

Thermodynamics of Tetra-*n*-octyltin + Hydrocarbon Systems by Gas-Liquid Chromatography

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*The activity coefficients of fifteen hydrocarbons at infinite dilution in tetra-*n*-octyltin were measured using gas-liquid chromatography at five temperatures between 40 and 60°C. Partial molar excess thermodynamic properties are calculated from the experimental results, and discussed within the framework of the equation of state theory of Flory and of the Ising fluid theory of Sanchez and Lacombe. Both theories result in binary mixture characteristic parameters (X_{12} and ΔP^* , respectively) that decrease linearly with the temperature. The results may be interpreted by assuming that there is orientational order in pure tetra-*n*-octyltin and in pure *n*-alkanes, but not in the remaining solutes; the destruction of this order on mixing the hydrocarbons with the tin compound results in important contributions to the excess thermodynamic properties.*

KEY WORDS: Tetra-*n*-octyltin; hydrocarbon solutions; activity coefficients; gas chromatography; Flory theory; Sanchez-Lacombe theory; excess enthalpy; orientational order.

1. Introduction

The absence of very strong or specific interactions gives to non-polar fluid mixtures an appearance of simplicity that was the subject of a large number of experimental and theoretical studies. The following contributions to the thermodynamic excess functions of such systems have been identified and constitute the present status of our knowledge.

a. A combinatorial contribution associated with the molecular size differences between the mixture components which results in a positive excess entropy calculable by means of the Flory equation⁽¹⁾ or by the Huggins-Miller-Orr and Guggenheim approximation.⁽²⁾

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b. Volume changes occur during the mixing process due to differences in the expanded states of the two species. For non-polar mixtures the contraction of the lower density component exceeds the expansion of the higher density component, this resulting in negative contributions to the enthalpy and entropy. Although Prigogine and co-workers⁽³⁾ were the first to consider a "structural contribution" of this type, it became more popular after the work of Flory and collaborators,⁽⁴⁾ who named it the "free volume effect" or "equation of state effect." It is also taken into account in the theory of Sanchez and Lacombe,⁽⁵⁾ founded on a model fluid characterized as a lattice that includes vacant sites (Ising fluid).

c. A positive contact interaction contribution to the excess enthalpy and entropy, that for alkane mixtures results from differences between the force fields around the methyl ends and the methylene interior segments of the chains, associated with the different proportions in which these groups participate in the molecules that constitute the mixture. Contact interactions are characterized by the parameter X_{12} in the theory of Flory, and by the parameter ΔP^* in the theory of Sanchez and Lacombe.

d. Depolarized Rayleigh scattering studies indicate that fluids formed from long non-branched molecular chains present, in the pure state, short range orientational order.⁽⁶⁾ This order is partially or totally destroyed during the mixing with molecules of more globular shape, giving rise to positive contributions both to the mixing enthalpy and entropy. Patterson and co-workers⁽⁷⁾ have indicated that unreasonably large force-field differences between methyl and methylene groups are required to justify the energetic effects observed during the mixing of paraffins and, on the basis of calorimetric measurements performed on carefully selected systems, have postulated the pre-eminence of order destruction processes.

e. Finally, the so-called "steric hindrance effect" or "condensation effect" occurs when rigid molecules (such as 3,3-diethylpentane) are mixed with molecules freer in motion (such as an *n*-alkane), and results in negative contributions to the excess enthalpy, entropy and volume.^(7b) The origin of this effect is not clear at present; Patterson^(7e) has suggested that the results could be interpreted as a restriction of rotation of the freer molecules or of segments of them, similar to their adsorption onto the rigid molecules.

Delmas and co-workers have performed a sequence of studies dealing with tetraalkyltin compounds, SnR_4 , including measurements of excess heats,^(8a-8e) volumes^(8d,9) and viscosities^(8e,10) in mixtures with

hydrocarbons, of heats of mixing in mixtures of tetraalkyltin compounds,⁽¹¹⁾ and determination of thermal expansion coefficients and thermal pressure coefficients for the pure compounds.⁽¹²⁾ The molecules of the shorter members of the series ($R = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7$ and C_4H_9) are almost spherical, and they behave as efficient order breakers when mixed with *n*-alkanes. Symptoms of orientational order appear when the chain length increases; this is incipient for $R = \text{C}_8\text{H}_{17}$, but clearly evident for $R = \text{C}_{12}\text{H}_{25}$.

Infinite dilution activity coefficients at three temperatures for a series of solutes (including hydrocarbons) in tetrabutyltin were measured by Chien and Laub⁽¹³⁾ using gas-liquid chromatography; this is the only recorded measurement of excess free energies for SnR_4 + hydrocarbon mixtures, and the only opportunity in which a tetraalkyltin compound has been used as the stationary phase in gas chromatography.

Fifteen tetra-*n*-octyltin + hydrocarbon mixtures are studied in the present paper using gas-liquid chromatography. The experimental results are discussed within the frameworks of the Flory⁽⁴⁾ and the Sanchez and Lacombe⁽⁵⁾ theories.

