

Volumes of Mixing and the P^* Effect: Part I. Hexane Isomers With Normal and Branched Hexadecane

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Received August 26, 1982; In Final Form December 14, 1982

The Prigogine-Flory theory of solution thermodynamics has been used to interpret molar excess volume data, V^E , for two series of alkane mixtures: the five isomers of hexane mixed with normal hexadecane (Data from Reeder, et al.) and the five hexane isomers mixed with a highly branched hexadecane isomer, 2,2,4,4,6,8,8-heptamethylnonane (this work). Values of V^E are negative and similar for both series, but vary considerably with the hexane within a series. According to the theory, V^E contains a ' P^ contribution' not found in the excess enthalpy and entropy, which depends strongly on the internal pressures and the derived P^* parameters of the components. Values of V^E are well predicted for both series, the variation of V^E corresponding to the different internal pressures or P^* parameters of the hexanes.*

KEY WORDS: Excess volume; Prigogine; Flory; internal pressure; hexane isomers; normal hexadecane; heptamethylnonane.

1. INTRODUCTION

An early theory⁽¹⁾ of liquid mixtures proposed a simple proportionality between the volume of mixing, ΔV_M , or excess volume, V^E and the enthalpy of mixing, ΔH_M , or excess enthalpy, H^E :

$$V^E = \frac{\beta}{1 + \alpha T} H^E \quad (1)$$

where α and β are respectively the thermal expansion coefficient and

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the isothermal compressibility of the mixture. Both H^E and V^E have their origin in the same energetic effect associated with the replacement of (1-1) and (2-2) contacts by (1-2) contacts, *i.e.* the interchange energy of the strictly regular solution theory.⁽²⁾ According to the more recent Prigogine-Flory theories,^(3,4) both H^E and V^E reflect another contribution beside that associated with the interchange energy, or in more recent terminology, the interaction parameter, X_{12} . The new contribution comes from volume changes occurring during the mixing of liquids of different degrees of thermal expansion or free volume. While H^E mainly reflects X_{12} , leading to positive values, V^E is usually dominated by the free volume term, which under typical conditions is negative. Thus positive H^E should often be accompanied by negative V^E as in fact suggested by any theory which introduces the liquid equation of state. The first such theory⁽⁵⁾ based on the Average Potential Model predicted the possibility of positive H^E and negative V^E for mixtures of spherical-molecule liquids of different cohesion or internal pressure. A requirement that the molecules be of very similar size suggested that the combination of positive H^E and negative V^E would be rarely found. However, the Average Potential Model greatly overestimates⁽⁶⁾ effects of molecular size-difference and many systems with positive H^E and negative V^E have been studied starting with those found^(7,8) directly after the prediction.

Recently Scott, Knobler and collaborators have studied H^E and V^E for the five hexane isomers + n-hexadecane^(9,10) and for the hexane isomers + polar liquids.⁽¹¹⁾ In all of these systems H^E is positive and in most V^E is negative. However, the most interesting feature of the results is the strong variation of V^E from one isomer to another. In the present work we show that the Prigogine-Flory theory, perhaps alone, gives good predictions of these features for the hexanes + $n\text{-C}_{16}$ and also of V^E for the hexane isomers mixed with another hexadecane of different structure, 2,2,4,4,6,8,8-heptamethylnonane ($br\text{-C}_{16}$).

2. THEORY

2.1. The Prigogine-Flory Theory and Negative Molar Excess Volumes

The Prigogine-Flory theory, in a corresponding-states formulation,⁽¹²⁾ gives for the molar excess volume, V^E :

$$V^E = (x_1 V_1^* + x_2 V_2^*) \tilde{V}\tilde{T} - x_1 V_1^* \tilde{V}(\tilde{T}_1) - x_2 V_2^* \tilde{V}(\tilde{T}_2) \quad (2)$$

or

$$\frac{V^E}{X_1V_1^* + x_2V_2^*} = \tilde{V}(\tilde{T}) - [\phi_1\tilde{V}(\tilde{T}_1) + \phi_2\tilde{V}(\tilde{T}_2)] \quad (3)$$

