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Application of equation-of-state theories to some polymeric liquids

Anna Edelman, and Alain Fradet*

Laboratoire de Synthèse Macromoléculaire, C.N.R.S. U.A. n°24, Université P. et M. Curie,
12, Rue Cuvier, F-75005 Paris, France

SUMMARY

Density-temperature data of some aliphatic block and branched α,ω-dihydroxy-polyesterethers, of some aliphatic α,ω-dihydroxy-polyesters, -polyethers, -polycarbonates and of 1,2,3-propanetriyl triacetate fit satisfactorily the equations of state of Flory's[1-3] and Lattice Fluid[4-6] theories. Characteristic specific volumes (or densities) and temperatures have been determined. Characteristic pressure of 1,2,3-propanetriyl triacetate and of α,ω-dihydroxy-polyoxyethylene have been calculated from these values and from literature compressibility data.

INTRODUCTION

In the conventional Flory-Huggins theory of polymer solutions[7], the free energy of mixing is the sum of a combinatorial entropy term related to the dispersion of the two species, and of an interaction enthalpy related to the difference in interactions between unlike and like neighbouring pairs. The combinatorial entropy term is calculated using a rigid lattice description of the solution, which limits the quantitative applications of this theory. Refinements taking into account the liquid nature of the components were introduced in more recent theories[1-6]. The behaviour of a pure fluid is described by an equation of state $f(\tilde{P}, \tilde{v}, \tilde{T}) = 0$ involving reduced specific volume, temperature and pressure:

$$\tilde{v} = v / v^*, \; \tilde{T} = T / T^*, \; \tilde{P} = P / P^*$$

where the starred quantities are the characteristic pressure, specific volume and temperature. They only depend on the fluid under consideration.

The determination of characteristic parameters is therefore a prerequisite for thermodynamic studies on polymer/solvent systems. However, only few quantitative determinations are available in the literature. This work is concerned with the determination of the characteristic parameters of some aliphatic block and branched α,ω-dihydroxy-polyesterethers the synthesis and characterisation of which were published in a preceding article[8] :

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* To whom offprint requests should be sent

poly(di(oxyethylene)oxysuccinyl) (**1**),
poly(tri(oxyethylene)oxysuccinyl) (**2**),
poly(oxyethyleneoxysuccinyl)-block-poly(oxyethylene) (**3**),
poly(oxy-3-(2-methoxyethoxy)propyleneoxysuccinyl) (**4**),

of some α,ω-dihydroxy-polyethers, -polyesters and -polycarbonates :

poly(di(oxyethylene)oxyadipyl) (**5**),
poly(hexamethylenecarbonate) (**6**),
poly(tetramethylenecarbonate) (**7**),
poly(oxypropylene) (**8**),
poly(oxyethylene) (**9**),

and of a high boiling point solvent, 1,2,3-propanetriyl triacetate (triacetin, **10**), used as solute in inverse gas chromatography studies on the preceding polymers for the determination of polymer-solvent interaction parameters[9].

RESULTS

According to Flory's equation of state theory[1-3], reduced parameters obey to the following relation:

$$\frac{\tilde{P}\,\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3} - 1} - \frac{1}{\tilde{v}\,\tilde{T}} \tag{1}$$

The characteristic values (P^*, v^*, T^*) of a given compound can be computed from equation (1) by non linear least square fit of experimental (P,v,T) data. v^* is related to the hard-core volume (volume at 0 K) of a polymer segment and P^* to the cohesive energy density of the polymer fluid. At atmospheric pressure $\tilde{P} \approx 0$ and equation (1) reduces to (3) and the starred quantities can be calculated from the thermal expansion coefficient α and the isothermal compressibility β through[1]:

$$\tilde{v} = v \;/\; v^* = \left(\frac{4\alpha T + 3}{3\alpha T + 3}\right)^3 \tag{2}$$

$$\tilde{T} = T \;/\; T^* = \tilde{v}^{-4/3}\,(\tilde{v}^{1/3} - 1) \tag{3}$$

$$P^* = (\alpha/\beta)\; T\, \tilde{v}^2 \tag{4}$$

Specific volumes v of compounds **1-10** were measured at atmospheric pressure in the range 100-160°C. v^* and T^* were determined by non-linear least-square fit of experimental (v,T) data with equation (3) (Table 1). Figure 1 shows that the Flory's equation of state fits satisfactorily the experimental data.

Table 1: Molecular weight (end group titration) and characteristic specific volumes v^*, densities ρ^*_{LF} and temperatures (T^* and T^*_{LF}) for polymers **1-9** and triacetin **10** calculated from Flory's and Lattice Fluid equations of state.

