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Validity of the Geometric Model of Ovaloid Polymers Based on Simpler Molecules

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ABSTRACT

The shape parameter obtained from the geometric model of Ishihara and Hayashida for ovaloid polymers, together with the scaled-particle theory, are applied to a mixture of methane and ethylene. The results are in good agreement with the experimental values, indicating the validity of the model and suggesting application to other polymer properties.

INTRODUCTION

Some of the properties of the solutions of high polymers can be described better by models which take into consideration the shape of the molecule. In order to accomplish this, Ishihara and Hayashida [1, 2] calculate the second virial coefficient, A_2, which appears when the osmotic pressure π of high polymers solutions is expanded in powers series of concentration, using a shape-dependent factor f. According to the theory of Zimm [3], they write

$$A_2 = \frac{4N_0 v}{M_2} f$$

where N_0 is Avogadro's number, M_2 is the molecular weight of the solute, and v is the volume of one molecule. They define f as

$$f = \frac{1}{8v} \int dv_B$$

where the integration is carried over all the configurations of one molecule where the common volume of two particles does not vanish.

To calculate f they use a geometric model which enables one to express the excluded volume of two convex bodies in term of their volume, their surface, and their mean radius. They apply the obtained formulas to such macromolecules as hemoglobin and serum albumin, thus underlining the parralelism between viscosity and osmotic pressure which has often been recognized experimentally.

Using the experimental value of the second virial coefficient for these molecules, they calculate their axial ratio as ellipsoids of revolution. The numbers obtained are in fair agreement with the accepted values.

In this work we look for the validity of the introduction of a shape factor in the description of the properties of a mixture applied to a simpler system than polymers. The system under investigation is a mixture of methane and ethylene, and the property considered is the compressibility factor.

METHOD

Gibbons [4], using scaled-particle theory [5], derived an equation of state for particles with nonspherical hard cores, which in the case of a spherical core reverts to the Percus-Yevick (PY) equation. The

Gibbons equation of state gives the exact second virial coefficient and excellent third and fourth virial coefficients as a function of the mean radius $\bar{R}$, surface area S, and volume v of the system's particles. Rigby [6] has emphasized that the van der Waals equations of generalized forms are of sufficient quality to represent the physical properties of a fluid. Recently [7], he has investigated the use of such forms for the case of nonspherical molecule. He uses the Gibbons equation to represent the contribution due to nonspherical repulsive core and the ordinary van der Waals term to represent the contribution due to attractive potentials.

Altogether the equation takes the form

$$\frac{PV}{NkT} = \frac{3 + (3\gamma - 6)d + (3 - 3\gamma + \gamma^2)d^2}{(1 - d)^3} - \alpha(T,V) \tag{1}$$

where $\gamma = \bar{R}S/v$ is the nonsphericity parameter. For a hard sphere, $\gamma = 3$, in which case the repulsive portion of the above expression reverts to the PY expression, while for nonspherical molecules $\gamma > 3$. The density is $d = Nv/V$, and $\alpha(T,V)$ is the attractive van der Waals term. By studying several properties as a function of the shape parameter γ, Rigby showed that Eq. (1) qualitatively accounts for several experimental trends due to a nonspherical core. The particles Rigby treated are not specific molecules but idealized particles in the form of spherocylinders. To our knowledge, the Gibbons-Rigby equation has not been applied to a real system. We have chosen CH_4 and C_2H_4, for which experimental data is available, for comparison purposes. Applying Gibbons equation [4] to a binary mixture and adding the attractive term, we obtain

$$Z = \frac{PV}{NkT} = \frac{1}{1 - d_1 - d_2} + \frac{1}{3}$$

$$\frac{y_1 d_1^2 \gamma_1^2 + y_2 d_2^2 \gamma_2^2 + y_2\left(\frac{\bar{R}_2}{\bar{R}_1}\right) d_1^2 \gamma_1^2 + y_1\left(\frac{\bar{R}_1}{\bar{R}_2}\right)^2 d_2^2 \gamma_2^2 + 2\gamma_1 \gamma_2 d_1 d_2 \left(y_1 \frac{\bar{R}_1}{\bar{R}_2} + y_2 \frac{\bar{R}_2}{\bar{R}_1}\right)}{(1 - d_1 - d_2)^3} +$$

