Solubilities of Heavy Hydrocarbons in Compressed Methane, Ethane, and Ethylene: Dew-Point Temperatures for Gas Mixtures Containing Small and Large Molecules

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Solubilities of heavy hydrocarbons in compressed gases were measured in the region 50° to 170°C for hexadecane, bicyclohexyl, diphenylmethane, and 1-methyl naphthalene and in the region 165° to 272°C for eicosane and squalane. Measurements were made in the pressure region 9 to 80 atm. The solubility data were reduced to yield second virial cross coefficients B_{12}. To interpret the B_{12} data, a square-well potential was used; the characteristic size of the large molecule is given by the mean radius of gyration which takes into account the variety of molecular conformations. Calculated results give good agreement with new as well as previously published B_{12} data.

Illustrative calculations indicate how the results obtained here may be used to make dew-point calculations in multicomponent systems containing both small and large molecules.

SCOPE

In design of a variety of industrial processes (for example, coal gasification), it is sometimes necessary to calculate dew-point temperatures at advanced pressures for asymmetric mixtures, that is, those comprising primarily light gases but containing also small amounts of heavy hydrocarbons. This work presents experimental and theoretical studies toward establishing a reliable method for prediction of dew-point temperatures of such mixtures.

At a fixed pressure, dew-point temperatures are determined primarily by the heavy component's vapor pressure and by its fugacity coefficient. The work reported here is concerned with the latter. A molecular-thermodynamic method is proposed for calculating fugacity coefficients in asymmetric mixtures; this method is based on a simple statistical-thermodynamic calculation using a few molecular parameters. Experimental gas-phase solubility measurements have been made to obtain and correlate the most important of these parameters.

CONCLUSIONS AND SIGNIFICANCE

Vapor-phase imperfections may have a significant effect on dew-point temperatures, even at moderate pressures. For gaseous mixtures containing traces of heavy hydrocarbons, these imperfections are highly sensitive to second virial cross coefficients. For reliable dew-point temperature calculations, therefore, these coefficients should be known accurately. A method is given for calculating fugacity coefficients of heavy hydrocarbons in gas mixtures containing primarily light components.

The correlation presented here for second virial coefficients is applicable to both small and large molecules of normal fluids and their mixtures. For large hydrocarbon molecules, the variety of molecular conformations is approximately taken into account through a mean radius of gyration. The correlation has only one adjustable parameter which can be estimated easily for typical mixtures encountered in natural gas, petroleum, and coal technology.

Solubility measurements for heavy hydrocarbons in compressed gases provide not only second virial cross coefficients (a quantity of fundamental physicochemical significance) but also an experimental base for establishing a correlation to estimate dew-point temperatures. Dew points are required for efficient design of typical chemical engineering operations, for example, heat exchangers in coal gasification and natural-gas processes. Although heavy hydrocarbons (such as eicosane, naph-

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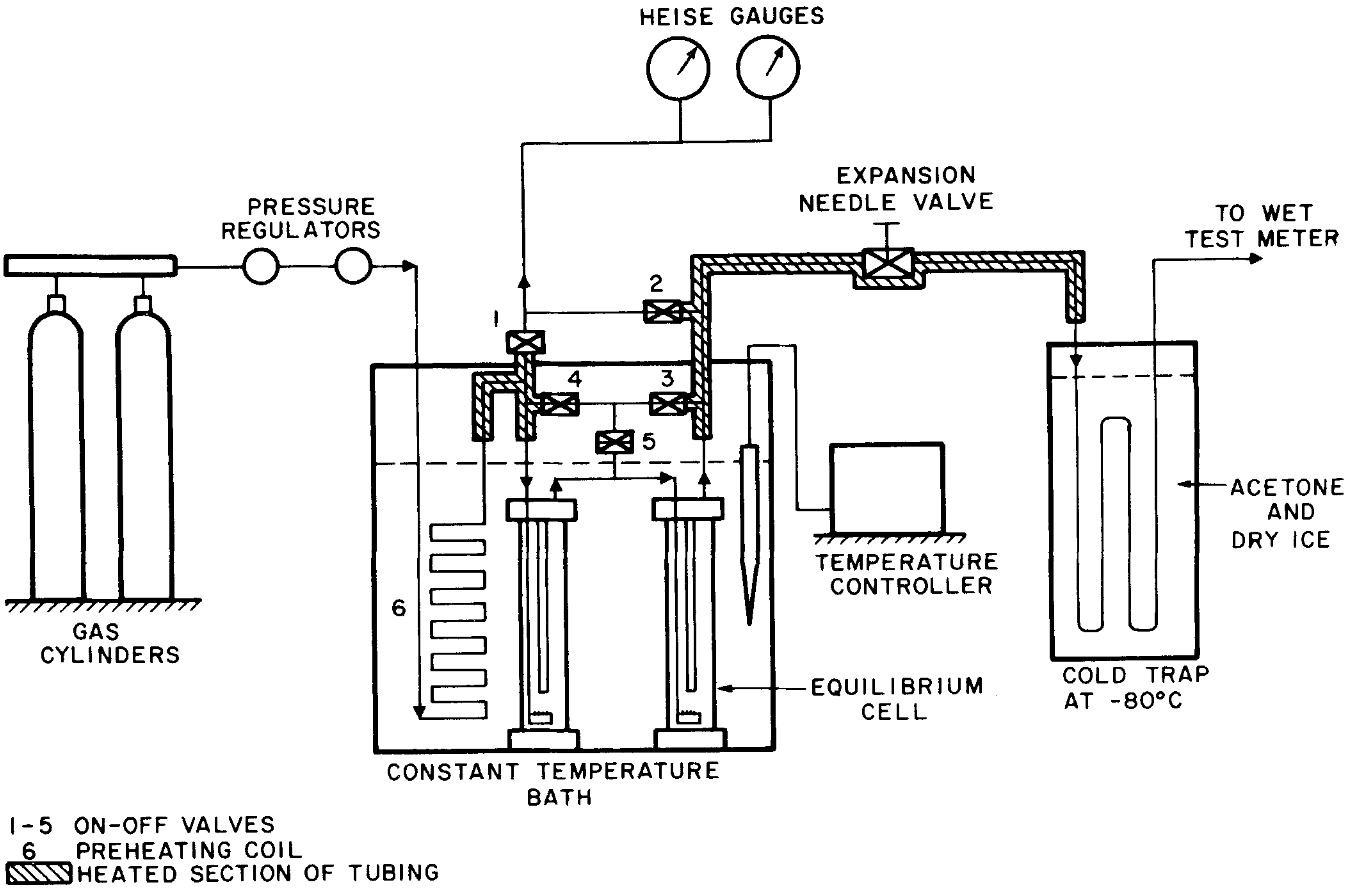

