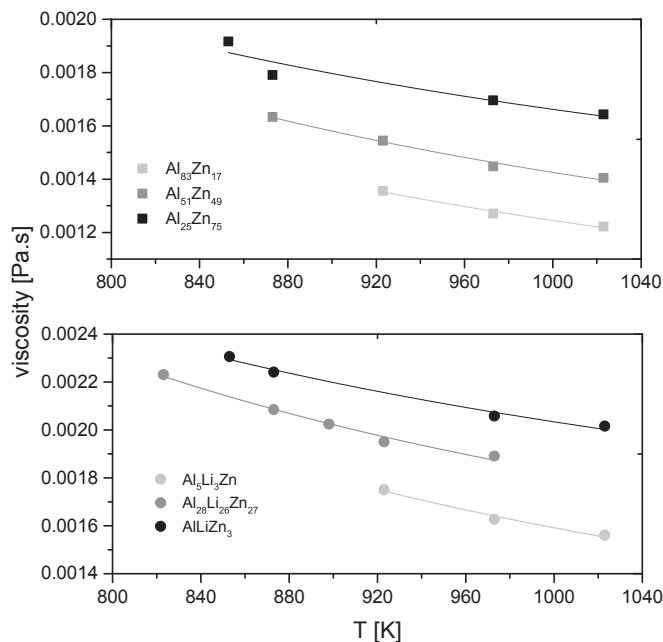

Fig. 5. Viscosity measured and computed using Arrhenius equation (Eq. (15)) of liquid binary Al-Zn (upper panel) and ternary Al-Li-Zn alloys (bottom panel). Coloured squares and balls represent binaries and ternaries investigated, respectively.

liquid ternary alloys due to its negligible value for pure liquid Li (see Fig. 7). Such a significant increase can be attributed to the presence of a ternary effect related to the associate forming tendency, which needs more attention and is subjected to discussion supplemented by modelling studies presented hereafter. As we mentioned above, these changes can also imply the increase in dense-packed liquid structure resulting from the occurrence of compact atomic structures. As it was recognized recently, atomic building blocks with five-fold symmetry are found to be the most abundant and compact structures occurring in liquid and undercooled Al as well as in alloys based on it [32−34]. Such considerations are beyond the scope of contribution addressed by this work.

In correspondence to the second point of the presented discussion, it can be easily read from Fig. 7, that in the examined composition range, viscosity increases with increasing Li content in
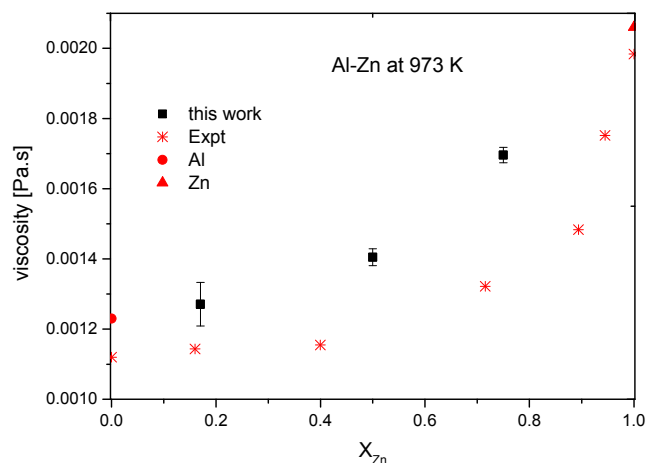

