Thermodynamic Interactions in Binary Mixtures of Styrene with *n*-Alkanes at 298.15 K

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Thermodynamic interactions in binary mixtures of styrene with *n*-alkanes have been studied in terms of excess quantities using the experimental results of density, viscosity, and speed of sound at 298.15 K. Flory as well as Prigogine–Flory–Patterson equations were used to calculate the excess molar volume in addition to enthalpy, entropy, and free-energy mixing functions. The viscosity results were analysed using Bloomfield and Dewan theory to predict viscosity deviations, while the speed-of-sound results were analysed by Benson and Kiyohara theory to predict the deviations in isentropic compressibility. The Prigogine–Saraga theory was used to calculate the deviations in internal pressure of liquids and liquid mixtures. Furthermore, isothermal compressibility values were predicted from the Flory equation of state and compared with the experimentally obtained values. Overall, the computed and experimental results are discussed in terms of thermodynamic interactions between the mixing components.

Thermodynamic interactions in liquids and liquid mixtures have been studied in the literature of solution chemistry ever since the development of classical theories of liquids. Such studies have been useful in many engineering disciplines. In the study of solution properties of nonelectrolytes, noteworthy contributions have been made by Flory,[1] Abe and Flory,[2] Prigogine,[3] Patterson and Delmas,[4] Patterson,[5] to mention a few. These studies have led to a better understanding of the mixing behavior of nonelectrolytes in terms of state effects, including order–disorder and packing phenomena. Over the past several years, we have been[6—13] engaged in systematic studies on the solution properties of binary nonelectrolyte liquids. In continuation of this program of research, we now present a complete analysis of the physical-property data on binary mixtures of styrene with *n*-alkanes. Only few such mixtures were discussed in the earlier literature.[10,14—19] Styrene is a useful monomer to prepare an industrially important polymer, polystyrene.

The principle objective of this study was to test the solution theories developed by Flory and co-workers[1,2,4,5] using the density results of styrene+*n*-alkanes[10] in order to calculate the excess molar volume (V^{E}) at 298.15 K. The excess enthalpy (H^{E}), excess entropy (S^{E}), and excess Gibbs free energy (ΔG^{E}) have also been calculated from the theory of Flory.[1,2] The viscosity deviations have been calculated from Bloomfield and Dewan theory.[20] From the speed-of-sound (u) results, the deviations in isentropic compressibility (Δk_S) have been calculated from Benson and Kiyohara equation.[21] Deviations in isothermal compressibility, (Δk_T) have also been calculated from Flory theory[1,2] and compared with those calculated from Benson–Kiyohara theory. Furthermore, efforts have been made to compute the deviations in internal pressure (ΔP_i) from the speed of sound using the Prigogine and Saraga equation.[22] All of the calculated excess quantities have been fitted to Redlich and Kister equation[23] to derive the coefficients and compute the standard errors between the experimentally calculated and fitted quantities. The sign and magnitude of these quantities are discussed in terms of thermodynamic interactions between the components.

Results

1. Volumetric Behavior. Here, we calculate three types of excess molar volumes (V^{E}): one calculated from Flory theory ($V^{\mathrm{E}}_{\mathrm{F}}$[1,2]) and the other[3] from Prigogine–Flory–Patterson theory ($V^{\mathrm{E}}_{\mathrm{PFP}}$[4,5]) and the experimentaly calculated value ($V^{\mathrm{E}}_{\mathrm{expt}}$). According to the Flory equation of state,[1,2] $V^{\mathrm{E}}_{\mathrm{F}}$ is given as

$$V^{\mathrm{E}}_{\mathrm{F}} = \left(\sum_{i=1}^{2} x_i V_i^*\right)\left(\tilde{V}^{\mathrm{o}\,7/3}/[4/3-(\tilde{V}^{\mathrm{o}})^{1/3}]\right)(\tilde{T}-\tilde{T}^{\mathrm{o}}), \qquad (1)$$

where $\tilde{V}^{\mathrm{o}}$ is the ideal reduced volume, calculated as

$$\tilde{V}^{\mathrm{o}} = \Phi_1 \tilde{V}_1 + \Phi_2 \tilde{V}_2. \qquad (2)$$

Here, $V_i^* = \frac{V_i}{\tilde{V}_i}$ is the characteristic volume of the i-th component, $\tilde{V}$ is the reduced volume and V_i is the molar volume. The redauced volume is calculated from the thermal expansion coefficient, $\alpha[\equiv -(1/\rho)(\partial\rho/\partial T)]$, as

$$\tilde{V}_i = \left[\frac{1+(4/3)\alpha_i T}{(1+\alpha_i T)}\right]^3. \qquad (3)$$

The reduced temperature ($\tilde{T}$) and the ideal reduced temperature ($\tilde{T}^{\mathrm{o}}$) in Eq. 1 are calculated using the following equations:

$$\tilde{T}^{o} = \frac{\left(\tilde{V}^{o1/3}-1\right)}{\tilde{V}^{o4/3}}, \tag{4}$$

$$\tilde{T} = \frac{(\Phi_1 P_1^* \tilde{T}_1 + \Phi_2 P_2^* \tilde{T}_2)}{(\Phi_1 P_1^* + \Phi_2 P_2^*)}. \tag{5}$$

In all of the above equations, the segment or hard-core volume fraction (Φ_i) is calculated as

$$\Phi_i = \frac{x_i V_i^*}{\sum_{i=1}^{2}(x_i V_i^*)} \quad \text{and} \quad \Phi_1 = 1 - \Phi_2. \tag{6}$$

The characteristic pressure (P^*) is calculated using

$$P_i^* = \frac{T\tilde{V}^2 \alpha_i}{k_T}, \tag{7}$$

where k_T is the isothermal compressibility, calculated from the isentropic compressibility, (k_S) and the heat capacity (C_p) of liquids as

$$k_T = k_S + T\alpha^2 V/C_p. \tag{8}$$

Here, the values of α have been calculated from the experimental densities at three temperatures.[10] In order to calculate P_i^* from Eq. 7, we used the C_p data of the mixtures from the individual (C_{p_1} and C_{p_2}) values of the heat-capacity data of components 1 and 2,

$$C_P = x_1 C_{p_1} + x_2 C_{p_2}. \tag{9}$$

The experimental excess molar volume can be calculated from the experimental density data using

$$V^E_{\text{expt}} = V_m - V_1 x_1 - V_2 x_2, \tag{10}$$

where $V_m = \frac{M_1x_1+M_2x_2}{\rho}$, $V_1 = M_1/\rho_1$ and $V_2 = M_2/\rho_2$ are, respectively, the molar volumes of the mixture, pure components 1 and 2; M_1 and M_2 are the respective molecular weights and ρ represents the density.

