Equation-of-State Parameters for Aliphatic Diesters and Aliphatic Polyesters

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ABSTRACT: Equation-of-state parameters for a series of aliphatic diesters and polyesters are reported. It is shown that: (a) the thermal pressure coefficients, γ, may be predicted with sufficient accuracy using a simple analytical expression, in terms of characteristic group contributions, for all fluids considered; (b) the hard-core volume of the class of compounds studied and of linear aliphatic monocarboxylic acid esters may be calculated with good accuracy with three common values (for 25°) expressing the contributions of the ester, methylene, and methyl groups, respectively. The dependence of the characteristic temperature value on other molecular parameters is briefly discussed.

Methyl and ethyl esters together with polymeric esters of aliphatic dicarboxylic acids, from succinic to sebacic acid, afford an interesting class of compounds for illustrating certain simple but useful structure–physical property correlations.

In this context and focussing attention on equilibrium properties of the liquid (or amorphous) state, the most important quantities to be considered are the molar volume, V_m, the thermal expansion coefficient, α, and either the thermal pressure coefficient ($\gamma = (\partial P/\partial T)_V$) or the isothermal compressibility ($K = \alpha/\gamma$).

These quantities suffice (when known with sufficient accuracy, of course) as equation-of-state parameters to derive the characteristic parameters p^*, $V_m{}^*$, and T^* for the fluid under consideration on the basis of current statistical-thermodynamic theories.[1]

In fact, structure–properties correlations for each given class of compounds should eventually be pursued utilizing appropriate characteristic parameter values. Moreover the same quantities are needed when it is wished to interpret the equilibrium properties of mixtures.[2]

In this paper, V_m, α, and γ data useful for a thermodynamic characterization of pure dimethyl and diethyl esters respectively of succinic, adipic, suberic, and sebacic acid are reported. Comparison is made with analogous properties of a few pure, amorphous aliphatic polyesters and polylactones for a common temperature (25°).

Thermodynamic features of binary mixtures of the diesters, of their solutions in dioxane and in toluene, and of mixtures of the polymeric esters with dioxane are illustrated in a companion paper.[3]

Results

(a) Molar Volumes, Thermal Expansion Coefficients, and Thermal Pressure Coefficients. The results of the measurements of molar volume (V_m), thermal expansion coefficient (α), and thermal pressure coefficient (γ) for the aliphatic diesters and polyesters considered, all referred to 25°, are given in Table I.

The γ values reported in parentheses are experimental values; the others were calculated with the aid of the semiempirical equation[4]

$$\gamma = (1/T)(\Sigma n_i a_i/V_m)^2 \qquad (1)$$

where a_i is the parametric value characteristic of a given atom or atomic grouping of which there are n_i per molecule of the pure liquid considered.

Equation 1 has been shown to express the thermal pressure coefficient for a number of nonpolar or moderately polar fluids (linear, cyclic, branched, and polymeric alkanes, ethers, ketones, esters, and aromatic hydrocarbons) generally within 1–2%, never beyond 5%, of the experimental figures on the basis of a consistent set of a_i values.

Figures given in Table I show that also for aliphatic diesters and polyesters the experimental γ values can be reproduced (within the uncertainty of our experimental data) when the following parametric a_i values are used (in $J^{1/2}$ $cm^{3/2}$): $a(\text{-C(O)O-}) = 705$; $a(CH_3) = 413$; $a(\text{-CH}_2\text{-}) = 309$.

This leads us to believe that all calculated γ's are of similar reliability, which is certainly sufficient for our purpose.

If one compares the physical properties listed in the first three columns of Table I with those for other less polar amorphous polymers and representative low molecular weight liquids,[5] the diesters and polyesters appear characterized by relatively large γ values. This should reflect the noticeable contribution from the ester groups to the cohesive energy density of such compounds (i.e., the large a(-C(O)O-) value).

