Thermodynamics of Aliphatic Diester and Polyester Solutions

G. Manzini, V. Crescenzi,* and R. Furlanetto

Laboratory of Macromolecular Chemistry, Institute of Chemistry, University of Trieste, 34127 Trieste, Italy. *Received July 31, 1974*

ABSTRACT: A thermodynamic characterization is partially achieved on the basis of calorimetric and volumetric data (25°) for a series of mixtures of different aliphatic diesters in 1,4-dioxane and toluene and for three aliphatic polyesters in dioxane. These data, together with similar ones previously obtained for two other polylactones,[1] are discussed with the use of the theory of Flory.[2] The possibility is explored of expressing the parameter X_{12} of this theory in terms of characteristic exchange enthalpies of contact ($X_{i,j}$) between chemically different segments (i, j, . . .) constituting the molecules of the components, each contributing a given fraction (α_i, α_j, . . .) to the total molecular surfaces.

The results of measurements at 25° of the enthalpy (ΔH_M) and excess volume (V^E) of mixing eight aliphatic diesters in equimolar pairs, and with 1,4-dioxane and toluene, respectively, are reported.

Diesters considered are: diacetoxyethane (DAE), dimethyl succinate (DMSucc), dimethyl adipate (DMAd), dimethyl suberate (DMSub), dimethyl sebacate (DMSeb), diethyl succinate (DESucc), diethyl adipate (DEAd), diethyl suberate (DESub), and diethyl sebacate (DESeb).

The results of similar experiments (heat of dilution and V^E measurements) on solutions of poly(δ-valerolactone) (PδL), poly(ethylene adipate) (PEA), and poly(hexamethylene adipate) (PHA) in 1,4-dioxane at 25° are also given.

Correlation of the data is attempted on the basis of a statistical thermodynamic formulation for liquid mixtures,[2] with use of the equation-of-state parameters for the pure diesters and polyesters reported in a preceding paper[3] and literature data for dioxane[4,5] and toluene.[4,5]

It is found expedient to express the exchange-energy density parameter (the X_{12} parameter of the above mentioned theory[2]) explicitly in terms of different contributions arising from pairwise contacts between chemically different segments constituting the ester molecules (or macromolecules) and the solvents studied.

Results

(a) Diester Mixtures. The results of the measurements of the enthalpy and volume changes on forming nearly equimolar binary mixtures of various aliphatic diesters are reported in Table I (ϕ is the volume fraction). As expected, the process of mixing is endothermic and characterized by small, positive V^E values except for the DAE–DMSucc pair for which, however, the observed effects are quite small indeed. Relatively large excess quantities are found for mixtures in which the two components have a large difference in molecular dimensions although, as expected, other factors also play a role (see, for instance, the DESucc-DMAd case). The significance (and method of calculation) of the X_{12} parameter of Table I will be discussed in the following.

(b) Diester Solutions in Dioxane and in Toluene. Heat and excess volumes of mixing of the various diesters with dioxane and with toluene, respectively, are reported in Figures 1–4, as a function of composition (diester volume fraction, ϕ_2). With dioxane we find that both ΔH_M (Figure 1) and V^E (Figure 2) are positive and increase in a rather regular fashion with an increasing number of carbon atoms in the diester molecules. (In each case the dotted and full line curves were drawn, on the basis of experimental V^E and ΔH_M data, respectively, employing analytical expressions given in the Discussion.)

In the case of toluene, on the contrary, the data of Figures 3 and 4 show that, for the dimethyl esters, ΔH_M and V^E decrease and change sign with increasing molecular weight of the latter, while both excess quantities are generally negative for the diethyl esters.

(c) Polyester Solutions in Dioxane. For the three polymers considered the measurements of the enthalpy of dilution and of the densities were carried out in a sufficiently wide range of solute concentration with dioxane as solvent. The experimental data on the heat of dilution are reported in Figure 5 as a plot of

$$X_H = \frac{\Delta Q}{\Delta n_1}\frac{1}{RT\phi_2'\phi_2''}$$

against

$$(\phi_2'\phi_2'')^{1/2}$$

ΔQ is the heat exchange measured (at 25°) when the number of moles of solvent in the solution was increased by Δn_1 thereby reducing the polymer volume fraction from ϕ_2' to ϕ_2''. The experimental points are rather scattered; the attainment of a higher precision would be, however, quite difficult in view of the very small heat effects to be measured. In all cases X_H is seen to be negative and small. The excess volumes (Figure 6) of the three polyester solutions in dioxane are likewise negative, the more pronounced effect being observed in the case of poly(ethylene adipate).