According to Prigogine–Flory–Patterson (PFP) theory,[4,5] the V^E_{PFP} values are calculated as follows:

$$\frac{V^E_{\text{PFP}}}{(x_1 V_1^* + x_2 V_2^*)} = V^E_{\text{int}} + V^E_{\text{fv}} + V^E_{\text{ip}}, \tag{11}$$

where

$$V^E_{\text{int}} = \frac{(\tilde{V}^{1/3}-1)\tilde{V}^{2/3}}{[(4/3)\tilde{V}^{-1/3}-1]}\psi_1\theta_2\left(\frac{X_{12}}{P_1^*}\right), \tag{11a}$$

$$V^E_{\text{fv}} = -\frac{(\tilde{V}_1-\tilde{V}_2)^2[(14/9)\tilde{V}^{-1/3}-1]\psi_1\psi_2}{[(4/3)\tilde{V}^{-1/3}-1]\tilde{V}}, \tag{11b}$$

$$V^E_{\text{ip}} = \frac{(\tilde{V}_1-\tilde{V}_2)(P_1^*-P_2^*)}{(P_1^*\psi_2+P_2^*\psi_1)}\psi_1\psi_2. \tag{11c}$$

The V^E_{int} term in Eq. 11 represents X_{12}, often called the contact interaction parameter. The second term (V^E_{fv}) represents the difference in the "free volume". The third term (V^E_{ip}) is the contribution of excess molar volume due to internal pressure. In order to calculate V^E_{PFP} from Eq. 11, we used the parameter values given in Table 1. For this, we needed the values of X_{12}. In view of the nonavailability of excess molar enthalpy (H^E), data for the present mixtures, we calculated the X_{12} parameter using the experimental V^E data at 298.15 K, as

$$X_{12} = \frac{1}{(\Phi_1\theta_2\tilde{T})}\left[\sum \Phi_i P_i^*\left(\tilde{T}-\tilde{T}_i\right)\right]. \tag{12}$$

The reduced temperature of the mixture was then calculated from

$$\tilde{T}(X_{12}) = \frac{(\Phi_1 P_1^* \tilde{T}_1 + \Phi_2 P_2^* \tilde{T}_2)}{(\Phi_1 P_1^* + \Phi_2 P_2^* - \Phi_1\theta_2 X_{12})}. \tag{13}$$

Here, the surface site fraction (θ_2) was calculalted as

$$\theta_2 = 1 - \theta_1 = \frac{\Phi_2}{\left[\Phi_2 + \Phi_1\left(V_2^*/V_1^*\right)^{1/3}\right]}, \tag{14}$$

and the contact energy fraction (ψ_i) was calculated as

$$\psi_i = \frac{x_i P_i^* V_i^*}{\sum_{i=1}^{2}(x_i P_i^* V_i^*)}. \tag{15}$$

Next, by following the Flory theory, the excess enthalpy (H^E), excess entropy (S^E), and excess Gibbs free energy (G^E) of mixing were calculated using the following equations:

$$H^E = \sum_{i=1}^{2} x_i P_1^* V_1^* \left(\frac{1}{\tilde{V}_i} - \frac{1}{\tilde{V}}\right) + \frac{x_1\theta_2 V_1^* X_{12}}{\tilde{V}}, \tag{16}$$

$$S^E = -3\left[\frac{x_1 P_1^* V_1^*}{T_1^*}\ln\frac{\tilde{V}_1^{1/3}-1}{\tilde{V}^{1/3}-1} + \frac{x_2 P_2^* V_2^*}{T_2^*}\ln\frac{\tilde{V}_2^{1/3}-1}{\tilde{V}^{1/3}-1}\right], \tag{17}$$

$$G^E = \sum_{i=1}^{2} x_i P_1^* V_1^* \left[\left(\frac{1}{\tilde{V}_i} - \frac{1}{\tilde{V}}\right) + 3\tilde{T}_i \ln\left(\frac{\tilde{V}_i^{1/3}-1}{\tilde{V}^{1/3}-1}\right)\right] + \frac{x_1\theta_2 V_1^* X_{12}}{\tilde{V}}. \tag{18}$$

The estimated values of H^E and G^E near to the equimolar compositions are compiled in Table 2.

Table 1. Values of Molar Volume (V), Thermal Expansion Coefficient (α), Heat Capacity (C_p), Isothermal Compressibility (k_T), Isentropic Compressibility (k_S), and Characteristic Parameters (P^*, V^*, and T^*) for Pure Liquids at 298.15 K

Liquid	V	V^*	$\tilde{V}$	C_p	$10^3\ \alpha$	k_S	k_T	P^*	T^*
	$\text{cm}^3\ \text{mol}^{-1}$	$\text{cm}^3\ \text{mol}^{-1}$		$\text{J K}^{-1}\ \text{mol}^{-1}$	K^{-1}	TPa^{-1}	TPa^{-1}	J cm^{-3}	K
Styrene	115.5	92.6	1.248	182.59	0.996	574	763	609	5240
n-Hexane	131.6	99.1	1.328	195.48	1.420	1310	1714	436	4391
n-Heptane	147.5	113.3	1.302	224.98	1.280	1147	1467	441	4608
n-Octane	163.5	128.1	1.276	254.15	1.142	1028	1278	434	4969
n-Decane	195.9	155.2	1.262	300.32	1.071	904	1127	451	5053
n-Dodecane	228.6	183.2	1.248	375.97	1.003	809	990	469	5239