Fig. 1. Schematic diagram of solubility apparatus.

thalene, etc.) are often present in only vanishingly small concentrations, in compressed gases (such as methane, hydrogen, etc.), vapor-phase imperfections have a large effect on dew-point temperatures even at moderate pressures. Therefore, to minimize condensation in tubes of heat exchangers or to estimate solvent losses in high-pressure absorbers, accurate estimation of dew points is an important design requirement.

Mixtures which contain both small and large molecules are called asymmetric mixtures. Second virial cross coefficients for such mixtures provide fundamental data concerning the interactions between small molecules (for example, hydrogen, nitrogen, and methane) and large molecules (for example, hexadecane, diphenylmethane, etc.). Such data for asymmetric systems are scarce.

For gas mixtures, the virial equation of state, truncated after the second term, represents the volumetric properties over a moderate range of pressure. The virial equation is

$$z_m = \frac{Pv}{RT} = 1 + \frac{B_m}{v} \tag{1}$$

Mixture Second Virial coefficient depends on composition according to

$$B_m = \Sigma_i \Sigma_j y_i y_j B_{ij} \tag{2}$$

where B_{ij} reflects the interaction between one molecule i and one molecule j.

The fugacity coefficient ϕ_i is easily calculated from the virial equation (Prausnitz, 1969)

$$\ln \phi_i = \ln \frac{f_i^V}{y_i P} = \frac{2}{v} \sum_{j=1}^{m} y_j B_{ij} - \ln z_m \tag{3}$$

Typically, the mole fraction of a heavy hydrocarbon in the gas phase is small; Equation (3) shows that when $y_i << 1$, ϕ_i is very sensitive to cross virial coefficients $B_{ij} (i \neq j)$. At moderate densities, ϕ_i is often much less than unity and hence may strongly influence calculation of the dew-point temperature T_d.

At the dew point

$$f_i(\text{liquid at } T_d) = \phi_i y_i P \tag{4}$$

where ϕ_i is given by Equation (3).

As discussed elsewhere (Prausnitz, 1969), the fugacity of component i in the liquid phase is determined primarily by the vapor pressure of liquid i. The major difficulty in calculating T_d at advanced pressures lies in obtaining a good estimate for ϕ_i.

Numerous correlations have been proposed for second virial coefficients. Among the most successful are those by Pitzer and Curl (1957), Tosonpoulos (1974), and by Hayden and O'Connell (1975). Although the latter two are also useful for polar components, all of these empirical correlations, when applied to so-called normal fluids, are derived from experimental data for molecules of modest size, that is, those with acentric factor no greater than (about) 0.35.

Recently, Kaul and Prausnitz (1977) have presented a method to estimate the second virial coefficients for both normal and large hydrocarbon gases. For large hydrocarbons, the new method takes into account the variety of conformations assumed by large molecules. Further, since critical data are often not available for large hydrocarbons, the new method does not require such data. In this work, we present, first, experimental

Table 1. Chemical Analysis by Gas-Liquid Chromatography

Internal standards for calibration of solute concentration

Solute	Internal standard	ppm by weight of internal standard	Column temperature, °C
Hexadecane	Dodecane	1 500	130
1-methyl naphthalene	Hexadecane	2 300	130
Bicyclohexyl	Hexadecane	2 300	130
Diphenylmethane	Hexadecane	2 300	130
Eicosane	Hexadecane	2 300	190
Squalane	Octadecane	1 000	220

data for solubilities of six heavy hydrocarbons in compressed methane, ethane, and ethylene in the range 50° to 272°C and 9 to 80 atm and, second, second virial cross coefficients obtained from data reduction. Finally, we present a correlation of the data followed by a discussion of how the correlation may be used for dew-point calculation in binary and multicomponent mixtures.

