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NOMENCLATURE

A_n = fitting parameter in excess properties equation
H = enthalpy of forming new surface, ergs per sq. cm.
d = density, g. per cc.
n = fitting parameter in excess properties equation
R = gas constant
S = entropy of forming new surface, ergs per deg. per sq. cm.
T = temperature, °K.
X_i = mole fraction of component i
t = temperature, °C.
Γ_i = individual Gibbs surface excess of component i, mole per sq. cm.
Γ_2^N = composite Gibbs surface excess, mole per sq. cm.
Σ = summation sign
σ = surface tension, dyne per cm. or free energy of forming new surface, ergs per sq. cm.

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Excess Volumes of Binary Liquid Mixtures of *n*-Alkanes

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The excess volume is presented for the binary *n*-alkane systems C_{10}–C_{12}, C_{12}–C_{14}, and C_{12}–C_{16} at 45°, 55°, and 65° C. and the systems C_{10}–C_{14} and C_{10}—C_{16} at 55° and 65° C. A pycnometric technique was used to observe the densities of mixtures and pure components of each system, from which the excess volume was calculated. The excess volume was found to be negative in all cases and to become more negative with increasing temperature. The data reaffirm the principle of congruence and its application to the form of $V(n)$ proposed by Hijmans and Holleman. Deviations from this correlation averaged 0.004 cc. per mole. The mixture volumes were also predicted using Flory's corresponding states theorem. Deviation from the prediction averaged 0.012 cc. per mole. The standard deviation in the experimental excess volumes was 0.007 cc. per mole.

IN AN EARLIER STUDY by Harrison (*4*), the excess volumes of the five binary *n*-alkane systems, C_{10}–C_{12}, C_{12}–C_{14}, C_{12}–C_{16}, C_{10}–C_{14}, and C_{10}–C_{16}, were determined at 25° and 35° C. and of C_{10}–C_{14} and C_{10}–C_{16} at 45° C. In that study the data were correlated using Hijmans and Holleman's equation (*6*), which incorporates an infinite series representation of $V(n)$ (in descending powers of n) and the principle of congruence proposed by Brønsted and Koefoed (*1*). It was shown that the equation was successful in correlating the data within experimental error.

Normal paraffins satisfy the requirements of a law of corresponding states when the concept of "segments" is adopted. A law of corresponding states for the *n*-paraffin liquids has been formulated by Prigogine and coworkers (*7*) from the consideration of a modified cell model and by Hijmans (*5*) from a phenomenological point of view. The partition function derived by Prigogine *et al.* has recently been refined by Flory and coworkers (*2*), and the tractable algebraic equations of state that they have derived can be used to predict the excess volume. These corresponding states treatments exploit the principle of congruence for the prediction of mixture properties.

THEORY

The method of correlating the data with Hijmans and Hollemans' equation and the principle of congruence was presented in an earlier paper (*4*).

To predict the excess volume from the law of corresponding states of Flory (*2*), the reduced volume and temperature of each pure component are required. Also needed are the parameters of hard-core segmental volume, V^*, and the end segment contribution to the total number of segments in a molecule, n_e. An empirical equation given by Flory relates the reduced temperature of a pure component to the chain length and temperature:

$$T = T/T^* = T[A + B/(n + 1)] \quad (1)$$

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A and B are functions of temperature only.

The reduced volume is related to the reduced temperature by Flory's equation of state of zero pressure:

$$(\overline{v}^{1/3} - 1)/\overline{v}^{4/3} = T \tag{2}$$

The reduced excess volume is the difference between the reduced volume and ideal reduced volume:

$$\overline{v}^E = \overline{v} - \overline{v}^0 \tag{3}$$

where

$$\overline{v}^0 = \Phi_1 \overline{v}_1 + \Phi_2 \overline{v}_2 \tag{4}$$

Since Equation 2 is implicit in $\overline{v}$, a Taylor series is used to approximate it and hence $\overline{v}^E$:

$$\overline{v}^E = \frac{\partial \overline{v}}{\partial T}(T_m - T^0) = 3(\overline{v}^0)^{7/3}[4 - 3(\overline{v}^0)^{1/3}]^1 (T_m - T^0) \tag{5}$$

The reduced ideal temperature, T^0, is calculated from the ideal volume using Equation 2.

The mixture reduced temperature, T_m, is the segment fraction weighted reduced temperature,

$$T_m = \Phi_1 T_1 + \Phi_2 T_2 \tag{6}$$

The molar excess volume is calculated from the reduced excess volume by

$$V^E = v^E v^* (n + n_e) \tag{7}$$

Thus the excess volume of any mixture of n-paraffins can be calculated if the reduced and hard-core segmental volumes, the reduced temperatures, and the end segment contribution are known. No mixture data are needed.

EXPERIMENTAL

To provide a continuous set of data, essentially the same procedure used by Harrison (*3, 8*) was again used in this investigation.

Sixteen or more separate determinations were made for each pure component density at each temperature, four for each mixture density. Nine mixture compositions corresponding to each tenth mole fraction were investigated for each system at each temperature.