2. Experimental

Tetra-*n*-octyltin was prepared according to the method of Jones *et al.*⁽¹⁴⁾ with slight modifications. A benzene solution of stannic chloride was added to a small excess of *n*-octylmagnesium bromide in ethyl ether; the reaction mixture was heated under steady reflux for four hours, and then allowed to stand overnight. The excess Grignard reagent was destroyed by adding saturated solution of ammonium chloride, and the organic layer was separated. The ether and benzene were removed by distillation at atmospheric pressure, and the remaining mixture was fraction-distilled under reduced pressure. A small quantity of hexadecane was thus obtained ($128^\circ\text{C} / 3$ torr), and the final product was collected at $230^\circ\text{C} / 3$ torr. The refractive index ($n_D^{20} = 1.4707$ vs. 1.4709 in Ref. 15) and infrared spectrum (contrasted with spectrum N 180 K, Sadtler Research Laboratories, 1970) were used in establishing the purity of the fractionated product. Tin content, as determined by decomposition with concentrated nitric and sulphuric acids followed by reduction with nickel and titration vs. potassium iodate,⁽¹⁶⁾ was 20.82% by weight (20.76% calculated). Densities ($\text{g}\cdot\text{cm}^{-3}$), measured with a 3 mL pycnometer (0.8 mm capillary tube, with a 4 cm stem, and carefully calibrated through the temperature interval) at twenty four temperatures between 20 and 65°C , were least squares fitted to the equation

$$d(t) = 0.97763 - 7.546 \times 10^{-4} t + 9.044 \times 10^{-9} t^2 + 6.777 \times 10^{-10} t^3 \quad (1)$$

where t is the centigrade temperature; experimental and interpolated results agreed up to the fourth decimal place. The thermal expansion coefficient at 25°C calculated with Eq. (1) is $7.85 \times 10^{-4} \text{ K}^{-1}$, in excellent agreement with the value $7.90 \times 10^{-4} \text{ K}^{-1}$ recorded in Ref. 12.

The hydrocarbons employed were of different origins, all of them were more than 99% pure, and were used without further purification. Chromosorb W AW DMCS 60/80 was used as the solid support; the packings were prepared in rotatory evaporator, under a slow nitrogen flow, using benzene as the volatile solvent. Coated supports were packed into 0.22 cm i.d. and 1-2 m in length stainless steel tubes.

Gas-chromatographic measurements were performed on a Hewlett-Packard 5880 A instrument, equipped with a flame ionization detector and an accessory that enabled measurement of the pressure at the injector. Nitrogen, at flow rates of about $20 \text{ mL} \cdot \text{min}^{-1}$, was used as the carrier gas. Solutes were injected individually or in mixtures, together with a small sample of methane, by means of $10 \mu\text{L}$ Hamilton syringes, applying the headspace sampling technique. Adjusted retention times, measured between the methane and the solute peak, were used to calculate specific retention volumes V_g in the usual form.⁽¹⁷⁾ The measurements were performed at 40, 45, 50, 55 and 60°C; each solute was subjected to not less than three runs involving the five mentioned temperatures, on different days, and the measurements at each temperature were made at least in quadruplicate. The scattering of the individual retention volumes did not exceed $\pm 0.5\%$ of the mean value.

3. Results

The hydrocarbons activity coefficients at infinite dilution in tetra-*n*-octyltin and zero pressure, $\gamma_1^{\circ}(T,0)$, were calculated by means of the equation

$$\begin{aligned} \ln \gamma_1^{\circ}(T,0) = & \ln(273.15R / V_g p_1^{\circ} M_2) - (B_{11} - V_1) p_1^{\circ} / RT \\ & + (2B_{13} - \bar{V}_1^{\circ}) P_0 J_3^{\circ} / RT \end{aligned} \quad (2)$$

where R is the gas constant, T the column temperature, M_2 the stationary phase molecular weight, p_1° and V_1 are the solute vapor pressure and molar volume at T , respectively, B_{11} the second virial coefficient of the solute and B_{13} the solute-carrier gas second cross-virial coefficient. \bar{V}_1° is the solute partial molar volume at infinite dilution, approximated by V_1 ,

Table I. Infinite Dilution Activity Coefficients of Hydrocarbons in Tetra-*n*-octyltin at Various Temperatures

Solute	<i>T</i> / °C				
	40	45	50	55	60
<i>n</i> -Pentane	0.575	0.574	0.575	0.575	0.577
<i>n</i> -Hexane	0.600	0.598	0.598	0.599	0.600
2,2-Dimethyl- butane	0.612	0.611	0.610	0.609	0.609
<i>n</i> -Heptane	0.627	0.626	0.626	0.625	0.625
3-Methyl- hexane	0.618	0.617	0.616	0.616	0.615
2,3-Dimethyl- pentane	0.589	0.589	0.588	0.587	0.587
<i>n</i> -Octane	0.655	0.651	0.649	0.648	0.647
2-Methyl- heptane	0.666	0.665	0.664	0.664	0.662
2,2,4-Trimethyl- pentane	0.675	0.671	0.671	0.670	0.670
2,3,4-Trimethyl- pentane	0.611	0.609	0.609	0.607	0.606
<i>n</i> -Nonane	0.694	0.690	0.688	0.684	0.682
Cyclohexane	0.468	0.465	0.464	0.463	0.462
Benzene	0.594	0.583	0.575	0.569	0.562
Toluene	0.591	0.585	0.579	0.574	0.569
Ethylbenzene	0.649	0.641	0.634	0.628	0.622

and J_3^4 is a function of the inlet (P_i) and outlet (P_o) pressures

$$J_3^4 = (3/4)[(P_i/P_o)^4 - 1] / [(P_i/P_o)^3 - 1] \quad (3)$$

Antoine equation, with the constants given in Dreisbach's compilation,⁽¹⁸⁾ was used to calculate p_i^0 ; molar volumes were calculated using the density data given by Orwoll and Flory^(4d) and by Dreisbach.⁽¹⁸⁾ B_{11} and B_{13} were computed by means of the corresponding states equation of McGlashan and Potter;⁽¹⁹⁾ critical constants were taken from Ref. 20. The results have been gathered in Table I.