Fig. 6. Viscosity isotherm of liquid Al-Zn alloys at 973 K, measured in this work (black squares, ■) and determined by Gebhardt et al. [9] (Expt, ✳). ● and ▲ correspond to pure Al and Zn taken from Refs. [27] and [21], respectively. Error bars for present data are also included.
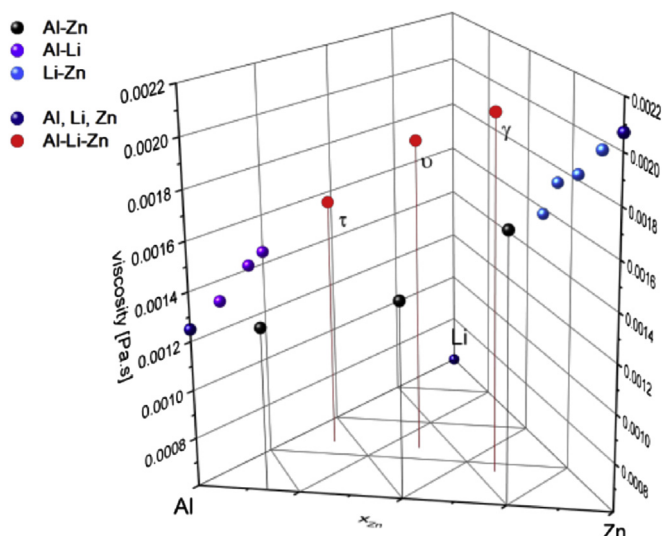
Fig. 7. Three-dimensional representation of viscosity isotherm at 973 K: black balls (●) — Al-Zn alloys. Dark blue balls (●) — pure liquid metals (Al [27], Li [28] and Zn [21]), violet (●) and blue (●) balls correspond to densities of Al-Li and Li-Zn alloys, taken from Refs. [10], respectively. Red balls (●) — represent τ(Al₅Li₃Zn), υ(Al₂₈Li₂₆Zn₂₇) and γ(AlLiZn₃) ternary alloys investigated in this work. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

liquid Al-Li alloys contrary to its decrease for liquid Li-Zn alloys [10]. Therefore, starting from the Al-Li edge of the Gibbs triangle, moving through ternaries towards the Li-Zn alloys, an almost linear increase in viscosity can be seen, up to the AlLiZn₃ alloy, followed by its diminishing towards the Li-Zn edge. Such a significant rise measured for viscosity, among the three ternary liquid alloys investigated, is attributed to the noticeable Zn composition change. In fact, it is equal to 49 at.% growth in comparison to slight (about 13 at.%) for Li and more visible (36 at.%) changes for Al, respectively. Invoking the mentioned above considerations and Fig. 7, which concern the noticeable difference in viscosity values between binaries and ternaries, a smooth viscosity pathway along the Al-Zn edge of the Gibbs triangle, plotted in Fig. 7, can be easily seen, contrary to the ternary liquids investigated.

For viscosity modelling, three best thermodynamics-based viscosity models given by Eqs. (7)–(9) were used, whereas parameters of Arrhenius relation (Eq. (15)) for pure elements (Al, Li and Zn) are taken as those collected in Table 4.

For a reminder, two variants were applied in the present considerations to determine the thermodynamic properties (ΔH_m, G^* and S^{xs}) required for viscosities evaluation of three liquid Al-Li-Zn alloys. On the margin, it should be noted that viscosity modelling performed for the binaries investigated in the present work, has not been considered due to its wide studies presented previously by Gasior [5]. Therefore, the first used approach takes into consideration two sets of ternary interaction parameters recently reported

Table 4
Parameters of Arrhenius equation (Eq. (15)), A_r and E_a, for viscosity computation of pure Al, Li and Zn metals.

Pure metal	A_r/Pa·s	E_a/J·mol^{-1}
Al[a]	0.000276	−12,511
Li[b]	0.000162	−4917
Zn[c]	0.000394	−13,497

[a] Data taken from Ref. [27].
[b] Data taken from Ref. [28].
[c] Data taken from Ref. [21].

in the literature, in principle, those elaborated by Guo et al. [12] and Trybula et al. [13], while the second one is limited to binary ones. Mentioned parameters of the Redlich-Kister polynomial (Eqs. (7 - 9)) for the binaries and ternaries are collected in Table 5.

