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**Validity of some regularities of dense fluids for ionic liquids**

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Keywords: Ionic liquids, Regularity, Bulk modulus, Isobaric expansion coefficient, Isothermal compressibility, Internal pressure.**1. Introduction**

Ionic liquids (ILs) are organic molten salts that have received special attention due to a negligible vapor pressure [1,2], a broad liquid range [3], thermal stability up to high temperatures, possess high solubility for both polar and nonpolar organic and inorganic substances, exhibit interesting solvation and coordination properties that depend on the nature of the cation and/or anion [4,5]. Ionic liquids usually consist of a large, asymmetric organic cation coupled with a generally smaller, weakly coordinating anion. Because a large number of cationic and anionic structure combinations are possible, their physicochemical properties can be easily tuned by changing the structure of the component ions. Among the many applications of ionic liquids that have been reported in the literature are the following: as media for clean liquid-liquid extraction processes, as solvents for electrochemical applications, for catalytic cracking of polyethylene, for radical polymerization, and in nanomaterial technologies. The design of industrial processes and new products based on ILs are only possible when their thermophysical properties are adequately known. Despite the fact that the description of dense fluids at the molecular level is very complicated, they obey some relatively simple regularity [6]. Five of the best known regularities, studied in this work, are the following:

- (1) Near linearity of the isothermal bulk modulus (reciprocal compressibility) of a liquid or supercritical fluid as a function of pressure.
- (2) Huang and O'Connell have found that isotherms of the bulk modulus as a function of density intersect at a common point [7].
- (3) It has been observed for many substances that isotherms of isobaric expansion coefficient versus pressure pass through a common intersection point.
- (4) There is a similar behavior for isothermal compressibility, namely isotherms of the isothermal compressibility of some liquids as a function of pressure intersect at a common point.
- (5) There exists a common intersection point for the isobars of internal pressure as a function of temperature.

2. Methods

In this work, two equations of states, Goharshadi-Morsali-Abbaspour (GMA) equation of state (EoS) and Tait EoS have been used to reproduce the regularities. The GMAEoS is based on the average potential energy and is given as [8]:

$$(2Z-1)V_m^{-1} = A(T) + B(T)\rho \quad (1)$$

where Z , V_m and ρ are compressibility factor, molar volume, and density, respectively. The intercept and slope of this equation depends on temperature via the equations:

$$A(T) = A_0 - \frac{2A_1}{RT} + \frac{2A_2 \ln T}{R} \quad (2)$$

$$B(T) = B_0 - \frac{2B_1}{RT} + \frac{2B_2 \ln T}{R} \quad (3)$$

where A_0 - A_2 and B_0 - B_2 are constants. To use the equation of state for a liquid, the A and B parameters must be known. To find these parameters, we may plot $(2Z-1)V_m^{-1}$ versus ρ for different isotherms. The slope and intercept of the straight lines can be fitted to Eqs. (2) and (3) from which A_0 - A_2 and B_0 - B_2 can be found, respectively. The Tait EoS has the following form [9]:

$$\frac{1}{\rho(P, T)} = \frac{1}{\rho(P_s, T)} \left(1 - c \ln \left(1 + \frac{P}{B(T)} \right) \right) \quad (4)$$

$$\frac{1}{\rho(P_s, T)} = a_0 + a_1 T + a_2 T^2 \quad (5)$$

$$B(T) = b_0 \exp(-b_1/T) \quad (6)$$



where $\rho(P_0, T)$ is the density at ambient pressure P_0 . The $B(T)$ is dependent on temperature; C is a constant; and a_0, a_1, a_2, b_0 and b_1 are the fitting parameters.

3. Results and discussion

In this paper different classes of ionic liquids, listed in Table 1 have been studied. The five regularities mentioned above have been checked using the existing experimental data. The results indicate that the some ionic liquids show these regularities.