Although the measurements were extended over a temperature interval of only 20°C, some of the plots of $\ln \gamma_i^0(T,0)$ vs. $1/T$ were decidedly non linear. Therefore, the activity coefficients were fitted to the following Taylor series expansion

Table II. Partial Molar Excess Thermodynamic Properties
at $\theta = 50^\circ\text{C}^a$

Solute	$-G_1^{E,o} \pm s^b$	$H_1^{E,o} \pm s^b$	$-C_{p,1}^{E,o} \pm s^c$
<i>n</i> -Pentane	1489.0 ± 1.7	-158.0 ± 49.0	44.0 ± 16.0
<i>n</i> -Hexane	1382.0 ± 1.3	-39.0 ± 39.0	59.0 ± 13.0
2,2-Dimethyl- butane	1328.0 ± 0.8	225.0 ± 22.0	15.0 ± 7.5
<i>n</i> -Heptane	1259.0 ± 0.6	139.0 ± 27.0	
3-Methylhexane	1300.0 ± 0.6	197.0 ± 27.0	
2,3-Dimethyl- pentane	1427.0 ± 0.7	177.0 ± 34.0	
<i>n</i> -Octane	1162.0 ± 1.2	498.0 ± 35.0	50.0 ± 12.0
2-Methylheptane	1100.0 ± 0.9	235.0 ± 41.0	
2,2,4-Trimethyl- pentane	1074.0 ± 2.4	275.0 ± 71.0	50.0 ± 24.0
2,3,4-Trimethyl- pentane	1335.0 ± 1.0	342.0 ± 47.0	
<i>n</i> -Nonane	1007.0 ± 1.0	757.0 ± 47.0	
Cyclohexane	2064.0 ± 1.9	516.0 ± 55.0	40.0 ± 18.0
Benzene	1486.0 ± 2.8	2332.0 ± 82.0	65.0 ± 28.0
Toluene	1467.0 ± 0.5	1644.0 ± 16.0	12.0 ± 5.4
Ethylbenzene	1224.0 ± 0.6	1826.0 ± 19.0	24.0 ± 6.3

^a *s*, standard deviation. ^b Units: J·mol⁻¹. ^c Units: J·K⁻¹·mol⁻¹.

$$G_1^{E,o}(T)/T = R \ln \gamma_1^o(T,0) = G_1^{E,o}(\theta)/\theta + H_1^{E,o}(\theta)[(1/T) - (1/\theta)] \\ + C_{p,1}^{E,o}(\theta)[1 - (\theta/T) + \ln(\theta/T)] + \dots \quad (4)$$

by applying the method of Clarke and Glew.⁽²¹⁾ θ in Eq. (4) is some reference temperature, and all the thermodynamic functions are partial molar excess quantities for the solute at infinite dilution.

The results of the regression analysis have been summarized in Table II. The *t*-test was used to estimate the statistical significance of $C_{p,1}^{E,o}(\theta)$, this parameter being given only in those cases where the probability that it differs from zero purely by chance is smaller than 20%. The remaining solutes displayed a linear relationship between $\ln \gamma_1^o(T,0)$ and $1/T$, and a temperature independent interval was assumed for them. The analysis cannot be extended with only five experimental points, even when each of them represents the mean of several determinations, and the excess heat capacities should be treated as only rough estimates.

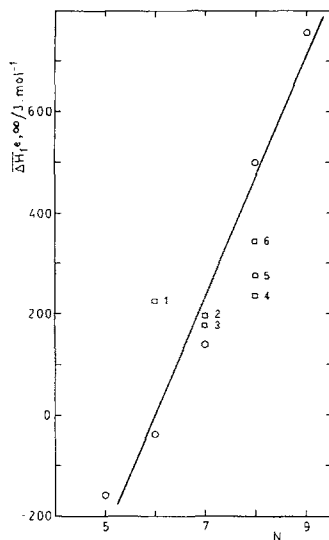


Fig. 1. Partial molar excess enthalpy at 50°C and infinite dilution of alkanes in $\text{Sn}(\text{C}_8\text{H}_{17})_4$. ○, *n*-alkanes; □, *br*-alkanes (1: 2,2-dimethylbutane; 2: 3-methylhexane; 3: 2,3-dimethylpentane; 4: 2-methylheptane; 5: 2,2,4-trimethylpentane; 6: 2,3,4-trimethylpentane).