The viscosity isotherm data computed at 973 K, using Kozlov-Romanov-Petrov [22], Kaptay [23] and Gasior [5] thermodynamics-based viscosity models, are compiled in Table 6 and confronted with the experimental results (second column in Table 6). Two important notes can be made for computed viscosity values which appropriately support the aforementioned experimental data. Basically, both variants used consistently reproduce the experiment, however each of them needs to be analysed separately to clarify the importance of ternary effects.

For the first, as it was applied KRP and Kaptay viscosity models for regular solution and their extension on ternary systems, underestimation of experiment has been found contrary to Gasior's model significantly overestimating the measured data in case of regular solution and using ternary interaction parameters devised by Guo et al. [12] Since the new proposition for ternary interaction parameters, developed by Trybula et al. [13], was employed, it can be easily seen that Gasior model [5] only slightly underestimates and overestimates viscosity data in comparison to a noticeable underestimation obtained from KPR and Kaptay's models. In fact, the values predicted using the Gasior's model (Eq. (9)), are smaller than the experimental data in case of the liquid Al₅Li₃Zn and Al₂₈Li₂₆Zn₂₇ alloys and higher for the third composition examined (AlLiZn₃). Despite this mismatch, they exhibit the best correlation among the three viscosity models applied in this work. The Gasior's model utilizes excess entropy, which is difficult to determine experimentally, whilst it gives the best reflection of the experimental data among the three viscosity models used in this work. It can be seen that KRP's and Kaptay's models give almost the same results with no regard on the variant used in contrary to be an important factor in case of Gasior's model [5]. It significantly differentiates the approximation applied, in particular, remarkably emphasized between two sets of ternary interaction parameters used. Invoking our thermodynamic description performed for the liquid Al-Li-Zn alloys, which also includes mixing enthalpy, a very good correlation between the one computed using the new ternary parameters (compiled in Table 6) and calorimetric data obtained by Kim & Sommer [11] (see Fig. 3 in Ref. [13]) was found and therefore, it is quite surprising to see the aforementioned difference. However, it is important to note a similar observation recently made by Gancarz & Gasior for liquid Sn-Zn-Na alloys that concerns almost perfect agreement between modelled and measured viscosities [17] contrary to present investigations, which found KRP and Kaptay's models to overestimate experiment.

The viscosity values modelled, employing ternary interaction parameters - first variant, are higher than those computed applying regular solution approximation (second variant) and, hence, they are closer to experimental results (second column in Table 6). Such appreciable convergence straightforwardly implies the ternary effect occurrence that might be suggestive of "associates" existence being not strong enough to be directly detected due to weak-coupling of atoms. Any experimental evidence of such remark has not been given yet. One could be brought to mind, in light of the available literature reports, three intermetallic phases had been experimentally detected by Badaeva & Sald'au [15] and, therefore, the viscosity increase with Li addition observed herein results from an energetic stability corresponding to these compounds. An adequate note we had made in the previous experimental and theoretical studies performed on the liquid Al-Li and Li-Zn alloys [10], concerning the presence of associative tendency in comparison to phase separation found in liquid Al-Zn alloys [6,30]. Undoubtedly, it is quite important to point out that Li addition in a

Table 5
Data set of ^mL − interaction parameters, defined by Eq. (10(a)), for liquid binary alloys: Al-Li, Li-Zn and Al-Zn, as well as liquid ternary Al-Li-Zn alloy.