Compound	$\overline{M_n}$ (g)	v^* ($cm^3 \cdot g^{-1}$)	T^* (K)	ρ^*_{LF} ($g \cdot cm^{-3}$)	T^*_{LF} (K)
1	890	0.6767	7209	1.3762	615.8
2	1250	0.7081	7158	1.2873	654.4
3	1810	0.7032	7262	1.3018	651.9
4	1820	0.7110	7353	1.2892	656.7
5	1913	0.7269	7027	1.2579	634.9
6	2410	0.7618	7056	1.1984	640.2
7	2208	0.7016	6992	1.2944	645.2
8	2007	0.8565	6730	1.0676	609.5
9	1570	0.7743	7190	1.1826	645.4
10	218	0.7083	5655	1.2828	523.4

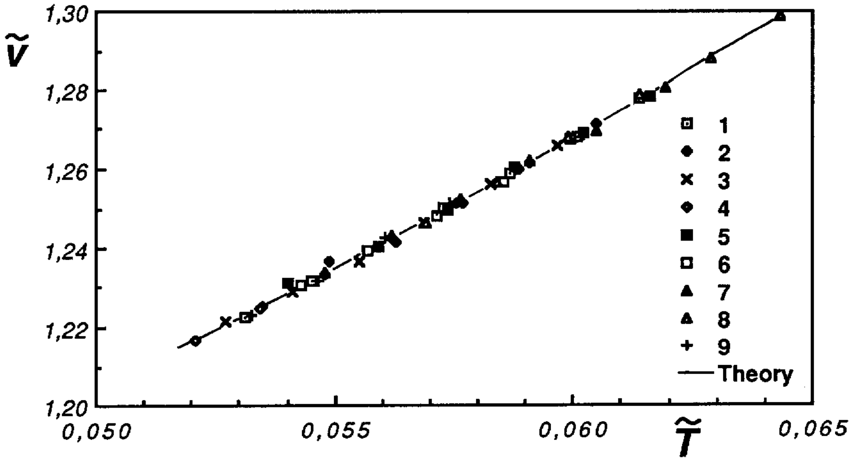

Figure 1 : Flory's equation of state. Variation of reduced specific volume with reduced temperature for polymers **1-9**.

The (v^*, T^*)values obtained for polyoxypropylene **8** and polyoxyethylene **9** can be compared to those obtained by Booth and Devoy[10,11] with a polyoxypropylene of $\overline{M_n}$ = 1900 at 61°C, (0.8424, 6330), and with a polyoxyethylene of $\overline{M_n}$ = 6100 at 57.9°C, (0.7532, 6469). The differences between these values and ours are relatively low for v^* (1-2%), but are higher for T^* (6-10%). This may be explained by the somewhat different molar masses of polymers and experimental temperature ranges used by these authors.

The compressibility $\beta = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$ of **10** at 95°C can be calculated from literature data[12] ($\beta = 0.7405\ 10^{-4}\ J^{-1}\cdot cm^3$). Relation (4) leads to $P^* = 942\ J\cdot cm^{-3}$.

The value of β for polyoxyethylene **9** can be calculated at 95°C by extrapolation from literature data[10] ($\beta = 0.6237\ 10^{-4}\ J^{-1}\cdot cm^3$), leading to $P^* = 682\ J\cdot cm^{-3}$, which is relatively close to the value found by Booth and Devoy[10], 672 $J\cdot cm^{-3}$.

As no compressibility data on polymers **1-8** could be found in the literature, the calculation of their characteristic pressures was not possible. It must be pointed out here that only the solvent P^* values are necessary for the determination of polymer-solvent interaction parameters by inverse gas chromatography[9].

In the Lattice Fluid theory (LF Theory) of Sanchez and Lacombe[4-6], a fluid is described as a system of N r-mer molecules and of N_0 vacant sites (holes). When temperature increases, the number of vacant sites increases. At equilibrium, the chemical potential is at minimum, leading to the following equation of state :

