Sound Velocity and Adiabatic Compressibility of Molten MCl + $NdCl_3$ Mixtures (M = Li, Na, K, and Cs)[†]

Vladimir I. Minchenko, Vladimir A. Khokhlov,* and Anna O. Kodintseva

Molten Salts Laboratory, Institute of High-Temperature Electrochemistry, Russian Academy of Sciences,
620219, Ekaterinburg, S. Kovalevskaya 22, Russia

New experimental data on the sound velocity and adiabatic compressibility of molten neodymium trichloride and its binary mixtures containing lithium, sodium, potassium, and cesium chlorides as a function of temperature and composition are reported. It is shown that the relative deviations of sound velocity and adiabatic compressibility of mixtures from their magnitudes inherent to hypothetical ideal solutions vary with ionic potentials of the alkali metal cations.

Introduction

Today there is a great body of experimental data on the temperature and concentration dependencies of the sound velocity and adiabatic compressibility of molten salt mixtures containing alkali and some alkaline-earth chlorides.[1] The properties of rare-earth-bearing salt melts have not been studied excluding our research concerned with molten MCl + $LaCl_3$ mixtures.[2,3] The reason is that experimental difficulties arise due to the complexity of preparing pure rare-earth trichlorides free of oxides or oxychlorides and high operating temperatures. Among other things, there is the necessity to obtain new data on the sound velocity in molten salt mixtures involving lanthanide compounds to improve our understanding of the structural peculiarities of MCl + $LnCl_3$ melts. Moreover, at present, sound velocity measurements are the only workable way to obtain trustworthy adiabatic compressibility values of molten salts and their mixtures at elevated temperatures.

We report here the sound velocities and adiabatic compressibilities of molten neodymium trichloride and its binary mixtures with alkali chlorides and discuss their temperature and concentration dependencies.

Experimental Section

Sound velocity (u) was measured by the direct pulse method using the original device developed in the Institute of High-Temperature Electrochemistry.[4] Special features of this device are the usage of sintered beryllium oxide and monocrystalline tungsten sound conductors that are inert to the molten salts studied as well as exact temperature control of the salt specimen. The measurements were made at an ultrasonic frequency of 5 kHz.

The ultrasonic velocity was calculated as

$$u = (x - x_0)/(t - t_0) \qquad (1)$$

where $(x - x_0)$ is the thickness of the salt gap between the inducing and receiving sound conductors and $(t - t_0)$ is the sound transmission time. The uncertainty of the sound velocity measurements which includes all sources of uncertainty did not exceed 0.5 %.

The chemically pure alkali chlorides (commercially produced) were carefully dried under vacuum at 550 K and melted. Then they were subjected to double zone recrystallization and cooled. The salts so prepared were stored in desiccators. Anhydrous neodymium trichloride was synthesized by treating high chemically pure Nd_2O_3 (commercially produced) by carbon tetrachloride vapors at 980 K. The $NdCl_3$ obtained was fused and placed into a desiccator filled with a dried inert gas (argon). All working operations associated with weighing and loading salts into platinum crucibles were performed in a glovebox under a nitrogen atmosphere.

Results and Discussion

The sound velocity u in molten neodymium trichloride and its binary mixtures with lithium, sodium, potassium, and cesium chlorides was measured over the temperature range of (900 to 1250) K. In all instances, the sound velocity diminishes as the temperature increases according to the linear equation

$$u = u_o + aT \pm \Delta u \qquad (2)$$

where u_o and a are the constants computed by the least-squares method, while Δu is the experimental data dispersion. These latter values are listed in Table 1 along with the operating temperature ranges ΔT.

As an example, the sound velocity isotherms at 1100 K are shown in Figure 1. It is seen that remarkable negative deviations of sound velocity from its additive values are observed for all salt mixtures under study which decrease in passing from the LiCl + $NdCl_3$ system to CsCl + $NdCl_3$.

The adiabatic compressibility of MCl + $NdCl_3$ molten mixtures was calculated using the sound velocities measured and available data on density[5,6] by the equation $\beta_s = u^{-2}\rho^{-1}$ over the same temperature ranges. For all melts, the temperature

---

[†] Part of the "Sir John S. Rowlinson Festschrift".

* Corresponding author. E-mail: v.khokhlov@ihte.uran.ru.