Our data show that this would correspond to relatively small isothermal compressibility values for the compounds of Table I, since our α data appear to be quite "normal." Finally, the α and V_m values seem to escape any attempt at simple, direct correlation with chemical composition; their appropriate, combined use may lead, however, to characteristic parameters much more useful for this purpose.

(b) Characteristic Parameters. Characteristic parameters $V_m{}^*$, T^*, and p^* have been calculated employing the equations of Flory et al.[1]

$$\tilde{v}^{1/3} = 1 + \alpha T/3(1 + \alpha T) \qquad (2)$$

$$\tilde{T} = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} \qquad (3)$$

$$p^* = \gamma T \tilde{v}^2 \qquad (4)$$

where $\tilde{v}$ and $\tilde{T}$ are the reduced volume and temperature defined respectively by $\tilde{v} = V_m/V_m{}^*$ and $\tilde{T} = T/T^*$ ($V_m{}^*$ is the "hard-core" volume per mole).

The results are listed in the last five columns of Table I. A plot of $V_m{}^*$ against the number of carbon atoms per molecule or per repeating unit of the compounds considered (*not* counting the carbons of the ester groups) is given in Figure 1. It has to be pointed out that, assuming an uncertainty of ±0.1% for V_m (see the Experimental Section) and since a 1% error in α implies an error of about 0.2% in $\tilde{v}$, the final uncertainty of our $V_m{}^*$ figures should be ±0.3%, approximately.

It is seen that all points fall nearly exactly on two parallel straight lines (Figures 1a and 1c). In any case, were a linear relationship to be strictly followed, the scatter of the points is well within experimental error in the primary parameters, α and V_m. For the polymers one can then imme-

Table I
Physical Properties and Characteristic Parameters of Pure, Liquid Compounds[a]

Compd	V_m, cm^3 mol^{-1}	$\alpha \times 10^3$ deg^{-1}	γ, J cm^{-3} deg^{-1}	$\tilde{v}$	$V_m{}^*$, cm^3 mol^{-1}	T^*, °K	p^*, J cm^{-3}	$\tilde{T}$
DAE	132.9	1.05_5	1.54	1.259	105.6	5080	732	0.0587
DMSuc	131.2	0.97_5	1.59	1.243	105.6	5300	732	0.0562
DESuc	168.2	1.01	1.43	1.250	134.6	5200	665	0.0573
DMAd	164.8	0.92_5	1.49 (1.56)	1.232	133.8	5460	674	0.0546
DEAd	201.8	0.96_5	1.38	1.240	162.7	5340	632	0.0559
DMSub	198.8	0.90_5	1.42	1.228	161.9	5530	640	0.0539
DESub	235.6	0.91	1.34	1.229	191.7	5520	603	0.0540
DMSeb[b]	232.4	0.85	1.38	1.216	191.1	5740	607	0.0579
DESeb	269.0	0.88	1.31 (1.27)	1.223	220.0	5630	586	0.0530
PβL	55.1	0.76	1.93 (1.98)	1.196	46.1	6150	824	0.0485
PδL	87.8	0.73	1.64	1.190	73.8	6310	692	0.0473
PϵL	104.2	0.72	1.56	1.187	87.8	6360	657	0.0469
PEAd	142.8	0.71	1.75 (1.80)	1.185	120.5	6420	734	0.0464
PHAd	209.4	0.68	1.55	1.178	177.7	6600	641	0.0451
PESeb	212.4	0.74	1.51	1.192	178.2	6250	638	0.0476

[a] All the data are for 25°. For the polymers, α values at 25° were extrapolated from dilatometric data as explained in the Experimental Section, and V_m and $V_m{}^*$ are in cm^3/mol of repeat unit. [b] For DMSeb (mp 26°) V_m was determined at 27 and 32° and the values were extrapolated at 25°.

