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Prediction of Density and Molar Volume for Mixtures of Nitrogen with Neon, Argon and Methane Using the Statistical-Mechanically Equation of State¶

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In this paper, the analytical equation of state (EoS) proposed by Ihm-Song-Mason (ISM) was applied to calculate molar volume and density of mixtures of nitrogen with neon, argon and methane. The pair interaction potential has been used to evaluate the second virial coefficients and the ISM EoS parameters (*i.e.* α and b). The calculated values of aforesaid quantities were applied to predict the molar volumes for mixtures of nitrogen with neon, argon and methane. Agreement with experiment was excellent for all the systems.

Key Words: Molar volume, Equation of state, Pair interaction potential, Statistical mechanics.

INTR ODUCTION

The lack of various data on thermodynamic properties severely limits the ability of scientists and engineers to propose innovative solutions to old or new problems of designing. Scientists and engineers are using computer frequently to predict thermodynamic properties of fluids. Because of time and financial constraints the computer-calculation can be carried out very fast. These methods are more efficient and cost effective. The laboratory experiments require much more effort and cast to determine the transport properties. Thermodynamic properties of gases are required to design heat transfer machinery and chemical processes. The quality and efficiency of chemical processing, including shrinking the time lines for industrial process scale-up and optimizing processes to maximize yields and maximize unwanted wastes and by products, can be greatly enhanced through theoretical studies. The thermodynamic properties of fluids are

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¶The authors wish to dedicate this paper to Prof. A. Maghari on the occasion of his 50th birthday.

essential for process design and control in the chemical, natural gas, aerospace, environmental and other related industries.

On the other hand, thermophysical properties of gases, such as the density, heat capacity, viscosity and thermal conductivity are important quantities in both science and engineering. Anyhow, volumetric properties are ubiquitous in chemical processes and form the building blocks of process designing. The importance of the volumetric properties of fluid in technology is maintained across the varied diversity.

All of the thermodynamic properties of a fluid are encapsulated in the mathematical relationship between the fluid's pressure, volume and temperature, which is commonly called its equation of state (EoS)[1]. It is therefore hardly surprising what an ability to predict such equations of state accurately and with a minimum of empiricism has been highly prized in engineering applications[2-8]. Though, an ability to understand equations of state on purely molecular level, using nothing more than information on intermolecular potentials and the tools of equilibrium statistical mechanics, would mean finally meeting a challenge posed over a century ago by van der Waals and would signify that one could, finally, claim some reasonable measure of understanding of at least the equilibrium properties of liquids and gases[9].

For the last decade, a considerable progress has been made in theoretical understanding of single fluids and their mixtures. Besides the theoretical importance, the knowledge of physico-chemical properties of multi-component mixtures are indispensable for many chemical process industries. Examples are all of the substances which are commonly used in industries where physico-chemical process is involved to handle the single fluids and their mixtures. Physico-chemical analysis method can be used for getting sound information for interaction between the components and the function of the binary interaction[10-17]. The thermodynamic studies of binary mixtures have attracted much attention of scientists and experimental data on a number of systems. Knowledge of the EoS is necessary to obtain densities and other thermodynamic properties. There exist a simple analytical EoS[18], based on statistical-mechanical perturbation theory[19,20]. Knowledge of the intermolecular potentials allows the complete specification of this equation[21-22]. Recently, Ihm-Song-Mason (ISM) EoS have received conspicuous attention[23-25]. The main objective of the present research is to compute the molar volume and density of some mixtures using the statistical mechanical EoS.

EXPERIMENTAL

The EoS that is obtained from the statistical-mechanical perturbation theory by ISM for mixtures is the form

$$P/\rho k_B T = 1 + \rho \sum_{ij} x_i x_j ((B)_{ij} - \alpha_{ij}) F_{ij} + \rho \sum_{ij} x_i x_j \alpha_{ij} G_{ij} \tag{1}$$

where P is the pressure, x is the mole fraction, ρ is the molar densities, B is the second virial coefficient, α is a correction factor for the softness of the repulsive forces, G is the average pair distribution function at contact for hard convex bodies, and k_BT is the thermal energy per one molecule. The summation run over all the components of mixture and the subscript ij refer to i-j interactions. The parameters F_{ij} and G_{ij} are defined as:

$$F_{ij} = \frac{1}{(1-\eta)} - \left(\frac{b_i b_j}{b_{ij}}\right)^{1/3} \frac{\rho \sum_k x_k b_k^{2/3} (\delta_k + 1/4)}{(1-\eta)(1+\rho) \sum_k x_k b_k \delta_k} \tag{2}$$

$$G_{ij} = \frac{1}{1-\eta} + \left(\frac{b_i b_j}{b_{ij}}\right)^{1/3} \frac{\rho \sum_k x_k b_k^{2/3} (\lambda_k - 1/4)}{(1-\eta)(1-\rho) \sum_k x_k b_k \lambda_k} \tag{3}$$