10.1021/je100554g

Table 1. Sound Velocity ($m \cdot s^{-1}$) in MCl + $NdCl_3$ Melts

melt composition	ΔT	u_o	$-a$	$\pm \Delta u$
mol fraction	K	$m \cdot s^{-1}$	$m \cdot s^{-1} \cdot K^{-1}$	$m \cdot s^{-1}$
	LiCl + $NdCl_3$			
LiCl	900 to 1150	2800	0.852	3
0.50 $NdCl_3$ + 0.50 LiCl	990 to 1170	1795	0.405	5
$NdCl_3$	1045 to 1218	1626	0.360	8
	NaCl + $NdCl_3$			
NaCl	1090 to 1190	2601	0.799	2
0.20 $NdCl_3$ + 0.80 NaCl	1053 to 1173	2343	0.783	11
0.365 $NdCl_3$ + 0.635 NaCl	1009 to 1175	2088	0.643	11
0.44 $NdCl_3$ + 0.56 NaCl	1090 to 1150	1998	0.596	5
0.75 $NdCl_3$ + 0.25 NaCl	1063 to 1176	1757	0.441	2
	KCl + $NdCl_3$			
KCl	1080 to 1230	2508	0.880	1
0.25 $NdCl_3$ + 0.75 KCl	1058 to 1213	2318	0.894	5
0.37 $NdCl_3$ + 0.63 KCl	1053 to 1188	1929	0.615	5
0.50 $NdCl_3$ + 0.50 KCl	1063 to 1203	1813	0.522	4
0.75 $NdCl_3$ + 0.25 KCl	1107 to 1163	1764	0.487	2
	CsCl + $NdCl_3$			
CsCl	1050 to 1200	1750	0.660	1
0.25 $NdCl_3$ + 0.75 CsCl	1150 to 1250	1372	0.352	1
0.45 $NdCl_3$ + 0.55 CsCl	900 to 1140	1632	0.572	2
0.80 $NdCl_3$ + 0.20 CsCl	1000 to 1150	1805	0.604	3

Table 2. Adiabatic Compressibility (Pa^{-1}) of MCl + $NdCl_3$ Melts

melt composition	$\beta_0 \cdot 10^{11}$	$\beta_1 \cdot 10^{14}$	$\beta_2 \cdot 10^{17}$
mol fraction	Pa^{-1}	$Pa^{-1} \cdot T^{-1}$	$Pa^{-1} \cdot T^{-2}$
	LiCl + $NdCl_3$		
LiCl	17.48	−19.90	20.60
0.5 $NdCl_3$ + 0.5 LiCl	13.035	−3.42	9.27
$NdCl_3$	15.292	−7.792	11.012
	NaCl + $NdCl_3$		
NaCl	29.290	−41.00	31.230
0.20 $NdCl_3$ + 0.80 NaCl	25.426	−37.495	30.952
0.365 $NdCl_3$ + 0.635 NaCl	20.598	−24.402	22.946
0.44 $NdCl_3$ + 0.56 NaCl	18.103	−17.523	18.750
0.75 $NdCl_3$ + 0.25 NaCl	14.742	−8.752	12.788
	KCl + $NdCl_3$		
KCl	39.876	−64,357	48.89
0.25 $NdCl_3$ + 0.75 KCl	52.138	−92.538	63.87
0.37 $NdCl_3$ + 0.63 KCl	25.212	−27.643	27.33
0.5 $NdCl_3$ + 0.5 KCl	22.121	−22.115	23.13
0.75 $NdCl_3$ + 0.25 KCl	18.143	−15.737	17.94
	CsCl + $NdCl_3$		
CsCl	48.0	−82.9	65.9
0.25 $NdCl_3$ + 0.75 CsCl	35.276	−34.31	33.9
0.45 $NdCl_3$ + 0.55 CsCl	30.328	−41.29	42
0.8 $NdCl_3$ + 0.2 CsCl	22.071	−26.91	27.1

dependency of the adiabatic compressibility may be well described by polynomial equations as follows

$$\beta_s = \beta_0 + \beta_1 T + \beta_2 T^2 \tag{3}$$

The β_0, β_1, and β_2 coefficients of this expression are listed in Table 2.

The concentration dependencies of adiabatic compressibility at 1100 K are plotted in Figure 2. The positive deviations of adiabatic compressibility from its additive values are observed, which increase in going from LiCl + $NdCl_3$ melts to CsCl + $NdCl_3$ melts.