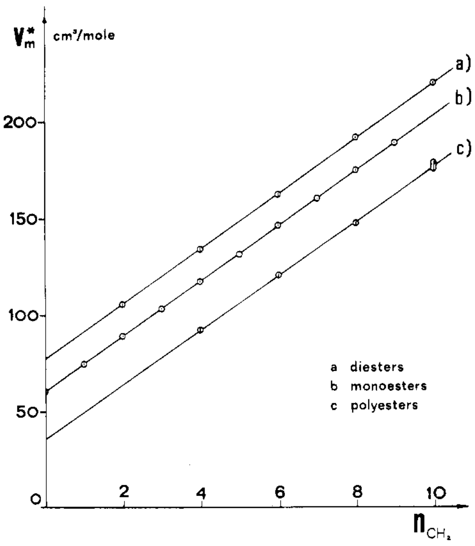

Figure 1. Dependence of the molar hard-core volume, $V_m{}^*$, on the number of methylene groups per molecule of aliphatic monoesters,[7] diesters, and polyesters. All the $V_m{}^*$ are calculated as indicated in the text, either from the data of Table I or from Timmermans' data[7] for the monoesters. For the latter, specification of compounds considered is superfluous in view of the nearly exact linear dependence of $V_m{}^*$ on n_{CH_2}, irrespective of the actual sequence of the methylene group in their linear molecules.

diately write for the hard-core volume per repeating unit

$$V_m{}^* = 2V_{COO}{}^* + nV_{CH_2}{}^* \tag{5}$$

where $V_{COO}{}^*$ and $V_{CH_2}{}^*$ represent the hard-core volumes per ester and per methylene group, respectively.

Our data (Figure 1) lead to $V_{CH_2}{}^* = 14.2$ cm^3/mol and $V_{COO}{}^* = 17.0$ cm^3/mol. Our figure for $V_{CH_2}{}^*$ compares well with the results obtained by Orwoll and Flory in their detailed, accurate analysis of the equation-of-state parameters for *n*-alkanes;[6] these authors find, in fact, that $V_{CH_2}{}^*$ changes with temperature from about 14.0 to 14.4 cm^3/mol in the range 20–160°. Moreover, examination of the V_m and α data reported by Timmermans[7] for several linear, aliphatic monoesters shows that, through application of eq 2, a list of $V_m{}^*$ values is obtained which is consistent with the analysis of our data in terms of group contributions to the molar hard-core volumes and leading to: $V_{CH_2}{}^* = 14.2$ cm^3/mol, and a residual hard-core volume for the ester *and* terminal methyl groups (two per molecule, of course) of 60.3 cm^3/mol (see Figure 1b) with a possible uncertainty of about 0.5%.

Considering now our data for the diesters (Figure 1) one immediately deduces that to each (CH$_3$ + –C(O)O–) atomic grouping a hard-core volume of 38.7 cm^3/mol may be associated. Therefore, we independently reproduce, within limits of experimental error, the value (2 × 38.7) − 60.3 = 17.1 cm^3/mol for the hard-core volume of an ester group for the low molecular weight compounds.

Such a finding is a demonstration of a structure–property correlation in terms of a characteristic parameter (for a given class of compounds) and affords an easy means of calculating from the group-hard-core volumes given above and one single experimental molar volume (at *T*) the thermal expansion coefficient (at *T*) for any linear aliphatic ester or polyester.

Such a result, being obtainable through the $\tilde{v} - \alpha$ link stipulated by eq 2, reinforces the validity of the equation of state.[3]

It would be interesting to extend a similar type of analysis to V_m and α data for other classes of compounds to see whether a sufficiently accurate prediction of the basic parameter α may be made in general (as for the thermal pressure coefficient, see eq 1) simply in terms of group contributions, at least for a given reference temperature.

Concerning the characteristic temperature, *T**, on the contrary, no simple linear relationship can in general be written to express it as a function of atomic groups and links building up molecules even within a given class of compounds.