EXPERIMENTAL

Apparatus

The experimental apparatus used is similar to that used by Benson (1959), Rigby (1968), and D'Avila (1976). Some modifications were made for operation at higher temperatures and for determination of gas-phase compositions by gas-liquid chromatography. Figure 1 shows a schematic diagram of the apparatus. The previously used Viton o rings in the high pressure equilibrium cells are replaced by knife-edge mating flanges with nickel-coated copper gaskets, and the previously used glass spargers are replaced by stainless-steel spargers with average pore size of 5 μ. Liquid is kept in each of two high-pressure equilibrium cells; gas bubbles slowly through the liquid before leaving the cells. Two cells are connected in series to assure saturation. Saturated gas leaving the cells is expanded, and the condensible component is removed by a cold trap, a mixture of acetone and dry ice at −80°C. The volume of the gas passed through the cold trap is measured with a calibrated wet-test meter. In the operating flow rate range used here, the calibration is independent of flow rate. Acuracy of volume measurement is within 0.5%. Since the flow rate of the gas after expansion is less than 30 cm^3/min for all measurements here reported, it is unlikely that liquid in the cells is entrained with the gas. However, to eliminate any possible entrainment, several layers of glass beads, supported by a perforated stainless-steel disk, are placed at the outlet of each cell. The solubility data reported here are independent of the flow rate provided that this rate is less than 50 cm^3 (STP)/min.

The equilibrium cells are placed in an agitated constant-temperature bath controlled by a Hallikainen Thermotrol. Temperatures in the cells were measured by copper-constantan thermocouples calibrated with National Bureau of Standards thermometers and a quartz thermometer; the estimated accuracy is within ±0.1°C. Dimethylpolysiloxane (Dow-Corning 200 fluid) is used as a bath fluid to 175°C, and a molten salt mixture (Hi-Tech from Du Pont Company) is used at higher temperatures.

The pressure in the second equilibrium cell is measured with a Bourdon-tube Heise pressure gauge calibrated with an Aminco dead-weight gauge; the uncertainty in pressure is ±1 lb/in.^{2} abs. A maximum pressure drop of 3 lb/in.^{2} abs through the cells was observed at 120 lb/in^2 abs inlet pressure. The influence of these and other uncertainties in measurements is discussed later in the error analysis.

Materials

Methane, ethane, and ethylene, obtained from Matheson Gas Products, have a reported minimum purity of 99.5%. Moisture content in these gases was undetectable. Hexadecane, diphenyl methane, and bicyclohexyl were supplied by Aldrich Chemical Company, eicosane and 1-methyl naphthalene by Chemical Sample Company, and squalane by Eastman Organic Chemicals. All of these have a reported purity of at least 99%, except squalane which had a maximum impurity of 2%. For all liquids, mass spectrometric measurements performed at Berkeley indicate that actual purities are higher than the minimum purities reported by the manufacturer. To eliminate volatile impurities, squalane was purged with nitrogen for several days at 230°C. Chromatographic analysis of purified squalane showed no extra peaks, even for sample size injections as large as 10 μl.

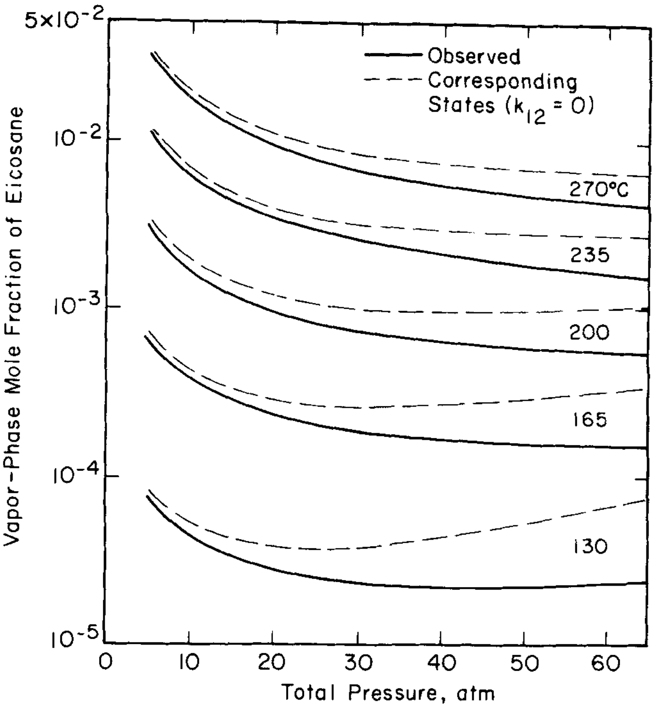

Fig. 2. Solubility of eicosane in compressed methane.

Gas Analysis

In previous studies reported from this laboratory (Benson, 1959; D'Avila, 1976), the amount of condensate collected was determined gravimetrically. However, for heavy hydrocarbons (solutes) used in the present study, the vapor pressures are so small that no appreciable amounts of condensate can be collected in a reasonable time. Therefore, a chromatographic method was used in this work.

To detect and record the concentration of solute, measurements were made with a Beckman Gas chromatograph (model GC-2A, with thermal conductivity detector) and a Wheelco 1 mv span recorder. Calibrations were made in the concentration range 700 to 6 000 ppm by weight, using an internal standard at constant concentration. Silica-gel columns supplied by Beckman Company provided good separation of peaks. Helium was the carrier gas, and for all systems the filament current was 200 mA. The flow rate of the carrier gas was less than 20 cm^3/min, and the sample size was less than 2 μl for all systems. A planimeter, used to measure peak area ratios, gave better accuracy and reproducibility than a Disc Integrator (Disc Instruments, Inc., model K-5). For replication of the calibration and of the condensate data, four samples were injected into the gas chromatograph; peak area ratios were carefully measured for each sample. Reproducibility was always within ±1%. Table 1 lists the internal standards used for different solutes along with the column temperature.

No change in peak area ratio was observed by using smaller sample sizes and lower flow rates than those given above. Sample injections for calibrations and for condensates were made at the same chromatograph operating conditions.

