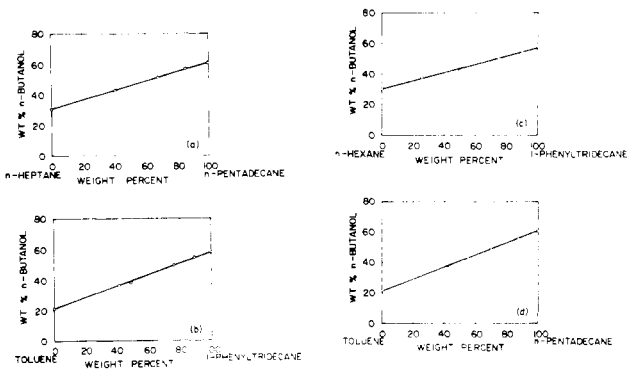

Figure 7. Miscibility relationships for hydrocarbon mixtures (wt % 1-butanol required for miscibility at 1:1 wt ratio of hydrocarbon to 2.5 *m* aqueous sodium *p*-cymenesulfonate solution; 25 °C).

The relatively simple dependence on EACN, whose applicability the Texas group demonstrated for hydrocarbon mixtures in their interfacial tension measurements, does not seem to apply to the miscibility relationships. Figure 6 compares 1-butanol–2.5 *m* cymenesulfonate systems containing octane, phenyloctane, and a 1:1 mixture of toluene and pentadecane. All three systems have, for the hydrocarbon, EACN = 8. The toluene–pentadecane system requires much more butanol for miscibility than the other two.

We were interested in establishing the basic mixing rules for the miscibility relationship. The studies were limited to the central portion of the phase diagrams where the weight ratio of hydrocarbon to aqueous cymenesulfonate solutions was one. The amount of butanol required for miscibility was established for the following four systems: hexane–pentadecane; hexane–1-phenyltridecane; toluene–pentadecane; toluene–1-phenyltridecane. The results are summarized in Figure 7. It may be noted that the amount of butanol required in all four systems varies approximately linearly with the weight fraction of one hydrocarbon in the hydrocarbon mixtures. Since some of the phase boundary diagrams are not completely symmetrical, one does not expect the linearity rule to hold generally at other hydrocarbon–aqueous ratios. However there is little doubt that the phase boundaries for the various hydrocarbon mixtures lie between those of the "pure" hydrocarbon systems.

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Excess Thermodynamic Properties of Binary Liquid Mixtures of 1,2-Dichloroethane with Normal Alkanes

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Excess volumes and isentropic compressibilities for binary liquid mixtures of 1,2-dichloroethane with hexane, heptane, octane, and nonane were determined at 303.15 K. Isothermal compressibilities were computed from isentropic compressibilities, heat capacities at constant pressure, and thermal coefficients of expansion. Excess isothermal compressibility was then calculated and the κ_T^E data were analyzed in light of both the original and modified versions of the Flory theory. The original theory fails to predict even the sign of κ_T^E while the modified theory correctly predicts the sign of κ_T^E in two systems.

A survey of the literature has shown that a number of attempts (*1–3*) have been made to predict excess volumes of binary liquid mixtures by using the values of the Flory interaction parameter derived from experimental excess enthalpy. Several attempts have also been made to predict excess enthalpy by employing the values of the Flory interaction parameter derived from experimental excess volume. However, very few attempts have been made to predict excess isothermal compressibility by employing the values of the interaction parameter from either experimental excess volume or excess enthalpy. These thermodynamic data have an important place in industrial and academic work. Hence an effort has been made to predict excess isothermal compressibility by using the values of the interaction parameter computed from the original Flory theory and that derived from experimental excess volumes. The mixtures studied include 1,2-dichloroethane + hexane, 1,2-dichloroethane + heptane, 1,2-dichloroethane + octane, and 1,2-dichloroethane + nonane. These mixtures have been chosen because they come under the category of *n*-alkane mixtures for which the Flory theory has been designed. The new experimental data reported here are excess volumes and isentropic compressibilities determined at 303.15 K.

