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Estimation of Thermodynamic Properties of Pure Molten Salts- Alkali Metal Halides

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Abstract: Keeping in view the importance of ionic liquids in science and industry we have undertaken the present work, Using the experimental sound velocity (u) and density (ρ) data, the adiabatic compressibility (β_s), internal pressure (P_i), Gruneisen parameter (Γ), available volume (V_a) and free valume (V_f) of four ionic liquids NaCl, NaBr, KBr and KCl were calculated at three different temperatures (1073 K, 1173 K and 1273 K). The experimental values of u and ρ were taken from literature. The results are discussed critically.

Keywords: Adiabatic compressibility, sound velocity , internal pressure , heat capacities ratio , available volume , free volume ,Gruneisen parameter.

1. Introduction

In view of numerous applications of molten salts[1,2] , we are making an attempt to calculate some of the thermodynamic properties of four alkali metal halide molten salts using sound velocity and density data[3]. These data are available at different temperatures. It has been stated earlier that sound velocity and density data are found to the most powerful tools for estimating a number of useful and important thermodynamic properties of liquid systems. Some of the properties e.g. adiabatic compressibility, Gruneisen

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parameter, intermolecular free length, Debey temperature and non-linearity parameter are not easily accessible by other methods, and can be deduced from the experimental values of sound velocity and density. The instruments required are quite cheap and procedures are quite simple, as well as quite accurate values are obtained. With this aim, we are presenting the results of calculation of adiabatic compressibility (β_s), sound velocity (u), internal pressure (P_i), heat capacities ratio (γ), available volume (V_a), free volume (V_f) and Gruneisen parameter (Γ) of four alkali metal halide molten salts (NaCl, NaBr, KBr and KCl) at 1073^0K, 1173^0K and 1273^0K. In order to test the procedure of using sound velocity as an instrumental property for estimating the thermodynamic properties, an attempt is being made here to calculate indirectly the value of u from the experimental data[3] of, V, $\square_T$, $\square$, C_P and C_v. The calculated values, thus obtained, are compared with the observed u.

Theoretical

Adiabatic compressibility β_s is obtained from the well known thermodynamic relation

(1) $$\beta_S = \beta_T - \frac{\alpha^2 TV}{C_P} \quad .$$

Ultrasonic velocity, internal pressure and Gruneisen parameter are obtained from the following equations:

(2) $$u = \sqrt{\frac{V}{\beta_S M}}$$

(3) $$P_i = \frac{\alpha T}{\beta_T}$$

$$\Gamma = \frac{\gamma - 1}{\alpha T} \tag{4}$$

Simultaneously available volume is calculated from the following equation[4]

$$V_{.a} = V\left(1 - \frac{u}{u_\infty}\right) \tag{5}$$

Here,

V_a = Available volume

V= Molar volume

u_∞ = Sound velocity at infinite frequency and its value is 1600 m s^{-1}.

For the evaluation of free volume, V_f, we have used Eyring relation[5] and Bockris equation[6].

Eyring relation:

$$V_f = V\left(\frac{u_g}{u_j}\right)^3 \tag{6}$$

were u_g is the ultrasonic velocity in vapour and obtained from

$$u_g = \left(\frac{\gamma RT}{M}\right)^{1/2} \tag{7}$$

were all the symbols have their usual notations.

Bockris relation:

$$V_f = \left[\frac{1}{u}\left\{\frac{RT}{2(M_a M_c)^{1/2}}\right\}^{1/2}\right]^3 V \tag{8}$$

here M_a and M_c are respectively the masses of anion and cation in the molten salt.

Hirschfelder-Stevenson-Eyring Equation[7,8]

$$V_f = \frac{\left[bRT/P + P_i\right]}{\left(1/V^2\right)} \quad (9)$$

were b is structural factor which is equal to 2 for simple cubic lattice.

Results and Discussion

Table –1 presents the experimental values of α, β_T, C_P and C_v for four alkali metal halide molten salts at three different temperatures 1073^0K, 1173^0K and 1273^0K. These are the input data needed for the calculations of various properties and taken from the literature[3]. The values of β_S, u, P_i, γ, V_a and Γ are calculated from equations (1), (2), (3), (4) and (5) respectively, and are recorded in Table - 2. Table- 3 enlists the calculated values of free volume, V_f from equations (6), (7), (8) and (9).

Table 1(a) Input data of α and β_T for molten salts

T (K)	V c.c mol^{-1}	β_T $Mbar^{-1}$		αX 10^4 K^{-1}	
		Theo(SST)	Expt	Expt	Theo(SST)
NaCl					
1073	37.60	15.87	28.70	4.47	3.60
1173	38.96	16.45	33.80	3.87	3.70
1273	40.43	18.48	40.00	2.65	3.90
NaBr					
1073	44.02	20.47	33.60	4.61	3.10
1173	45.63	21.57	38.60	4.20	3.20
1273	47.35	24.05	44.90	4.04	3.40
KBr					
1073	37.32	29.39	43.80	5.19	3.80
1173	59.72	32.49	52.10	4.92	3.90
1273	62.33	37.08	62.10	4.83	4.10
KCl					
1073	49.38	22.97	38.40	4.75	3.90
1173	51.28	24.49	45.70	4.65	4.00
1273	53.33	27.38	54.70	4.51	4.20