4. Discussion

The alkanes heats of mixing have been plotted vs. the number of carbon atoms, N , in Fig. 1; the straight line was drawn through the *n*-alkane ($n\text{-C}_N$) points. There is a linear increase for the heats of mixing of $n\text{-C}_N$ with N , in parallel with the trend postulated for the orientational order; this behavior resembles that observed for the systems $n\text{-C}_N + \text{Sn}(\text{CH}_3)_4$, $+ \text{Sn}(\text{C}_2\text{H}_5)_4$, and $+ \text{Sn}(\text{C}_4\text{H}_9)$.^(8a) The heats of mixing for the branched alkanes (*br*- C_N) are positive, relatively high and not very different values; this could be attributed to the existence of orientational order in $\text{Sn}(\text{C}_8\text{H}_{17})_4$. The heats of mixing with *br*- C_N are larger than those with *n*- C_N for $N = 6$, almost coincident for $N = 7$, and smaller for $N = 8$; since there are only small differences between the free volume contributions for alkanes with the same number of carbon atoms, this behavior suggests that contact interactions do not play an important role in these systems. The data could be tentatively explained on the basis of the existence of orientational order both in the *n*- C_N and in $\text{Sn}(\text{C}_8\text{H}_{17})_4$. A substantial increase in the heats of mixing is observed when aromatic hydrocarbons are considered, attributable in principle to important con-

tact interaction contributions and to the destruction of the orientational order in the tin compound.

4.1. Prigogine-Flory Theory⁽⁴⁾

The reduction parameters (asterisk) were calculated by means of the equations

$$\tilde{v}_i = V_i / V_i^* = \{1 + \alpha_i T / 3(1 + \alpha_i T)\}^3 \quad (5a)$$

$$\tilde{T}_i = T / T_i^* = (\tilde{v}_i^{1/3} - 1) / \tilde{v}_i^{4/3} \quad (5b)$$

$$\tilde{p}_i = p / p_i^* = p / \gamma_i T \tilde{v}_i^2 \quad (5c)$$

using molar volumes (V_i), thermal expansion coefficients (α_i) and thermal pressure coefficients (γ_i) at 20°C, taken from Refs. 4d, 22 and 23. Density data for our experimental temperature range are available from many sources.^(4d,18) The hydrocarbon reduction parameters can be read on Table IV; those for $\text{Sn}(\text{C}_8\text{H}_{17})_4$ were computed from the value of α at 20°C calculated with Eq. (1).

The Flory equation for the solute partial molar excess free energy at infinite dilution and zero pressure is

$$G_1^{E,0} = \Delta G(\text{comb}, F) + \Delta G(\text{fv}, F) + \Delta G(\text{chem}, F) \quad (6a)$$

$$\Delta G(\text{comb}, F) = RT[\ln(V_1^*/V_2^*) + 1 - (V_1^*/V_2^*)] \quad (6b)$$

$$\begin{aligned} \Delta G(\text{fv}, F) = p_1^* V_1^* \{ & 3\tilde{T}_1 \ln[(\tilde{v}_1^{1/3} - 1) / (\tilde{v}_2^{1/3} - 1)] \\ & + (1/\tilde{v}_1) - (1/\tilde{v}_2) \} \end{aligned} \quad (6c)$$

$$\Delta G(\text{chem}, F) = V_1^* X_{12} / \tilde{v}_2 \quad (6d)$$

$\Delta G(\text{comb}, F)$ is the combinatorial contribution, expressed in terms of the "hard core molar volume" instead of molar volumes, and $\Delta G(\text{fv}, F)$ is the free volume contribution. Within the context of the original theory, $\Delta G(\text{chem}, F)$ was attributed exclusively to differences in the molecular force fields; more recent works^(6,8) have assumed that the only parameter characteristic of the binary mixture X_{12} somehow reflects all the effects described under c., d. and e. in the Introduction to this paper. From Eq. (6)

$$H_1^{E,0} = \Delta H(\text{fv}, F) + \Delta H(\text{chem}, F) \quad (7a)$$

$$\Delta H(\text{fv}, F) = p_1^* V_1^* \{ \alpha_2 T (\tilde{T}_1 - \tilde{T}_2) / \tilde{v}_2 \tilde{T}_2 + 1 / \tilde{v}_1 - 1 / \tilde{v}_2 \} \quad (7b)$$

$$\Delta H(\text{chem}, F) = V_1^* X_{12} (1 + \alpha_2 T) / \tilde{v}_2 \quad (7c)$$

On calculating X_{12} from the activity coefficients it was found that: 1) X_{12} is a decreasing function of the temperature for all the systems studied in this paper. A temperature independent X_{12} would be expected if it originated exclusively in contact interactions; the observed behavior is consistent with a decrease in orientational order when the temperature increases; and 2) the heats of mixing calculated by using these X_{12} values in conjunction with Eqs. (7) are negative for all the mixtures of tetra-*n*-octyltin with alkanes and with cyclohexane; the results calculated for aromatics are positive but markedly lower than the experimental values. In the course of a study on mixtures of *n*-hexane, 2,2-dimethylbutane and cyclohexane with a series of hexadecane isomers, Barbe and Patterson^(6d) found that the X_{12} parameters obtained by fitting to experimental heats of mixing were always larger than those obtained by fitting to excess free energies. Some years before Orwoll and Flory^(4d) had verified that experimental excess free energies for *n*-alkanes mixtures were smaller than those calculated using X_{12} parameters obtained from calorimetric measurements.