The V^E values are small, however, and may be affected by an error of about $\pm 2 \times 10^{-3}\ \phi_2$ mainly as a consequence of the uncertainty in the value of the specific volumes of the pure amorphous polymers at 25°, estimated to be around 0.2%.

Discussion

(a) Theoretical Framework. In an attempt to correlate the experimental findings given above we make recourse to the theory of Flory.[2] In this theory the characteristic pressure p^* of a mixture is given as a function of those of the components and of a parameter, X_{12} (J cm^{-3}), chosen to express the difference between interactions of neighboring pairs of like and unlike species, by the equation

$$P^* = \phi_1 P_1^* + \phi_2 P_2^* - \phi_1\theta_2 X_{12} \tag{1}$$

where

$$\phi_1 = 1 - \phi_2 = N_1\bigg/\left(N_1 + \frac{V_2^*}{V_1^*}N_2\right) \tag{2}$$

and

$$\theta_2 = 1 - \theta_1 = \frac{(s_2/s_1)\phi_2}{\phi_1 + (s_2/s_1)\phi_2} \tag{3}$$

The $V_{1,2}^*$ are the molar hard-core volumes of the components present with $N_{1,2}$ molecules in number and s_2/s_1 is the ratio of contact sites per segment of the components.[2]

Table I
Aliphatic Diesters (Enthalpy and Volumes Changes on Mixing at 25°)

1–2	ϕ_2	ΔH_M, J/mol	X_{12},[a] J/cm^3	ϕ_2	V^E, cm^3/mol	X_{12},[b] J/cm^3	V^E from X_{12},[a] cm^3/mol
DMSucc–DMAd	0.53	120	4	0.50	0.09	4.5	0.08
DMSucc–DESub	0.60	480	14	0.50	0.25	12	0.32
DMSucc–DESeb	0.58	700	19	0.50	0.32	10.5	0.48
DMAd–DESub	0.55	210	5	0.50	0.08	3.5	0.12
DMAd–DESeb	0.56	380	9	0.51	0.14	4.5	0.24
DESub–DESeb	0.51	35	1	0.51	0.02	1	0.02
DAE–DMSucc	0.48	−12	−0.5	0.40	0.0	1	−0.02
DESucc–DMAd	0.50	180	5.5	0.49	0.02	2.5	0.07

[a] From ΔH_M data. [b] From V^E data.

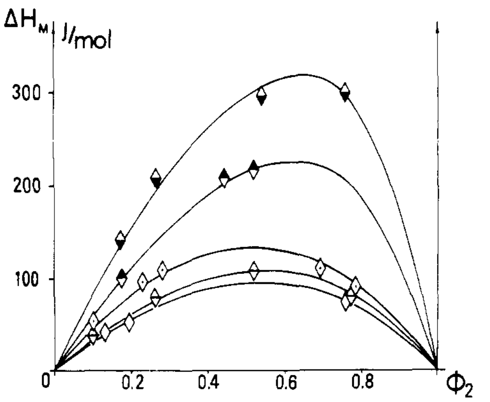

Figure 1. Enthalpy changes on mixing aliphatic diesters with 1,4-dioxane at 25°. (——) Enthalpies calculated using X_{12} values (eq 6) chosen to get the best fit with experimental data: ◊, DAE; ◊, DMSucc; ◊, DMAd; ◊, DESub; ◊, DESeb.

The characteristic temperature, T^*, of the mixture may then be written as

$$T^* = P^* \Big/ \left(\phi_1 \frac{P_1^*}{T_1^*} + \phi_2 \frac{P_2^*}{T_2^*}\right) \tag{4}$$

and the analytical forms of the equation of state ($p \rightarrow 0$) and of the thermal expansion coefficient of the mixture are identical, respectively, to those for the pure components

$$\tilde{T} = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} \tag{5}$$

$$\tilde{v}^{1/3} - 1 = \alpha T/3(1 + \alpha T) \tag{5'}$$

where $\tilde{T}$ and $\tilde{v}$ are the reduced temperature and volume.[2] With these premises the expression for the enthalpy of mixing will have the form (per mole of mixture)

$$\Delta H_M = x_1 P_1^* V_1^* \left(\frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}}\right) + x_2 P_2^* V_2^* \left(\frac{1}{\tilde{v}_2} - \frac{1}{\tilde{v}}\right) + \frac{x_1 V_1^* \theta_2}{\tilde{v}} X_{12} \tag{6}$$

where x_1 and x_2 are mole fractions.