with, $$\eta \equiv \frac{\rho}{4} \sum_k x_k b_k \tag{4}$$

$$B = 2\pi \int_0^{\infty} (1 - e^{-u(r)/k_B T}) r^2 d\tau$$

$$\alpha = 2\pi \int_0^{r_m} (1 - e^{-u^0(r)/k_B T}) r^2 d\tau$$

$$b = 2\pi \int_0^{r_m} (1 - [1 + u^0(r)/k_B T] - e^{-u^0(r)/k_B T}) r^2 d\tau$$

Here, b is a temperature dependent parameter analogous to the van der Waals co-volume, λ is an adjustable parameter and δ = 0.22 λ. The intermolecular potential is identified by the u(r) whereas the repulsive part, $u^0(r)$ has its usual meaning of decomposition of u(r) according to the Weeks-Chandler-Anderson formulation[19] of the thermodynamic perturbation theory[20]. This equation of state has been derived from the pressure equation in conjunction with the assumption that the intermolecular potentials are pair-wise additive. The major feature of the ISM EoS is its sound statistical-mechanical basis. The purpose of the present work is to find the second virial coefficients as well as the parameters α and b for pure components and their mixtures. The interaction parameters B_{ij}, α_{ij} and b_{ij} for i ≠ j correspond to a hypothetical single substance whose molecules interact according to a pair-wise ij potential. For i = j the parameters are those for pure substance i. The mathematical expressions for B_{ij}, α_{ij} and b_{ij} are as the same as for pure fluids, but the intermolecular potential energy for pure substances should be replaced by the interaction potential for unlike molecules.

RESULTS AND DISCUSSION

The pair intermolecular potentials[26,27] as input data to determine the cross second virial coefficients for mixtures of nitrogen with neon, argon and methane has been used present work. The calculated values of α and b have been inserted to the eq. 1. The values of λ_k of that appear in eqs. 2 and 3 were found empirically from P-V-T data of dense pure components and are as follow: 0.402, 0.430, 0.380 and 0.420 for nitrogen, neon, argon and methane, respectively. Knowing the temperature-dependent parameters; second virial coefficient, α and b, along with the values of λ parameters the ISM EoS for mixtures can be employed to predict P-V-T properties of the aforesaid mixtures. The used values of the experimental density and molar volume are adopted from the Streett[28], Ricardo *et al.*[29] and Nunes da Ponte *et al*[30] for aforesaid mixtures. As it is clear from Figs. 1-3, our calculated values are in satisfactory agreement with those from Streett[28], Ricardo *et al.*[29] and Nunes da Ponte *et al.*[30] data. The overall agreement between our predicted values and the experimental data is fairly good.

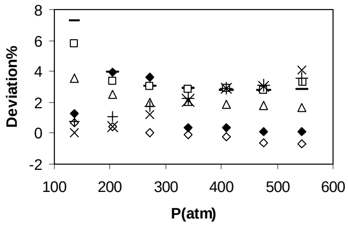

Fig. 1. Deviation $(100(\rho_{cal} - \rho_{exp})/\rho_{exp})$ plot for the density of 0.054 Ne + 0.946 N_2 (◇), 0.1528 Ne + 0.8472 N_2 (υ), 0.3322 Ne + 0.6678 N_2 (△), 0.5385 Ne + 0.4615 N_2 (=), 0.6365 Ne + 0.3635 N_2 (□), 0.8145 Ne + 0.1855 N_2 (+) and 0.9545 Ne + 0.0455 N_2 (×) at 100.78 K. The experimental data have been adopted from Ref. [28]

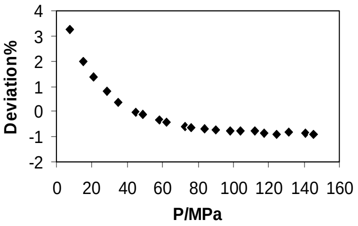

Fig. 2. Deviation $(100(V_{cal} - V_{exp})/V_{exp})$ plot of the molar volume of 0.476 Ar + 0.524 N_2 at 119.33 K. The experiment data have been adopted from Ref. [29]

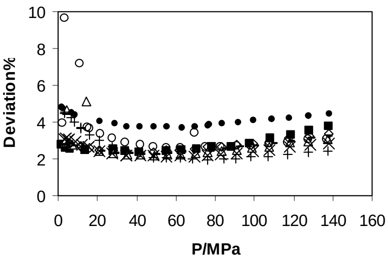

Fig. 3. Same as Fig. 2 for 0.320 N_2 + 0.680 CH_4 (●), 0.503 N_2 + 0.497 CH_4 (■), and 0.706 N_2 + 0.294 CH_4 (○) at 110.09 K, 0.503 N_2 + 0.497 CH_4 (=) at 113.70 K, 0.503 N_2 + 0.497 CH_4 (△) at 116.30 K, 0.320 N_2 + 0.680 CH_4 (□), 0.503 N_2 + 0.497 CH_4 (×) and 0.706 N_2 + 0.294 CH_4 (+) at 120.00 K. The experimental data have been adopted from Ref. [30].