In fact, considering that, for the compounds which concern us, the characteristic pressure, *p**, can be expressed in our notation (eq 1 and 4) as

$$p^* = \left(\frac{n_{COO}a_{COO} + n_{CH_2}a_{CH_2} + n_{CH_3}a_{CH_3}}{n_{COO}V_{COO}{}^* + n_{CH_2}V_{CH_2}{}^* + n_{CH_3}V_{CH_3}{}^*}\right)^2 \tag{6}$$

and that the characteristic parameters obey the equation[1]

$$p^*V_m{}^* = CRT^* \tag{7}$$

one can see that *T** is also proportional to the inverse of *C*, the number of external degrees of freedom per molecule, a quantity which eludes independent determination (i.e., if not through eq 7, knowing T^*, of course) or reliable prediction in terms of molecular structure.

One can only anticipate that the value of C/V_m^* may markedly decrease with increasing chain-like character for a given type of linear molecule, leading eventually to a maximum T^* value for the "polymeric" compound of appropriate chemical constitution. In Figure 2 values of T^* are plotted against $1/V_m^*$ with use of a few of our data from Table I and the data deduced from Timmermans[7] for *n*-alkyl acetates and propionates. The characteristic temperatures of the dimethyl esters are seen to be substantially higher than those of the other compounds of comparable hard-core molar volume, including the diethyl esters. This must reflect a lower C value, i.e., a comparatively lower molecular flexibility for the former, consistent with the well-known fact that they melt at higher temperatures than the corresponding diethyl esters. In any case it appears that all data for the different compounds may actually be extrapolated, without excessive arbitrariness, to the characteristic T^* value of polyethylene[5] for vanishing $1/V_m^*$, as expected.

Experimental Section

(a) Samples. The diesters were reagent grade samples from Merck, Schuchardt, or EGA. Diacetoxyethane was a Fluka product, while dimethyl sebacate was synthesized in our laboratory. The degree of purity of all samples was about 99% except for diethyl sebacate (ca. 95%). The diesters were therefore fractionally distilled under vacuum and middle cuts were used in each case without further purification.

Dimethyl sebacate, prepared using pure sebacic acid and ethanol in the presence of H_2SO_4, was washed, dried over anhydrous Na_2SO_4, distilled under vacuum, and finally crystallized (mp 26°). Poly(ϵ-caprolactone), PϵL (mol wt = 17,000), a Union Carbide sample, was purified by precipitation with petroleum ether from benzene solutions. Poly(β-propiolactone), PβL, was synthesized in our laboratory as already described.[8]

Poly(δ-valerolactone) was prepared by ring-opening polymerization of pure δ-valerolactone, initiated by CF_3COOH, in toluene solution at 20°. After 24 hr the polymer was precipitated with ethyl ether, washed, and finally dried under vacuum.

The intrinsic viscosity of PϵL and PδL was 0.2 dl/g (benzene, 25°). Melting points of the polymer samples, recorded by differential scanning calorimetry, were: PϵL, 65°; PβL, 83°; PδL, 56°. Poly(ethylene adipate), PEAd, poly(hexamethylene adipate), PHAd, and poly(ethylene sebacate), PESeb, were prepared in our laboratory by transesterification of dimethyl adipate and dimethyl sebacate, respectively, with ethylene- or hexamethyleneglycol following the procedure described by Billmeyer.[9] After purification, the intrinsic viscosity of PEAd, PHAd, and PESeb was close to 0.15 dl/g (benzene, 25°). The three polyesters melt at 54° (PEAd), 56° (PHAd), and 77° (PESeb).

(b) Density Measurements. The density of liquid samples was determined with the aid of a pycnometer (about 7 cm^3 volume, 1 mm^2 capillary section) at three temperatures (20, 25, and 30°) in a thermostatic bath. Constancy of temperature better than ±0.01° was assured in each case. Thermal expansion coefficient, α, values at 25° were derived from these density data.