$$\frac{y_1 d_1 \gamma_1 + y_2 d_2 \gamma_2 + y_1 d_2 \gamma_2 \left(\frac{S_1}{S_2} + \frac{\bar{R}_1}{\bar{R}_2}\right)}{(1 - d_1 - d_2)^2} - \alpha(T,V) \tag{2}$$

where y_1 and y_2 are the mole fractions. The subscripts 1 refer to methane and the subscripts 2 to ethylene. For the binary mixture, $\alpha(T,V)$ takes the form

$$\frac{y_1{}^2 a_1 + 2y_1 y_2 \sqrt{a_1 a_2} + y_2{}^2 a_2}{NkTV}$$

where a_1 and a_2 are the van der Waals coefficients, respectively $a_1(CH_4) = 2.25$ liter^2 atm/mole^2 and $a_2(C_2H_4) = 4.47$ liter^2 atm/mole^2, as given by the Handbook of Chemistry and Physics, 42nd ed. (Chemical Rubber Publishing Co.). The use of the geometric mean for a_{12} is an approximation which could introduce an error from zero to about 2% in the value of $\alpha(T,V)$ [8]. The values of α are listed in Table 2. In order to apply Eq. (2) to a concrete case, we need to know the values for $\bar{R}$, S, and v. This is where we use the geometric model of Ishihara and Hayashida [1, 2] with the addition of the constants given for methane and ethylene by Kihara [9], and we obtain the values shown in Table 1. These data yield shape parameters $\gamma = 3.39$ and 3.37 for methane and ethylene, respectively.

TABLE 1

	CH_4	C_2H_4
v, Å^3	19.2	26.40
S, Å^2	36.74	45.40
$\bar{R}$, Å	1.77	1.96
γ	3.39	3.37

We have used Eq. (2) to calculate the compressibility at a constant temperature of 77°F over a range of volumes from 252 to 116 ml. For reference purposes we have repeated the calculations considering methane and ethylene to be hard spheres of density d_1 and d_2. This implied $\gamma_1 = \gamma_2 = 3$, yielding the PY analog of Eq. (2).

RESULTS

Our results are tabulated in Table 2, from which we may draw the following conclusions. The results obtained from the generalized

TABLE 2. Results Obtained Using Eq. (2). For Nonspherical Molecules, z_{ns}; for Spherical Molecules, z_{py}. z_{exp} Refers to Experimental Results of Ref. 11

y_1	y_2	$\alpha(T = 77^\circ F)$	V (ml)	Z_{ns}	Z_{py}	Z_{exp}
1	0	0.365	252.0	0.860	0.835	0.869
0.788	0.212	0.459	236.5	0.801	0.775	0.817
0.572	0.428	0.600	214.4	0.725	0.691	0.742
0.384	0.616	0.750	189.9	0.647	0.607	0.645
0.184	0.816	1.050	155.0	0.491	0.436	0.506
0	1	1.577	116.5	0.301	0.211	0.336

van der Waals equations of state used here reproduced the experimental results fairly well. The calculations corresponding to the nonspherical hard core Z_{ns} are consistently closer to the experimental results than the analogous hard sphere calculation Z_{py}. This points up the importance of taking proper account of the shape of the hard core in equations of state for real molecules. Intuitively, we would expect a proper accounting of the shape to be increasingly important at higher densities. This is borne out in Table 2.

DISCUSSION

It is well known that some polymer properties such as light scattering are shape-independent when the dimensions of the particles are small as compared to the wavelength of the light. When the particles are larger, though, the dissymetry factor [10] will play a role. In consequence, for ovaloid-shaped polymers, some shape factor related to γ might prove valuable in the data correlations. As far as osmotic pressure and viscosity are concerned, it was shown [1, 2] that they are shape-dependent and can be approximated theoretically with the help of the parameter f which is related to γ by the simple relation

$$f = \frac{1}{4} + \frac{\gamma}{4}$$

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