For polymer solutions for which, in general, accurate heat of dilution data are more easily collected than integral heats of mixing, the experimental calorimetric data may be made to fit the equation for the limiting ($\phi_2 \rightarrow 0$) reduced partial molar enthalpy of the solvent, $X_{H,1}$

$$X_{H,1} = \frac{P_1^* V_1^*}{\tilde{v}_1 RT}\left[Y_{12}(1 + \alpha_1 T) - \frac{2}{3} A^2 \alpha_1^2 T^2 (1 + \alpha_1 T)\right] \tag{7}$$

derivable from eq 6 by writing

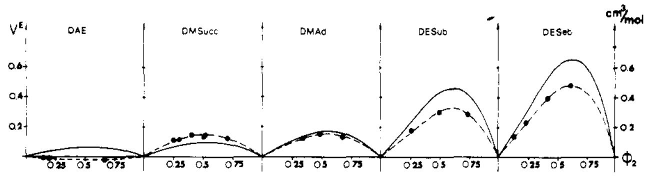

Figure 2. Excess volumes on mixing aliphatic diesters with 1,4-dioxane at 25°: (⊙) experimental data; (- - -) excess volumes calculated with X_{12} values chosen to fit experimental data; (——) excess volumes calculated using X_{12} values from calorimetric data.

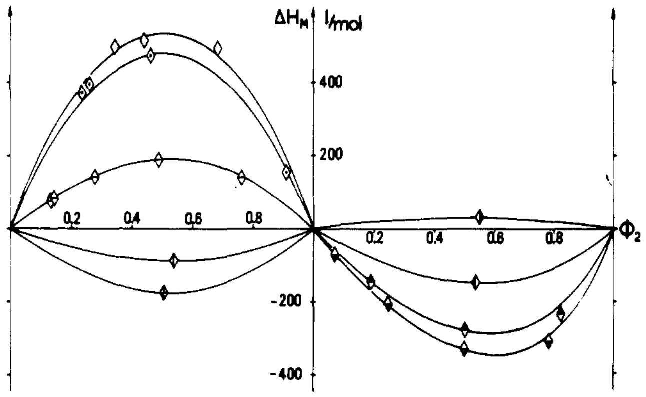

Figure 3. Enthalpy changes on mixing aliphatic diesters with toluene at 25°. (——) Enthalpies calculated using X_{12} values (eq 6) chosen to get the best fit with experimental data: ◊, DAE; ◊, DMSucc; ◊, DMAd; ◊, DMSub; ◊, DMSeb; ◊, DESucc; ◊, DEAd; ◊, DESub; ◊, DESeb.

$$Y_{12} = X_{12} \frac{(s_1/s_2)^2}{P_1^*}$$

$$A = \left(1 - \frac{T_1^*}{T_2^*}\right)\frac{P_2^*}{P_1^*} - X_{12}\frac{(s_2/s_1)}{P_1^*} \tag{8}$$

To evaluate the basic parameter X_{12} for a given binary mixture one may proceed as follows. The experimental molar volume of the solution, V_m [$V^E = V_m - (x_1 V_{m,1} + x_2 V_{m,2})$], is used to obtain $\tilde{v} = V_m/(x_1 V_1^* + x_2 V_2^*)$ once the hard-core volumes of the components have been calculated from their thermal expansion coefficients with the aid of eq 5′. Hence T^* is deduced from the equation of state (eq 5) and its insertion in 4 and 1 yields X_{12}, once appropriate values of the s_2/s_1 ratio have been chosen (see the following section).