System	^mL-parameters for liquid phase of binaries and ternaries				Ref.
Al-Li	$^0L_{Al-Li} = 44,200 + 20.6 \cdot T$	$^1L_{Al-Li} = 13,600 - 5.3 \cdot T$	$^2L_{Al-Li} = 14,200$	$^3L_{Al-Li} = -12,100$ $^4L_{Al-Li} = -7100$	[35]
Li-Zn	$^0L_{Li-Zn} = 45258.6 + 26.36 \cdot T$	$^1L_{Li-Zn} = 22887.2 - 4.19 \cdot T$	$^2L_{Li-Zn} = -4552.6 + 4.07 \cdot T$	– –	[36]
Al-Zn	$^0L_{Al-Zn} = 10466.6 - 3.39 \cdot T$	–	–	– –	[37]
Al-Li-Zn	$^0L_{Al-Li-Zn} = -50834 + 0.57 \cdot T$	$^1L_{Al-Li-Zn} = 47262.7$	$^2L_{Al-Li-Zn} = -94780.8 - 36.88 \cdot T$	– –	[12]
Al-Li-Zn	$^0L_{Al-Li-Zn} = -7700 - 53 \cdot T$	$^1L_{Al-Li-Zn} = -112,500 - 4 \cdot T$	$^2L_{Al-Li-Zn} = 29,000 - 14 \cdot T$	– –	[13]

Table 6
Comparative analysis of viscosity, including experimental (Expt[+]) and modelled[*] values obtained at 973 K. Regular solution corresponds to binary interactions considered only (first sum in. Eq. (10))[a] and ternary parameters relate to second term in Eq. (10)[b,c]. Experimental values are displayed three times for easier comparison with modelled data.

Alloy	Viscosity of liquid Al-Li-Zn alloys, Pa·s			
	Expt[+]	KRP[*1]	Kap[*2]	Gas[*3]
	Regular solution[a]			
$Al_5Li_3Zn^\#$	0.001642	0.001184	0.001088	0.002145
$Al_{28}Li_{26}Zn_{27}^\#$	0.001881	0.001345	0.001263	0.002635
$AlLiZn_3^\#$	0.002074	0.001725	0.001611	0.003031
	Ternary parameters[b]			
$Al_5Li_3Zn^\#$	0.001642	0.001310	0.001148	0.001474
$Al_{28}Li_{26}Zn_{27}^\#$	0.001881	0.001554	0.001351	0.001558
$AlLiZn_3^\#$	0.002074	0.001788	0.001672	0.002314
	Ternary parameters[c]			
$Al_5Li_3Zn^\#$	0.001642	0.001280	0.001128	0.002068
$Al_{28}Li_{26}Zn_{27}^\#$	0.001881	0.001654	0.001390	0.002108
$AlLiZn_3^\#$	0.002074	0.002167	0.001791	0.002234

\# Al-Li-Zn alloys' compositions − listed in Table 1.
+ Data determined in this work (see Table 3).
* Modelled viscosities employing Kozlov-Romanov-Petrov's (*1, KRP [22]), Kaptay's (*2, Kap [23]) and Gasior's (*3, Gas [5]) models.
a $^mL_{Al-Li}$, $^mL_{Li-Zn}$ and $^mL_{Al-Zn}$ taken these from Refs [35], [36] and [37], respectively.
b $^mL_{123}$ taken these of Trybula et al. [13] (see Table 5).
c $^mL_{123}$ taken these of Guo et al. [12] (see Table 5).

relevant amount (listed in Table 1) allows to find the change in mixing behaviour. An important observation made very recently by Gancarz, investigating eutectic Al-Zn alloys with Li content up to 8 at.%, which entirely agrees with the ones made in this work (results to be published). The last point of the present discussion on viscosity modelled relates to the linear viscosity trend observed, the least and highest viscosity values are found for Al_5Li_3Zn and $AlLiZn_3$ ternary alloys plotted in the Gibbs triangle (Fig. 7), correspondingly.

3.3. Surface tension

Surface tension values, both measured (points) and computed (solid lines) using parameters of linear equation ($\sigma = A + B \cdot T$, $N \cdot m^{-1}$), collected in Table 7, are graphically presented in Fig. 8. Upper panel relates to liquid binary Al-Zn alloys and bottom one corresponds to the ternaries investigated in this work. As a result, we found the surface tension decrease with increasing temperature and Zn-content in liquid binary Al-Zn alloys. Consequently, the relatively good correspondence of the fitted lines to experimental points can be seen, and also a small deviation from the linearly dependent surface tension manifested by the liquid $Al_{28}Li_{26}Zn_{27}$ and $AlLiZn_3$ alloys, in principle, the most pronounced one has been recorded for the $Al_{28}Li_{26}Zn_{27}$ alloy.