RESULTS

Solubility data were obtained for hexadecane, diphenylmethane, bicyclohexyl, 1-methyl naphthalene in com-

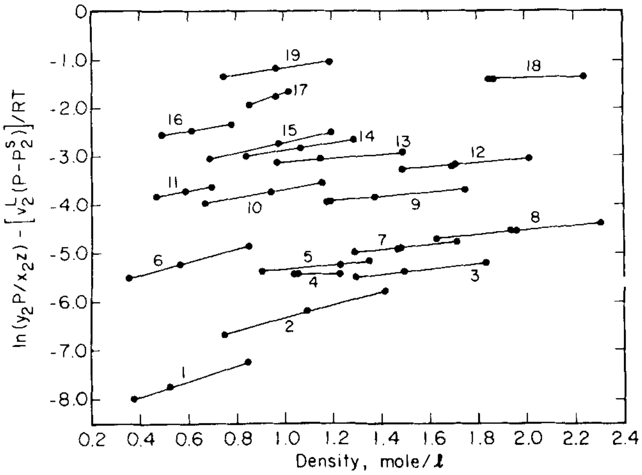

Fig. 3. $\ln(y_2P/x_2z)-[v_2^L(P-P_2^S)]/RT$ vs density for 19 binary mixtures. 1. Ethylene-hexadecane, 75°C; 2. ethylene-diphenylmethane, 65°C; 3. methane-1-methyl naphthalene, 75°C; 4. methane-squalane, 230°C; 5. methane-eicosane, 165°C; 6. ethane-1-methyl naphthalene, 75°C; 7. methane-hexadecane, 125°C; 8. methane-diphenylmethane, 100°C; 9. methane-hexadecane, 150°C; 10. ethane-diphenylmethane, 120°C; 11. ethane-eicosane, 200°C; 12. methane-diphenylmethane, 135°C; 13. methane-hexadecane, 175°C; 14. ethylene-1-methyl naphthalene, 125°C; 15. ethane-1-methyl naphthalene, 125°C; 16. ethane-eicosane, 235°C; 17. ethane-diphenylmethane, 175°C; 18. methane-bicyclohexyl, 170°C; 19. ethane-1-methyl naphthalene, 175°C.

TABLE 2. SECOND VIRIAL CROSS COEFFICIENTS B_{12} FOR SIXTEEN BINARY SYSTEMS

Components	Temperature, °C	$-B_{12}$, cm³/mole
Methane-hexadecane	75	371 ± 15
	100	260 ± 14
	125	214 ± 12
	150	170 ± 10
	175	103 ± 10
Methane-1-methyl naphthalene	75	205 ± 10
	125	146 ± 10
	175	91 ± 10
Methane-bicyclohexyl	50	299 ± 15
	90	223 ± 10
	130	104 ± 10
	170	96 ± 10
Methane-diphenylmethane	65	295 ± 15
	100	268 ± 12
	135	237 ± 10
	170	176 ± 10
Methane-eicosane	165	214 ± 10
	200	149 ± 10
	235	103 ± 10
	270	56 ± 5
Methane-squalane	230	48 ± 6
	272	−43 ± 4
Ethane-hexadecane	75	928 ± 40
	125	645 ± 30
	175	434 ± 21
Ethane-1-methylnaphthalene	75	672 ± 28
	125	462 ± 23
	175	322 ± 15
Ethane-bicyclohexyl	50	777 ± 32
	110	545 ± 27
	170	326 ± 15
Ethane-diphenylmethane	65	734 ± 35
	120	481 ± 25
	175	343 ± 20
Ethane-eicosane	165	517 ± 25
	200	402 ± 20
	235	336 ± 15
	270	256 ± 10
Ethane-squalane	230	293 ± 20
	272	165 ± 10
Ethylene-hexadecane	75	735 ± 32
	125	524 ± 21
	175	357 ± 20
Ethylene-1-methylnaphthalene	75	571 ± 20
	125	381 ± 16
	175	235 ± 15
Ethylene-bicyclohexyl	50	607 ± 25
	110	432 ± 25
	170	257 ± 12
Ethylene-diphenylmethane	65	645 ± 27
	120	416 ± 22
	175	293 ± 10

pressed methane, ethane and ethylene from 50° to 170°C, and for eicosane and squalane in compressed methane and ethane in the region 165° to 272°C. Complete data are given elsewhere (Kaul, 1977). Measurements were made in the pressure range 9 to 80 atm. To illustrate, Figure 2 shows results for methane-eicosane.

DATA REDUCTION

To obtain second virial cross coefficients from solubility data, we use the experimentally measured vapor-phase fugacity coefficient ϕ and relate it to the virial equation as indicated in Equation (3).

The equilibrium relation for heavy component 2 is given by

$$f_2^V = f_2^L \tag{5}$$

The fugacity coefficient is related to mole fractions y and x by

$$\phi_2 = \frac{\gamma_2(1-x_1)P_2^s\phi_2^s \exp\left[\dfrac{v_2^L(P-P_2^s)}{RT}\right]}{y_2P} \tag{6}$$

Solubility x_1 was calculated (or estimated) from direct solubility data (Chappelow and Prausnitz, 1974; Cukor and Prausnitz, 1971; Battino and Clever, 1966); in no case did x_1 exceed 0.3. Since we are here concerned with nonpolar systems, γ_2 is very near unity. However, to estimate γ_2 we used regular solution theory coupled with the Flory-Huggins entropy correction (Prausnitz, 1969).