The chemicals used were the same as those used previously, obtained from the Humphrey Chemical Co., North Haven, Conn. The purity was listed as olefin-free research grade. No further purification was carried out, but all chemicals were degassed prior to use (*3*).

RESULTS

The systems C_{10}–C_{14} and C_{10}–C_{16} at 55° and 65° C. and the systems C_{10}–C_{12}, C_{12}–C_{14}, and C_{12}–C_{16} at 45°, 55°, and 65° C. were investigated. The excess volume data were smoothed by separately fitting the data of each system at each temperature (by least squares) to the equation of Hijmans and Holleman. Also, the data of all systems at a particular temperature were simultaneously fitted to the equation for a general representation of the data at that temperature. The values of the two constants in the equation of Hijmans and Holleman found by these fittings are listed in Table I along with standard deviations from the all-data smoothed curves of the observed data. Pictured in Figure 1 are the data points of a system and smoothed data curves of both types of fits.

PREDICTED EXCESS VOLUME

For this study, the value of A to be used in Equation 1 was linearly interpolated from the values found by Flory *et al.* at 20° and 100° C., and the value of B is an arithmetic average of those found at 20°, 100°, and 150° C. The calculated values appear in Table II. The reduced temperatures and volumes were calculated as described earlier. Using the experimental densities of pure components the net hard-core volume was calculated from

$$V^* = M/\overline{v}\rho \tag{8}$$

n_e was evaluated by setting $V_{10^*}/(10 + n_e)$ equal to $V_{12^*}/(12 + n_e)$ and solving for n_e. v^* was found from the equation

$$v^* = V^*/(n + n_e) \tag{9}$$

Use of any other pair of n-alkanes to calculate n_e results in differences in v^* of only 0.003 cc. per mole. Values of n_e and v^* appear in Table III. The excess volume for a given mole fraction of a given system was computed by the use of Equations 5 through 7. In Figure 2 are pictured the results of the calculations carried out for one system at two temperatures. Listed in Table IV are the standard deviations from the observed data of the predicted excess volume.

DISCUSSION

The experimental error in excess volumes based on the maximum error of ±2 × 10^{-5} gram per cc. in the mixture densities lies between the limits of ±0.005 and ±0.009 cc. per mole, depending on the system being considered.

Figure 1 illustrates that the Hijmans-Holleman equation, using all systems at a given temperature to determine the constants, gives the more reasonable fit of the data. Although the curve calculated from the individual system lies closest to each set of data, it is skewed toward the heavy end. Because of the shape of V (n) for these n-paraffins, however, the curves should always be skewed

Table I. Constants in the Hijmans and Holleman Equation from Curve Fits

Temp., ° C.	Constants	All Systems	System C_{10}–C_{12}	 C_{12}–C_{14}	 C_{12}–C_{16}	 C_{10}–C_{14}	 C_{10}–C_{16}
45	A_1	−7.8869	90.232	10.797	88.752		
	A_2	84.672	−205.22	−216.01	−293.67		
55	A_1	19.876	−69.457	98.303	57.271	−1.0668	20.991
	A_2	−1.3379	273.94	−299.75	−146.75	63.129	−4.4787
65	A_1	29.435	1.7501	−54.414	112.16	82.229	20.949
	A_2	−23.485	58.594	276.12	−341.11	−190.39	4.1225

	Standard Deviation, Cc./Mole C_{10}–C_{12}	 C_{12}–C_{14}	 C_{12}–C_{16}	 C_{10}–C_{14}	 C_{10}–C_{16}
45	0.0022	0.0008	0.0041		
55	0.0040	0.0014	0.0029	0.0042	0.0049
65	0.0021	0.0017	0.0048	0.0074	0.0067

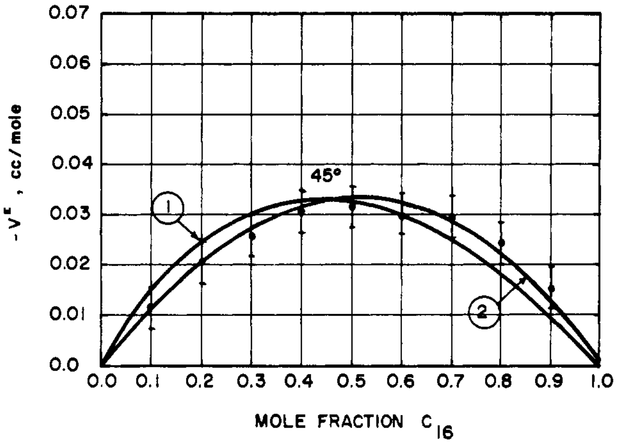

Figure 1. Comparison of data with Hijmans-Holleman equation

C_{12}–C_{16} at 45° C.