On the basis of calorimetric data one can directly use eq 6 or 7 to calculate X_{12}, with the introduction of the necessary set of parameters for each component prescribed by eq 1–5. The same X_{12} value should obviously be obtained according to theory, independent of the experimental source of information. As a matter of fact more or less divergent

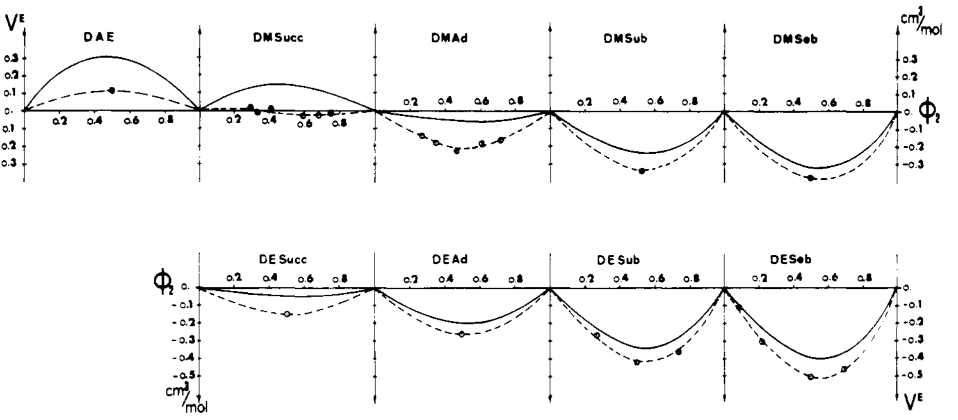

Figure 4. Excess volumes on mixing aliphatic diesters with toluene at 25°: (⊙) experimental data; (- - -) excess volumes calculated with X_{12} values chosen to fit experimental data; (——) excess volumes calculated using X_{12} values from calorimetric data.

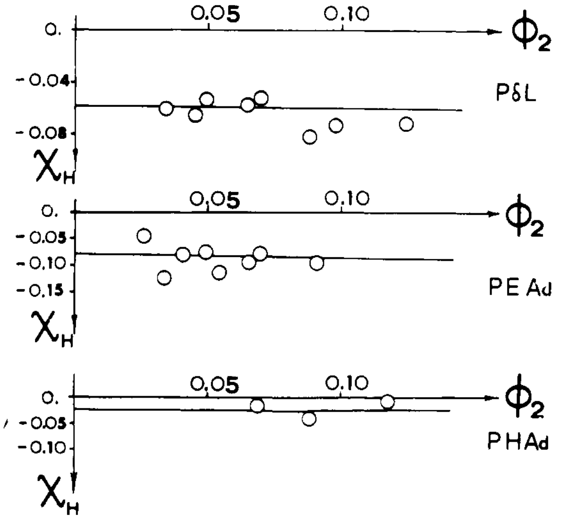

Figure 5. Reduced partial molar residual enthalpies, X_H, on diluting 1,4-dioxane solutions of three polyesters at 25°: O, experimental data; (——) X_H calculated using X_{12} values chosen to fit the experimental data (eq 7).

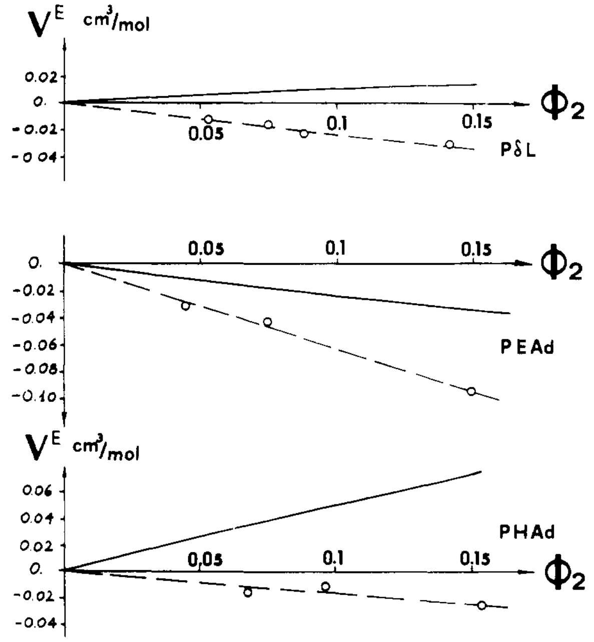

Figure 6. Excess volumes V^E on mixing three polyesters with 1,4-dioxane at 25°: O, experimental data; (- - -) V^E calculated using X_{12} chosen to fit experimental data; (——) V^E calculated using X_{12} from calorimetric data (see Figure 5).