Surface isotherm at 973 K as a function of Zn content of liquid Al-Zn alloys investigated in this work (black squares) and those examined by Goicoechea et al. [4] (red stars) are plotted in Fig. 9. A slight mismatch between the present and literature data was found

in comparison to a significant one for viscosity discussed above. Both surface tension results, plotted in Fig. 9, demonstrate its decrease with increasing Zn content, however much pronounced decrease demonstrates Goicoecha et al. [4] data in contrast to results determined in this work. Apart from this, surface tension of pure Al is lower than Goicoecha measured that could result from Al surface oxidation.

Three dimensional representation of surface tension isotherm at 973 K is illustrated in Fig. 10, which includes three ternary Al-Li-Zn alloys, three reference binary liquid alloys and pure metals. Two distinct features can be easily read from Fig. 10 which we would discuss with regard to the contributions given above.

The first relates to liquid Al-Zn alloys, namely the slight surface tension decrease with increasing Zn-content (lowering X_{Al}/X_{Zn} molar ratio) has been measured that results from lower surface tension value of pure Zn compared to pure Al. It needs to be noted for data collected in Tables 2 and 3, concerning liquid Al-Zn alloys' properties, both density and viscosity demonstrate an increase with Zn content growth of liquid Al-Zn alloys contrary to the decrease found in the case of surface tension. Principally, the monitored surface tension trend, the linear decrease is compatible with expected one. An adequate note has also been made by Gancarz & Gasior for Sn-Zn-Na liquid alloys [17] as well as that found by Gancarz for eutectic Al-Zn alloy composition with Li addition (results to be published).

The second remark concerns the analysis of Li addition influence on surface tension of the liquid ternaries investigated. Hence, lithium addition results in a surface tension decrease due to its lowest surface tension value out of the three components of the Al-Li-Zn alloy. It is interesting to point out the surface tension change found within three liquid ternary alloys - a slight drop in surface tension towards $Al_{28}Li_{26}Zn_{27}$ ternary alloy has been observed.

Butler's formulation for surface tension modelling, in the form of Eq. (14(a−c)), has been applied for liquid ternaries. For surface tension calculation, two variants were employed adequate to those used for viscosity studies. The first one includes two sets of ternary interaction parameters, "ternary1" and "ternary2" stand in Table 8 for parameters developed by Trybula et al. [13] and Guo et al. [12], respectively. Whereas the second variant considers only the binary ones. Both data sets of employed interaction parameters are gathered in Table 5, and the modelled surface tension values are collected in Table 8 including experimental ones at 973 K (second column). Surface tension values of pure elements i.e. Al, Li and Zn, were taken as follows,

$$\sigma_{Al} = 1036.1 - 0.17745 \cdot T$$
$$\sigma_{Li} = 467.9 - 0.15 \cdot T$$
$$\sigma_{Zn} = 1018.1383 - 0.2854 \cdot T$$

from Refs. [27], [28] and [21], respectively.

Analysis of the modelled surface tension, utilizing the two variants mentioned above, allowed to see two distinct features, concerning correlation between experimental and modelled data. In correspondence to the first, it has been found the underestimated

Table 7
Coefficients and their errors[a] of linear temperature dependence of surface tension ($\sigma = \mathbf{A} + \mathbf{B} \cdot \mathbf{T}$) measured for liquid binary Al-Zn and ternary Al-Li-Zn alloys as a function of temperature. The last two columns present surface tension values and its errors[b] computed at 973 K.[c]