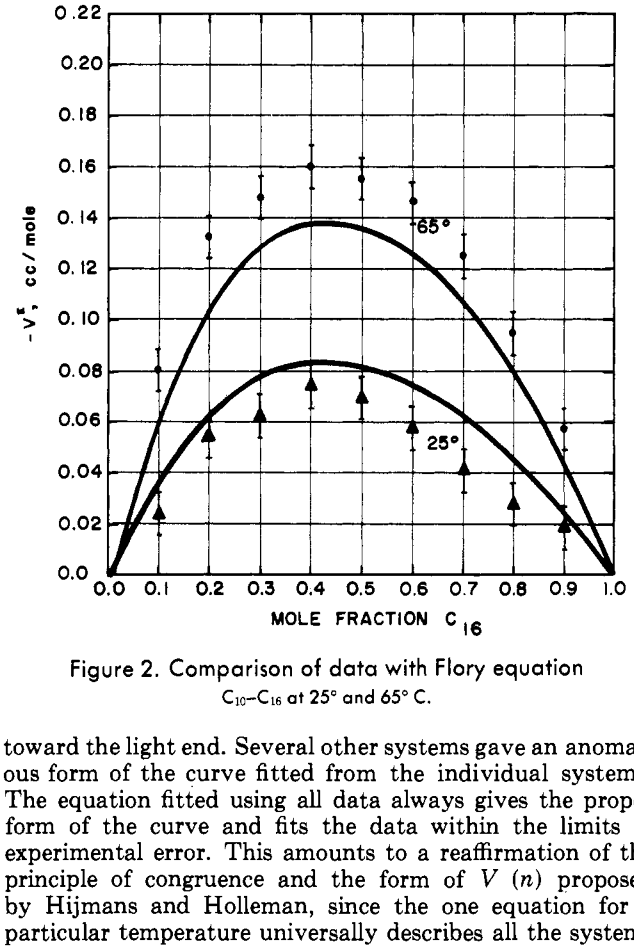

Figure 2. Comparison of data with Flory equation

C_{10}–C_{16} at 25° and 65° C.

toward the light end. Several other systems gave an anomalous form of the curve fitted from the individual systems. The equation fitted using all data always gives the proper form of the curve and fits the data within the limits of experimental error. This amounts to a reaffirmation of the principle of congruence and the form of V (n) proposed by Hijmans and Holleman, since the one equation for a particular temperature universally describes all the systems investigated.

The $V^E(X)$ curves computed by the method of Flory *et al.* are all properly negative and of the proper form—i.e., parabolic and skewed toward the light end. [This skewing is expected, because the curve of $V(n)$ *vs.* n for the n-alkanes has less curvature as n increases.] When compared with the data of the present work, the method generally underpredicted the excess volume beyond the limits of experimental error. With the system C_{12}–C_{14}, however, agreement was excellent. The reason for this is unknown. Comparison of predicted excess volumes with Harrison's data shows both positive and negative deviations.

Computed values of the parameters v^* and n_e agree with those reported by Flory (*2*). The same slow increases of v^* with temperature and chain length and of T^* with temperature that were noted by him were also observed here.

Table II. Values of Constants Used in Equation 1

Temp., ° C.	Constants $A \times 10^4$	 $B \times 10^4$
25	1.411	5.67
35	1.408	5.67
45	1.404	5.67
55	1.400	5.67
65	1.397	5.67

Table III. End Segment Contribution and Hard-Core Segmental Volume

Temp., ° C.	n_e	v^*, Cc./Mole
25	1.033	14.198
35	1.040	14.202
45	1.059	14.205
55	1.051	14.218
65	1.050	14.220

Table IV. Standard Deviation of Predicted (Flory) Excess Volume from Observed Data

Temp., ° C.	Standard Deviation, Cc./Mole C_{10}–C_{12}	 C_{12}–C_{14}	 C_{12}–C_{16}	 C_{10}–C_{14}	 C_{10}–C_{16}
25	0.0050	0.0030	0.0454	0.0058	0.0217
35	0.0072	0.0068	0.0068	0.0109	0.0193
45	0.0081	0.0008	0.0039	0.0322	0.0358
55	0.0077	0.0012	0.0060	0.0084	0.0194
65	0.0042	0.0019	0.0112	0.0167	0.0206

NOMENCLATURE

A_1, A_2 = constants in Hijmans and Holleman equation
A, B = constants in Equation 1
M = molecular weight, grams per mole
n = chain length of molecule, dimensionless
n_e = end segment contribution to total number of segments per molecule, dimensionless
T = temperature, ° K.
T^* = characteristic temperature, ° K.
T = reduced temperature, dimensionless
T_m = reduced temperature of a mixture, dimensionless
V = molar volume, cc. per mole
V^* = net hard-core volume of molecule, cc. per mole
V^E = molar excess volume, cc. per mole
v^* = segmental hard-core volume, cc. per mole
$\bar{v}$ = reduced volume, dimensionless
$\bar{v}^0$ = ideal reduced volume, dimensionless
$\bar{v}^E$ = reduced excess volume, dimensionless
X = mole fraction, dimensionless
Φ_i = segment fraction of component i, $X_i(n_i + n_e)/\Sigma_i X_i(n_i + n_e)$, dimensionless
ρ = density, grams per cc.

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