X_{12} figures are in general calculated from enthalpy or V^E data, which reflects some inaccuracy in the theory.

(b) Application of the Theory to the Experimental Data. To apply the above theoretical approach to our data the characteristic parameters for the pure components previously reported[3] have been used (for dioxane[4,5] and toluene[4,5] literature values have been retained).

By adopting the method of calculation of Flory et al.[6] the s_2/s_1 values for the different mixtures involving the diesters were found to be nearly unity. In practice, $s_2/s_1 = 1$ was imposed in all these cases. For the polymer solutions in dioxane, by approximating the solvent molecule by a disk of volume V_1^*/N and height equal to $\frac{3}{2}$ of the radius, and the polymer repeating unit by a cylinder of volume V_u^*/N and the height of its fully extended zig-zag planar structure the resulting s_2/s_1 values are: 0.80 for PEAd, 0.85 for PδL, and 0.90 for PHAd. X_{12} values were finally derived as outlined in the previous section; these are reported in Tables I and II. For simplicity, in Table II only the X_{12} values obtained from calorimetric data are given.

For the diester mixtures (Table I) the theory reproduces the experimental findings with reasonably good agreement for X_{12}, from ΔH_M and from V^E data, although the latter are systematically lower. For the solutions of the diesters in dioxane and in toluene a similar discrepancy between the two sets of X_{12} values was found.

More important, a perspective view of all of our data for the diesters (Table I and Figures 1–4) indicates the following. (1) The enthalpy of mixing is nearly quantitatively determined by the term containing X_{12} in eq 6, the contribution from equation-of-state terms accounting for a few percent of the measured heats. (2) For the excess volumes, on the contrary, calculations made taking $X_{12} = 0$ correctly predict the sign of V^E and yield values amounting to at least 50% of the experimental data. In particular for the diester solutions in dioxane, V^E calculated in this way agrees within a few percent with experiment in each case. In other words, the theory correctly predicts and nearly quantitatively describes the influence on the excess volume of mixing of differences in equation-of-state parameters between components in the case mentioned above. (3) The interaction parameter X_{12} is seen to vary in a rather regular fashion with increasing chain length of the diesters, depending, of course, of the other partner in the binary mixtures (i.e., dioxane or toluene). For the solutions in toluene, however, one has to assume negative X_{12} values to account for the observed ΔH_M values (and also to let the calculated and experimental V^E values coincide) for the

Table II
X_{12} from Calorimetric Data (J/cm^3)

Diester or polyester	In toluene	In 1,4-dioxane
DAE	20	5
DMSucc	18	6
DESucc	1	
DMAd	5	4.5
DEAd	−5	
DMSub	−2.5	
DESub	−8	8.5
DMSeb	−5.5	
DESeb	−9.5	11
PβL[a]		25
PδL		0
PεL[a]		1.5
PEAd		0
PHAd		2

[a] Data from previous work.[1]

diesters having the *smaller* linear density of ester groups per molecule (see Figure 7).

For the polyesters, X_{12} values practically equal to zero satisfy the heat of dilution data on the basis of eq 7. Differences in equation-of-state parameters between polymeric solute and solvent do therefore determine sign and absolute value of the enthalpy (Figure 5). The excess volumes are then not so well reproduced, however, by the theory, which appears to lead systematically to too high V^E figures (see Figure 6). For the polylactone dioxane solutions considered in a previous work[1] the same result occurs in the case of poly(ϵ-caprolactone), while in the case of poly(β-propiolactone) it is necessary to assume a positive value for X_{12} in order to account for the heat of dilution data.

The Dependence of the X_{12} Parameter on Component Chemical Structure. The complete set of X_{12} values calculated from our calorimetric data is given in Tables I and II. These data pertain to mixtures of homologous components, and it appears logical to look for a possible correlation between X_{12} and the chemical structure of the species considered. To this end, let us define

$$X^* = (V_1^*/S_1)X_{12} \tag{9}$$

where S_1 is the total number of contact sites which 1 mol of component 1, with hard-core volume V_1^*, can establish in a binary mixture. Recalling the definition of X_{12},[2] we see that X^* has the meaning of an average characteristic exchange energy connected with the establishment of contacts between unlike species (1–2) at the expense of 1–1 and 2–2 contacts.