where the tilde refers to a reduced quantity, V^* are the hardcore volumes or volume reduction parameters, and the segment or hardcore volume fractions, ϕ , are defined by

$$\phi_1 = 1 - \phi_2 = x_1V_1^* / (x_1V_1^* + x_2V_2^*) \quad (4)$$

The reduced temperature \tilde{T} of the liquids are ratios of the cohesive energies (U^*) and the kinetic energies of the external degrees of freedom (S^*T) of the molecules:

$$\tilde{T} = \frac{S^*T}{U^*} = \left(\frac{S^*}{V^*}\right)\left(\frac{T}{P^*}\right) \quad (5)$$

In the case of a small-molecule liquid, $S^* \approx R$, whereas for a polymer S^*/V^* decreases with the number of segments, becoming a constant dependent on the chain flexibility. The quantities P^* , V^* , S^* , and \tilde{T} may be obtained for the component liquids from equation-of-state data using, for instance, relations from the Flory model. Thus, P^* is related to the thermal pressure coefficient (γ) or internal pressure (γT) through:

$$P^* = (\gamma T) \tilde{V}^2 \quad (6)$$

For the solution, \tilde{T} is given by

$$\tilde{T} = \frac{\psi_1\tilde{T}_1 + \psi_2\tilde{T}_2}{1 - \psi_1\theta_2(X_{12}/P_1^*)} \quad (7)$$

Here the surface fraction

$$\theta_2 = \phi_2s_2 / (\phi_1s_1 + \phi_2s_2) \quad (8)$$

s being the molecular surface/volume ratios and the composition variables ψ are defined by

$$\psi_1 = 1 - \psi_2 = x_1U_1^* / (x_1U_1^* + x_2U_2^*) \quad (9)$$

$$= \phi_1P_1^* / (\phi_1P_1^* + \phi_2P_2^*) \quad (10)$$

The ψ have been termed contact-energy fractions and only for $P_1^* =$

P_2^* will ϕ and ψ be equal. The $\tilde{V}(\tilde{T})$ functions may be obtained through reduction of empirical $\tilde{V}(\tilde{T})$ data or from a theoretical prediction, e.g. that of Flory.⁽⁴⁾ In either case, $\tilde{V}(\tilde{T})$ has positive curvature, as shown schematically in Fig. 1 where V^E is related to the difference of two values of \tilde{V} . In Eq. (3), the reduced volume of the pure components $\phi_1\tilde{V}(\tilde{T}_1) + \phi_2\tilde{V}(\tilde{T}_2)$ lies on the dashed straight line at a \tilde{T} value of

$$\tilde{T} = \phi_1\tilde{T}_1 + \phi_2\tilde{T}_2 \quad (11)$$

On the other hand, \tilde{V} of the solution corresponds to a point on the full curve at \tilde{T} given by Eq. (7) which, taking $X_{12} = 0$ for simplicity, is:

$$\tilde{T} = \psi_1\tilde{T}_1 + \psi_2\tilde{T}_2 \quad (12)$$

If $P_1^* = P_2^*$ so that $\psi_1 = \phi_1$ the two average values of \tilde{T} given in Eqs. (11) and (12) are equal, and due to the positive curvature of $\tilde{V}(\tilde{T})$, the \tilde{V} value of the solution lies below that of the pure substances so that the contribution to V^E due to the curvature of $\tilde{V}(\tilde{T})$ is negative. This contribution has been emphasized in discussions^(13,14) of the theory. If $X_{12} > 0$, as for dispersion forces, then \tilde{V} of the solution moves upward giving the *interactional contribution* to V^E which has the same sign as X_{12} . However, if $P_1^* \neq P_2^*$ a third P^* effect occurs in V^E . In Fig. 1, component 1 has been chosen to have the higher degree of thermal expansion, i.e. $\tilde{T}_1 > \tilde{T}_2$. If also $P_1^* < P_2^*$, then $\psi_1 < \phi_1$ and Eq. (11) gives a larger value of \tilde{T} than Eq. (12), leading to a negative P^* effect in V^E as illustrated in Fig. 1. This situation corresponds to the liquid of higher degree of thermal expansion having a lower internal pressure, essentially the P^* parameter. Clearly this is the usual state of affairs where both the component molecules are small and of similar V^* , and follows from Eq. (5); the less usual case may arise where $\tilde{T}_1 > \tilde{T}_2$ and $P_1^* > P_2^*$ giving a positive P^* effect in V^E . The negative P^* effect leads typically to negative V^E whereas H^E dominated by X_{12} will be positive, as originally predicted in Ref. 5, and now found in many systems.