The vapor pressure of component 2 is small; therefore, fugacity coefficient ϕ_2^s of the pure liquid at saturation is essentially unity. Vapor pressures and molar liquid volumes were taken from smoothed data of Myers and Fenske (1955) and from API Projects 42 and 44.

Since $y_2 << y_1$, Equation (3) shows that the fugacity coefficient is sensitive to B_{12}. Reliable measurements of y_2, therefore, yield accurate values of B_{12}. Values of z and v are essentially those for the pure gas, for which good experimental data are available (Goodwin, 1974; Goodwin et al., 1976; Miller, 1969). However, corrections due to composition are included in z and v, as indicated by Equations (1) and (2). An approximate value of B_{22} is sufficient because $y_2 << y_1$. Estimates for B_{22} are based on the correlation of Kaul and Prausnitz (1977). The value chosen for B_{22} has only a small effect on B_{12} at higher temperatures; at lower temperatures, the effect is negligible. The desired cofficient B_{12} is found by iteration but convergence is extremely fast.

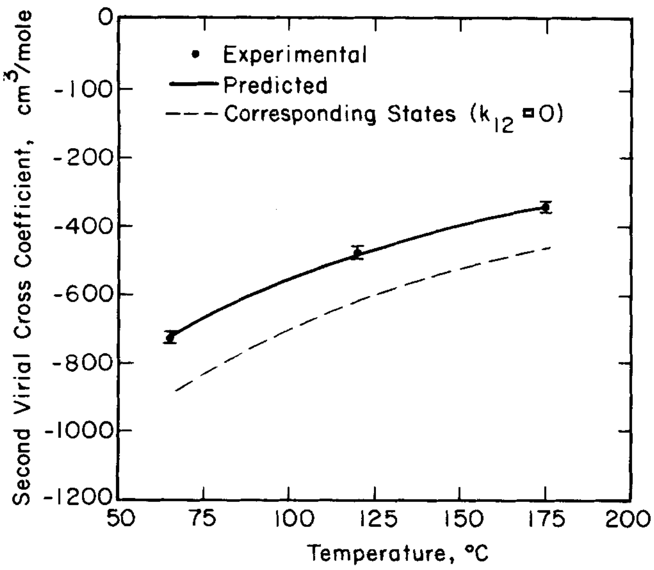

Fig. 4. Experimental and predicted second virial cross coefficients for ethane-diphenylmethane.

For a binary system, the contribution of third virial coefficients to the fugacity coefficient is given by

$$\ln \phi_2 = \frac{2}{v}(y_1B_{12} + y_2B_{22}) + \frac{3}{2v^2}[y_1^2C_{112} + 2y_1y_2C_{122} + y_2^2C_{222}] - \ln z_m \quad (7)$$

where C is the third virial coefficient characterizing interactions between three molecules.

When fugacity coefficient ϕ_2, given by Equation (6), is substituted into Equation (7), rearrangement (assuming $\gamma_2 = 1$) yields

$$\ln\left(\frac{y_2P}{x_2z_m}\right) - \frac{v_2^L(P - P_2^s)}{RT} = \ln P_2^s - \frac{2}{v}(y_1B_{12} + y_2B_{22}) - \frac{3}{2v^2}[y_1^2C_{112} + 2y_1y_2C_{122} + y_2^2C_{222}] \quad (8)$$

Thus, if the contribution of third virial coefficient is insignificant, a plot of $\ln\left(\frac{y_2P}{x_2z_m}\right) - \frac{v_2^L(P - P_2^s)}{RT}$ vs. density should give a straight line. Figure 3 shows such a plot for nineteen binary systems. For the systems and vapor-phase densities considered here, third virial coefficients have no significant effect.

Table 2 presents second virial cross coefficients for sixteen binary systems. As shown in Figures 4 and 5, the experimental second virial cross coefficients are significantly more positive than those predicted by corresponding states correlations using simple rules for the characteristic *i-j* parameters, namely, Lorentz rule for the critical volume, linear rule for the critical compressibility factor, and Berthelot rule (geometric mean with no correction) for critical temperature. In Figure 5 for methane-eicosane, line (b) is based on the correlation of McGlashan and Wormald (1964) for normal paraffins.

ERROR ANALYSIS

Possible sources of errors are random errors and errors in measurement of temperature, pressure, and mole fraction. Random errors were estimated from the observed scatter in the data.

The uncertainty in temperature arises from temperature gradients in the bath and from temperature measurements. Under worst conditions, the maximum inaccuracy is ±0.1°C; this uncertainty gives less than 0.7% uncertainty in vapor pressure and, from Equations (3) and (6), introduces less than 1% uncertainty in B_{12}.

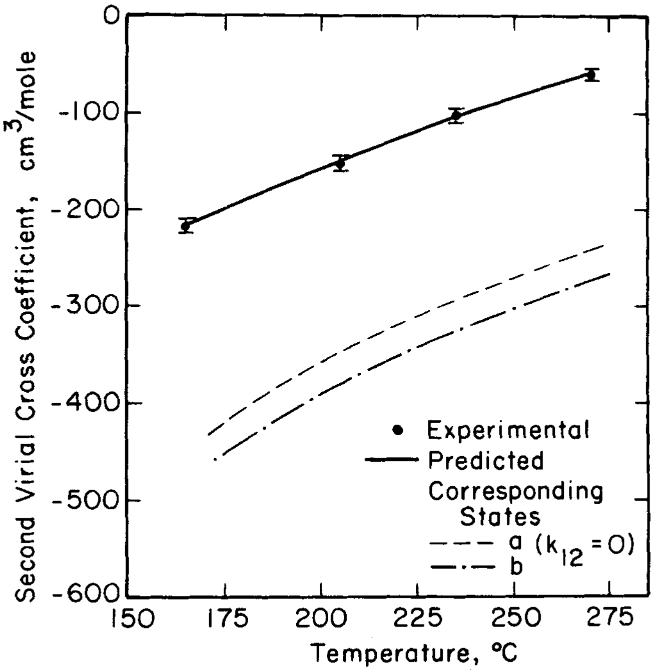

Fig. 5. Experimental and predicted second virial cross coefficients for methane-eicosane.