We assume that X^* for a given binary mixture can be expressed in terms of contributions from characteristic exchange energies X_{ij}^*, associated with the formation of contacts between dissimilar *chemical groupings*, i and j, of the components, and with the interruption of an equivalent number of i–i and j–j ones (j and i may indicate an alkyl group or an ester group, etc., respectively).

The following expression linking X^* to the X_{ij}^*'s may then be written, with the hypothesis of completely random mixing

$$X^* = -\sum_{i>j}(\alpha_{i,1} - \alpha_{i,2})(\alpha_{j,1} - \alpha_{j,2})X_{ij}^* \tag{10}$$

where $\alpha_{i,1(2)}$ and $\alpha_{j,1(2)}$ are the site fractions of contacts of the ith and jth type (e.g., aliphatic, ester, etc.) per mole of component 1 (or 2).

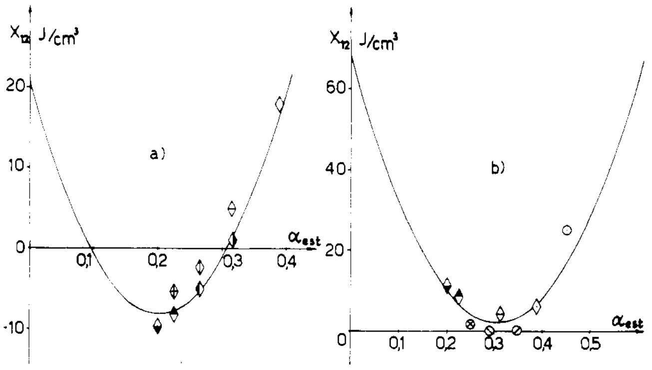

Figure 7. X_{12} parameter *vs.* ester group surface (contact sites) fraction: (A) for toluene solutions symbols as in Figure 3, (——) calculated values (see text); (B) for 1,4-dioxane solutions diamond symbols as in Figure 1, (⊙) PβL, (⊘) PEAd, (⦸) PδL, (⊗) PεL and PHAd, (——) calculated values (see text).

We then assume that X_{12} is simply proportional to X^* since the V_1^*/S_1 ratio (see eq 9) is nearly a constant for most monomeric liquids. Equation 10 thus becomes

$$X_{12} \simeq -\sum_{i>j}(\alpha_{i,1} - \alpha_{i,2})(\alpha_{j,1} - \alpha_{j,2})X_{ij} \tag{11}$$

where the X_{ij} are exchange-energy density parameters.

Finally, to evaluate the site fractions α_i, we consider the diester molecules to exhibit only two types of contact surfaces: "aliphatic" (including methylene and methyl groups) and "ester," respectively. Similarly, for toluene "aromatic" and "aliphatic," and for 1,4-dioxane "aliphatic" and "ether" type surfaces are considered.

In practice, we use the approximate van der Waals group surfaces as given in the well-known paper of Bondi,[7] i.e., 35.2, 22.4, 36.5, 88.5, and 12.5 Å^2, for the groups CH_3, $-CH_2-$, $-COO-$, Ph, $-O-$, respectively.

Our approach is basically not new; in our opinion it represents, however, a more logical application of known formalisms.[8,9] Equation 11, in fact, aims at an interpretation of the enthalpy of mixing residual from equation-of-state contributions and *not* of the total heat effect.[9] Our method of evaluation of the α_i values, although roughly approximate, seems to us more realistic then that adopted by others.[9]

Moreover, methods of calculation of the number of sites of *whole molecules*[6] are not easily applicable to the case of *single constituent groups*.

For the diesters of Table I, eq 11 becomes

$$X_{12} \simeq -(\alpha_{al,1} - \alpha_{al,2})(\alpha_{est,1} - \alpha_{est,2})X_{al,est} = (\alpha_{est,1} - \alpha_{est,2})^2 X_{al,est} \tag{12}$$

since for these compounds $\alpha_{al} = 1 - \alpha_{est}$.

For the diester–toluene mixtures we write

$$X_{12} \simeq X_{al,est}\alpha_{est}^2 - 0.72(X_{al,arom} + X_{al,est} - X_{arom,est})\alpha_{est} + 0.5184X_{al,arom} \tag{13}$$

while for the diesters and polyesters in dioxane

$$X_{12} \simeq X_{al,est}\alpha_{est}^2 - 0.22(X_{al,est} + X_{al,et} - X_{est,et})\alpha_{est} + 0.0484X_{al,et} \tag{14}$$

where we take for toluene $\alpha_{arom} = 0.72$, $\alpha_{al} = 0.28$ and for dioxane $\alpha_{al} = 0.78$, $\alpha_{et} = 0.22$ on the basis of the group surfaces given above.

