NOMENCLATURE

A = zero intercept
A_0 = constant in BWR equation of state
a = constant in BWR equation
B = second virial coefficient defined by Equation 4
B' = second virial coefficient defined by Equation 3
B'' = second virial coefficient defined by Equation 7
B_0 = constant in BWR equation of state
b = constant in BWR equation of state
C = third virial coefficient defined by Equation 4
C' = third virial coefficient defined by Equation 3
C'' = third virial coefficient defined by Equation 7
C_0 = constant in BWR equation of state
c = constant in BWR equation of state
D = gas density, lb. moles per cubic foot
D' = fourth virial coefficient in Equation 3
M.F. = mole fraction
N = volumetric constant
P = pressure, atmospheres
X_A = mole fraction of component A in a mixture
Z = compressibility factor
γ = constant in BWR equation of state
α = constant in BWR equation of state

Subscripts and Exponents

n = number of expansions
$^\circ$ = initial conditions

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Excess Volume of Mixing of *n*-Alkane Mixtures

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The excess volume of mixing for five normal alkane mixtures was determined by pycnometric technique. The mixtures investigated were the normal alkane mixtures C_{10}-C_{12}, C_{12}-C_{14}, C_{10}-C_{14}, C_{12}-C_{16}, and C_{10}-C_{16}. The investigations were carried out at three temperatures, 25°, 35°, and 45° C., over the entire range of compositions. A volume contraction was observed in all cases, ranging up to −0.14 cc. per mole. The maximum error observed was 0.008 cc. per mole or about 0.0032% of the total volume. The data were correlated using equations based on the principle of congruence. Deviations averaged about 0.002 cc. per mole.

THE MOST successful correlative technique for the thermodynamic excess properties of liquid mixtures was postulated by Brønsted and Koefoed (*1*) in 1946 for alkane mixtures; however, this technique could apply to chain molecules in general. Only Brønsted and Koefoed's own vapor pressure data and heat of mixing data by Van der Waals and Hermans (*8*) were available until the late 1950's when Desmyter and Van der Waals (*3*) measured the volume changes on mixing for six alkane mixtures. These data bore out Brønsted's principle of congruence, at least for short-chain-length molecules at moderate temperatures.

THEORY

Brønsted postulated that the excess thermodynamic properties were a function of the index of the mixture. This index is equal to the average chain length and is defined by the equation:

$$N = \sum_i N_i x_i \tag{1}$$

N_i is the number of carbon atoms in the chain of the ith species and x_i is the mole fraction of that species. Brønsted called this theory the principle of congruence, according to

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which mixtures within a homologous series having the same index or average chain length should have the same properties. Two mixtures are said to be congruent if they have the same index. An example would be 0.5 mole fraction C_{10} in C_{16} and 0.75 mole fraction C_{12} in C_{16}, both of which have an average chain length of 13 carbon atoms.

In 1961, Hijmans and Holleman (5) derived Equation 2 based on the principle of congruence.

$$V^e = A_1\left[\frac{(N_2-N)(N-N_1)}{(N-2)(N_1-2)(N_2-2)}\right] + A_2\left[\frac{(N_2-N)(N-N_1)}{(N-2)(N_1-2)(N_2-2)}\right] \cdot \left[\frac{1}{(N-2)} + \frac{1}{(N_1-2)} + \frac{1}{(N_2-2)}\right] \quad (2)$$

If the values of the constants A_1 and A_2 in Equation 2 are known, the excess volume of mixing for any binary mixture in a homologous series may be estimated.

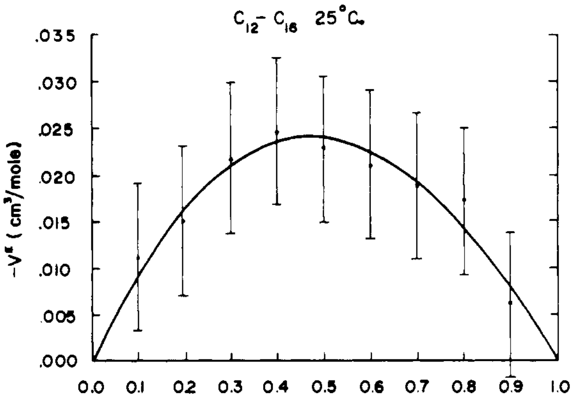

Figure 1. Volume change on mixing for dodecane-hexadecane

Fit using constants from Table I

EXPERIMENTAL

The systems decane-dodecane, dodecane-tetradecane, dodecane-hexadecane, decane-tetradecane, and decane-hexadecane were selected to be investigated. Their excess volumes were calculated from density data rather than measured directly.

