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An Improved Corresponding States Method For Liquid Heat Capacities

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In a recent paper (Tarakad and Danner, 1977) we have discussed the development of a new set of corresponding states parameters for nonpolar and polar fluids. These parameters were used to correlate both pure and cross second virial coefficients. In this paper we discuss the use of the new parameters in correlating configurational liquid heat capacities.

The fourth parameter Φ, developed in the previous paper, was defined in terms of the second virial coefficient. We, therefore, assume that this parameter accounts for the polar contribution to the interactions involving two molecules at a time. However, while Φ is based on two-body interactions, it is to be used primarily as an indicator of overall polar and association effects. The magnitude of these effects may be assumed to be proportional, whether we are concerned with two-, three-, or more body interactions. Thus, the two-body measure may well be expected to be able to correlate the overall effects of polarity.

DEVELOPMENT OF THE CORRELATION

Using a theoretical equation developed by Rowlinson (1959), Bondi (1966) obtained the following semitheoretical correlation for the configurational liquid heat capacity of normal fluids:

$$\frac{C_\sigma - C_p{}^o}{R} = 2.56 + \frac{0.436}{1 - T_r} + \delta\left[17.11 + \frac{25.2}{T_r}(1 - T_r)^{1/3} + \frac{17.42}{1 - T_r}\right] \quad (1)$$

where δ is related to the Pitzer acentric factor by $\delta = 0.40\omega$. This equation (usually referred to as the Rowlinson-Bondi equation) was developed using data on liquid argon. Though Equation (1) has not been widely used, it does offer an excellent starting point for developing a correlation for standard fluids. (See our previous paper for the definition of standard fluids.)

In the newly developed corresponding states formulation, the radius of gyration $\overline{R}$ is the size-shape parameter. A functional form identical to Equation (1) will not adequately fit standard fluid data when $\overline{R}$ is used in place of δ as the size-shape parameter. This is because of the nonlinear relationship between $\overline{R}$ and δ (or ω, the Pitzer acentric factor). Several modifications of Equation (1) were tried so as to best fit a selected set of experimental points for fifty-eight standard fluids in the temperature range $0.35 < T_r < 0.96$. The following equation was chosen:

$$\left[\frac{C_\sigma - C_p{}^o}{R}\right]_{\substack{\text{standard}\\ \text{fluid}}} = 1.136 + \frac{0.297}{1 - T_r} + \frac{0.718(1 - T_r)^{1/3}\overline{R}}{T_r} + \frac{0.012\,\overline{R}^2}{T_r} + 1.01\,T_r{}^3\overline{R} \quad (2)$$

All the data used were for the saturated liquid. Since this already fixes one degree of freedom, Equation (2) contains no terms in P_r.

When $\overline{R}$ is zero (that is, for simple, monoatomic fluids), Equation (2) does not correctly represent the data on liquid argon. By replacing the constant 1.136 by 2.85, however, C_σ for argon can be predicted with only 0.7% average deviation. Thus, for simple fluids, the recommended equation is

$$\left[\frac{C_\sigma - C_p{}^o}{R}\right]_{\substack{\text{simple}\\ \text{fluids}}} = 2.85 + \frac{0.297}{1 - T_r} \quad (3)$$

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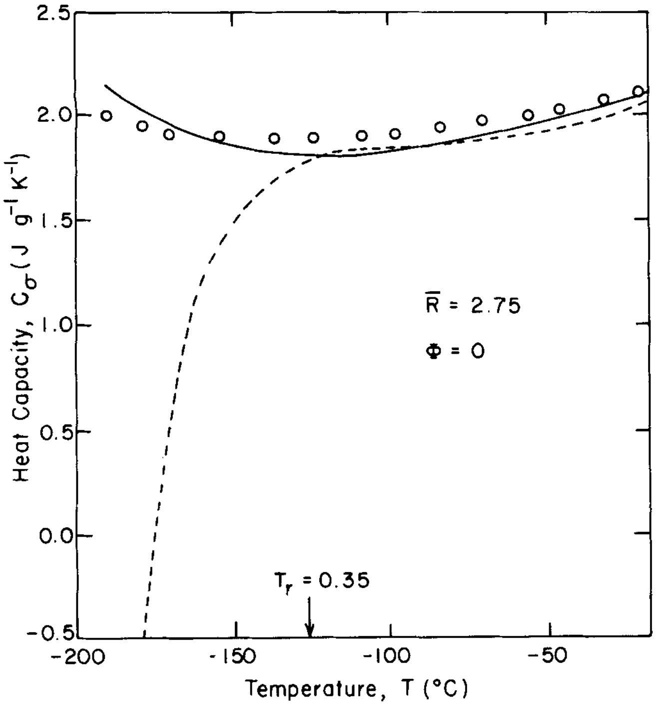