As for sound velocity, the departures reflect qualitatively the weakening counteraction of alkali metal cations on the strong bond of Nd^{3+} with Cl^- in the $NdCl_n^{(n-3)-}$ complex anions[7] as the ion potential μ_i ($\mu_i = z_i e r_i^{-1}$, where e is the elementary electric charge and z_i and r_i are the formal oxidation number and cation radius, respectively) decreases from Li^+ to Cs^+.

This regularity is best demonstrated by concentration changes of the relative departures of sound velocity ($\Delta u/u_{id}$) and adiabatic compressibility ($\Delta \beta_s/\beta_{id}$) from their values inherent to a hypothetical ideal solution (Figure 3), u_{id} and β_{id} being calculated with the following formulas[8,9]

$$u_{id} = (n_1/u_1 + n_2/u_2)^{-1} \tag{4}$$

$$\beta_{sid} = n_1 \beta_{s1} + n_2 \beta_{s2} \tag{5}$$

Here, u_1, u_2 and β_{s1}, β_{s2} are the sound velocity and adiabatic compressibility of molten individual components, respectively, while n_1 and n_2 are their volume fractions in the salt mixtures.

The absolute values of the deviations decrease with rising ion potential of alkali metal cations. This correlation is clearly visible in Figure 4 where dependencies of maximum relative deviations of sound velocity and adiabatic compressibility vs the inverse cation radii[10] are plotted.

The regular trends of changing concentration dependencies of sound velocity and adiabatic compressibility found are adequately described in the terms of the complexing model in halide melts containing salts of alkali, alkaline-earth, and rare-earth metals[11] corroborated by the results of X-ray diffraction,[12] Raman spectroscopy,[13] thermodynamics of mixing,[14,15] and

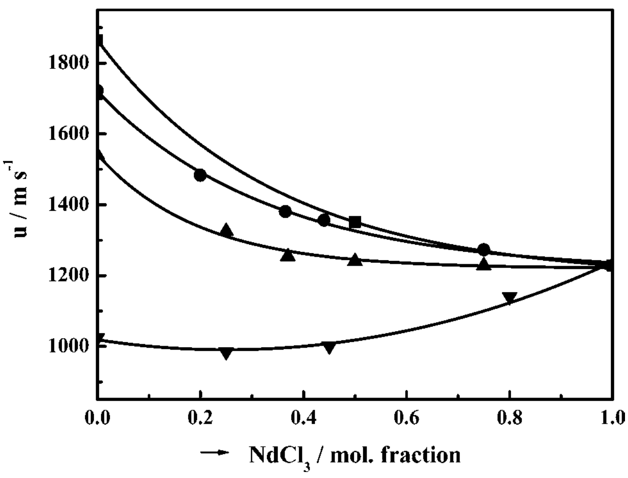

Figure 1. Isotherms of sound velocity in molten ■, LiCl + $NdCl_3$; ●, NaCl + $NdCl_3$; ▲, KCl + $NdCl_3$; and ▼, CsCl + $NdCl_3$ mixtures at 1100 K.

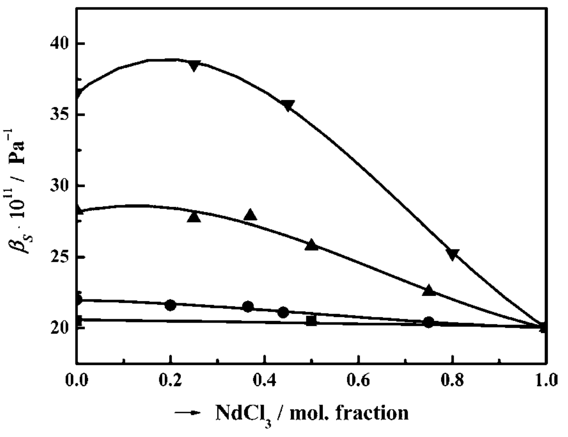

Figure 2. Isotherms of adiabatic compressibility of molten ■, LiCl + $NdCl_3$; ●, NaCl + $NdCl_3$; ▲, KCl + $NdCl_3$; and ▼, CsCl + $NdCl_3$ mixtures at 1100 K.