Uncertainty in pressure measurement is less than 1 lb/in.^{2} abs, giving an error in B_{12} of less than 0.5% at a total pressure of 140 lb/in.^{2} abs. At higher pressures, the uncertainty in pressure measurement becomes insignificant.

Uncertainties in vapor-phase mole fraction arise from wet-test meter and gas-chromatographic measurements. Considering the errors in volumetric measurement obtained from the wet-test meter, peak area measurements, etc., these are less than 2%. In general, this introduces an error near 1.5% in B_{12} at 14 atm; at higher pressures these errors diminish.

Table 2 gives overall estimated uncertainties for each value of B_{12}.

CORRELATION OF SECOND VIRIAL CROSS COEFFICIENT

As discussed elsewhere (Kaul and Prausnitz, 1977), B_{12} values for asymmetric systems are conveniently correlated with the square-well potential using a constant well width of 2Å. The effective diameter of a molecule is given by the radius of gyration, normalized with respect to methane:

$$\tfrac{1}{2}\sigma_i = (\tfrac{1}{2}\sigma \text{ for methane molecule}) + (\overline{R} \text{ for molecule } i) - (\overline{R} \text{ for methane molecule}) \quad (9)$$

For methane, $\overline{R}$ = 0.443Å (Moelwyn-Hughes, 1961) and $\frac{1}{2}\sigma$ = 1.675Å in the square-well potential (Sherwood and Prausnitz, 1964). For normal alkanes, the theoretical expression obtained by Bellemans (1973) is used to find the average radius of gyration:

$$\overline{R}^2 = 0.164\, n^{1.2}(1 + 0.547/n) \quad (10)$$

To use Equation (10), $n \geqq 1$. Values of $\overline{R}$ obtained from Equation (10) must be multiplied by the distance of one chain linkage (1.573Å). For normal paraffins, Equations (9) and (10) were used to find the diameter σ. For other hydrocarbons, σ was calculated from Equa-

TABLE 3. POTENTIAL ENERGIES ϵ_{12} DETERMINED FROM EXPERIMENTAL SECOND VIRIAL CROSS COEFFICIENTS

Binary mixture	σ_{12} (Å)*	Temperature range, °K	No. of data points	(ϵ_{12}/k),
Methane-hexadecane	6.40	348-448	5	327.7
Methane-1-methylnaphthalene	5.50	348-448	3	294.0
Methane-bicyclohexyl	5.70	323-443	4	292.0
Methane-diphenylmethane	5.59	338-443	4	338.9
Methane-eicosane	6.69	438-543	4	367.2
Methane-squalane	8.40	503-545	2	392.3
Ethane-hexadecane	6.74	348-448	3	467.3
Ethane-1-methylnaphthalene	5.80	348-448	3	437.4
Ethane-bicyclohexyl	6.00	323-443	3	432.2
Ethane-diphenylmethane	5.89	338-443	3	440.5
Ethane-eicosane	7.03	438-543	4	477.0
Ethane-squalane	8.70	503-545	2	476.0
Ethylene-hexadecane	6.57	348-448	3	436.7
Ethylene-1-methylnaphthalene	5.67	348-448	3	401.9
Ethylene-bicyclohexyl	5.87	323-443	3	397.9
Ethylene-diphenylmethane	5.76	338-448	3	419.6
Ethylene-naphthalene	5.47	296-342	7	394.5

* Parameter σ_{12} is not fitted to the data. It is calculated using Equations (9) and (12).

