Applications of Generalized Hole Theory to Molten Salts and their Mixtures – Computation of Thermoacoustical Properties

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Abstract

Recently developed generalized hole theory has been applied for the first time to molten salts (ionic liquids) and their binary mixtures. Various thermodynamic parameters (internal pressure, energy of vaporization, cohesive energy density, solubility parameter, heat of vaporization and Vander Waals constant) have been computed .The results are found to be quite successful indicating the applicability of the theory to ionic liquids and their binary mixtures.

***Keywords**: Hole creation energy, Hole radius, Isothermal compressibility, Internal pressure, Energy of vaporization, solubility parameter.*

Introduction

Recently we have developed a generalized version of hole theory which is a modification of Frenkel hole theory. This modified version of hole theory has been successfully applied to pure liquids[1], binary[2-3] and multi- component[4-5] liquid mixtures. Molten salts (ionic liquids) from an interesting class of liquids because of the presence of columbic forces between the particles, contract to the phenomena involved in the molecular liquids or dilute aqueous salt solutions. For the last 50 years the field of molten salts (ionic liquids) has been a subject of renewed interest and has attracted the attention of scientists in research and technology. Exhaustive works has been done and still in progress on the experimental and theoretical studies of ionic liquids. various thermodynamic and transport properties of these liquids have been calculated on the basis of various liquid state models including quasi- lattice model, Flory`s statistical theory, significant structure theory of Eyring and coworkers. The purpose of the present works is to apply the generalized version of hole theory to calculate various thermodynamic properties related to the ultrasonic propagation parameters for molten salts and their binary mixtures. Such works has, so far, not been reported in the literature.

Theoretical Formulation

For applying the generalized hole theory to molten salts and their mixtures, the following relevant equations have been employed. For further detail one may refer to the recent papers[2- 3]. Recently[6] we have, also succeeded in applying this theory successfully to the viscosity of liquid mixtures,

Hole creation energy

$$E_h = \frac{4}{3}\pi r^2 \sigma \quad (1)$$

$$V = \frac{4}{3}\pi r^3 = \frac{32}{3} \times \pi\sigma^3/P_{int}^3 \quad (2)$$

Hole Radius

$$r_h = \frac{2\sigma}{P_{int}} \quad (3)$$

$$a = \frac{V}{V_h} \quad (4)$$

$$V = \frac{V}{N} \quad (5)$$

Isothermal compressibility

$$\beta_T = \frac{aNV_h^2 \ exp\left(1-\frac{1}{a}\right) \ exp\frac{E_h+PV_h}{KT}}{VKT\left[exp\left(1-\frac{1}{a}\right)exp\frac{E_h+PV_h}{KT}-1\right]^2} \quad (6)$$

Thermal expansion coefficient

$$\alpha = \frac{1}{VKT^2}\frac{aNV_h \ 2exp\left(1-\frac{1}{a}\right)\left[exp\frac{E_h+PV_h}{KT}\right]\left(E_h+PV_h\right)}{\left[\exp\left(1-\frac{1}{a}\right)\exp\frac{\left(E_h+PV_h\right)}{KT}-1\right]^2} \quad (7)$$

Internal pressure

$$P_{int(mix)} = \frac{\alpha_{(mix)}}{\beta T_{mix}} T \quad (8)$$

Energy of vaporization

$$\Delta E_{V(mix)} = P_{int(mix)} V_{(mix)} \quad (9)$$

Solubility parameter

$$\delta_{mix} = \sqrt{P_{int(mix)}} \quad (10)$$

Cohesive Energy Density (ced)

$$ced = \frac{\Delta E_{V(mix)}}{V_{(mix)}} \quad (11)$$

Heat of vaporization

$$\Delta E_{V_{mix}} = \Delta H_{V(mix)} + RT \quad (12)$$

Van der Waals constant

$$a_{Vdw} = P_{int(mix)} V_{(mix)}^2 \quad (13)$$

Results and Discussion

The generalized hole theory is applied here, for the first time, to molten salts and their binary mixtures. Various equations outlined in the previous section have been used to obtain basic parameters of hole theory for pure molten salts KCl, LiCl, RbCl, CsCl, NaCl and KBr. The experimental data needed for the computation of hole radius r_h, hole volume v_h and hole creation energy E_h are taken from the different sources[7-9]. Table -1 enlists the literature values of molar volume (V), density (ρ), thermal expansion coefficient (α) ,isothermal compressibility (β_S), surface tension (σ) and internal pressure (P_i) for above mentioned pure molten salts at 1073K. The thermodynamic parameters viz. internal pressure (P_{int}), energy of vaporization (ΔE_v),cohesive energy density (ced) solubility parameter (δ) heat of vaporization(ΔH_v) and van der Waals constant (a) have been computed at 298.15 K for the ten binary molten salts and compared with their experimental findings. The above thermodynamic parameters are calculated from eqs (6) to (13). The results are shown in Table-2.

Table 1: Properties of molar volume (V), density(ρ), thermal expansion coefficient (α), hole radius (r_h),hole volume (V_h), hole energy (E_h),Van der Waals constant (a), average percentage velocity (%u), average percentage internal pressure (%P_{int}), average percentage thermal expansion coefficient (% α) and average percentage isothermal compressibility (%β_T) of pure molten salts at 1073 K.