2. Internal Pressure. The internal pressure (P_i) of liquids and liquid mixtures has been the subject of active interest in the literature.[24,25] Internal pressure has been calculated using the speed-of-sound data in conjunction with other thermodynamic parameters[26,27] as

$$P_i = \frac{2^{1/6}RT}{2^{1/6}V - dN^{1/3}V^{2/3}}, \tag{19}$$

where V (m^3/10^{-6} mol^{-1}), N (6.023×10^{23} molecules/mole), and d (calculated in SI units) are respectively, the molar volume, Avogadro's number, and molecular diameter; R is the molar gas constant in SI units and T is the temperature in Kelvin. The values of d needed to calculate P_i from Eq. 19 were calculated using the following semiempirical relation:[25]

$$d^{5/2} = \frac{1}{7.21\times10^{19}}\cdot\frac{V\gamma^{1/4}}{T_C^{1/4}}, \tag{20}$$

where γ (N m^{-1}) is the surface tension and T_C (Kelvin) is the critical temperature. The surface tension of liquids, or their mixtures, is related to speed-of-sound, as[22,27]

$$\gamma = 6.3\times10^{-4}\rho u^{3/2}. \tag{21}$$

Here, ρ (kg m^{-3}) and u (m s^{-1}) were used in SI units. The T_C of the mixture was obtained from the following additive relation:

$$T_{C(\text{mix})} = \sum_{i=1}^{2} T_{C(i)}x_i. \tag{22}$$

The deviation in the internal pressure (ΔP_i) of the liquid mixture was then calculated as[11,28]

$$\Delta P_i = P_{\text{mix}} - \sum_{i=1}^{2} P_i x_i. \tag{23}$$

3. Viscosity Behavior. Several empirical correlations have been proposed to study the viscosity behavior of liquid mixtures that generally require adjustable parameters.[29,30] However, the most commonly used equation to predict the deviation in logarithmic viscosity ($\Delta \ln \eta$) from the experimental viscosity is given by

$$\Delta \ln \eta_{\text{expt}} = \ln \eta - (x_1 \ln \eta_1 + x_2 \ln \eta_2). \tag{24}$$

Bloomfield and Dewan[20] developed a theoretical relation to compute $\Delta \ln \eta_{\text{th}}$ without using any adjustable parameters. This theory correlates the viscosity of a mixture with such thermodynamic properties as H^E, S^E, and G^E. The theory is based on the free volume and absolute reaction-rate concepts[31] as well as that of the Flory equation.[1,2] From the equation proposed by Bloomfield and Dewan,[20] we have

$$\Delta \ln \eta_{\text{th}} = \ln \eta_G + \ln \eta_{\text{fv}}, \tag{25}$$

where $\ln \eta_G$ and $\ln \eta_{\text{fv}}$ are, respectively, the contributions from the free energy and free-volume effects. Equation 25 can be further rewritten by splitting the $\ln \eta_G$ term into enthalpy and entropy contributions,

$$\Delta \ln \eta_{\text{th}} = \ln \eta_H + \ln \eta_S + \ln \eta_{\text{fv}} = -G^E/RT + \ln \eta_{\text{fv}}. \tag{26}$$

By splitting G^E into enthalpy and entropy contributions, one obtains

$$\Delta \ln \eta_{\text{th}} = -H^E/RT + S^E/R + \left[\frac{1}{\tilde{V}-1} - \left(\sum_{i=1}^{2}\frac{x_i}{(\tilde{V}_i - 1)}\right)\right]. \tag{27}$$

To calculate $\Delta \ln \eta_{\text{th}}$ (in the absence of experimental data), the values of H^E and S^E calculated from Eqs. 16 and 17, respectively, were used. The free-volume contribution to deviations in the viscosity was then calculated in the usual manner from Flory theory.[1,2]

Table 2. Calculated Near Equimolar H^E and G^E Values at 298.15 K for the Binary Mixtures of Styrene with n-Alkanes

n-Alkane	x_1	H^E/J mol^{-1}	G^E/J mol^{-1}
n-Hexane	0.4992	677	577
n-Heptane	0.4989	657	532
n-Octane	0.4971	558	435
n-Decane	0.4959	615	472
n-Dodecane	0.5183	627	482

Using the theory of Eyring et al.,[31] we also calculated the excess molar Gibbs energy of activation (ΔG^{*E}) for viscous flow using

$$\Delta G^{*E} = RT(\ln \eta V - x_1 \ln \eta_1 V_1 - x_2 \ln \eta_2 V_2), \tag{28}$$

where η and V are, respectively, the viscosity and molar volume of the mixture; η_i and V_i represent similar quantities for the i component, of the mixture and RT has the usual meaning. The ΔG^{*E} is a kinetic-energy barrier which impeaches the system to immediately reach the minimal level of free energy corresponding to complete thermodynamic equilibrium. However, it is possible to split this contribution between the enthalpy or entropy i.e., ΔH^{*E} of ΔS^{*E}, terms, which could be obtained from the temperature dependence of ΔG^{*E}. Such ΔH^{*E} or ΔS^{*E}, referring to activation energy values, cannot be fundamentally replaced by the H^E or S^E obtained based on pure thermodynamic considerations.

4. Ultrasonic Behavior. The ultrasonic properties of liquids and their mixtures are useful in predicting deviations in the isentropic compressibility (Δk_S) and the isothermal compressibility (Δk_T) using a general equation of the type[12,13]

$$\Delta k_S = k_S(\text{or } k_T)^{\text{mix}} - k_S(\text{or } k_T)^{\text{ideal}}. \tag{29}$$

The ideal terms in Eq. 29 are the volume-fraction averages calculated from the individual components of the mixture. However, Benson and Kiyohara[21] proposed the following relation to calculate k_S^{ideal}:

$$k_S^{\text{ideal}} = k_{S,1}\phi_1 + k_{S,2}\phi_2 + T\left\{\phi_1 V_1 \alpha_1^2/C_{P,1} + \phi_2 V_2 \alpha_2^2/C_{P,2} - \frac{V_m^{\text{ideal}}(\alpha^{\text{ideal}})^2}{C_P^{\text{ideal}}}\right\}. \tag{30}$$

Here, $\phi_i = \frac{x_i V_i}{\sum_{i=1}^{2}(x_i V_i)}$ is the volume fraction of the i-th component of the mixture. The values of C_{P_i} for pure components of the mixtures were taken from Riddick et al.[32]