In order to improve their predictions of chemical potentials Flory and co-workers introduced a second adjustable parameter for binary mixtures, Q_{12} . The proposed modification consists in making in Eq. (6d) the substitution

$$X_{12} = X_{12}^\ddagger - Q_{12} \tilde{v}_2 T \quad (8)$$

where X_{12}^\ddagger and Q_{12} , with enthalpic and entropic connotations respectively, are both temperature independent. X_{12}^\ddagger substitutes to X_{12} in Eq. (7c).

X_{12}^\ddagger and Q_{12} parameters, obtained by fitting X_{12} values to Eq. (8), can be found in Table III. No negative parameters have been obtained, and the correlation coefficients indicate that (with the exceptions of *n*-pentane and *n*-hexane) the experimental results are satisfactorily interpreted by Eq. (8). The temperature dependence of X_{12} for two representative solutes is shown in Figs. 4 and 5. Experimental heats of mixing differ from those calculated using X_{12}^\ddagger in less than 5% of the alkanes and in less than 1% of the aromatics; the exceptions are

Table III. Results of Regression vs. Temperature of Mixture Parameters X_{12} and $\Delta P^*{}^a$

	$X_{12} = X_{12}^\ddagger - Q_{12}T\tilde{v}_2$			$\Delta P^* = \Delta P^\ddagger - QT/\tilde{p}_2$		
	$X_{12}^\ddagger{}^b$	$10^3Q_{12}{}^c$	$-r$	$\Delta P^\ddagger{}^b$	$10^3Q{}^c$	$-r$
<i>n</i> -Pentane	5.80	3.68	0.864	7.43	6.26	0.912
<i>n</i> -Hexane	5.19	6.88	0.915	5.80	6.83	0.908
2,2-Dimethyl- butane	7.19	11.26	0.997	8.18	12.74	0.999
<i>n</i> -Heptane	4.91	7.82	0.990	5.38	8.89	0.995
3-Methyl- hexane	4.82	6.77	0.998	5.78	10.57	0.997
2,3-Dimethyl- pentane	4.92	10.28	0.996	5.28	10.68	0.992
<i>n</i> -Octane	6.63	13.87	0.987	6.53	14.51	0.989
2-Methyl- heptane	4.30	6.07	0.997	4.93	9.25	0.986
2,2,4-Trimethyl- pentane	5.21	9.16	0.961	5.11	8.80	0.958
2,3,4-Trimethyl- pentane	5.21	11.97	0.995	5.26	12.82	0.993
<i>n</i> -Nonane	7.44	15.82	0.997	7.06	16.44	0.997
Cyclo- hexane	10.32	22.30	0.990	8.83	17.02	0.985
Benzene	38.03	45.24	0.989	30.80	35.62	0.985
Toluene	21.37	22.52	0.999	17.84	19.88	0.999
Ethyl- benzene	19.96	24.53	0.999	16.54	21.98	0.998

^a r , correlation coefficient. ^b Units: J-cm⁻³. ^c Units: J-K⁻¹-cm⁻³.

n-pentane, *n*-hexane and 2,2-dimethylbutane, whose differences amount to as much as 20%, these being the three solutes with smaller retention volumes and therefore with the larger experimental error.

4.2. Sanchez-Lacombe Theory

The theory⁽⁵⁾ is founded on a lattice model description of a fluid; the main difference from classic Flory theory⁽¹⁾ is that the lattice is allowed to have vacant sites or "holes." Each molecule occupies r lattice sites, corresponding to a rv^* close-packed molecular volume. The state equation for such a fluid is

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}[\ln(1 - \tilde{\rho}) + (1 - 1/r)\tilde{\rho}] = 0 \quad (9)$$

when $\tilde{\rho}$, \tilde{P} and \tilde{T} are the reduced density, pressure and temperature, defined by Sanchez and Lacombe as

$$\tilde{\rho} = \rho / \rho^* \quad \rho^* = M / rv^* \quad (10a)$$

$$\tilde{P} = p / P^* \quad P^* = \varepsilon^* / v^* \quad (10b)$$

$$\tilde{T} = T / T^* \quad T^* = \varepsilon^* / k \quad (10c)$$

where k is the Boltzmann constant and ε^* is the interaction energy between two adjacent molecular segments.

A pure fluid is characterized by three parameters: ρ^* , P^* and T^* , or equivalently ε^* , r and v^* . From the several alternatives proposed by Sanchez and Lacombe for their determination, that based on the use of the heats of vaporization and the liquid and vapor densities at a given temperature^(5c) was chosen for the hydrocarbons in the present paper, using data at 25°C taken from Dreisbach.⁽¹⁸⁾ Since no reliable vapor pressure or heat of vaporization data are available for tetra-*n*-octyltin, its molecular parameters were determined by fitting liquid density data at atmospheric pressure ($\tilde{P} \cong 0$) to the state equation by a non-linear adjustment method. The results can be found in Table IV; there are some small differences with the values given in the original paper,^(5a) but they do not affect the conclusions resulting from the application of the model to the mixtures studied in the present paper.