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REFERENCES

1. J.R. MacDonald, *Rev. Mol. Phys.*, **41**, 316 (1969).
2. U.K. Deiters and K.M. de Reuck, *Pure Appl. Chem.*, **69**, 1237 (1997); *Fluid Phase Equil.*, **161**, 205 (1999).
3. Y.S. Wei and R.J. Sadus, *AIChE J.*, **46**, 169 (2000).
4. J.O. Valderrama, *Ind. Eng. Chem. Res.*, **42**, 1603 (2003).
5. B. Haghighi, M.R. Laee, M.R. Husseindokht and N.S. Matin, *J. Ind. Eng. Chem.*, **10**, 316 (2004).
6. B. Haghighi, M.R. Laee and N.S. Matin, *Cryogenics*, **43**, 393 (2003).
7. N.S. Matin and B. Haghighi, *Fluid Phase Equil.*, **175**, 273 (2000).
8. B. Haghighi, M. Fathabadi and M. M. Papari, *Fluid Phase Equil.*, **203**, 205 (2002); *Indian J. Chem.*, **43A**, 1824 (2004).
9. B. Haghighi and N. Farhami, *Asian J. Chem.*, **17**, 45 (2005) and references therein.
10. B. Haghighi, N. M. Oghaz and M. Najafi, *Asian J. Chem.*, **15**, 1355 (2003) and references therein; **14**, 1341 (2002) and references therein.
11. M.M. Papari, D.M.-Aghaei, B. Haghighi and A. Boushehri, *Fluid Phase Equil.*, **232**, 122 (2005).
12. M.M. Papari, *Chem. Phys.*, **288**, 249 (2003).
13. B. Haghighi, A.H. Djavanmardi, M. Najafi and M. Papari, *J. Theor. Comput. Chem.*, **2**, 371 (2003); **3**, 69 (2004).
14. B. Haghighi, *Indian J. Chem. Tech.*, **10**, 483 (2003).
15. B. Haghighi and M. Najafi, *Indian J. Chem.*, **41A**, 687 (2002).
16. B. Haghighi, M. Fathabadi and M.M. Papari, *Int. J. Trans. Phenom.*, **6**, 63 (2004).
17. B. Haghighi, M. Fathabadi and M.M. Papari, *Int. J. Chem. Sci.*, **1**, 371 (2003).
18. G. Ihm, Y. Song and E.A. Mason, *Fluid Phase Equil.*, **75**, 105; 117 (1992) .
19. J.D. Weeks, D. Chandler and H.C. Anderson, *J. Chem. Phys.*, **54**, 5237 (1971).
20. J.A. Barker and D. Henderson, *Rev. Mol. Phys.*, **48**, 587 (1976).
21. B. Haghighi, M.M. Papari, M. Niafari and H. Ghasemi, *J. Mol. Liq.*, **123**, 134 (2006); M.M. Papari, B. Haghighi and R. Rastegari, *High Temp.-High Press.*, **35/36**, 549 (2003/2006).
22. H. Eslami, M.M. Papari and A. Boushehri, *J. Phys. Soc. Japan.*, **70**, 1015 (2001); **69**, 1731 (2000).
23. M.M. Papari, A. Boushehri, A.A. Rostami and B. Haghighi, *J. Chin. Chem. Soc.*, **25,** 209 (2005).
24. S. Sheikh, M.M. Papari and A. Boushehri, *Ind. Eng. Chem. Res.*, **41**, 3274 (2002).
25. B. Haghighi, M.M. Papari, M. Niafari and H. Ghasemi, *J. Chin. Chem. Soc.*, **52**, 227 (2005).
26. F.M. Mourits and F.H.A. Rummens, *Can. J. Chem.*, **55**, 3007 (1977).
27. M. Edalat, S.S. Lan, F. Pang and G.A. Mansoori, *Int. J. Thermophys.*, **1**, 177 (1980).
28. W.B. Streett, *Cryogenics*, **8**, 88 (1968).
29. A.A. Ricardo, S.F. Barreiros, M. Nunes da Ponte, G.M.N. Albuquerque and J.C.G. Calado, *J. Chem. Thermodyn.*, **24**, 1281 (1992).
30. M.N.da Ponte, W.B. Streett and L.A.K. Staveley, *J. Chem. Thermodyn.*, **10** 151 (1978).

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