The deviations in the speed of sound (Δu) were calculated from the experimental values of u of the binary mixtures and of the individual components (u_i) using

$$\Delta u = u_{\mathrm{mix}} - u_1 x_1 - u_2 x_2. \tag{31}$$

A survey of the literature indicates that very few attempts[33] have been made to predict Δk_T theoretically. Thus, we have calculated Δk_T of mixtures using Flory theory,[1,2]

$$\Delta k_T = 3\tilde{V}^2/[P^*\{(\tilde{V}^{1/3}-1)^{-1}-3\}] - \sum_{i=1}^{2}(\Phi_i \tilde{V}_i k_{T,i})/\tilde{V}. \tag{32}$$

In order to judge the validity of the speed-of-sound data for the present mixtures, we also computed the theoretical values of u from the Prigogine–Saraga equation[22] and that of Auerbach,[34]

$$u = [\gamma \cdot 104/6.3\rho]^{2/3}, \tag{33}$$

where γ is the surface tension. To obtain u in $\mathrm{m\,s^{-1}}$, the input values of γ and ρ were taken in the c.g.s. units,

$$\gamma = \gamma^* \tilde{\gamma}, \tag{34}$$

where γ^* and $\tilde{\gamma}$ are the characteristic and reduced surface tension, respectively. According to Patterson and Rastogi,[35] γ^* is related to the state parameters,

$$\gamma^* = k^{1/3} \cdot T^{*1/3} \cdot P^{*2/3}, \tag{35}$$

where k is the Boltzmann constant. Following Prigogine and Saraga,[22] we may write the relationship for reduced surface tension as

$$\tilde{\gamma} = M\tilde{V}^{-5/3} - \frac{\tilde{V}^{1/3}-1}{\tilde{V}^2}\ln\left[\frac{\tilde{V}^{1/3}-0.5}{\tilde{V}^{1/3}-1}\right]. \tag{36}$$

Here, M is the fractional decrease in the nearest neighbors of a cell due to migration from the bulk phase to the surface phase; its value varies from 0.25 to 0.29 for a closely packed lattice. In this calculation, we took M as 0.25. These data reproduced the experimental values of u within 3—5% when compared with the published results.[6—13]

5. Least-Squares Estimations. All of the calculated parameters [V^{E} from Eq. 10, ΔP_{i} from Eq. 23, $\Delta \ln \eta$ from Eq. 24, $\Delta G^{*\mathrm{E}}$ from Eq. 28, Δk_S from Eq. 29, and Δu from Eq. 31] were fitted to the Redlich-and-Kister equation[23] to obtain the coefficients (A_j),

$$\Delta Y = C_1 C_2 \sum_{j=1}^{k} A_j (C_2 - C_1)^{j-1}, \tag{37}$$

where ΔY refers to V^{E}, ΔP_{i}, $\Delta \ln \eta$, $\Delta G^{*\mathrm{E}}$, Δk_S, and Δu; C_{i} is a mixture composition. To calculate Δk_S, we used the volume fraction (ϕ_i), while to calculate the other quantities (V^{E}, $\Delta \ln \eta$, ΔP_{i}, $\Delta G^{*\mathrm{E}}$, and Δu) the mole fraction (x_{i}) was used. The standard errors (σ) between the calculated and observed data points were obtained using

$$\sigma = \left(\sum (Y_{\mathrm{calcd}} - Y_{\mathrm{obsd}})^2/(n-m)\right)^{1/2}, \tag{38}$$

where n is the number of data points and m represents the number of parameters to be estimated. The values of the coefficient, A_j and σ are given in Table 3. In all of these calculations, no more than three coefficients were required in the polynomial for a proper fit while minimizing the data using the Marquardt algorithm.[36]

Discussion

Styrene has an oriented structure, which is rather stabilised by dipole–dipole interactions. As can be seen from the data given in Table 1, styrene has a lower value of α and k_T than all of the *n*-alkanes. When it is mixed with lower *n*-alkanes (*n*-hexane or *n*-heptane) having higher values of k_T, the binary mixture exhibits large free-volume effects (see Table 4). This also explains the observed high negative V^{E} for mixtures of styrene+*n*-hexane when compared to other *n*-alkane-containing mixtures (Fig. 1). However, the variation in the thermodynamic properties of *n*-alkanes with increasing molecular chain lengths is influenced by changes in the free volume i.e., equation-of-state effects and of the orientational order between chains and/or due to packing effects involving *trans*-to *gauche* conformational proportions.[37]

For mixtures of styrene+*n*-octane, although both the calculated and $V^{\mathrm{E}}_{\mathrm{PFP}}$ values are positive, the $V^{\mathrm{E}}_{\mathrm{F}}$ values are negative, as shown in Table 4. Even the H^{E} values calculated from the PFP theory for these mixtures are positive (Table 2). This is attributed to the order creation in view of: (i) the intramolecular interactions due to a change in the *trans*-to-*gauche* population of the *n*-alkanes produced by a favorable interaction between the *trans*-conformer and styrene or (ii) through hindering of the rotational segmental motion in flexible *n*-alkanes. Since the rotational and conformational orders are not very different, it is possible that the order-creation might be due to a combination of both processes. Hence, of all of the systems investigated, styrene+*n*-hexane

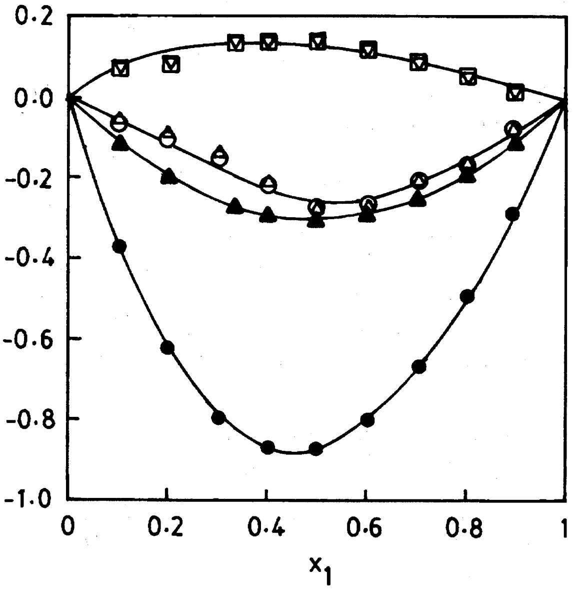

Fig. 1. Comparison of V^{E} data for mixtures of styrene with *n*-hexane, (○) Expt; (●) Flory theory; (△) PFP theory and for mixtures of styrene with *n*-octane, Symbols: (□) Expt; (▲) Flory theory and (▽) PFP theory at 298.15 K.