It is of interest that the P^* effect occurs only in V^E and not in H^E , TS^E or G^E at zero pressure. This follows from their having dimensions of energy, whence in a schematic representation similar to that in Fig. 1 for V^E the \tilde{H} , $\tilde{T}\tilde{S}$, and \tilde{G} reduced quantities for the pure components occur at average values of \tilde{T} given by Eq. (12) in ψ rather than Eq. (11) in ϕ . Thus only two contributions appear, the interactional and that due to the curvature of the reduced \tilde{H} , $\tilde{T}\tilde{S}$, and \tilde{G} as

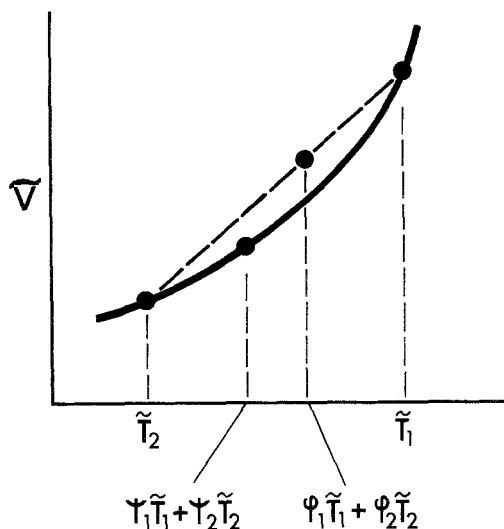


Fig. 1. A plot of the reduced volume against the reduced temperature, illustrating the P^* effect arising from the difference in two average \tilde{T} values, one in ϕ for the pure components and the other in ψ for the solution.

functions of \tilde{T} . While H^E , TS^E , and G^E depend only slightly on the P^* of the components, V^E requires the accurate determination of P^* .

2.2. Approximate Expressions for Molar Excess Volumes

Using the Flory model equation of state which relates \tilde{V} and \tilde{T} , together with a knowledge of X_{12} , V^E may be predicted directly from Eq. (2). Insight may be gained, however, from an approximate expression for V^E which separates the three contributions, Eq. (21) of Ref. 12. With a slight change of nomenclature,

$$\begin{aligned} \frac{V^E}{x_1 V_1^* + x_2 V_2^*} &= \tilde{T} \frac{\partial \tilde{V}}{\partial \tilde{T}} \psi_1 \psi_2 \frac{X_{12}}{P_1^*} && \text{(interactional)} \\ &- 1/2 \left[\frac{(\tilde{V}_1 - \tilde{V}_2)}{(\partial \tilde{V} / \partial \tilde{T})} \right]^2 \left(\frac{\partial^2 \tilde{V}}{\partial \tilde{T}^2} \right) \psi_1 \psi_2 && \text{(\tilde{V} curvature)} \\ &+ \frac{(\tilde{V}_1 - \tilde{V}_2)(P_1^* - P_2^*)}{P_2^* \psi_1 + P_1^* \psi_2} \psi_1 \psi_2 && \text{(P* effect)} \end{aligned} \tag{13}$$

