Latin American Applied Research 34:41-47 (2004)

A GENERALIZED CORRELATION FOR THE SECOND VIRIAL COEFFICIENT BASED UPON THE STOCKMAYER POTENTIAL

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***Abstract*— We have approximated the second virial coefficients obtained from the Stockmayer potential using a two parameter, analytical correlation. The correlation eliminates the need for integration of the potential over nearly the entire range of reduced temperatures. The equation is valid from 0 to 1.5 reduced dipole moment and uses the Boyle temperature as a normalizing variable. Because the equation is a correlation, the parameters do not necessarily have any physical meaning. We have applied the new equation to nonpolar compounds, aromatics, freons, alcohols, ethers, aldehydes, and acids.**

***Keywords*— Second Virial Coefficient, Correlation, Stockmayer Potential, Boyle Temperature.**

I. INTRODUCTION

The precise basis in statistical mechanics of the virial equation is one of its attractions. The virial equation, when truncated after the second virial coefficient, can predict accurate thermodynamic properties in the vapor phase up to about one-half the critical density. Therefore, experiments and correlations have emphasized determination of the second virial coefficient. Correlation use is preferable to experiment if the accuracy in the prediction is close to the experimental error.

Several correlations have appeared in the literature. Among the most popular are those developed by: Pitzer and Curl, (1957); O'Connell and Prausnitz, (1967); Halm and Stiel (1971); Tsonopoulos (1974); and Tanakad and Danner (1977). These correlations, based upon the corresponding states principle, provide generalized expressions for the second virial coefficient. The characteristic parameters for simple molecules in these equations are the acentric factor, the critical pressure and the critical temperature. To predict the second virial coefficient for more complex molecules, the correlations utilize the reduced dipole moment and adjustable parameters. For non-polar and slightly polar substances, prediction of the second virial coefficient is relatively close to experimental values, but the correlations cannot predict strongly polar and associating substances adequately.

Another way to obtain the second virial coefficient is through integration of a pair potential. Hirschfelder *et al.* (1954) give the theoretical expressions for the second and third virial coefficient using different potential functions. The resultant equations can correlate the second virial coefficient fairly well, but they tend to fail at low temperatures.

One of the pair potentials used to represent the second virial coefficient of polar substances is the Stockmayer potential (Hirschfelder *et al.*, 1954). The expression for the second virial coefficient of the Stockmayer fluid is a two characteristic constant equation that requires a numerical integration. Polak and Lu (1972) and Johnson and Eubank (1973) obtained the intermolecular forces constants of alcohols and other polar molecules. They used an iterative least squares method because of the complexity and non-linearity of the expression for the second virial coefficient.

Recently, Tellez-Morales (1998) have developed a simple straight line to correlate the pure and interaction second virial coefficient data and Iglesias-Silva and Hall, (2001) have developed a correlation using the Boyle temperature as a reducing parameter. In this work, we use a new correlation that has the Boyle temperature as a normalizing parameter. This new function can correlate the second virial coefficient from the Stockmayer potential within a maximum error of 3% at low temperatures and within less than 1% at other temperatures. We have generalized the parameters from this correlation in terms of the Stockmayer reduced dipole moment and the Boyle temperature. Also, we use the new equation to represent the second virial coefficient of nonpolars, aromatics, freons, alcohols, ethers, aldehydes, and acids. The force constants used in the new equation agree with the force constants obtained from the Stockmayer expression.

II. DEVELOPMENT

Many correlations for the second virial coefficient are based upon the corresponding states principle. The reduced second virial coefficient is:

$$B^{*}\left(T/T_c\right)=\frac{BP_c}{RT_c}=B^{*}_{np,s}\left(T/T_C\right)+\omega B^{*}_{np,ns}\left(T/T_c\right) \tag{1}$$
$$+\mu^{*}B^{*}_{p}\left(T/T_c\right)+\cdots$$

where B is the second virial coefficient, T is the absolute temperature, P_c is the critical pressure, T_c is the critical