Table 3. Estimated Parameters of Eq. 38 for Various Functions for Binary Mixtures of Styrene with *n*-Alkanes

Function	T/K	A_0	A_1	A_2	σ
		Styrene(1)+*n*-Hexane(2)			
$V^E/10^{-6}\text{m}^3\text{mol}^{-1}$	298.15	−1.024	0.268	0.545	0.015
$\Delta\ln\eta$/mPa s	298.15	−0.383	−0.008	0.097	0.007
ΔG^{*E}/J mol^{-1}	298.15	−953.1	−0.915	291.1	16.16
$\Delta P_i\cdot 10^7$/TPa	298.15	5.98	−3.98	−0.58	0.202
Δk_S/TPa^{-1}	298.15	−314	11.47	−11.10	1.711
		Styrene(1)+*n*-Heptane(2)			
$V^E/10^{-6}\text{m}^3\text{mol}^{-1}$	298.15	−0.069	0.462	−0.128	0.004
$\Delta\ln\eta$/mPa s	298.15	−0.427	0.086	−0.032	0.001
ΔG^{*E}/J mol^{-1}	298.15	−988.2	209.8	−61.75	4.47
$\Delta P_i\cdot 10^7$/TPa	298.15	−12.6	−3.61	0.66	0.123
Δk_S/TPa^{-1}	298.15	−154	−20.7	8.2	1.43
		Styrene(1)+*n*-Octane(2)			
$V^E/10^{-6}\text{m}^3\text{mol}^{-1}$	298.15	0.546	0.235	−0.273	0.006
$\Delta\ln\eta$/mPa s	298.15	−0.452	0.060	0.118	0.005
ΔG^{*E}/J mol^{-1}	298.15	−960.8	135.3	289.9	11.18
$\Delta P_i\cdot 10^7$/TPa	298.15	−30.63	−6.61	4.96	0.153
Δk_S/TPa^{-1}	298.15	−122.3	−48.2	−14.02	1.49
		Styrene(1)+*n*-Decane(2)			
$V^E/10^{-6}\text{m}^3\text{mol}^{-1}$	298.15	1.245	0.294	−0.036	0.007
$\Delta\ln\eta$/mPa s	298.15	−0.369	0.140	−0.085	0.004
ΔG^{*E}/J mol^{-1}	298.15	−553.3	285.3	−201	11.02
$\Delta P_i\cdot 10^7$/TPa	298.15	−92.3	10.64	1.54	0.155
Δk_S/TPa^{-1}	298.15	−44.9	−13.1	−28.8	1.61
		Styrene(1)+*n*-Dodecane(2)			
$V^E/10^{-6}\text{m}^3\text{mol}^{-1}$	298.15	1.712	0.024	0.348	0.013
$\Delta\ln\eta$/mPa s	298.15	−0.205	0.069	0.064	0.003
ΔG^{*E}/J mol^{-1}	298.15	93.2	231.8	−191.5	34.46
$\Delta P_i\cdot 10^7$/TPa	298.15	−162.8	26.8	−13.39	0.29
Δk_S/TPa^{-1}	298.15	35.78	−115.3	−71.9	2.85

Table 4. Comparison of Theoretical Excess Volume with the Experimental Data at 298.15 K for Near Equimolar Mixtures of Styrene+*n*-Alkanes

n-Alkane	$\partial V^E/\partial T$	θ_2	X_{12}[a)]	V^E_{expt}	V^E_{PFP}	V^E_{F}	V^E_{int}	V^E_{fv}	V^E_{ip}
	cm^{3}mol^{-1} K^{-1}		Jmol^{-1}	cm^{3}mol^{-1}	cm^{3}mol^{-1}	cm^{3}mol^{-1}	cm^{3}mol^{-1}	cm^{3}mol^{-1}	cm^{3}mol^{-1}
n-Hexane	−0.0048	0.5122	28.48	−0.272	−0.269	−0.874	0.596	0.224	−0.640
n-Heptane	−0.0028	0.5346	26.01	−0.024	−0.021	−0.570	0.545	0.114	−0.451
n-Octane	0.0035	0.5568	21.02	0.138	0.140	−0.298	0.437	0.033	−0.263
n-Decane	0.0036	0.5893	21.83	0.322	0.324	−0.136	0.460	0.009	−0.127
n-Dodecane	0.0032	0.5943	21.12	0.438	0.440	ca. 0	0.440	ca. 0	ca. 0

a) From V^E

mixtures, show the largest negative values of V^E_{expt} (see Table 4). On the other hand, a greater degree of order is found with *n*-decane or *n*-dodecane, due to their greater segment density values (or lower free volumes) inspite of their more elongated molecular shapes.