Fig. 1. Predicted and experimental liquid heat capacities for 1-butene [○ experimental data, —— Equation (5), – – – Lyman-Danner equation].

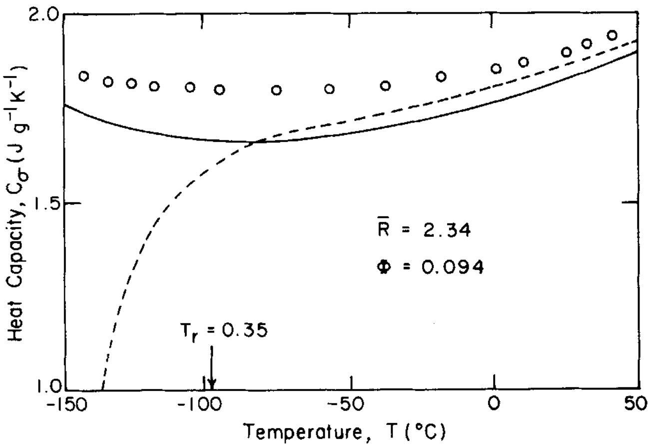

Fig. 2. Predicted and experimental liquid heat capacities for ethyl mercaptan [○ experimental data, —— Equation (5), – – – Lyman-Danner equation].

Experimental heat capacity data on nonstandard fluids are rather scarce. Moreover, existing data do not evenly span the entire reduced temperature range. From the limited amount of data available, the polar contribution to the configurational saturation heat capacity of twenty-three nonstandard fluids was correlated by

$$\left[\frac{C_\sigma - C_p^o}{R}\right]_{\substack{\text{polar}\\ \text{contribution}}} = \left[\frac{C_\sigma - C_p^o}{R}\right]_{\text{total}} - \left[\frac{C_\sigma - C_p^o}{R}\right]_{\substack{\text{standard}\\ \text{fluid}}} = \Phi\left(6.82\,T_r^2 + 12.2\,T_r^5 - \frac{0.056}{T_r^2} - \frac{0.465\,\Phi}{1 - T_r}\right) \quad (4)$$

The form of the equation and the constants in Equation (4) were obtained by statistical analysis of the available data.

Table 1. Summary of Results for Predicting Heat Capacities of Saturated Liquids in the Temperature Range $0.35 < T_r < 0.96$

Compound class	No. pts	% deviations* Proposed equation	Lyman Danner
Normal alkanes	447	1.8	1.0
Isomeric paraffins	272	1.0	1.7
Olefins, diolefins, and alkynes	282	3.0	3.5
Cyclohexane and alkyl cyclohexanes	83	2.7	1.8
Benzene and alkyl benzenes	126	1.8	2.7
Alcohols and water	230	7.2	8.6
Ethers and ketones	192	3.5	2.5
Halogen compounds	53	5.1	5.0
Sulfur compounds	47	7.0	4.7
CO_2, NH_3, N_2, and Ar†	46	8.7	6.2
Overall	1 778	3.3	3.2

* Percent deviation is defined as

$$\frac{\sum \left(\dfrac{\text{calculated} - \text{experimental}}{\text{experimental}}\right) \times 100}{\text{number of points}}$$

The deviations quoted here are for the total heat capacity and not for the configurational portion alone.

† Equation (3) was used for argon.

Combining Equations (2) and (4), we can express the configurational heat capacity for any fluid, standard or nonstandard, in generalized form by

$$\frac{C_\sigma - C_p^o}{R} = 1.136 + \frac{0.297}{1 - T_r} + \frac{0.718(1 - T_r)^{1/3}\overline{R}}{T_r} + \frac{0.012\,\overline{R}^2}{T_r} + 1.01\,T_r^3\overline{R} + \Phi\left(6.82\,T_r^2 + 12.2\,T_r^5 - \frac{0.056}{T_r^2} - \frac{0.465}{1 - T_r}\Phi\right) \quad (5)$$

For simple fluids, Equation (3) should be used.