Here \tilde{V} and \tilde{T} for the solution, without subscripts, are evaluated at an average reduced volume given by

$$\tilde{V} = \psi_1 \tilde{V}_1 + \psi_2 \tilde{V}_2 \quad (14)$$

In Eq. (13) introduction of expressions from the Flory model gives:

$$\begin{aligned} \frac{V^E}{x_1 V_1^* + x_2 V_2^*} &= \frac{(\tilde{V}^{1/3} - 1) \tilde{V}^{2/3}}{(4/3 \tilde{V}^{-1/3} - 1)} \psi_1 \theta_2 \frac{X_{12}}{P_1^*} && \text{(interactional)} \\ &- \frac{(\tilde{V}_1 - \tilde{V}_2)^2 (14/9 \tilde{V}^{1/3} - 1)}{(4/3 \tilde{V}^{-1/3} - 1) \tilde{V}} \psi_1 \psi_2 && (\tilde{V} \text{ curvature}) \\ &+ \frac{(\tilde{V}_1 - \tilde{V}_2)(P_1^* - P_2^*)}{P_2^* \psi_1 + P_1^* \psi_2} \psi_1 \psi_2 && (P^* \text{ effect}) \end{aligned} \quad (15)$$

Ref. 12 gives for H^E at zero pressure, *i.e.* U^E , the following equation which corresponds to Eq. (13) for V^E

$$\begin{aligned} \frac{H^E}{x_1 U_1^* + x_2 U_2^*} &= (-\tilde{U} + \tilde{T} \tilde{C}_p) \psi_1 \theta_2 \frac{X_{12}}{P_1^*} && \text{(interactional)} \\ &- 1/2 \left[\frac{(\tilde{V}_1 - \tilde{V}_2)}{(\partial \tilde{U} / \partial \tilde{T})} \right]^2 \frac{\partial^2 \tilde{U}}{\partial \tilde{T}^2} \psi_1 \psi_2 && (\tilde{U} \text{ curvature}) \end{aligned} \quad (16)$$

Here reduced quantities for the solution, without subscript, are to be evaluated at an average reduced volume defined in Ref. 12 which may for present purposes be taken as that given by Eq. (14). Eq. (16) may be written in terms of the Flory model to give an equation analogous to Eq. (15) for V^E . Here, however, we shall only show that Eq. (1) follows from the assumption of van der Waals liquids as in the Flory model, which gives:

$$-\tilde{U} = \tilde{V}^{-1}; \quad \tilde{C}_p = \alpha \tilde{V}^{-1}; \quad \tilde{\beta} = \alpha \tilde{T} \tilde{V}^2 \quad (17)$$

Considering only the interactional terms of Eqs. (13) and (16), we have:

$$\frac{V^E \text{ (interact.)}}{H^E \text{ (interact.)}} = \frac{x_1 V_1^* + x_2 V_2^*}{x_1 U_1^* + x_2 U_2^*} \frac{\alpha \tilde{T} \tilde{V}^2}{1 + \alpha T} = \frac{\beta}{1 + \alpha T} \quad (18)$$

Thus Eq. (1) reappears in the newer theory when only the interactional term is considered in V^E and H^E . Eq. (1) would therefore be

Table I. Equation of State Parameters for the Components at 25°C

Components	γ (J-cm ⁻³ -K ⁻¹)	P^* (J-cm ⁻³)	$10^3\alpha$ (K ⁻¹)	d (g-cm ⁻³)	s (A) ⁻¹
22/4 ^a	0.714 ^b	380	1.465 ^f	0.64446 ^f	0.88 ^h
2/5	0.765 ^b	403	1.433 ^f	0.64852 ^f	0.96 ⁱ
23/4	0.783 ^c	410	1.409 ^c	0.65705 ^c	0.88 ⁱ
3/5	0.797 ^b	415	1.382 ^f	0.65976 ^f	0.96 ⁱ
<i>n</i> -C ₆	0.814 ^d	423	1.386 ^d	0.6548 ^f	1.04 ^h
<i>n</i> -C ₁₆	1.0314 ^d	463	0.901 ^d	0.76996 ^f	0.90 ^h
<i>br</i> -C ₁₆	0.896 ^e	399	0.855 ^g	0.7813 ^e	0.77 ^h