The equations of Sanchez and Lacombe for the excess partial molar properties at infinite dilution are

$$G_1^{\text{E},\infty} = \Delta G(\text{comb, SL}) + \Delta G(\text{fv, SL}) + \Delta G(\text{chem, SL}) \quad (11a)$$

$$\Delta G(\text{comb, SL}) = RT[\ln(r_1 v_1^* / r_2 v_2^*) + 1 - (r_1 v_1^* / r_2 v_2^*)] \quad (11b)$$

$$\begin{aligned} \Delta G(\text{fv, SL}) = RT r_1 [(\tilde{\rho}_1 - \tilde{\rho}_2) / \tilde{T}_1 + (\tilde{v}_2 - 1) \ln(1 - \tilde{\rho}_2) \\ - (\tilde{v}_1 - 1) \ln(1 - \tilde{\rho}_1) + (1 / r_1) \ln(\tilde{\rho}_2 / \tilde{\rho}_1)] \end{aligned} \quad (11c)$$

$$\Delta G(\text{chem, SL}) = r_1 v_1^* \tilde{\rho}_2 \Delta P^* \quad (11d)$$

$$H_1^{\text{E},\infty} = \Delta H(\text{fv, SL}) + \Delta H(\text{chem, SL}) \quad (12a)$$

Table IV. Flory and Sanchez-Lacombe Molecular Parameters

Solute	Flory			Sanchez-Lacombe		
	V'^a	p^{*b}	T^*/K	ρ^{*c}	P^{*b}	T^*/K
<i>n</i> -Pentane	85.5	4093	4178	0.758	3029	442
<i>n</i> -Hexane	99.5	4395	4430	0.779	3085	459
2,2-Dimethyl- butane	100.0	3741	4318	0.773	2680	456
<i>n</i> -Heptane	113.5	4310	4632	0.796	3127	472
3-Methyl- hexane	113.4	4062	4685	0.801	3017	471
2,3-Dimethyl- pentane	112.0	4233	4675	0.806	2945	479
<i>n</i> -Octane	127.6	4367	4806	0.809	3158	481
2-Methyl- heptane	128.6	4060	4827	0.807	3013	478
2,2,4-Trimethyl- pentane	128.7	3851	4719	0.800	2628	481
2,3,4-Trimethyl- pentane	125.2	4233	4879	0.826	2930	488
<i>n</i> -Nonane	141.6	4420	4957	0.821	3193	488
Cyclo- hexane	84.2	5377	4710	0.890	3667	501
Benzene	69.1	6263	4686	1.000	4538	507
Toluene	84.5	5505	5008	0.973	4179	525
Ethyl- benzene	98.3	5383	5173	0.969	4020	530
Sn(C ₈ H ₁₇) ₄	495.5		5998	1.042	2494	577

^a Units: cm³-mol⁻¹. ^b Units: atm. ^c Units: g-cm⁻³.

$$\begin{aligned} \Delta H(\text{fv, SL}) = & Rr_1 \{ T_1^* [\tilde{\rho}_1 - \tilde{\rho}_2 - T(\alpha_1 \tilde{\rho}_1 - \alpha_2 \tilde{\rho}_2)] \\ & + T^2 [(\alpha_1 / \tilde{\rho}_1) \ln(1 - \tilde{\rho}_1) - (\alpha_2 / \tilde{\rho}_2) \ln(1 - \tilde{\rho}_2) \\ & + (\alpha_1 - \alpha_2)(1 - 1/r_1)] \} \end{aligned} \quad (12b)$$

$$\Delta H(\text{chem, SL}) = r_1 v_1^* \tilde{\rho}_2 (1 + \alpha_2 T) \Delta P^* \quad (12c)$$

ΔP^* is the only parameter characteristic of the binary mixture; it is defined as

$$\Delta P^* = P_1^* + P_2^* - 2\xi(P_1^* P_2^*)^{1/2}$$

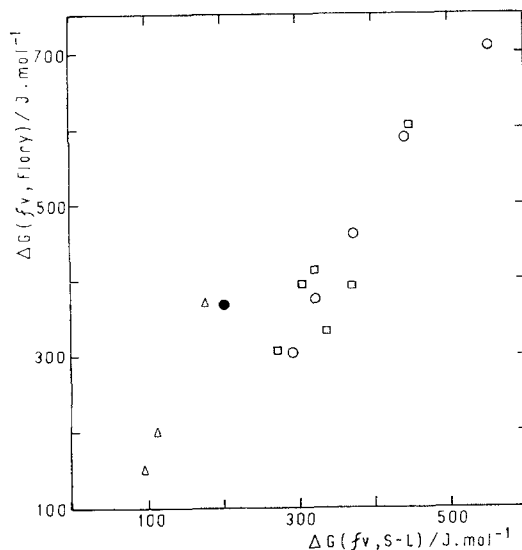


Fig. 2. Free volume contribution to the partial molar excess free energy at infinite dilution in the theory of Flory [Eq. (6c)], vs. the prediction for the same property in the theory of Sanchez and Lacombe [Eq. (11c)]. o, *n*-alkanes; □, *br*-alkanes; ●, cyclohexane; Δ, aromatics.

where ξ is a dimensionless parameter which measures the deviations from the geometric mean. Making $r_i v_i^* = V_i^*$ and $\tilde{\rho}_i = 1 / \tilde{v}_i$ in Eqs. (11b, 11d and 12c), expressions for the combinatorial and chemical contributions are obtained that coincide with those of the Flory theory, with ΔP^* playing a role equivalent to that of X_{12} . Furthermore, since both theories give values almost identical for the quotients between the solute and the solvent hard core volumes, V_1^*/V_2^* , there is a coincidence between the combinatorial excess free energy values.