TESTING AND COMPARISON OF THE PROPOSED CORRELATION

Based on an evaluation of the available methods to predict liquid heat capacities, San Jose and Reid (1976) recommended the correlations of Lyman and Danner (1976) or Yuan and Stiel (1970) as the preferred corresponding states methods. Lyman and Danner gave an extensive comparison of their method with Yuan and Stiel's method. In this paper, therefore, a comparison has been made only with the Lyman-Danner correlation. The test data set consisted of 1 778 experimental points for eighty-nine compounds. This set is almost identical to the one used by Lyman and Danner, who have given detailed references to the data. Since the recommended range for the Lyman-Danner correlation is $0.35 < T_r < 0.96$, only data in this temperature range were used initially.

Table 1 summarizes the results of the evaluation for various classes of compounds. Detailed results for each compound are given in the supplement to this paper. Table 1 shows that the two correlations tested here are equivalent in accuracy. The proposed correlation, however, uses fewer empirical constants. Moreover, the present correlation requires no association correction for simple fluids and hydrocarbons; the Lyman-Danner method does need such a correction for all compounds other than normal paraffins.

EXTRAPOLATION TO LOW TEMPERATURES

Heat capacities at low reduced temperatures are often needed in process calculations. An evaluation of the two methods discussed above was made to see how the correlations perform when extrapolated to low temperatures. The results of these extrapolations for 1-butene and ethyl mercaptan are shown in Figures 1 and 2. The Lyman-Danner predictions, like most empirical correlations, deviate dramatically when extrapolated outside the recommended reduced temperature range $0.35 < T_r < 0.96$. This illustrates clearly why such extrapolations should generally not be made.

On the other hand, extrapolations of the present correlation are reasonably well behaved. For the low temperature data set consisting of 217 experimental points for forty-three compounds, Equation (5) gave an average deviation of only 4.2%, which indicates that this equation may be extrapolated with little loss in accuracy.

The success of the present correlation upon extrapolation to lower temperatures is attributable to two factors. Firstly, a semitheoretical equation, Equation (1), was employed to get an approximate form of the fitting function. Secondly, the new correlation represents a more appropriate and physically meaningful choice of parameters. The fourth parameter κ, used by Lyman and Danner, assumes both positive and negative values. This renders it mathematically difficult to obtain suitable functions that contain odd powers of κ (the same term could add or subtract, depending on whether κ is positive or negative).

The results of this study further demonstrate the usefulness and superiority of the new set of parameters in correlating configurational properties of fluids.

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NOTATION

C_p^o = isobaric heat capacity of ideal gas
C_σ = saturation heat capacity of the liquid
P_r = reduced pressure
R = gas constant
$\overline{R}$ = radius of gyration, Å
T = temperature
T_c = critical temperature
T_r = reduced temperature
δ = Rowlinson's third parameter
κ = Passut fourth parameter, used by Lyman and Danner
Φ = newly developed fourth parameter
ω = Pitzer acentric factor

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Quantum Effects in the Diffusion of Gases in Liquids

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Measurements of diffusion coefficients is important both for industrial use and fundamental research. It is of major use in testing current models of the liquid state and for formulating models of mass transfer. Our understanding of industrially important, complex chemical reactions, where combined kinetic and diffusional effects determine product distribution, will depend on our knowledge of the diffusional process.

Diffusion in liquids has been studied for many years beginning with the Stokes-Einstein equation in 1905. Since then, many equations have appeared in the literature. Available expressions have only been partially successful. The problem of accurately predicting diffusion coefficients still remains to be solved.

Previous predictive relationships for gas-liquid diffusivities have been derived from four main theoretical approaches: hydrodynamical theories, kinetic theory, absolute rate theory, and semiempirical expressions based on the first two theories. Among all available equations, the absolute rate theory approach of Akgerman and Gainer (1972) seems to be most successful. This model of the liquid state assumes that liquids contain holes in their structure and solute molecules move into these holes in the process of diffusion.