^aHexane isomers listed as methyl positions/no. of chain carbons. ^bThis work. ^cM. B. Ewing and K. N. Marsh, *J. Chem. Thermodyn.*, **6**, 35 (1974). ^dP. J. Flory, J. L. Ellenson, and B. E. Eichinger, *Macromolecules*, **1**, 279 (1968). ^eP. de St. Romain, Ph.D. Thesis, McGill University, 1977. ^fFrom density data in R. R. Dreisbach, *Physical Properties of Chemical Compounds*, Adv. Chem. Series, (A.C.S., Washington, D C), No. 22. ^gJ. M. Bardin, Ph.D. Thesis, McGill University, 1972. ^hV. T. Lam, P. Picker, D. Patterson, and P. Tancrede, *J.C.S. Faraday Trans. II* **70**, 1465 (1970). ⁱP. Tancrede, P. Bothorel, P. de St. Romain and D. Patterson, *J.C.S. Faraday Trans. II* **73**, 15 (1977).

expected to hold for a system where the thermal expansion coefficients of the components are similar, *i.e.* the P^* effect and curvature terms are small.

3. EXPERIMENTAL RESULTS

3.1. Thermal Pressure Coefficients

Values of the thermal pressure coefficient γ were obtained at 25°C (extrapolated to zero pressure) for 2- and 3-methylpentane. They are listed in Table I together with the P^* values derived therefrom using Eq. (6). The apparatus was similar to that of Flory and collaborators.⁽¹⁵⁾ Thermal pressure coefficients for the other hexane isomers and for the two hexadecane isomers are available from the literature as listed in Table I.

3.2. Calorimetry

A Picker flow microcalorimeter⁽¹⁶⁾ was used to obtain enthalpies of mixing for 2- and 3-methylpentane and 2,3-dimethylbutane mixed

Table II. Experimental and Predicted Molar Excess Volumes for Hexane Isomers-Normal and Branched Hexadecane Mixtures

Comp. 1	Equimolar $H^{E,k}$	x_{12}^i	Eq. (19) Constants ⁱ		Theoret. V^E terms			$10^3 dV^E/dt^j$				
			c_0^d	c_1	c_2	Interact. \bar{V} Curvature	P^*		Total V^E	Exptl.	Theor.	
					$n-C_{16}$ (Component 2)							
22/4	235 ^a	8.35	-0.85 ^e	-	-	0.26	-0.57	-0.73	-1.04	-17 ^f	-12	
2/5	184 ^a	6.77	-0.63 ^e	-	-	0.21	-0.53	-0.49	-0.80		-10	
23/4	187 ^a	6.78	-0.53 ^e	-	-	0.21	-0.49	-0.40	-0.68		-8	
3/5	171 ^a	6.21	-0.46 ^e	-	-	0.19	-0.44	-0.36	-0.61		-8	
$n-C_6$	114 ^a	4.23	-0.54 ^e	-	-	0.14	-0.45	-0.30	-0.61		-10 ^g	-8
					$br-C_{16}$ (Component 2)							
22/4	-55 ^b	0.56	-0.88	-1.60	-0.43	0.02	-0.73	-0.20	-0.91	-11 ^h	-11	
2/5	-71 ^c	0.10	-0.64	-0.94	-3.04	0.00	-0.67	0.04	-0.63		-9	
23/4	-48 ^c	0.56	-0.58	-1.05	-0.24	0.02	-0.63	0.11	-0.60		-8	
3/5	-72 ^c	-0.17	-0.50	-0.81	-0.47	-0.01	-0.58	0.14	-0.44		-7	
$n-C_6$	-68 ^b	-0.02	-0.44	-0.60	-0.03	0.00	-0.59	0.21	-0.38	-6 ^f	-7	

^aJ. A. Larkin, D. V. Fenby, T. S. Gilman and R.L. Scott, *J. Phys. Chem.* **70**, 1959 (1966). ^bV. T. Lam, P. Picker, D. Patterson, and P. Tancrede, *J.C.S. Faraday II*, **70**, 1465 (1974). ^cM. Barbe and D. Patterson, *J. Solution Chem.* **9**, 753 (1980). ^d $c_0/4$ = equimolar V^E . ^eRef. 10. ^fJ. M. Bardin, Ph.D. Thesis, McGill University, 1972. ^gM. Diaz-Peña and M. Benitez de Soto, *Anales Real Soc. Españ. Fis. Quím.* **61**, 1163 (1965). ^hS. N. Bhattacharyya, work in this laboratory. ⁱUnits: $cm^3 \cdot mol^{-1} \cdot K^{-1}$. ^jUnits: $cm^3 \cdot mol^{-1} \cdot K^{-1}$. ^kUnits: J-mol⁻¹. ^lUnits: J-cm⁻³.