Order destruction and order-creation processes in binary mixtures have also been studied[38)] in terms of the second-order thermodynamic mixing quantities, $\partial V^E/\partial T$. These values are negative for styrene+*n*-hexane or +*n*-heptane mixtures (see Table 4), suggesting the presence of a short-range orientational order between the long-chain *n*-alkanes in the pure state. When a rigid plate-like molecule like styrene is mixed with elongated *n*-alkanes, the order is destroyed, since styrene has an order-breaking ability. Because of the destruction of order during mixing, we observed a negative contribution to $\partial V^E/\partial T$. For styrene+*n*-octane or +higher *n*-alkanes, $\partial V^E/\partial T$ is positive (see Table 4), suggesting the presence of long-range orientational order between the styrene and higher *n*-alkanes in the pure state. Thus, order is created in these mixtures, leading to positive V^E_{expt}. The contributions of an order effect for $\partial V^E/\partial T$ have also been studied by others.[39—42]

The computed values of θ_2 and X_{12} are given in Table 4 along with a comparison of the near-equimolar V^E_{expt} values with those of the V^E_F and V^E_{PFP} values. The X_{12} values are positive and decrease with an increasing size of *n*-alkanes. This could be explained in view of the fact that the H^E and G^E results (Table 2) are also positive. In the original PFP theory, V^E_{int} is generally positive in the absence of a H-bond and other specific interactions. This is indeed the case for all *n*-alkanes. Since the V^E_{int} term is dominant in H^E these values are positive. The free-volume terms are also positive because $d^2\tilde{V}/dT^2$ is negative. On the other hand, the internal-pressure contribution can be positive or negative, depending upon the sign of the $(\tilde{V}_1-\tilde{V}_2)(P^*_1-P^*_2)$ term. The P^* contribution of the PFP theory therefore depends either on the difference in the thermal–pressure coefficient or the internal pressure of liquids. The P^* term often dominates V^E_{PFP}, particularly if one of the components has a higher P^* (internal pressure) value and a lower $\tilde{V}$ (thermal expansion coefficient) than the other. This situation leads to a negative V^E_{PFP} with positive H^E, as originally predicted by Prigogine and Mathot.[43] This observation is prevalent for styrene+*n*-hexane or *n*-heptane mixtures, but not for those containing higher *n*-alkanes. However, the P^* contribution to V^E is negative for all mixtures.

The V^E_F and V^E_{PFP} values are compared with the V^E_{expt} values for mixtures of styrene with *n*-hexane or *n*-octane as well as with *n*-decane or *n*-dodecane at 298.15 K in Figs. 1 and 2. In all cases, the V^E_{PFP} values are almost identical to the V^E_{expt} values, but the V^E_F values are more negative than the experimental V^E_{expt} values and also deviate drastically from the experimental data. A plot of the equimolar V^E_{expt} as a function of the number of carbon atoms of *n*-alkanes is shown in Fig. 3. In all the cases, the equimolar values of V^E_{expt} increase with increasing size of *n*-alkanes. The calculated curves of the equimolar V^E_{expt} values from the theories of Flory and PFP are also included in Fig. 3. Since V^E_{PFP} curves are in good agreement with the V^E_{expt} curves, a single curve is drawn to show their dependencies. However, the V^E_F curves are lower than both the V^E_{expt} and V^E_{PFP} curves.

Figure 4 shows plots of ΔP_i vs. ϕ_1 for all binary mixtures. A positive deviation in ΔP_i is observed for a styrene+*n*-hexane mixture, indicating that the attractive forces are greater than those of the repulsive interactions, while for other *n*-

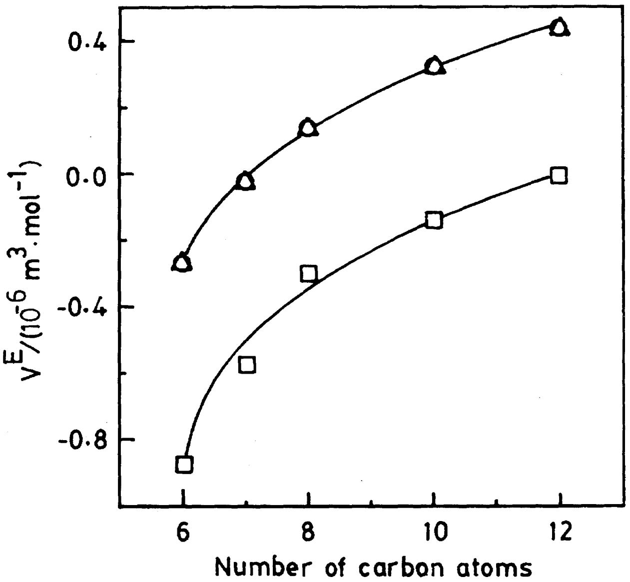

Fig. 3. Equimolar V^E vs. number of carbon atoms for (○) Expt, (□) Flory theory and (△) PFP theory at 298.15 K.

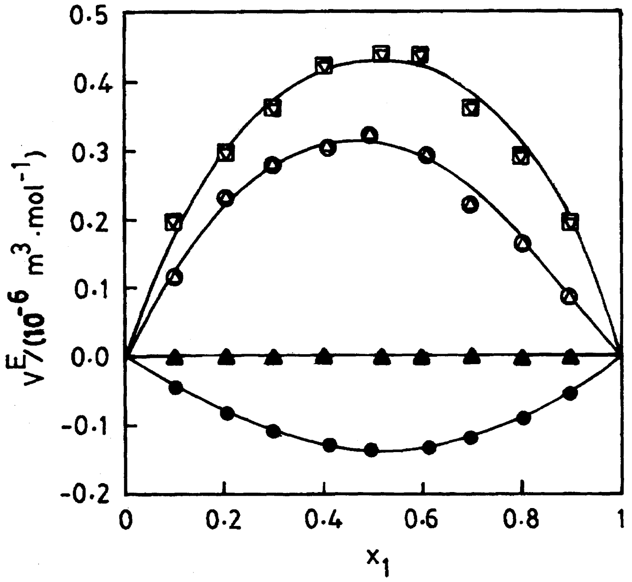

Fig. 2. Comparison of V^E data for mixtures of styrene with *n*-decane, (○) Expt; (●) Flory theory; (△) PFP theory and for mixtures of styrene with *n*-dodecane, (□) Expt; (▲) Flory theory and (▽) PFP theory at 298.15 K.