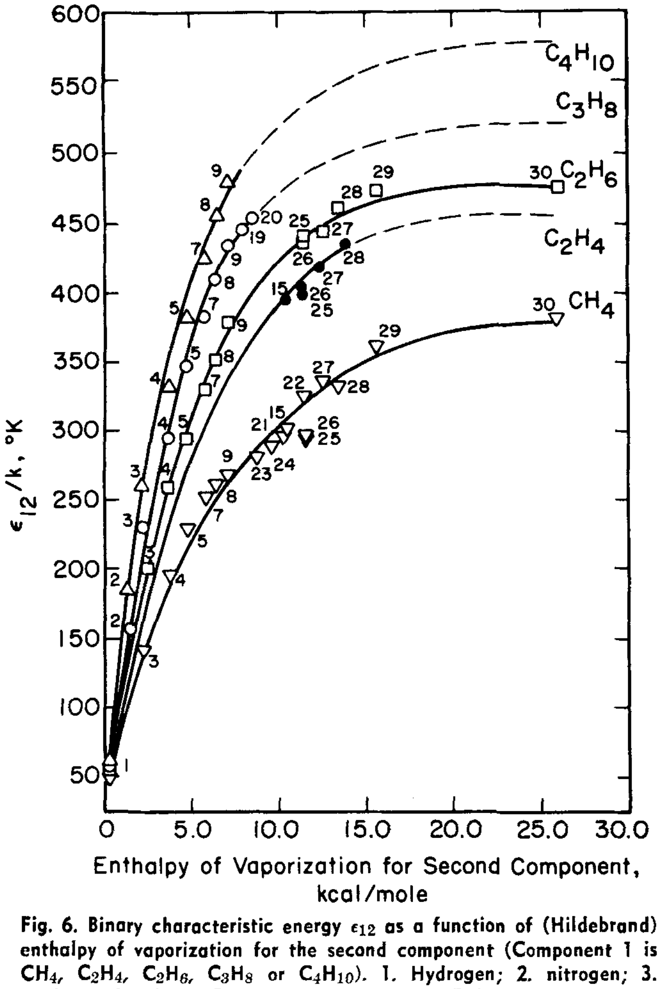

Fig. 6. Binary characteristic energy ϵ_{12} as a function of (Hildebrand) enthalpy of vaporization for the second component (Component 1 is CH_4, C_2H_4, C_2H_6, C_3H_8 or C_4H_{10}). 1. Hydrogen; 2. nitrogen; 3. methane; 4. ethane; 5. propane; 6. isobutane; 7. butane; 8. pentane; 9. hexane; 10. benzene; 11. cyclohexane; 21. decane; 22. dodecane; 24. tert. butyl benzene; 15. naphthalene; 23. 2,2,5 trimethyl hexane; 17. carbon monoxide; 19. heptane; 20. octane; 25. bicyclohexyl; 26. 1-methyl naphthalene; 27. diphenyl methane; 28. hexadecane; 29. eicosane; 30. squalane.

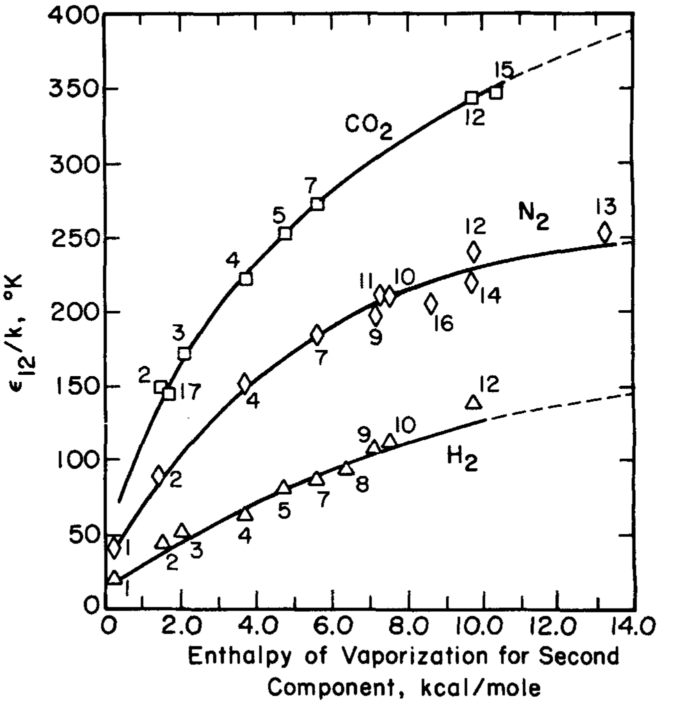

Fig. 7. Binary characteristic energy ϵ_{12} as a function of (Hildebrand) enthalpy of vaporization for the second component (component 1 is CO_2, N_2 or H_2). 1. hydrogen; 2. nitrogen; 3. methane; 4. ethane; 5. propane; 6. isobutane; 7. butane; 8. pentane; 9. hexane; 10. benzene; 11. cyclohexane; 12. decane; 13. dodecane; 14. tert. butyl benzene; 15. naphthalene; 16. 2,2,5 trimethyl hexane; 17. carbon monoxide.

tion (9) using the most probable molecular configuration. The value of $\overline{R}$ was calculated from its definition, using bond-angle and bond-distance data given by Moelwyn-Hughes (1961) and Bower and Sutton (1965). Some details are given in the appendix.

The expression for B_{ij}, using the square-well potential with fixed well width of 2Å, is given by (Hirschfelder et al., (1954)

$$\frac{B_{ij}}{b_{oij}} = 1 - (g_{ij}^3 - 1)\left[\exp\left(\frac{\epsilon_{ij}}{kT}\right) - 1\right] \quad (11)$$

TABLE 4. ENTHALPY OF VAPORIZATION OF SELECTED NONPOLAR FLUIDS CALCULATED BY HILDEBRAND'S RULE*

Fluid	ΔH^v (kcal/mole)
Hexadecane	13.53
1-methyl naphthalene	11.65
Bicyclohexyl	11.66
Diphenylmethane	12.47
Eicosane	15.61
Squalane	26.02

* Volume of saturated vapor is 49.5 l/mole.

where

$$b_{oij} = \frac{2\pi N}{3}\sigma_{ij}^3$$

$$g_{ij} = \frac{\sigma_{ij} + 2}{\sigma_{ij}} \quad (\sigma \text{ in Å})$$

and

$$\sigma_{ij} = \tfrac{1}{2}(\sigma_i + \sigma_j) \qquad (12)$$

In these equations, ϵ is the only adjustable parameter; values of ϵ_{12}, obtained for the systems studied in this work, are given in Table 3. For a fixed first component, the binary characteristic energy ϵ_{12} correlates smoothly with Hildebrand's enthalpy of vaporization for the second component, as shown in Figures 6 and 7. Table 4 gives enthalpy of vaporization (Hildebrand and Scott, 1950) for several heavy hydrocarbons; the enthalpy of vaporization is evaluated at the constant saturated volume of 49.5 l/mole. In Figure 6, ϵ_{12} rises sharply. Then, as the molecules of component 2 become large, component 1 cannot "see" and interact with all of molecule 2; therefore, ϵ_{12} remains nearly constant. Figures 6 and 7 can be used to predict second virial cross coefficients of heavy nonpolar molecules with light gases (hydrogen, methane, carbon monoxide, etc.). The curve for carbon monoxide is very close to that for nitrogen. In Figure 6, the dashed curves indicate interpolation and slight extrapolation. To predict B_{12} using Equation (11), we require no arbitrary mixing rules and no critical constants for the heavy hydrocarbons.