with *br*-C₁₆ at 25°. The equimolar values of H^E for these systems and for the other systems are listed in Table II. Values of the X_{12} parameter have been derived for these systems from the equimolar H^E values. Although Eq. (16) would have been adequate, in fact a somewhat different approximation was used as in previous publications.⁽¹⁷⁾

3.3. Excess Volumes

Using a densitometer of the vibrating cell type (Sodev, Sherbrooke, Canada), densities were obtained for the five hexane isomers mixed with *br*-C₁₆ at 25°C. The equimolar values, $c_0/4$, of the molar excess volumes for these and other systems are found in Table II, which also contains constants obtained through fitting the V^E values to the Redlich-Kister equation:

$$V^E = \sum_i c_i x_1 x_2 (x_1 - x_2)^i \quad (19)$$

4. DISCUSSION

4.1. Equation-of-State Parameters

The equation-of-state parameters of Table I are of interest apart from their more important role in the interpretation of V^E . The α and hence \tilde{T} values of the C₁₆ isomers lie below those of the hexanes and this is interpretable through Eq. (5), the molecular entropy/volume ratio S^*/V^* being smaller for the larger molecules. The variations within each set of isomers are more significant. For instance, α and \tilde{T} increase and P^* decreases with increasing hexane chain branching. This is probably due to the decrease of molecular surface area and hence decrease of the energy of molecular cohesion U^* . However, it is also evident that when a methyl group is at the 3-position of the alkane chain, the values of α and V^* are decreased while those of P^* are increased. It has been suggested⁽¹⁷⁾ that this behavior is not related to any change of molecular shape, but rather to steric crowding of the groups within the molecule and/or the number of gauche conformations.⁽¹⁸⁾ Between *n*-C₁₆ and *br*-C₁₆ there is a decrease of P^* which may be ascribed to the decrease of molecular surface area. The accompanying decrease of α and \tilde{T} is perhaps due to steric crowding of the *br*-C₁₆ and lower flexibility of this highly branched molecule.

4.2. Comparison of the Molar Excess Volume and Enthalpy

Comparing the two sets of results for the hexanes + n -C₁₆ and the hexane + br -C₁₆, H^E values for the n -C₁₆ systems are all substantially positive, while the V^E are large and negative and therefore not in accord with Eq. (1). The H^E values for the br -C₁₆ systems are smaller and *negative*, yet the V^E values are remarkably similar to those obtained using n -C₁₆. Within each set of systems, the variations of H^E and V^E values are again out of harmony with Eq. (1). Thus, for the hexanes + n -C₁₆ there are large changes of both H^E and V^E but with almost an inverse correlation from that given by Eq. (1), *e.g.* the 2,2-dimethylbutane + n -C₁₆ system has the most positive value of H^E but the most negative V^E . For the hexanes + br -C₁₆, the H^E values change little from system to system, while the same wide variation of the experimental V^E values is found as with the n -C₁₆ systems.

Perhaps the most striking feature of the results is the similarity of V^E between the two sets of systems in spite of the very different H^E values. The similarity is, however, more apparent than real as indicated by the dV^E/dT values in Table II which are much larger for the n -C₁₆ systems than for those containing br -C₁₆. This suggests a difference in the origin of V^E for these two series of mixtures.

4.3. Interpretation of Molar Excess Volumes through the Prigogine-Flory Theory

Using Eq. (15) together with pure component data and X_{12} values from Table I, equimolar values of the three contributions to V^E have been calculated for the systems. They are shown in Table II, together with the predicted total V^E values. The total V^E have also been calculated directly using Eq. (2), which shows that the approximate Eq. (15) is satisfactory. Although the approximate V^E are more negative than the exact values, the difference is never more than 4%. The predicted total V^E agree well with experiment, both as to the absolute value and the variation of V^E with the hexane isomer. Inspection of the separate terms listed in Table II explains the origin of V^E in the various mixtures.