Table I. Densities of the Pure Components

component	temp, K	ρ/g cm^{-3} present work	ρ/g cm^{-3} lit.[5]
1,2-dichloroethane	303.15	1.238 30	1.238 31
hexane	303.15	0.650 64	0.650 70
heptane	303.15	0.675 30	0.675 38
octane	303.15	0.694 59	0.694 50
nonane	303.15	0.709 98	0.709 99

Experimental Section

Materials. 1,2-Dichloroethane, hexane, and heptane, supplied by B.D.H. Chemicals, England, and octane and nonane supplied by Veb Chemicals, West Germany, were purified by the methods

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Table II. Parameters of the Pure Components at 303.15 K

component	$10^3\alpha$/ deg^{-1} [a]	K_T/ TPa^{-1} [b]	V/cm³ mol^{-1} [a]	$\tilde{v}$ [c]	V^*/cm³ mol^{-1}	P^*/J cm^{-3} [d]	$\tilde{T}$ [c]
1,2-dichloroethane	1.189	856.7	79.92	1.289	62.00	699.1	0.062 95
hexane	1.404	1791.7	132.45	1.329	99.65	419.7	0.068 09
heptane	1.260	1526.3	148.39	1.303	113.92	424.7	0.064 76
octane	1.195	1373.5	164.46	1.290	127.47	439.0	0.063 11
nonane	1.062	1217.3	180.65	1.264	142.94	422.5	0.059 41

[a] Experimentally determined. [b] Computed from eq 3. [c] Computed from the thermal expansion coefficient. [d] Computed from isothermal compressibility.

Table III. Experimental Values of V^E for the Binary Systems of 1,2-Dichlorethane + n-Alkanes[a]

1,2-dichloroethane + hexane		1,2-dichloroethane + heptane		1,2-dichloroethane + octane		1,2-dichloroethane + nonane	
x_1	V^E	x_1	V^E	x_1	V^E	x_1	V^E
0.1225	0.312	0.1452	0.471	0.1472	0.542	0.1502	0.605
0.2058	0.453	0.2561	0.712	0.2360	0.773	0.2793	0.911
0.3609	0.598	0.3821	0.844	0.4078	1.015	0.4385	1.090
0.4826	0.597	0.5295	0.854	0.4802	1.043	0.5431	1.097
0.6105	0.525	0.6230	0.775	0.5775	1.021	0.6746	0.974
0.7255	0.409	0.7250	0.643	0.6797	0.898	0.8154	0.698
0.8328	0.265	0.8154	0.468	0.8012	0.654	0.8732	0.532
0.9020	0.162	0.9090	0.247	0.9216	0.289	0.9263	0.337

[a] x_1 indicates mole fraction of 1,2-dichloroethane; V^E in cm³ mol^{-1}.

described by Reddick and Bunger (*4*). The purity of the samples was checked by comparing the measured densities of the samples with those reported in literature (*5*). The densities were measured by using a bicapillary pycnometer. The measured data of densities along with the literature values are reported in Table I.

Excess Volumes and Compressibilities. The excess volumes were determined by using a single composition per loading type dilatometer described by Rao and Naidu (*6*). The values were accurate to ±0.003 cm³ mol^{-1}.

Isentropic compressibilities (κ_s) were computed from ultrasonic sound velocities (u) and densities (ρ) by using the relation

$$\kappa_s = u^{-2}\rho^{-1} \tag{1}$$

Ultrasonic sound velocities were determined with a single-crystal ultrasonic interferometer at a frequency of 2 MHz and were accurate to ±0.15% (*7*). The densities were computed from experimental V^E, using the relation

$$\rho = \frac{x_1M_1 + x_2M_2}{V + V^E} \tag{2}$$

where x_1 and x_2 and M_1 and M_2 denote the mole fractions and molecular weights of 1,2-dichloroethane and normal alkanes, respectively. V stands for molar volume and V^E for excess molar volume. Isothermal compressibilities (κ_T) were calculated by using the relation

$$\kappa_T = \kappa_s + \alpha^2VT/C_P \tag{3}$$

where α, V, T, and C_p denote thermal expansion coefficient, molar volume, temperature, and heat capacity at constant pressure. In the case of mixtures the thermal coefficient of expansion and heat capacity at constant pressure were assumed to be additive in terms of volume fraction and mole fraction, respectively.