Density measurements were reproducible to better than 0.01%, however, allowing for a residual 0.5% impurity in each sample (presumably homologous diesters) and assuming its density to differ by 10% from that of the major component, the final accuracy of the V_m data should be ±0.05% approximately. Analogously the α figures can be considered accurate to nearly 1%, or better.

The density of the polyesters, which are partially crystalline solids at room temperature, was determined at 25° either using a pycnometer for solids or measuring the density of aqueous $BaCl_2$ solutions in which the polymer samples were in hydrostatic equilibrium. Specific volumes, V_{sp}, were measured up to about 100° by mercury weighing dilatometers as already described.[6] Data from above the polymers melting temperatures could be extrapolated to 25° to obtain sufficiently reliable "amorphous" specific volumes. This in view of the linear dependence of V_{sp} on temperature and of the low melting points of the polymers considered.

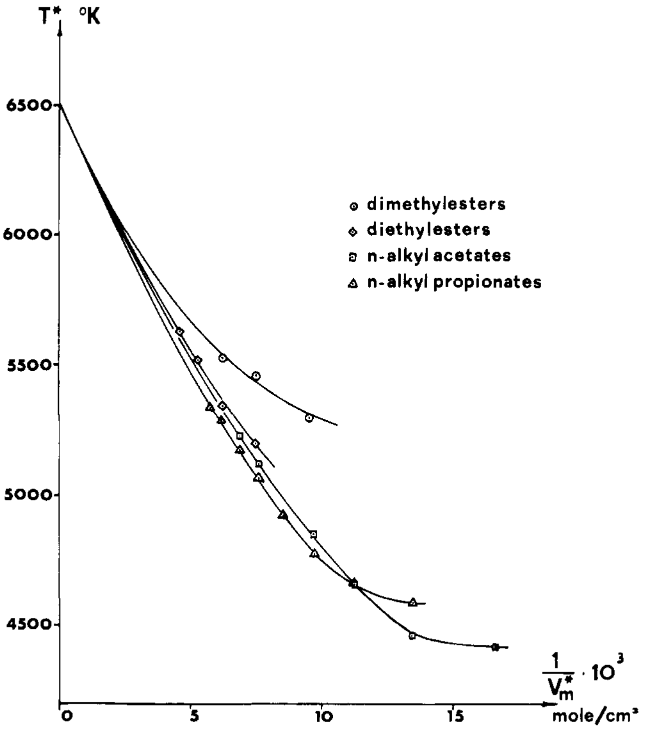

Figure 2. Dependence of the characteristic temperature, T^*, on the reciprocal of the molar hard-core volume for aliphatic monocarboxylic acid esters and dicarboxylic acid esters. The following compounds of increasing T^* within each series have been considered: (⊙) $[(CH_3)COO]_2-(CH_2)_x$, x = 2, 4, 6; (⊡) $(CH_3COO)C_xH_{2x+1}$, x = 1–7; (◇) $[(C_2H_5)COO]_2-(CH_2)_x$, x = 2, 4, 6, 8; (▲) $(C_2H_5COO)C_x \cdot H_{2x+1}$, x = 1–8.

The α values were finally calculated with the assumption that they are independent of temperature in the range 25–100° (which generally holds true to 2–3% for different polymers).

(c) Thermal Pressure Coefficient Measurements. The experimental set-up has already been described.[10] For two of the diesters (see Table I) the thermal pressure coefficient was determined at three temperatures in the range 20–50° and the figure at 25° was deduced by linear interpolation. The experimental error should not exceed ±3% of the final figure.

For the polymers, γ values were determined at two or three temperatures above their melting temperatures T_m and then linearly extrapolated down to 25°. Figures obtained in this way differ by less than 3% from those calculated on the basis of the equation[6] $d \ln \gamma/dT = (1 + 2\alpha T)/T$.

Acknowledgment. This work has been sponsored by the Italian Consiglio Nazionale delle Ricerche, Rome.

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