Table 1(b) Input data of $C_p$and C_v for molten salts

T (K)	V c.c mol^{-1}	C_pX10^{-7} erg mol^{-1}		C_vX10^{-7} erg mol	
		Theo(SST)	Expt	Theo(SST)	Expt
NaCl					
1073	37.60	97.81	66.88	46.94	48.91
1173	38.96	88.20	66.88	46.65	47.65
1273	40.43	64.37	66.88	44.89	47.23
NaBr					
1073	44.02	95.72	63.954	46.65	49.74
1173	45.63	89.45	63.954	45.73	49.32
1273	47.35	86.11	63.954	45.02	48.91
KBr					
1073	37.32	102.83	68.552	46.69	48.49
1173	59.72	97.81	68.552	45.86	48.07
1273	62.33	94.89	68.552	45.23	47.23
KCl					
1073	49.38	102.41	66.88	46.86	46.40
1173	51.28	99.07	66.88	46.02	45.56
1273	53.33	95.71	66.88	45.31	45.14

In Table - 2 two sets of values are given as obtained from two different values of input data reported in Table- 1. Vilcu and Misdolea[3] applied significant structure theory (SST) to four molten halides and calculated the values of β_T, α, C_p and C_v at three different temperatures. They also reported the experimental values of these properties. One set of values reported in Table - 2 are the calculated values obtained from the theoretical values of input data derived from SST by Vilcu and Misdolea. The second set (experimental) of the values of β_S, u, P_i, γ, V_a and Γ are obtained from experimental input data. It is interesting to note that the trend of variation of all the calculated properties (except V_a) with temperature is the same as observed experimentally. The agreement in magnitudes is not very much encouraging. This is due to various approximations involved in the

theoretical methods. At some places the values of V_a comes out to be negative which is due to the lower values of u_∞ then in equation (5). The Gruneisen parameter, Γ can not be determined experimentally. The values reported in the last column of Table- 2 are those obtained from experimental values of α and γ in equation (4).

Table-2(a) Calculated Values of β_s, u and P_i

T K	β_s(Mbar^{-1})		U(ms^{-1})		P_i X 10^3 (Mbar)	
	Theo(SST)	Expt	Theo(SST)	Expt	Theo(SST)	Expt
NaCl						
1073	14.2	20.88	2141.56	1755.13	30.22	13.45
1173	14.45	23.93	2148.30	1668.99	27.59	13.18
1273	16.36	28.29	2056.17	1563.53	18.25	12.41
NaBr						
1073	18.19	26.50	1533.44	1270.59	24.16	9.63
1173	19.05	29.48	1525.43	1226.34	22.84	9.89
1273	21.22	34.00	1472.61	1163.36	21.38	10.02
KBr						
1073	27.36	36.22	1070.49	1159.24	18.94	8.81
1173	28.96	37.34	1316.24	1108.22	17.76	8.55
1273	33.04	42.64	1259.01	930.43	16.48	8.40
KCl						
1073	20.51	26.35	1796.99	1585.49	22.18	10.89
1173	21.66	31.21	1781.71	1482.14	22.27	10.26
1273	24.18	36.79	1719.87	1394.25	20.96	9.77

In conclusion we can say that the calculated values of β_S, μ, P_i, γ, V_a and Γ for four molten alkali metal halides yield the similar trend of variation as observed experimentally. However, the agreement in the magnitude of calculated properties is not so encouraging.

Table-2(b) Calculated Values of ϒ, V_a and Γ

T K	ϒ		Va(cc mol^{-1})		Γ	
	Theo(SST)	Expt	Theo(SST)	Expt	Theo(SST)	Expt
NaCl						
1073	2.08	1.44	-12.73	-3.65	2.259	0.95
1173	1.89	1.47	-13.35	-1.68	1.962	0.91
1273	1.43	1.48	-11.53	0.92	1.286	0.84
NaBr						
1073	2.05	1.29	1.83	9.06	2.127	0.86
1173	1.96	1.30	2.13	10.66	1.941	0.77
1273	1.91	1.31	3.77	12.92	1.775	0.71
KBr						
1073	2.20	1.41	12.35	15.62	2.159	1.07
1173	2.13	1.43	10.59	16.45	1.963	0.96
1273	2.10	1.45	13.28	19.16	1.786	0.86
KCl						
1073	2.19	1.44	-6.08	0.45	2.326	1.05
1173	2.15	1.47	-5.82	3.78	2.113	1.00
1273	2.11	1.48	-4.00	6.86	1.938	0.90

The free volumes of the molten salts under the present study are calculated by using Eyring equation (6), Bockris relation (8) and Hirschfelder et al equation (9). As the free volume of a liquid is very complicated, and its definition depends on the specific model of liquid state. All the equations employed here obtained from entirely different theoretical considerations. Hence, there is no question of agreement between the V_f value obtained from various equations. Moreover, V_f can not be determined experimentally. A perusal of Table - 3 shows that the V_f values calculated from the three methods increase by increasing temperature for all the molten salts.

Table-3 Calculated Values of free volume

T (K)	V_f c c mol^{-1}		
	Eq(7)	Eq(9)	Eq(10)
NaCl			
1073	0.6866	0.2361	0.0042
1173	0.6964	0.2770	0.0047
1273	0.7154	0.3706	0.0071
NaBr			
1073	0.9161	0.4098	0.0038
1173	1.0262	0.4931	0.0041
1273	1.2940	0.6431	0.0044
KBr			
1073	2.0410	0.6872	0.0068
1173	2.2138	0.6761	0.0095
1273	2.5171	0.9115	0.0134
KCl			
1073	1.1382	0.3532	0.0033
1173	1.3547	0.4301	0.0035
1273	1.7216	0.5622	0.0036

However the numerical values obtained from all the methods are quite different. So, it is not possible to make any conclusion about the free volume results.

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