The excess isothermal compressibilities were evaluated from the relation

$$\kappa_T^E = \kappa_T - \phi_1\kappa_{T,1} - \phi_2\kappa_{T,2} \tag{4}$$

Table IV. Values of the Parameters in Equation 12 and the Standard Deviation

system	a_0	a_1	a_2	$\sigma(V^E)$/ cm³ mol^{-1}
1,2-dichloroethane + hexane	2.378	−0.699	−0.037	0.003
1,2-dichloroethane + heptane	3.466	−0.548	−0.046	0.004
1,2-dichloroethane + octane	4.185	−0.154	0.009	0.004
1,2-dichloroethane + nonane	4.389		0.727	0.006

where κ_T, $\kappa_{T,1}$, and $\kappa_{T,2}$ are isothermal compressibilities of the mixture and pure components and ϕ_1 and ϕ_2 are volume fractions of 1,2-dichloroethane and n-alkanes.

Theory and Calculations

Flory (*8*, *9*) formulated the following theoretical equations for excess volume and excess isothermal compressibility:

$$V^E = \tilde{v}^E(x_1V_1^* + x_2V_2^*) \tag{5}$$

$$\kappa_T^E = \frac{3\tilde{v}^2(\tilde{v}^{1/3} - 1)}{P^*[1 - 3(\tilde{v}^{1/3} - 1)]} - \frac{1}{\tilde{v}}(\phi_1\tilde{v}_1\kappa_{T,1} + \phi_2\tilde{v}_2\kappa_{T,2}) \tag{6}$$

where

$$\tilde{v}^E = (\tilde{v}^\circ)^{7/3}[4/3 - (\tilde{v}^\circ)^{1/3}]^{-1}(\tilde{T} - \tilde{T}^\circ) \tag{7}$$

$$\tilde{T} = \frac{(\phi_1P_1^*\tilde{T}_1 + \phi_2P_2^*\tilde{T}_2)}{(\phi_1P_1^* + \phi_2P_2^* - \phi_1\theta_2X_{12})} \tag{8}$$

$$\theta_2 = \frac{\phi_2}{\phi_1(S_1/S_2) + \phi_2} \tag{9}$$

$$X_{12} = P_1^*[1 - (S_1/S_2)^{1/2}(P_2^*/P_1^*)^{1/2}]^2 \tag{10}$$

$$P^* = (\phi_1P_1^* + \phi_2P_2 - \phi_1\theta_2X_{12}) \tag{11}$$

The quantities in eq 5–11 have the same significance described by Flory (*8*, *9*).

In application of the original theory of Flory to excess isothermal compressibilities, the numerical evaluation of characteristic and reduced parameters for the pure components and mixtures was carried out according to the procedure adopted by Flory (*8*, *9*). The values of the parameters for pure components are included in Table II. To predict κ_T^E on the basis of the modified Flory theory, we obtained the values of the interaction parameter from experimental V^E at each composition.

Results and Discussion

The experimental excess volumes for the four binary mixtures determined at 303.15 K are given in Table III. The experimental values of V^E are represented by an empirical equation

$$V^E/\text{cm}^3\ \text{mol}^{-1} = x_1x_2\sum_{i=0}^{k} a_i(x_1 - x_2)^i \tag{12}$$