Table 1. Formula, critical properties, and temperature and pressure ranges of ionic liquids of studied

Compound	Formula	T_c (K) ^a	P_c (MPa)	$10^3 V_c$ (m ³ /mol)	ΔP (MPa)	ΔT (K)
[Gmim][CF ₃ SO ₃]	C ₈ H ₁₁ NF ₃ SO ₃	985.2	3.58	653.4	0.1-35	293.15-393.15
[Cmpyr][NTf ₂]	C ₁₁ H ₁₄ NF ₆ SO ₄	1228.9	2.75	981.7	0.1-35	293.15-393.15
[Cmpyr][NTf ₂]	C ₁₀ H ₁₃ NF ₆ SO ₄	1196.9	2.67	969.8	0.1-35	293.15-393.15
[Cmpyr][NTf ₂]	C ₁₀ H ₁₁ NF ₆ SO ₄	1209.2	2.48	1026.9	0.1-35	293.15-393.15
[Gmim][OS]	C ₁₀ H ₁₃ N ₂ O ₅	1189.8	2.02	1116.7	0.1-60	318.15-428.15
[Gmim][NTf ₂]	C ₈ H ₁₃ NF ₆ SO ₄	1259.3	2.99	933.0	0.1-59.59	313.15-333.15
[Gmim][NTf ₂]	C ₁₁ H ₁₃ NF ₆ SO ₄	1281.1	2.56	1047.2	0.1-59.59	313.15-333.15
[Gmim][NTf ₂]	C ₁₀ H ₁₃ NF ₆ SO ₄	1265.0	2.76	1007.1	0.1-150	298.15-323.15
[Gmim][NTf ₂]	C ₁₂ H ₁₄ NF ₆ SO ₄	1287.3	2.39	1121.3	0.1-150	298.15-323.15
[Gmim][BF ₄]	C ₈ H ₁₃ N ₂ BF ₄	632.3	2.04	672.0	0.1-150	298.15-323.15
[Gmim][PF ₆]	C ₈ H ₁₃ N ₂ PF ₆	708.9	1.73	779.5	0.1-40	298.15-323.15
[Gmim][PF ₆]	C ₁₀ H ₁₃ N ₂ PF ₆	754.3	1.55	893.7	0.1-200	312.8-472.3
[Gmim][PF ₆]	C ₁₂ H ₁₅ N ₂ PF ₆	800.1	1.40	1007.9	0.1-200	312.8-472.3
[Gmim][BF ₄]	C ₁₀ H ₁₃ N ₂ BF ₄	679.1	1.79	786.2	0.1-200	313.3-472.5
[Gmim][PF ₆]	C ₈ H ₁₁ N ₂ PF ₆	663.5	1.95	665.3	0.1-200	312.8-472.4

^aCritical properties taken from Ref 10 & 11.

GMA EoS is able to show the linearity of bulk modulus versus pressure. EoS can not predict the second, third, and fourth regularities for ILs. Tait EoS is not able to predict the second and fourth regularities for ILs, although the Tait EoS can predict these regularities for other compounds.

4. Conclusions

In summary, five of the best known regularities have been investigated experimentally and theoretically for different classes of ILs to develop solution theories for ionic liquids. All of this work points to the need for more experimental and theoretical research to extend our understanding of ILs so that researchers will have additional key information to help them systematically design IL systems to meet their specific target applications.

References

- [1] M. J. Earle, J. M. S. S. Esperanca, M. A. Gilea, J. N. C. Lopes, L. P. N. Rebelo, J. W. Magee, K. R. Seddon, J. A. Widegren, *Nature* 439 (2006) 831.
- [2] D. H. Zaitsau, G. J. Kabo, A. A. Strechan, Y. U. Paulechka, A. Tschersich, S. P. Verevkin, A. Heintz, *J. Phys. Chem. A* 110 (2006) 7303.
- [3] K. J. Baranayai, G. B. Deacon, D. R. MacFarlane, J. M. Pringle, J. L. Scott, *Aust. J. Chem* 57 (2004) 145.
- [4] A. Heintz, *J. Chem. Thermodyn* 37 (2005) 525.
- [5] L. P. N. Rebelo, J. N. C. Lopes, J. M. S. S. Esperanca, E. Filipe, *J. Phys. Chem. B* 109 (2005) 6040.
- [6] G. Parsafar, N. Sohraby, *J. Phys. Chem* 100 (1996) 12644.
- [7] A. C. Colin, S. Cancho, R. G. Rubio, A. Copostizo, *J. Phys. Chem* 97 (1993) 10796.
- [8] E. K. Goharshadi, A. Morsali, M. Abbaspour, *Fluid Phase Equilib* 230 (2005) 170.
- [9] J. M. S. S. Esperanca, H. J. R. Guedes, M. Blesic, L. P. N. Rebelo, *J. Chem. Eng. Data* 51 (2006) 237.
- [10] J. O. Valderrama, P. A. Robles, *Ind. Eng. Chem. Res* 46 (2007) 1338.
- [11] J. O. Valderrama, W. W. Sanga, J. A. Lazzs, *Ind. Eng. Chem. Res* 47 (2008) 1318.