Components	V (cm^3mol^{-1})	ρ ($g\ cm^{-3}$)	α $x10^3$ (K^{-1})	r_h $x10^{10}$ (m)	V_h $x10^{29}$ (m^3)	E_hX10^{21} (j)	$aX10^{-6}$	%u	%P_{int}	%α	%β_T
KCl	49.38	1.51	0.386	1.7946	2.4199	8.0636	3.39	9.96	6.81	9.33	2.7
LiCl	29.84	1.421	0.305	1.6345	1.8281	8.2598	2.71	10.15	-0.23	-15.26	-15
RbCl	55.65	2.173	0.406	1.8719	2.7462	8.6848	3.36	8.38	5.46	12.79	7.76
CsCl	63.97	2.632	0.406	1.8274	2.555	7.967	4.16	1.5	-8.04	13.84	20.25
NaCl	37.6	1.5544	0.36	1.73	2.1676	8.9904	2.88	13.35	11.2	1.43	-11.01
KBr	57.32	2.076	0.38	1.8179	2.5151	13.2581	3.78	-0.33	-13.25	8.6	19.29

Table 2: Calculated values of thermodynamic properties of hole radius (r_h), hole volume (V_h), hole energy (E_h), average percentage deviation isothermal compressibility (β_T %Δ), average percentage deviation thermal expansion coefficient (α% Δ), average percentage deviation internal pressure (P_{int}% Δ), average percentage deviation energy of vaporization (E_v%Δ), average percentage deviation of cohesive energy density (ced%Δ), average percentage deviation of solubility parameter(δ%Δ), average percentage deviation heat of vaporization(H_v %Δ), average percentage deviation of van der Waals constant (a%Δ), and average percentage deviation of ultrasonic velocity (u%Δ)of binary molten salt mixtures by hole theory at 1073 K

ρ	r_hx10^{10}	v_h	E_h	β_T	α	P_{int}	E_v	ced	δ	ΔH_v	a
(g/cm^3)	**(m)**	**(m^3)**	**(j)**	**%Δ**	**%Δ**	**%Δ**	**%Δ**	**%Δ**	**%Δ**	**%Δ**	**%Δ**
1.5177	1.8	2.43	8.35	3.92	7.68	3.91	3.91	3.91	1.98	3.91	3.91
1.5304	1.9	2.89	9.88	-10.39	4.48	7.77	7.77	7.77	3.96	7.77	7.77
1.5404	1.98	3.25	11.14	-20.52	3.23	10.06	10.06	10.06	5.16	10.06	10.06

2.0609	1.87	2.74	9.06	7.91	10.15	2.43	2.43	2.43	1.22	2.47	2.43
1.9258	1.99	3.3	10.75	-8	7.22	7.47	7.47	7.47	3.81	7.47	7.47
1.7606	2.11	3.93	12.71	-24.86	5.99	11.83	11.83	11.83	6.1	11.83	11.83
2.4572	1.87	2.76	8.75	13.9	10.69	-3.73	-3.73	-3.73	-1.85	-3.73	-3.73
2.2357	2.07	3.69	11.28	-7.57	7.86	5.68	5.68	5.68	2.88	5.68	5.68
1.9465	2.26	4.82	14.39	-29.73	8.95	13.39	13.39	13.39	6.94	13.39	13.39
2.0219	1.86	2.67	8.58	11.96	11.87	-0.1	-0.1	-0.1	-0.05	-0.1	-0.1
1.8616	1.84	2.59	8.45	10.47	10.98	0.57	0.57	0.57	0.28	0.57	0.57
1.6913	1.82	2.51	8.28	8.87	10.12	1.37	1.37	1.37	0.69	1.37	1.37
1.5001	1.82	2.53	8.53	-0.46	5.2	5.63	5.63	5.63	2.86	5.63	5.63
1.4722	1.84	2.61	9.33	-14.26	-4	8.98	8.98	8.98	4.6	8.98	8.98
1.4607	1.83	2.58	9.54	-18.06	-7.22	9.18	9.18	9.18	4.7	9.18	9.18
1.9752	1.82	2.53	8.08	13.12	8.22	-5.64	-5.64	-5.64	-2.78	-5.64	-5.64
1.8134	1.82	2.51	8.14	10.7	8.59	-2.37	-2.37	-2.37	-1.18	-2.37	-2.37
1.7563	1.81	2.5	8.15	9.95	8.73	-1.36	-1.36	-1.36	-0.68	-1.36	-1.36
1.6369	1.81	2.47	8.13	8.5	9.01	0.56	0.56	0.56	0.28	0.56	0.56
1.9181	1.94	3.05	10.18	-9.75	0.88	9.69	9.69	9.69	4.97	9.69	9.69
2.2582	1.98	3.24	10.37	-6.43	1.17	7.14	7.14	7.14	3.63	7.14	7.14
2.4182	1.86	2.69	8.36	17.92	13.26	-5.69	-5.69	-5.69	-2.8	-5.69	-5.69
2.1436	1.84	2.59	8.27	15.02	11.39	-4.27	-4.27	-4.27	-2.11	-4.27	-4.27

The values of internal pressure decrease with the increase in mole fraction of the first components of each molten salts. It is worthwhile to mention that the agreement between the observed and calculated values of internal pressure is good for all the systems and excellent for the binary mixtures of KCl + RbCl and KCl + KBr. The percentage deviations in case of KCl + RbCl and KCl +KBr are -0.10 and 0.56 respectively. It is worthwhile to mention that for obtaining hole creation energy E_h and hole radius r_h in the present case, some changes are made from the original procedure. These changes are σ surface tension used in the calculation of hole creation energy is calculated by the most familiar and tested Auerbach equation [10]

$$\sigma = 6.3 \times 10^{-4} \rho u^{3/2}$$

In the case of hole radius, the surface tension of pure components is used.

As far as the energy of vaporization, ced, solubility parameter and heat of vaporization for the investigated binary salt mixtures are concerned, it is observed that the above parameters decrease with the mole fraction of the first component. It is obvious from the values reported that the calculated values of all the thermodynamic parameters obey the same trend as it is observed experimentally. The agreement between observed and calculated values is excellent for all the aforesaid mixtures.

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