Table V. Experimental and Predicted Values of κ_T^E for the Binary Systems of 1,2-Dichloroethane + Alkanes at 303.15 K[a]

system	ϕ_1	κ_s	original theory		modified theory		κ_T^E (exptl)
			$\theta_2 X_{12}$	κ_T^E	$\theta_2 X_{12}$	κ_T^E	
1,2-dichloroethane + hexane	0.0777	1329	16.5250	−47	53.5708	−4	2
	0.1352	1286	15.3142	−75	49.1883	−8	5
	0.2541	1194	12.8980	−114	41.4447	−14	8
	0.3601	1112	10.8385	−132	34.4640	−31	10
	0.4860	1010	8.4984	−134	27.0549	−44	9
	0.6146	902	6.2218	−119	19.9433	−49	4
	0.7503	791	3.9322	−89	12.7152	−43	2
	0.8474	711	2.3620	−59	7.7562	−30	1
1,2-dichloroethane + heptane	0.0838	1152	11.8064	−25	54.1383	25	6
	0.1564	1111	10.7385	−42	48.6228	34	10
	0.2498	1058	9.3477	−59	41.1726	34	15
	0.3774	982	7.5415	−71	32.6802	25	17
	0.4709	922	6.2812	−73	26.8137	15	13
	0.5867	849	4.7881	−68	20.5186	5	11
	0.7040	772	3.3463	−56	14.2747	−3	7
	0.8432	684	1.7232	−34	7.3434	−6	2
1,2-dichloroethane + octane	0.0774	1061	7.1467	−19	58.3895	17	9
	0.1305	1040	6.6409	−30	53.2869	47	15
	0.2507	981	5.5472	−47	42.9387	59	17
	0.3099	952	5.0345	−61	38.5884	59	19
	0.3991	906	4.2862	−56	32.7922	56	18
	0.5077	850	3.4205	−47	25.8367	45	17
	0.6620	767	2.2647	−40	17.1839	28	11
	0.8511	667	0.9564	−22	7.2124	9	7
1,2-dichloroethane + nonane	0.0725	985	7.2005	−3	49.5117	30	17
	0.1463	963	6.4889	−4	44.6741	51	26
	0.2568	922	5.4784	−8	44.2345	62	31
	0.3446	886	4.7170	−10	28.8268	60	31
	0.4784	826	3.6244	−12	21.3552	52	27
	0.6615	741	2.2458	−12	13.5004	36	16
	0.7529	700	1.6030	−10	9.9674	28	13
	0.8476	656	0.9669	−7	6.1672	19	8

[a] $\phi_2 X_{12}$ in J mol^{-1}, V^E in cm^3 mol^{-1}, κ_s and κ_T^E in TPa^{-1}, and ϕ_1 indicates the volume fraction of 1,2-dichloroethane.

where a_0, a_1, ..., a_k are adjustable parameters. The values of the parameters, obtained by the least-squares method, are included in Table IV along with the standard deviation, $\sigma(V^E)$.

The experimental isentropic compressibilities determined at 303.15 K are included in column 3 of Table V. The predicted and experimental isothermal compressibilities for the four binary systems are shown in columns 5, 7, and 8 of Table V. The data show that the original theory fails even to predict the correct sign of κ_T^E in all cases. Further, the modified theory correctly predicts the sign of κ_T^E in the systems of 1,2-dichloroethane with octane and nonane and fails to predict even the sign of κ_T^E for the system of 1,2-dichloroethane with heptane in mixtures rich in 1,2-dichloroethane and over the whole range of composition for the system 1,2-dichloroethane with hexane. This shows though the modified theory is superior to original theory it fails to predict correctly the sign of κ_T^E which is sensitive to molecular geometry unlike excess enthalpy.

Glossary

ρ	density, g cm^{-3}
κ_T	isothermal compressibility, TPa^{-1}
κ_s	isentropic compressibility, TPa^{-1}
α	thermal expansion coefficient, deg^{-1}
T	temperature, K
V	molar volume, cm^3 mol^{-1}
V^E	excess molar volume, cm^3 mol^{-1}
C_p	heat capacity at constant pressure, J mol^{-1}
ϕ_i	segment fraction of component i
θ_2	site fraction
$\tilde{v}_i$	reduced volume of component i
$\tilde{v}^0$	ideal reduced volume of mixture
$\tilde{v}^E$	excess reduced volume
V_i^*	characteristic volume of component i, cm^3 mol^{-1}
P_i^*	characteristic pressure of component i, J cm^{-3}
$\tilde{T}_i$	reduced temperature of component i
S_i	site fraction of component i
X_{12}	interaction parameter, J mol^{-1}

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