The density determinations were made using a standard pycnometric technique (4). The pycnometers were filled in a Hallikainen constant temperature bath, controlled to ±0.005° C. Atmospheric temperature control was provided by a glove box fitted over the bath. An on-off controller maintained the air space to ± 3° C.

Decane, dodecane, tetradecane, and hexadecane were obtained from the Humphrey Chemical Co., North Haven, Conn. The purity was listed as research olefin free grade, but an analysis of the actual purities was not available. The pure components densities compared favorably with data found in the literature (2). The calibration water was Fisher catalog number W-2 and the wash acetone was Fisher catalog number A-18, obtained from the Fisher Chemical Co.

RESULTS

Excess volumes of mixing were determined for five binary normal alkane systems at 25°, 35°, and 45° C. Nine compositions, each tenth mole fraction, for each system were studied: decane-dodecane, 25°, 35° C.; dodecane-tetradecane, 25°, 35° C.; dodecane-hexadecane, 25°, 35° C.; decane-tetradecane, 25°, 35°, 45° C.; and decane-hexadecane, 25°, 35°, 45° C. The pure component densities were also measured at each temperature. Figure 1 is a graphical representation of one set of raw data as compared with the values calculated using Hijmans and Holleman's Equation 2 and constants determined solely from that particular system at 25° C. The fit is similar for all other systems. Table I lists the constants obtained for each system. These are the most accurate analytical representations of the data.

TREATMENT OF DATA

All the data points were used at a given temperature in order to get the best over-all fit for all systems studied. A technique of this nature would allow each system and each data point to exercise its proper weight on the constant. This means that each average chain length also exercises its proper weight and a reasonable over-all prediction for all systems studied should be accomplished. Sample fits of the experimental data with curves obtained with these "universal" constants appear as Figures 2 and 3. The other systems fit similarly against the calculated curves. The constants are listed in Table II.

McGlashan (7) suggests that the system exhibiting the largest volume change would yield constants for Equation 2 that would be most generally applicable. The system decane-hexadecane was best because if one considers the entire composition range for this mixture, all possible average chain lengths investigated have been considered. This would not be so for any of the other systems. These constants were determined at each temperature. The calculated excess volumes for all mixtures compared with the experimental data with relative error very similar to that shown in Figures 2 and 3.

Table I. Constants from Curve Fit Using Individual System Data

Temp., °C.	Constants	System $C_{10}-C_{12}$	$C_{12}-C_{14}$	$C_{12}-C_{16}$	$C_{10}-C_{14}$	$C_{10}-C_{16}$
25	A_1	-35.713	94.059	-16.398	-40.231	8.193
	A_2	88.317	-400.523	24.730	98.321	-58.962
35	A_1	16.956	-11.983	47.891	16.050	9.561
	A_2	-68.590	-44.512	-230.259	-97.884	-78.750
45	A_1				97.242	37.010
	A_2				-385.725	-190.426

Standard Error, Cc./Mole

	$C_{10}-C_{12}$	$C_{12}-C_{14}$	$C_{12}-C_{16}$	$C_{10}-C_{14}$	$C_{10}-C_{16}$
25	0.0005	0.0008	0.002	0.003	0.005
35	0.001	0.001	0.002	0.002	0.004
45				0.004	0.005