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}\left[\ln(1-\tilde{\rho}) + \left(1-\frac{1}{r}\right)\tilde{\rho}\right] = 0 \qquad (5)$$

where $\tilde{\rho}$, $\tilde{P}$, and $\tilde{T}$ are the reduced density, pressure and temperature and r is the number of lattice sites occupied by the r-mer. They are given by the relations:

$$\tilde{\rho} = \rho \,/\, \rho^*_{LF} \qquad (6)$$

$$\tilde{T} = T \,/\, T^*_{LF} \qquad (7)$$

$$\tilde{P} = P \,/\, P^*_{LF} \qquad (8)$$

$$r = \frac{M\ P^*_{LF}}{R\ T^*_{LF}\ \rho^*_{LF}} \qquad (9)$$

where ρ^*_{LF}, T^*_{LF} and P^*_{LF} are the characteristic density, pressure and temperature, M the molar mass and R the ideal gas constant. P^*_{LF} is equal to the cohesive energy density of the fluid in the close packed state and is a direct measure of the strength of the intermolecular interactions in the pure fluid[5]. At atmospheric pressure, $\tilde{P} \approx 0$. Assuming $(1 - 1/r) \approx 1$ for the polymers[6], the non linear least square fit of simplified equation (10):

$$\tilde{\rho}^2 + \tilde{T}\left[\ln(1-\tilde{\rho}) + \tilde{\rho}\right] = 0 \tag{10}$$

to experimental (ρ,T) data yields characteristic density and temperature ρ^*_{LF} and T^*_{LF}. The characteristic pressure P^*_{LF} can be obtained from equation (11) and compressibility β[5]:

$$P^*_{LF}\,\beta = \frac{\tilde{v}^2}{\tilde{T}\tilde{v}\left[\frac{1}{\tilde{v}-1} + \frac{1}{r}\right] - 2} \tag{11}$$

The ρ^*_{LF} and T^*_{LF} values are reported in table 1.

P^*_{LF} and r for **10** were determined from the value of β at 95°C and equations (9) and (11):

$$P^*_{LF} = 778\ \mathrm{J{\cdot}cm^{-3}},\ r = 30.4\ .$$

In the same way , for polyoxyethylene **9** :

$$P^*_{LF} = 572\ \mathrm{J{\cdot}cm^{-3}},\ r = 142\ .$$

The approximation $(1 - 1/r) \approx 1$ for such polymers is reasonable, since it leads only to a 0.3-0.4% underestimation of the third term in equation (5).

As in the case of Flory's equation of state, figure 2 shows a good agreement between the experimental data and the theoretical curve calculated from the LF equation of state.

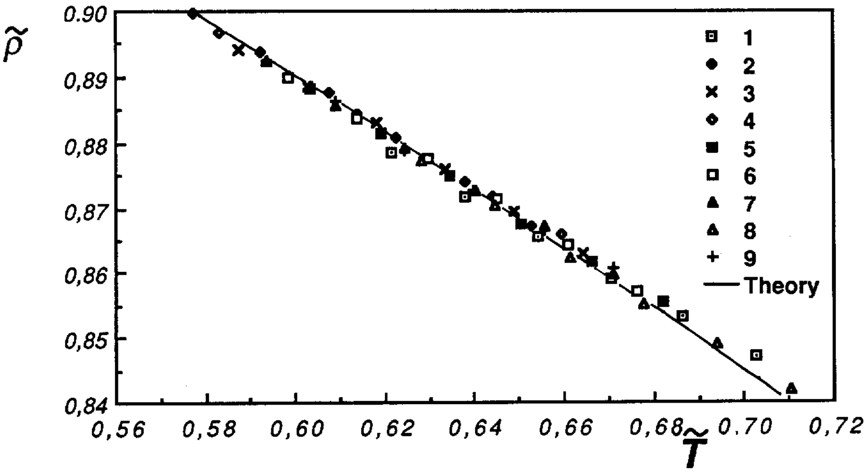

Figure 2 LF equation of state. Variations of reduced density with reduced temperature for polymers **1**-**9**.

EXPERIMENTAL

The synthesis and the characterization of α,ω-dihydroxy-poly(di(oxyethylene)-oxysuccinyl) (**1**), -poly(tri(oxyethylene)oxysuccinyl) (**2**), -poly(oxyethyleneoxysuccinyl)-block-poly(oxyethylene) (**3**), and -poly(oxy-3-(2-methoxyethoxy)propyleneoxysuccinyl) (**4**) were described in a previous article[8]. α,ω-dihydroxy-poly(di(oxyethylene)oxyadipyl) (**5**), -poly(hexamethylene-carbonate) (**6**), -poly(tetramethylenecarbonate) (**7**), -poly(oxypropylene) (**8**) and -poly(oxyethylene) (**9**) were obtained from S.N.P.E.(France). The molar masses of polymers are reported in table 1. Analytical grade triacetin (Prolabo) was used without further purification

Specific volumes v were measured with an accuracy of 0.25% using a thermostated Le Chatelier densitometer in the range 100-160°C at atmospheric pressure.

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