T − range/K	Surface tension of liquid Al-Zn alloys						
	X_{Zn}	A/N·m^{-1}	u(A)	B/N·m^{-1}·T^{-1}	u(B)	$\sigma(973)$/N·m^{-1}	U(σ)
923−1023	0.17	1.0600	0.00337	−0.000218	0.000003	0.84788	0.00026
873−1023	0.49	1.0371	0.00596	−0.000236	0.000006	0.80747	0.00085
873−1023	0.75	1.0206	0.01360	−0.000250	0.000014	0.77675	0.00175

T − range/K	Surface tension of liquid Al-Li-Zn alloys						
	X_{Li}	X_{Zn}	A/N·m^{-1}	u(A)	B/N·m^{-1}·T^{-1}	u(B)	$\sigma(973)$/N·m^{-1}	U(σ)
923−1023	0.33	0.11	1.1688	0.00090	−0.000510	0.000009	0.67177	0.00159
823−1023	0.32	0.33	1.1796	0.03403	−0.000535	0.000038	0.65844	0.00543
853−1023	0.20	0.60	1.0290	0.00970	−0.000340	0.000010	0.69818	0.00200

[a] Estimated from linear regression error as implemented in Grapher Softaware Package.

[b] Estimated from difference computed between experimental and calculated from linear surface tension fit, $u\ (m) = \frac{1}{N}\sum_{i=1}^{N}|m^{exp} - m^{fit}|$, where N is number of experimental points (i.e. for $Al_{83}Zn_{17}$ and Al_5Li_3Zn alloy N = 3, whereas for remaining binary and ternary alloys N is equal to 4) and the combined expanded uncertainty U(σ) (0.95 level of confidence with k = 2).

[c] Standard uncertainties u are u(T) = 1 K, u(p) = 0.1 kPa at atmospheric pressure p = 0.1 MPa, u(X) = 0.005 for and Zn, whereas u(X) = 0.01 for Li.
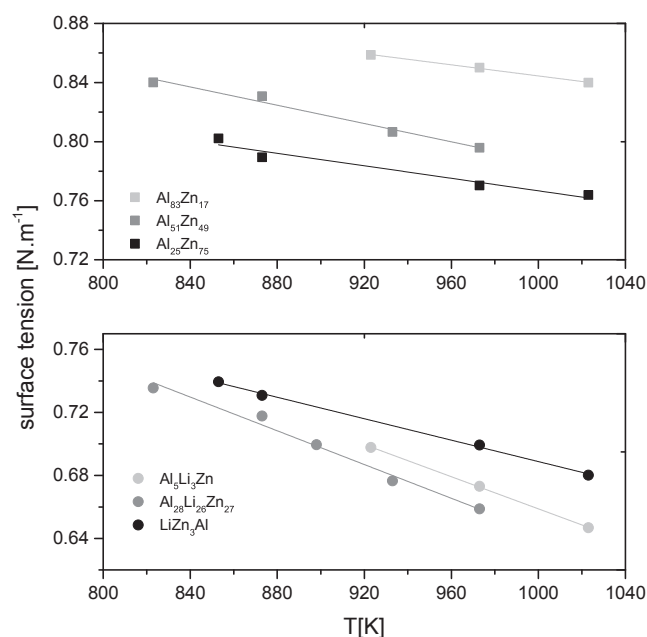

Fig. 8. Surface tension measured and computed using linear temperature dependence of liquid binary Al-Zn (upper panel) and ternary Al-Li-Zn (bottom panel). Coloured squares and balls represent binaries and ternaries investigated.