Sanchez and Lacombe expressions for the free volume contributions to the excess free energy and to the excess enthalpy are however markedly different from those of Flory. Values for $\Delta G(\text{fv})$ and for $\Delta H(\text{fv})$ resulting from both theories are compared in Figs. 2 and 3, respectively. Both plots display non negligible dispersions, attributable to a combination of inadequacies of the state equations and the combining rules, to approximations in the estimation of molecular parameters and to errors in the physical properties. However, there is a significant correlation between both pairs of values, with the Flory theory resulting in more positive values of $\Delta G(\text{fv})$ and less negative values of $\Delta H(\text{fv})$ than the Sanchez and Lacombe theory. Since the chemical contributions

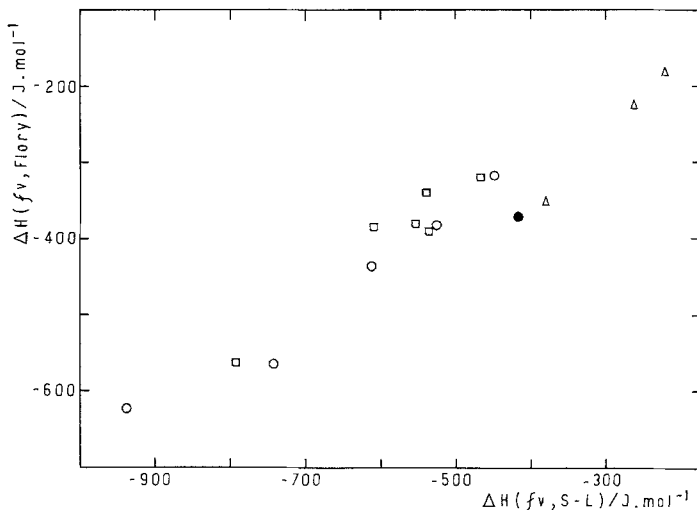


Fig. 3. Predicted values of the free volume contribution to the partial molar excess enthalpy at infinite dilution in the theory of Flory [Eq. (7b)] vs. the prediction for the same property in the theory of Sanchez and Lacombe [Eq. (12b)]. See Fig. 2 for symbols.

are obtained by subtracting the free volume contributions from the experimental data, the results for both theories are different in spite of the correlation between Eqs. (6d, 11d) on one side, and between Eqs. (7c, 12c) on the other.

As to the rest, the conclusions are analogous to those obtained by applying the theory of Flory: 1) ΔP^* decrease when the temperature increase; 2) the heats of mixing calculated using ΔP^* are markedly lower than the experimental results; and 3) if ΔP^* is treated analogously to X_{12} , and a temperature dependence parameter Q is introduced, an expression similar to Eq. (8) is obtained

$$\Delta P^* = \Delta P^\ddagger - QT/\tilde{\nu}_2 \quad (13)$$

The results that appear in Table III are obtained by fitting the experimental data to Eq. (13). The worst regressions are those corresponding to *n*-pentane and to *n*-hexane (as it was for X_{12}), with Eq. (13) interpreting satisfactorily the data for the remaining solutes. Representative data have been plotted in Figs. 4 and 5.

5. Conclusion

Some years ago, in a note to a paper, Barbe and Patterson^(6d) pointed out that to treat X_{12} as a temperature dependent parameter is 'an

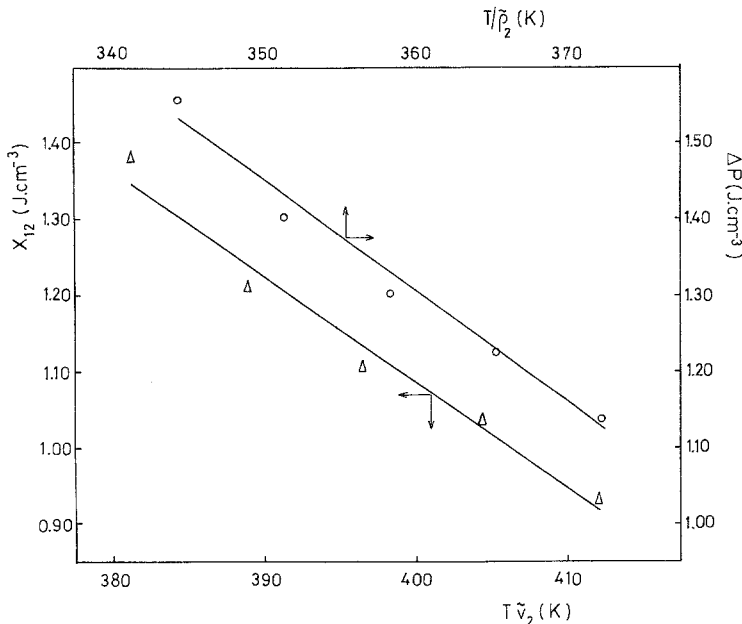


Fig. 4. Plots of X_{12} vs. $T^*\bar{\nu}_2$ and of ΔP^* vs. $T/\bar{\rho}_2$ for octane.

empirical way of dealing with orientational order within the framework of the present Prigogine-Flory theory.' The mixture theory is obtained from the pure component theory by applying combination rules based on the random mixing assumption and, as mentioned above, Patterson and co-workers have presented plentiful evidence pointing to the importance of orientational order in mixtures of non-polar fluids. In the opinion of Sanchez and Lacombe, whose theory was founded on assumptions that are similar to those used in the Prigogine-Flory theory, the mean field approximation is the most important imperfection of their model.⁽⁵⁾ Notwithstanding these criticisms, at the present time both theories remain the best available tools to advance the understanding of this type of mixture.