For the diester solutions in dioxane and in toluene, the X_{12} values of Table II are plotted in Figure 7 against α_{est}. Before proceeding further, let us point out that in such plots, with α_{est} estimated as indicated above, the points for the dimethyl esters lie systematically above those for the diethyl esters.

When relying upon the theory according to which the X_{12} values were derived and to our scheme of reasoning as embodied in eq 11, it appears that α_{est} should be calculated in a different manner for the two types of esters. This is not unrealistic, but would entail a degree of sophistication which does not seem warranted at present.

For $\alpha_{est} = 0$ one should place on the ordinates of Figure 7 the X_{12} values for alkane–benzene mixtures and for alkane–dioxane mixtures, respectively. For the former, literature data[6,10,11] lead to $X_{al,arom}$ values in the range 35–50 J/cm^3 at 25°. The fact that $X_{al,arom}$ depends on the hydrocarbon considered is very likely due to the inaccuracy underlying our position $X_{12} \simeq X_{al,arom}$ for benzene solutions of any saturated aliphatic hydrocarbon.

For the $X_{al,et}$ exchange-energy parameter we can consider the average value which we estimate from a few of the calorimetric data of Kehiaian et al.[9] for *n*-alkane–aliphatic ether mixtures. In view of the lack of information necessary to treat quantitatively the above-mentioned data by means of the theory of Flory, we can only say that $X_{al,et}$ should have a high value in the neighborhood of 1300 J/cm^3.

Evaluation of literature data[12] for cyclohexane–dioxane mixtures yields: $X_{al,et} \simeq X_{12}/(\alpha_{et})^2 = 80/(0.22)^2 \simeq 1600$ J/cm^3 at 25°. It is evident that the $X_{al,et}$ parameter is particularly sensitive to the choice of the van der Waals surface of an ether group, anyhow a relatively small figure.

To simplify the matter, and in view of the nature of our approach, which is presently confined to a qualitative level mainly by the roughly approximate estimate of the α_i values, we have therefore taken $X_{al,arom} = 40$ J/cm^3 and $X_{al,et} = 1400$ J/cm^3 and have drawn best-fit curves (eq 13 and 14) through the points of Figure 7 (curves a and b) by further imposing $X_{al,est} = 700$, $X_{arom,est} = 350$, and $X_{est,et} = 150$ J/cm^3. Use of data of Table I and eq 12 leads to $X_{al,est} = 650 \pm 50$ J/cm^3.

It has to be realized that properly made concomitant variations up to 20% in the above listed X_{ij} figures do lead to curves fitting the points of Figure 7 in similarly satisfactory ways, among which it is difficult to make a rational choice in view of what has been said above. In other words, fixing the α_{est} values, as at the present stage, entails an uncertainty of about 20% in the X_{ij} figures.

It is interesting to report, however, that application of Flory's theory to the calorimetric data of Meares[13] for mixtures of aliphatic diesters with ethyl acetate (by assuming literature V_M and α data,[13] and calculating the γ values with the aid of eq 1 of the preceding paper[3]) leads, on the basis of eq 11, to $X_{al,est} \simeq 800$ J/cm^3. This figure should be considered in satisfactory agreement with that derived from our data.

Finally it should be pointed out that our curve of Figure 7a predicts a very large X_{12} value for PβL ($\alpha_{est} = 0.45$) in toluene. In fact PβL is not soluble in this solvent. Likewise, our figure for $X_{al,est}$ leads to a very large positive value for X_{12} (about 105 J/cm^3) in the case of mixtures of saturated aliphatic hydrocarbons with DAE and DMSucc; in fact, these diesters exhibit large miscibility gaps when mixed with *n*-hexane and cyclohexane near room temperature. We also predict for alkane solutions of the other diesters considered X_{12} values less than 70 J/cm^3; these diesters are freely soluble in *n*-hexane and cyclohexane at room temperature.