Fig. 9. Surface tension isotherm at 973 K: for measured data in this work (black squares, ■) and determined by Goicoechea et al. [4] (Expt, ✳). ● and ▲ correspond to pure Al and Zn taken from Refs. [27] and [21], respectively. Error bars for present data are also included.

experimental surface tension by regular solution approximation (first sum in Eq. (10) − second variant used) and using ternary interaction parameters of Trybula et al. [13]. Whereas, a slightly overestimated one can be seen employing Guo et al. [12] ternary interaction parameters. In fact, each of the variants used, gave the same trend in surface tension change, namely it is increasing through AlLiZn$_3$ ternary alloy. However, regular solution approximation (third column in Table 8) and Trybula's parameters allowed to observe a drop in surface tension towards $Al_{28}Li_{26}Zn_{27}$ alloy, much remarkable for latter compared to its disappearance in the case of Guo's parameters usage. Invoking the surface tension data collected in Table 7 for binary Al-Zn alloys, it can be concluded, apart from the recorded mismatch between models and experiment, that the observed trend in modelled surface tension change is correct. Principally, lithium addition should substantially reduce surface tension as has been found in this work and also Gancarz observed for the eutectic Al-Zn liquid alloy with Li addition up to 8 at.%.
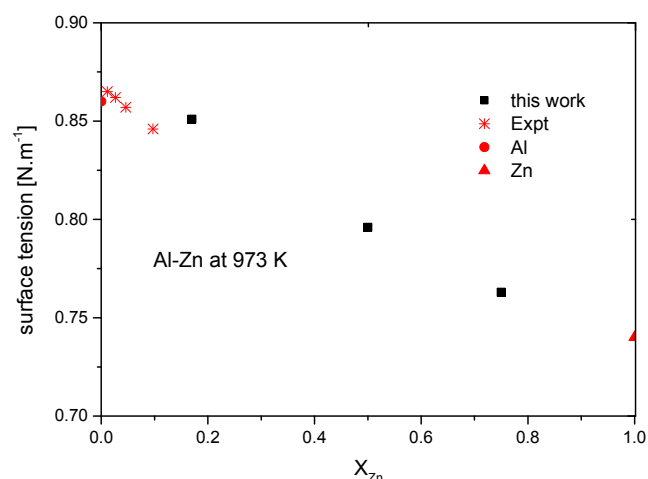
With regard to the discussion on presented above, both density and viscosity are changing linearly with increasing Li and Zn content, through ternaries investigated, in comparison to a slight drop found for surface tension in the liquid ternary Al-Li-Zn alloys. Whilst we could expect a deviation for the $Al_{28}Li_{26}Zn_{27}$ alloy composition as it is demonstrated by the present surface tension studies. Density and viscosity are bulk properties in contrast to surface tension being a surface one, therefore the atomic interactions in the bulk phase differ from those on the surface due to the existence of unsaturated chemical bonding of surface atoms. This consideration requires to be assisted by atomistic calculations which are beyond the scope of present contribution.

4. Summary

We have examined the influence of Li addition to Al-Zn based alloys on thermophysics of three ternary alloys, whose compositions correspond to atomic concentration of experimentally determined intermetallic phases occurring in the solid state of Al-Li-Zn system. Particularly, density, surface tension and viscosity of liquid binary Al-Zn and ternary Al-Li-Zn alloys have been determined by means of draining crucible method. Performed
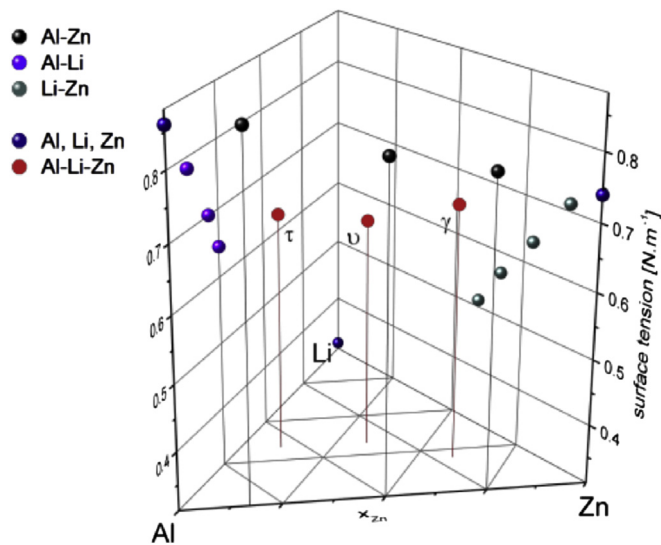
Fig. 10. Three-dimensional representation of surface tension isotherm at 973 K: black balls (●) — Al-Zn alloys. Dark blue balls (●) — pure liquid metals (Al [27], Li [28] and Zn [21]), violet (●) and blue (●) balls correspond to densities of Al-Li and Li-Zn alloys, taken from Refs. [10], respectively. Red balls (●) — represent τ(Al$_5$Li$_3$Zn), υ(Al$_{28}$Li$_{26}$Zn$_{27}$) and γ(AlLiZn$_3$) ternary alloys investigated in this work. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 8
Comparative analysis of surface tension, including experimental (Expt)+ and modelled values obtained at 973 K "binary" denotes regular solution approximation used (first sum in Eq. (10))[a], "ternary" corresponds to ternary interaction parameters[b,c] consideration into Eq. (10).