It has been mentioned above that the predicted free volume contributions are different, and that the mixture parameters (X_{12} or ΔP^*) must be treated as functions of temperature. In spite of the differences in their origins, X_{12}^\ddagger and ΔP^\ddagger are surprisingly alike: the mean of the quotients $\Delta P^\ddagger / X_{12}^\ddagger$ for our sample of fifteen systems is 1.02, and its standard deviation is 0.14.

An explanation of our results can be attempted on the basis of the existence of orientational order both in the *n*-alkanes and in

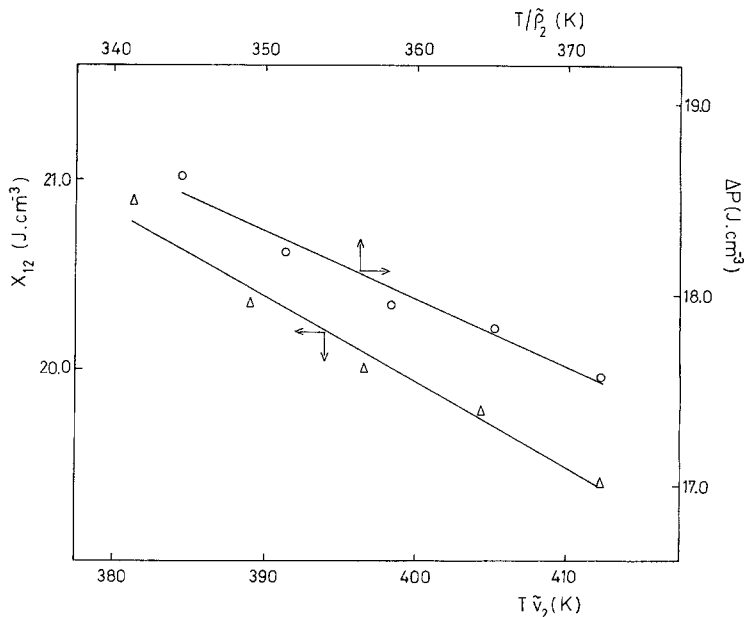


Fig. 5. Plots of X_{12} vs. $T\bar{v}_2$ and of ΔP^* vs. T/\bar{p}_2 for benzene.

tetra-*n*-octyltin. The most important effects of this order on the excess properties should be detected at infinite dilution, because under this condition the hydrocarbon molecules shall be totally isolated (and therefore in the most disordered state), and because the first hydrocarbon molecules to get into solution shall find the stationary phase in its most ordered state, it should promote the largest destruction.

On dissolving a normal alkane, both the disorder that this process generates between its own molecules and the order destruction that is promoted in the solvent have to be considered. It would be reasonable to expect a monotonous increase of X_{12}^\ddagger and of ΔP^\ddagger as the solute chain length increase, but both parameters display a minimum for *n*-heptane. This minimum is most probably a consequence of an overestimation of the free volume contribution to the heat of mixing for systems whose components have a large difference in their expanded state (*i.e.*, for *n*-pentane and *n*-hexane; this effect has already been observed in solutions of polybutene in alkanes).⁽²⁴⁾

When the behavior of normal and branched alkanes with the same number of carbon atoms are compared it has to be considered that although the branched molecule is expected to be a more efficient destroyer of the solvent order, its dissolution does not involve contribu-

tions originating in the destruction of its own order (considered as non-extant). Since the *n*-alkanes orientational order increases with chain length, it can be predicted that the relation $X_{12}^{\ddagger}(br-C_N) > X_{12}^{\ddagger}(n-C_N)$ holds for small *N*, and the opposite for larger size molecules. Corroborating this prediction, the data in Table III indicate that X_{12}^{\ddagger} is larger for 2,2-dimethylbutane than for *n*-hexane, that the three branched octanes show a smaller X_{12}^{\ddagger} than *n*-octane, and that the values are almost coincident for all the isomeric heptanes; the values of ΔP^{\ddagger} show the same trends.

There is a strong structural similarity between 3,3-diethylpentane and the tetraalkyltins, and Delmas and co-workers⁽⁸⁾ have investigated the existence of steric hindrance effects in mixing of SnR₄ compounds with hydrocarbons. The heats of mixing of most of the hydrocarbons with Sn(C₃H₇)₄ are surprisingly low, only a little higher with Sn(C₄H₉)₄, and increase markedly both for lighter and heavier tetraalkyl compounds. The authors concluded that this behavior was a manifestation of steric hindrance, that was most effective for Sn(C₃H₇)₄ and for Sn(C₄H₉)₄. The effect disappears when the chain length increases, probably because the hydrocarbons do not reach the sterically hindered part of the SnR₄ molecule, and is expected to be null for R = C₈H₁₇.

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