Concluding Remarks

Our experimental data reinforce the opinion that the theory of Flory[2] can give a fair representation of the influence of equation-of-state parameters on the thermodynamics of binary mixtures. We have tried to find an explicit, consistent expression for the X_{12} parameter of that theory in terms of exchange-enthalpy parameters associated with the different contacts that chemically different groupings of the component molecules may establish (at random) with each other.

The present approach still leaves a certain latitude of choice, and hence of arbitrariness, in the values of the above parameters. This is mainly due, in our opinion, to our rather crude estimate of the number of contact sites for the different atomic groupings.

With more experimental data for different classes of compounds, a refinement in this direction should be feasible. At present we can maintain that eq 10 in the text may provide a sound representation of the dependence of X_{12} on chemical composition of binary nonpolar mixtures, as envisaged by the plots of Figure 7.

In closing, it is worth mentioning that our approach obviates assumption of "specific" interactions to account for negative X_{12} values.[14] As a matter of fact, such an assumption is not at all justified in our case, since more negative X_{12} values in toluene have been found for those diesters with a lower density of ester groups per molecule (see Figure 7), i.e., of those groups which might be assumed to give rise to specific interactions with the aromatic solvent.

Experimental Section

(a) Samples. Origin and purity of the diester and polyester samples have already been specified in the preceding paper.[3] Toluene and dioxane (C. Erba, R.P. Products) were distilled under reduced pressure, dried, and stored over sodium wire.

(b) Density Measurements. The excess volumes of mixing were derived in all cases from density data at 25°. Density measurements were made using a pycnometer (7 cm^3 volume; 1-mm diameter capillary) calibrated with bidistilled water, mercury, and anhydrous toluene at 25° (temperature control ±0.005°) with reproducibility within 0.003%. All solutions were prepared by weight (±0.1 mg). The reproducibility of the pycnometric measurements was better than 0.01%. Buoyancy corrections were made by assuming 1.2 mg/cm^3 and 8 g/cm^3 for the density of air and of the balance's weights, respectively.

(c) Calorimetric Measurements. Integral heats of mixing were determined at 25 ± 1° for the nonpolymeric esters with use of an LKB batch microcalorimeter 10700-2. In the case of dimethyl sebacate the measurements were taken at 27°. In each run, given amounts of the two components to a total of about 5 cm^3 were mixed in the calorimeter and the heat exchange (from −10 to +15 J, depending, of course, on the mixture) was determined by measuring the surface under the recorded thermogram with the aid of a calibration curve. This procedure involves an error of less than 1%. However, the existence of a vapor space in the calorimeter cells (about 5–6 cm^3) may entail, when working with dioxane or toluene, a larger uncertainty in the final enthalpy of mixing figures, which we roughly estimate to be about 3–6 J/mol. Heats of dilution of the polyester solutions in dioxane were measured with the same LKB calorimeter as previously described.[1]

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

References and Notes

(1) G. Manzini and V. Crescenzi, *Polymer*, **14**, 343 (1973).
(2) P. J. Flory, *J. Amer. Chem. Soc.*, **87**, 1833 (1965).
(3) G. Manzini and V. Crescenzi, *Macromolecules*, preceding paper.
(4) G. Allen, G. Gee, and G. J. Wilson, *Polymer*, **1**, 456 (1960).
(5) J. Timmermans, "Physico-Chemical Constants of Organic Compounds," Elsevier, New York, N.Y., 1950.
(6) A. Abe and P. J. Flory, *J. Amer. Chem. Soc.*, **87**, 1838 (1965).
(7) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).
(8) O. Redlich, E. L. Derr, and G. J. Pierotti, *J. Amer. Chem. Soc.*, **81**, 2285 (1959).
(9) H. V. Kehiaian, K. Sosnkowska-Kehiaian, and R. Hryniewicz, *J. Chim. Phys. Phys.-Chim. Biol.*, **68**, 922 (1971).
(10) P. Callot, *Eur. Polym. J.*, **8**, 1209 (1972).
(11) G. C. Benson and J. Singh, *J. Phys. Chem.*, **72**, 1345 (1968).
(12) A. W. Andrews and K. W. Morcom, *J. Chem. Thermodyn.*, **3**, 519 (1971).
(13) (a) P. Meares, *Trans. Faraday Soc.*, **45**, 966 (1949); (b) *ibid.*, **45**, 1066 (1949).
(14) C. Booth and C. J. Devoy, *Polymer*, **12**, 309 (197)).