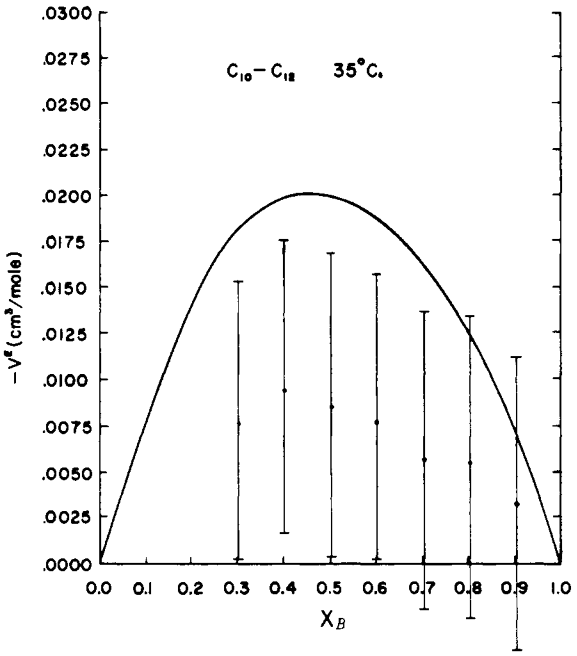

Figure 2. Volume change on mixing for decane-dodecane

Fit using constants from Table II

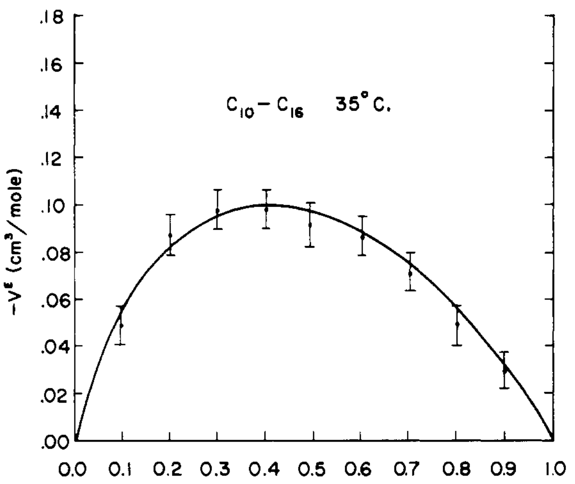

Figure 3. Volume change on mixing for decane-hexadecane

Fit using constants from Table II

DISCUSSION

Either of the latter two methods of fitting the data allows the prediction of the excess volumes for all systems using one set of constants at any temperature.

The only comparison of these data with any in the literature was one point (*3*) for 0.5 mole fraction decane in hexadecane. Values of volume change on mixing of −0.07 and −0.09 cc. per mole for 20° and 30° C., respectively, are reported. This yields an estimate of −0.08 cc. per mole at 25° C. compared with −0.075 cc. per mole obtained in this work.

Table II. Constants from Curve Fit Using All Data

Method of Fit	Constants	Temperature, ° C. 25	35	45
Equation 2	A_1	−10.537	−4.236	44.477
	A_2	4.695	−30.892	−216.020

Temp., ° C.	Average Standard Error, Cc./Mole $C_{10}-C_{12}$	$C_{12}-C_{14}$	$C_{12}-C_{16}$	$C_{10}-C_{14}$	$C_{10}-C_{16}$
25	0.004	0.003	0.002	0.003	0.007
35	0.01	0.007	0.004	0.003	0.007
45				0.008	0.005

Figure 1 shows that the individual systems fit of Hijmans and Holleman's equation is excellent. A maximum error for all systems of about 0.008 cc. per mole occurs at the worst point. However, one set of constants in Equation 2 will fit most systems at any temperature within experimental error. Figures 2 and 3 are representative curves showing the fit obtained using a single pair of constants at a given temperature. Figure 3 appears to be a much more accurate representation of the data than Figure 2, however, there is a 10-fold difference in excess volume of mixing between decane-hexadecane and decane-dodecane. Figure 2 is the worst fit obtained using constants determined from all systems at one temperature.

NOMENCLATURE

$A_{1,2}$ = constants in Equation 2
C_{10}, etc. = normal decane, etc.
N = average chain length of mixture, defined by Equation 1
N_i = chain length of pure component i
V^e = excess volume of mixing, cc. per mole
x_i = mole fraction component i

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