Alloys	Surface tension of liquid Al-Li-Zn alloys, N·m^{-1}			
	Expt+	Butler model*		
		binary[a]	ternary1[b]	ternary2[c]
Al$_5$Li$_3$Zn[#]	0.67177	0.58730	0.65260	0.61660
Al$_{28}$Li$_{26}$Zn$_{27}^{\#}$	0.65844	0.57400	0.61170	0.67700
AlLiZn$_3^{\#}$	0.69818	0.62800	0.67750	0.70130

[#] Al-Li-Zn alloys' compositions — listed in Table 1.
+ Data determined in this work (see Table 7).
* Modelled surface tension employing Bultler's model [18].
[a] ^{m}L$_{Al-Li}$, ^{m}L$_{Li-Zn}$ and ^{m}L$_{Al-Zn}$ taken as these from Refs [35], [36] and [37], respectively.
[b] ^{m}L$_{123}$ taken these of Trybula et al. Ref. [13] (see Table 5).
[c] ^{m}L$_{123}$ taken these of Guo et al. Ref. [12] (see Table 5).

experimental studies for these three thermophysical properties are confronted with modelled data obtained in this work.

Basically, very good agreement between determined in this work and available experimental data for liquid binary Al-Zn alloys has been found for density and surface tension compared to viscosity demonstrating much pronounced inconsistence. Consequently, the linear changes in the three thermophysical properties investigated, namely the increase in density and viscosity Al-Zn alongside of Gibbs triangle, while the decrease has been found for surface tension.

Experimental data for ternary alloys, i.e. Al$_5$Li$_3$Zn, Al$_{28}$Li$_{26}$Zn$_{27}$, AlLiZn$_3$ demonstrate the decrease in density and surface tension in comparison to the viscosity increase since Zn content is increasing. With regard to complete properties' isotherms examined at 973 K, nonlinear changes have been found for each thermophysical property measured since their analysis is started from Al-Li liquid alloys through ternaries towards Li-Zn alloys. In case of surface tension a slight drop towards Al$_{28}$Li$_{26}$Zn$_{27}$ has been found.

Two variants used for modelling studies revealed the

importance of ternary interaction parameters in viscosity estimation, using three best thermodynamics-based models, which could suggest the existence of a ternary effect related to an associate forming tendency, previously found in liquid Al-Li and Li-Zn alloys. Particularly, Gasior model applied, employing ternary interaction parameters developed by Trybula et al. [13], gave almost perfect reflection of the data measured compared to more pronounced scatter recorded for Kozlov-Romanov-Petrov's [22] and Kaptay's [23] models. An adequate importance of ternary parameters in surface tension assessment has also been observed. Basically, the slight drop in surface tension towards Al$_{28}$Li$_{26}$Zn$_{27}$ has been reproduced using regular solution approximation and Trybula et al. [13] ternary interaction parameters since the latter gave much more consistent agreement with data measured.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.fluid.2016.03.013.

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