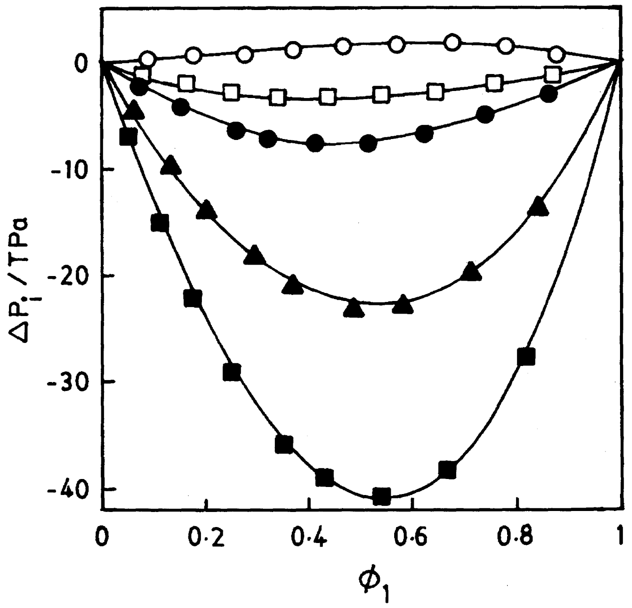

Fig. 4. Deviations in internal pressure vs. volume fraction at 298.15 K for mixtures of styrene+(○) *n*-hexane, (□) *n*-heptane, (●) *n*-octane, (▲) *n*-decane, and (■) *n*-dodecane.

alkanes these values are negative. The negative ΔP_i values indicate qualitatively that the repulsive forces between the interacting molecules have a predominant effect. Thus, the ΔP_i results are in agreement with those expected from theoretical predictions. The ΔP_i values decrease systematically with increasing size of the *n*-alkanes.

The Bloomfield and Dewan[20] values of $\Delta \ln \eta_{th}$ are compared in Table 5 with those of the experimental $\Delta \ln \eta_{expt}$ calculated from Eq. 24. The three contribution terms of Eq. 26 ($\ln \eta_H$, $\ln \eta_S$, and $\ln \eta_{fv}$) to $\Delta \ln \eta_{th}$ are also listed. The $\Delta \ln \eta_{th}$ values are in agreement with the $\Delta \ln \eta_{expt}$ results. Figure 5 displays the dependence of $\Delta \ln \eta$ on x_1. In all cases, we find that $\Delta \ln \eta$ are negative. However, any difference between the experimental and predicted values is attributed to: (i) an overestimation of the entropy contribution, i.e., the S^E/R term, determined from free-volume difference and (ii) due to conformational effects in *n*-alkanes. The $\ln \eta_H$ contribution is negative and becomes dominant in the overall contribution to $\Delta \ln \eta_{th}$. The results of ΔG^{*E} vs. x_1 are plotted in Fig. 6, wherein for all mixtures, except for styrene+*n*-dodecane, the ΔG^{*E} values are negative.

The results of Δk_S calculated from Eq. 29 and those predicted from Benson–Kiyohara theory,[21] i.e. Eq. 30, are presented in Fig. 7. The Benson–Kiyohara values of Δk_S are less negative than those obtained from the experiments. In both cases, the Δk_S values exhibit a systematic dependence on the size of the *n*-alkanes. Negative values of Δk_S suggest that the system is less compressible than the corresponding ideal mixture; the positive values indicate the opposite behavior. Hexane is a disordered liquid, and when it is mixed with styrene the "free volume" of the mixture decreases. However, larger *n*-alkanes are more ordered liquids than *n*-hexane, and upon mixing their order is partially destroyed due to an additional creation of free volume. Thus, for longer *n*-alkanes, smaller values of Δk_S are observed. The theoretically calculated Δk_T values are compared with the experimental Δk_T in Fig. 8 in the case of styrene+*n*-hexane, +*n*-octane or +*n*-decane mixtures. It is observed that although the theoretical results of Δk_T are lower than the experimental curves, quite identical dependecies are observed between theory and experiments.

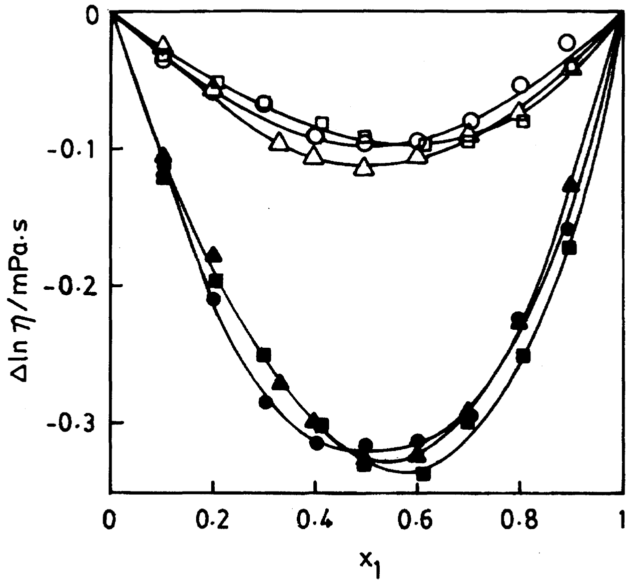

Fig. 5. Deviations in experimental ln η vs. mole fraction of styrene with (○) *n*-hexane, (△) *n*-octane, and (□) *n*-decane with those calculated from Bloomfield–Dewan for (●) *n*-hexane, (▲) *n*-octane, and (■) *n*-decane at 298.15 K.

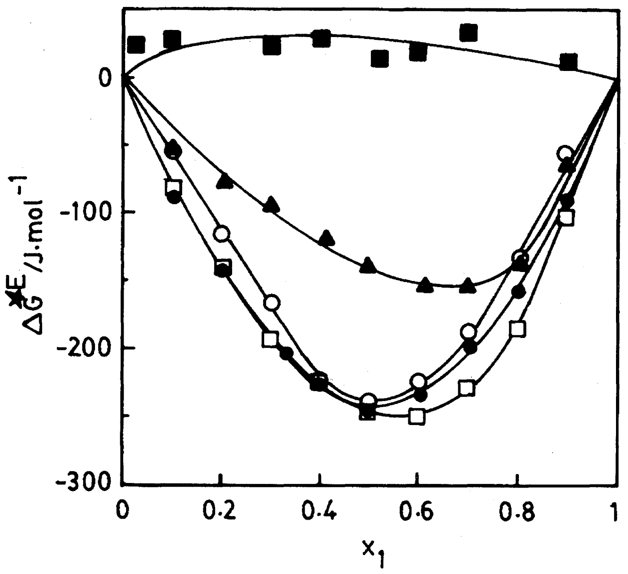

Fig. 6. Excess molar Gibbs energy of activation of flow vs mole fraction of styrene at 298.15 K for the same mixtures with the same symbols as given in Fig. 4.