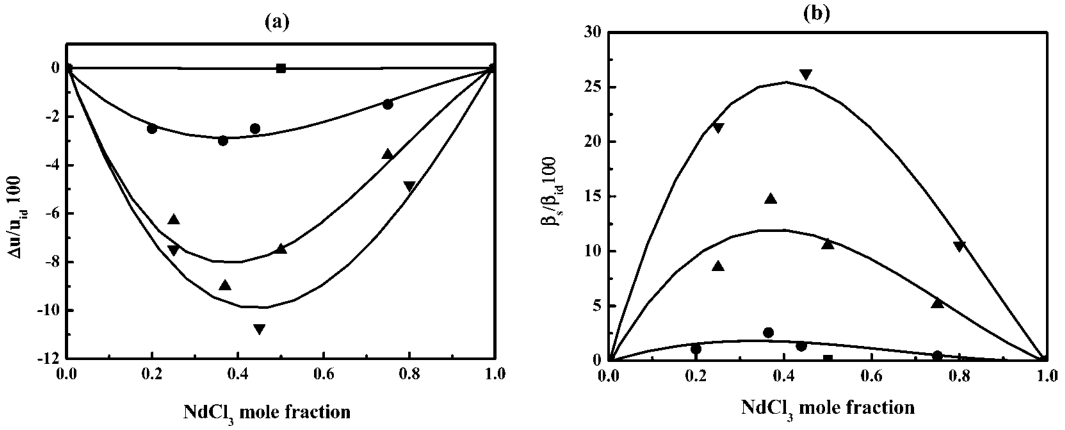

Figure 3. Relative deviations of the sound velocity (a) and adiabatic compressibility (b) of molten ■, LiCl + $NdCl_3$; ●, NaCl + $NdCl_3$; ▲, KCl + $NdCl_3$; and ▼, CsCl + $NdCl_3$ mixtures from their values inherent to hypothetic ideal solutions at 1100 K.

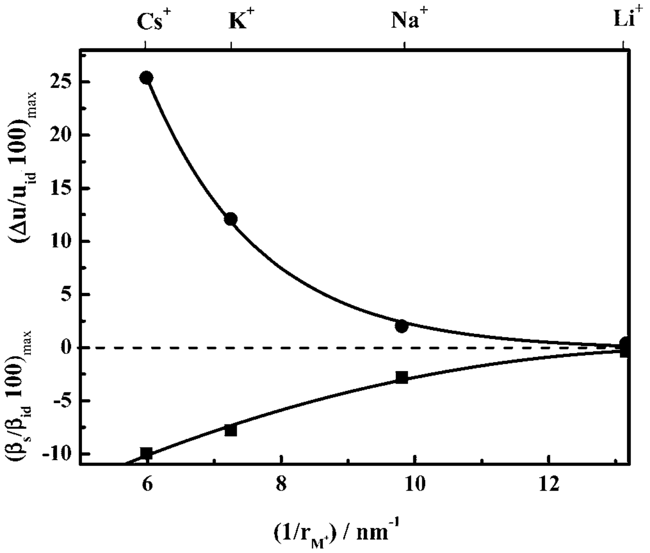

Figure 4. Correlation between maximum deviations of ■, sound velocity and ●, adiabatic compressibility in molten MCl−$NdCl_3$ mixtures at 1100 K and reverse radii of alkali cations.

molecular dynamics[16] analysis. Indeed, while dissolving trichloride neodymium in molten alkali chloride, the $NdCl_6^{3-}$ complex ions form which are surrounded by alkali metals cations.

As the ion potential μ_i decreases as $Li^+ > Na^+ > K^+ > Cs^+$, the Ln−Cl bond elasticity and intensity of stretching vibration band increase, while the distance between the complexing ion (Ln^{3+}) and addend (Cl^-) reduces.[16,17] This leads to diminishing sound velocity with regard to its values for salt mixtures when there is no interaction between components. One would expect that local structure compacting had to result in a relative reduction of adiabatic compressibility of mixed melt too. However, as is evident from the density measurements of melts under study and (MCL + $LnCl_3$) melts investigated earlier,[1] decreasing bond length Nd−Cl in the complex particle is less than the increasing distance $M^+{-}LnCl_6^{3-}$. The difference between them rises progressively passing from $LnCl_3$ + LiCl melts to $LnCl_3$ + CsCl melts. This clearly demonstrates growing structure loosening with a decrease in M^+ ionic potential results in a build up of excess adiabatic compressibility of $NdCl_3$ + MCl mixtures relative to its "ideal" value. Similar regularity was observed for molten $LaCl_3$ + MCl mixtures.[2,3]

Conclusions

From the original experimental data on sound velocity and adiabatic compressibility of molten $NdCl_3$ + MCl (M = Li, Na, K, and Cs) mixtures, correlations between their relative deviations from "ideal" characteristics have been found. The regular trends observed are directly associated to structure transformations caused by interaction between salt components.