In Table II, X_{12} and the corresponding interactional term are substantial for systems containing n -C₁₆ but are virtually zero for those containing br -C₁₆. The original view that X_{12} arises from CH₃-CH₂ interactions is not in accord with experiment. Instead, the X_{12} values for the n -C₁₆ systems reflect the presence of short-range orientational order between the n -C₁₆ pairs in the pure liquid which is lost when the

C₆-C₁₆ pairs are formed in the mixture. The values found with the different isomers have been interpreted⁽¹⁷⁾ in terms of the hexane molecular shape and degree of steric crowding. On the other hand, the X_{12} values for the hexanes+*br*-C₁₆ are almost negligible, consistent with the relatively minor amount of orientational order in *br*-C₁₆. The interactional contributions to V^E calculated from Eq. (15) are thus virtually zero for the *br*-C₁₆ systems and still moderate for those containing *n*-C₁₆, reaching 0.267 cm³·mol⁻¹ for 2,2-dimethylbutane+*n*-C₁₆ where the globular shape of the hexane results in the largest destruction of orientational order during mixing.

The term arising from the curvature of $\bar{V}(\bar{T})$ depends on $(\bar{V}_1 - \bar{V}_2)^2$ and hence on the difference of thermal expansion coefficients of the two component liquids. In Table II, this term varies little from system to system.

The P^* term calculated from Eq. (15) and listed in Table II shows the largest variations of the three contributions to V^E . The P^* values of the hexane isomers increase on descending the table, approaching the P^* value for *n*-C₁₆. Corresponding to this the P^* term is negative but decreasing in magnitude. It is this variation which leads to the large change in total V^E which in the absence of the P^* term, would be ≈ -0.3 cm³·mol⁻¹ for all the hexane+*n*-C₁₆ systems. In the case of the mixtures containing *br*-C₁₆, the value of P^* for *br*-C₁₆ lies above that for 2,2-dimethylbutane but below the values for the other hexanes where the calculated P^* term is therefore positive. Here the role of the P^* term is less important than for the *n*-C₁₆ systems but the variation of V^E from system to system is better represented by its inclusion. The reasonable agreement between the predicted and experimental V^E for the hexanes+*n*-C₁₆ indicates that the interactional term in V^E does not depend strongly on the origin of X_{12} , *i.e.* the destruction of orientational order rather than on the dispersion force interactions between unlike molecules as suggested in the original theory. However, since orientational order of the *n*-C₁₆ falls rapidly with increase of T leading to a rapid decrease of the effective value of X_{12} , we expect that the prediction of dV^E/dT will be insufficiently negative if X_{12} is constant as in the Prigogine-Flory theory. On the other hand, good predictions should be found for the hexanes+*br*-C₁₆. This is seen to be the case in Table II.

4.4. Predictions of Molar Excess Volume by Other Theories

The Prigogine-Flory theory requires the fitting of three param-

eters, U^* , V^* and S^* to equation-of-state data of the pure components, whereas other recent theories require only two parameters of dimensions equal to energy (ϵ) and distance (σ), similar to U^* and V^* . However, the Prigogine-Flory theory appears particularly suited to systems containing polyatomic molecules which are allowed more than three external degrees of freedom, $S^* > R$ in Eq. (5), while the other theories, corresponding to $S^* = R$, are more suited to molecules which may be considered as structureless spheres. Calculations of V^E were made using the single-fluid van der Waals theory⁽¹⁹⁾ considering hexanes and hexadecanes as spheres and using the combining rules as recommended by Scott⁽²⁰⁾ for chain-molecules, *i.e.* $\langle \sigma \rangle^3 = x_1 \sigma_{11}^3 + x_2 \sigma_{22}^3$. Results are unsatisfactory which is perhaps not surprising when the theory is applied to molecules such as hexadecane. We believe the Prigogine-Flory theory to be uniquely successful in interpreting V^E for the present systems.

5. ACKNOWLEDGMENTS

We are grateful to the Natural Sciences and Engineering Research Council of Canada for support to which the Ministère de l'Éducation du Québec also contributed.

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