Conclusions

The theories of Flory and that of Prigogine–Flory–Patterson were employed to predict the excess molar volumes for binary mixtures of styrene+*n*-alkanes.[10] The trends in the calculated values of V^E_{expt} with *n*-alkane carbon numbers agree with those predicted from the theories, indicating the importance of the P^* contribution to the prediction of

Table 5. Comparision of Experimental and Computed Values of $\Delta \ln \eta$ from Bloomfield–Dewan Equation at 298.15 K for Near Equimolar Mixtures of Styrene +*n*-Alkanes

n-Alkanes	$\ln \eta_H$	$\ln \eta_S$	$\ln \eta_{fv}$	$\Delta \ln \eta_{th}$	$\Delta \ln \eta_{expt}$	$\Delta \ln \eta_{expt} - \Delta \ln \eta_{th}$
n-Hexane	−0.308	0.040	−0.051	−0.318	−0.097	0.222
n-Heptane	−0.315	0.051	−0.069	−0.333	−0.107	0.226
n-Octane	−0.313	0.050	−0.062	−0.325	−0.115	0.210
n-Decane	−0.327	0.059	−0.069	−0.337	−0.092	0.245
n-Dodecane	−0.336	0.058	−0.052	−0.330	−0.055	0.275

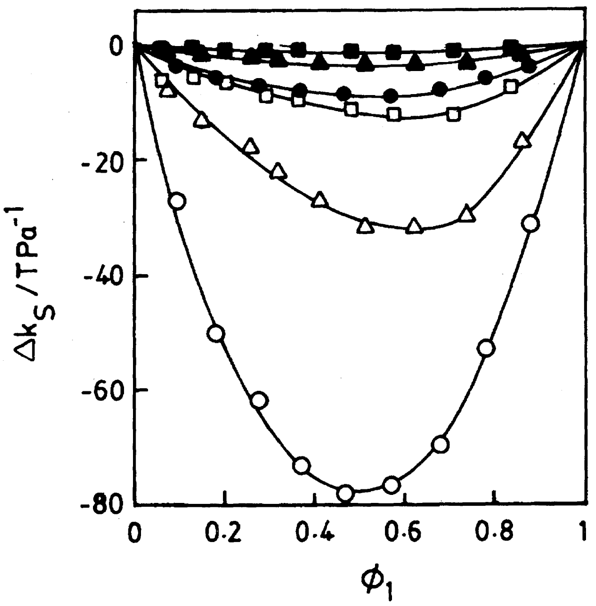

Fig. 7. Comparison of experimental deviations in isentropic compressibility for styrene with (○) *n*-hexane, (△) *n*-octane, and (□) *n*-decane with those calculated from Benson–Kiyohara theory at 298.15 K for mixtures of styrene with (●) *n*-hexane, (▲) *n*-octane, and (■) *n*-decane.

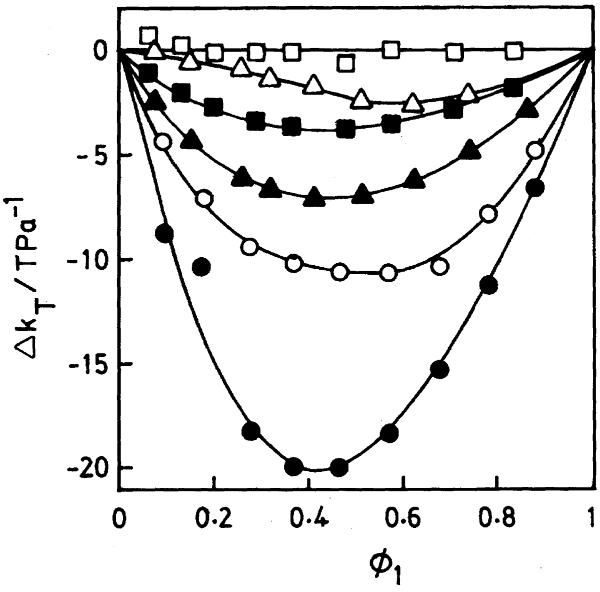

Fig. 8. Comparison of experimental deviations in isothermal compressibility for styrene with (○) *n*-hexane, (△) *n*-octane, and (□) *n*-decane with Flory theory for styrene with (●) *n*-hexane, (▲) *n*-octane, and (■) *n*-decane at 298.15 K.

V^E_{PFP}. Usually, if one of the components, viz. styrene, has a higher value of P^* than the other components, i.e., *n*-alkanes, and a lower value of thermal expansion coefficient, H^E is always positive, but V^E_{PFP} is negative. However, both the Flory and PFP theories successfully predict the main features of V^E_{expt}. For mixtures of styrene+*n*-hexane or +*n*-heptane, V^E_{expt} is negative at all temperatures. The negative V^E_{expt} indicates the organized packing effect between molecules of the mixtures.

The present research also shows the importance of the three contributions to V^E_{expt} i.e., X_{12} (heat of mixing), the difference in free volume and the internal-pressure effect. Further efforts have been made to estimate the H^E and G^E data of mixtures using the PFP theory. The experimental viscosities were used to calculate $\Delta\ln\eta_{exp}$ as well as the theoretical calculation of $\Delta\ln\eta_{th}$ from the Bloomfield–Dewan theory.[20] Here, the $\ln\eta_H$ and $\ln\eta_{fv}$ contributions, being positive, seem to dominate the overall contribution to the $\Delta\ln\eta_{th}$ values.

From the speed-of-sound data, the results of deviations in the isentropic and isothermal compressibility were calculated and compared with those calculated from the Benson–Kiyohara equation. Though the sings of these quantities remain the same, the theoretically calculated Δk_S values are more negative than the experimental data. However, the isothermal compressibility data, calculated from Flory equation, are not comparable to the experimental values. The speed-of-sound data were used to calculate the internal-pressure deviations in binary mixtures. In summary, the present study is an advancement toward an understanding of the mixing behavior in liquid mixtures consisting of a flat molecule+short-to-long chain *n*-alkanes by using developed theories, and will add to the wealth of information on interactions in binary mixtures.

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