Supporting Information Available:

Additional experimental data. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Minchenko, V. I.; Stepanov, V. P. *Ionic melts: elastic and caloric properties*; UB RAS: Ekaterinburg, 2008.
(2) Minchenko, V. I.; Korzun, I. V.; Khokhlov, V. A.; Vinogradov-Zhabrov, S. O. Ultrasonic velocity, inner pressure and heat capacity of $LaCl_3$-RbCl melts. *Melts* **2001**, *2*, 28–33.
(3) Minchenko, V. I.; Korzun, I. V.; Khokhlov, V. A.; Vinogradov-Zhabrov, S. O. Ultrasonic velocity, heat capacity and inner pressure of $LaCl_3$-LiCl melts. *Melts* **2001**, *4*, 33–37.
(4) Smirnov, M. V.; Minchenko, V. I.; Bukharov, A. N. Sound absorption in molten alkali chlorides, bromides, iodides and their mixtures. *Electrochim. Acta* **1988**, *33*, 213–220.
(5) Mochinaga, J.; Igarachi, K. Densities and molar volumes of molten binary $PrCl_3$-KCl, $PrCl_3$-NaCl, $PrCl_3$-$CaCl_2$, $NdCl_3$-KCl, $NdCl_3$-KCl, $NdCl_3$-$CaCl_2$ systems. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 713–714.
(6) Vogel, G.; Schneider, A. Chemie der seltenen Erden in geschmolzenen Alkalihalogeniden. X. Schmelzen von Alkalichloriden mit Neodimchlorid und Gadoliniumchlorid. *Z. Anorg. Allg. Chem.* **1972**, *388*, 97–104.
(7) Chrissanthopoulos, A.; Papatheodorou, G. N. Temperature dependence of the f←f hypersensitive transitions of Ho^{3+} and Nd^{3+} in molten salt solvents and the structure of the $LaCl_3$-KCl melts. *J. Mol. Struct.* **2006**, *782*, 130–142.
(8) Sternberg, S.; Vasilescu, V. Ultrasonic velocity and compressibility and excess volume of molten salts: NaCl + (Li, K, Rb, Cs) Cl. *Rev. Roum. Chim.* **1970**, *15*, 1665–1673.
(9) Minchenko, V. I.; Smirnov, M. V. Sound velocity in molten alkali halides and their ideal mixtures. *Melts* **1994**, *2*, 42–48.
(10) Shannon, R. D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.* **1976**, *A 32*, 751–767.
(11) Smirnov, M. V. *Electrode potentials in molten chlorides*; Nauka: Moscow, 1973.
(12) Matsumiya, M.; Takagi, R. A Molecular Dynamics simulation of the electric and thermodynamic properties in molten ($Nd_{1/3}$, Na or K)Cl mixtures. *Z. Naturforsch.* **2001**, *56a*, 466–472.
(13) Photiadis, G. M.; Brresen, B.; Papatheodorou, G. N. Vibrational modes and structures of lanthanide halide-alkali halide binary melts $LnBr_3$-KBr (Ln=La, Nd, Gd) and $NdCl_3$-ACl (A=Li, Na, K, Cs). *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 2605–2613.

(14) Gaune-Escard, M.; Bogacz, A.; Rycerz, L.; Szczepaniak, W. Calorimetric investigation of $NdCl_3$-MCl liquid mixtures (where M is Na, K, Rb, Cs). *Thermochim. Acta* **1994**, *236*, 67–80.
(15) Gaune-Escard, M.; Rycerz, L.; Hoch, M. Analysis of the enthalpy of mixing data of binary and ternary {Rare Earth (Dy, Nd, Pr, Tb) - Alkali metal} halide systems. *J. Mol. Liq.* **1999**, *83*, 83–94.
(16) Glover, W. J.; Madden, P. A. Raman spectra of ionic liquids: A simulation study of $LaCl_3$ and its mixtures with alkali chlorides. *J. Chem. Phys.* **2004**, *121*, 7293–7303.
(17) Iwadate, Y.; Yamoto, H.; Fukushima, K. Structural analysis of molten samarium trichloride - alkali chloride by Raman spectroscopy and Molecular Dynamics calculation. *Molten Salt Forum* **1998**, *5*—*6*, 193–196.

Received for review June 2, 2010. Accepted September 3, 2010.

JE100554G