Figures 4, 5, and 8 show predicted and experimental values of B_{12}. The B_{12} values predicted by corresponding states are too negative because in corresponding states, the effective diameter varies as $n^{1/3}$; this follows from the assumption that σ^3 is proportional to critical volume v_c, and v_c is (nearly) proportional to n when n is large. However, for large n we see from Equations (9) and (10) that the effective diameter varies as $n^{0.6}$. Therefore, Belleman's result indicates that for large normal paraffins, the excluded volume (positive contribution to B) is larger than that calculated from a customary corresponding-states theory.

For the cross coefficient B_{12} in highly asymmetric systems, customary corresponding states also predicts an excluded volume that is too small. To force agreement with experiment, it is common practice to modify the Berthelot (geometric mean) mixing rule by introducing the correction factor $(1 - k_{12})$; positive values of k_{12} lower the absolute value of B_{12}, making it less negative. While this correction achieves the desired goal, its physical significance is doubtful. For asymmetric systems, substantial values of k_{12} ($k_{12} \approx 0.2$ for methane-eicosane) are required to reproduce the experimental data.

The results of our analysis here suggest that in applying corresponding states to highly asymmetric systems, simple mixing rules for the characteristic molecular size are also in error; for physically significant calculations, it is not sufficient to modify only the mixing rule for the characteristic energy. A more careful estimate is needed for the volume characterizing the 1-2 interaction whenever molecules 1 and 2 differ appreciably in size, as suggested previously by Gunn (1958) and by Benson (1959).

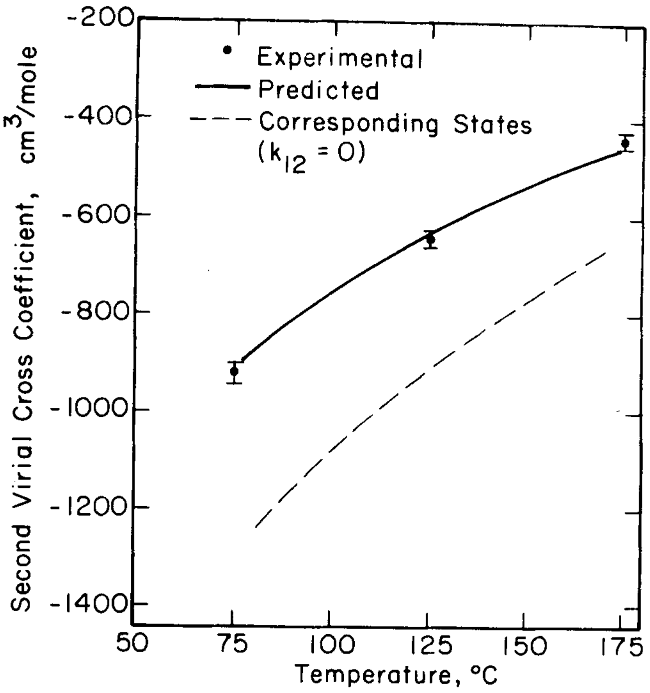

Fig. 8. Experimental and predicted second virial cross coefficients for ethane-hexadecane.

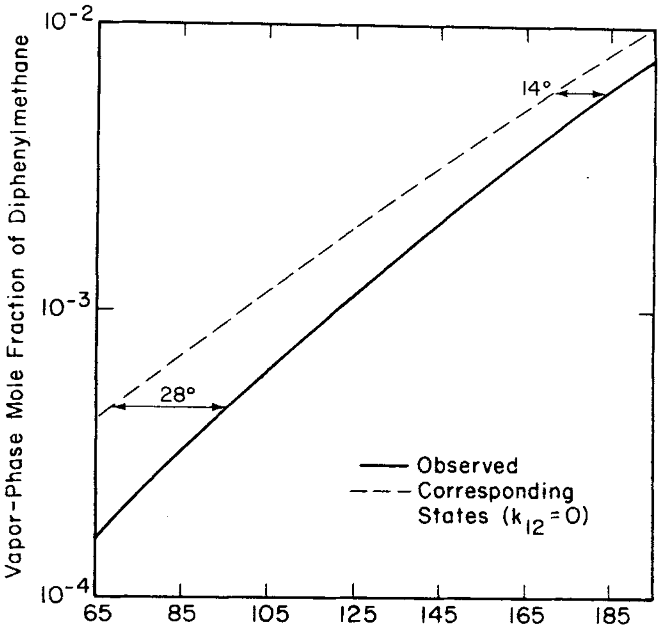

Fig. 9. Dew-point temperature for ethane-diphenylmethane mixture at 45 atm.

The square-well potential, coupled with the radius of gyration concept, provides an alternate to the corresponding states method. This alternate is particularly useful for those large hydrocarbons where critical constants are not known and cannot be estimated accurately. The square-well potential method uses no critical data.

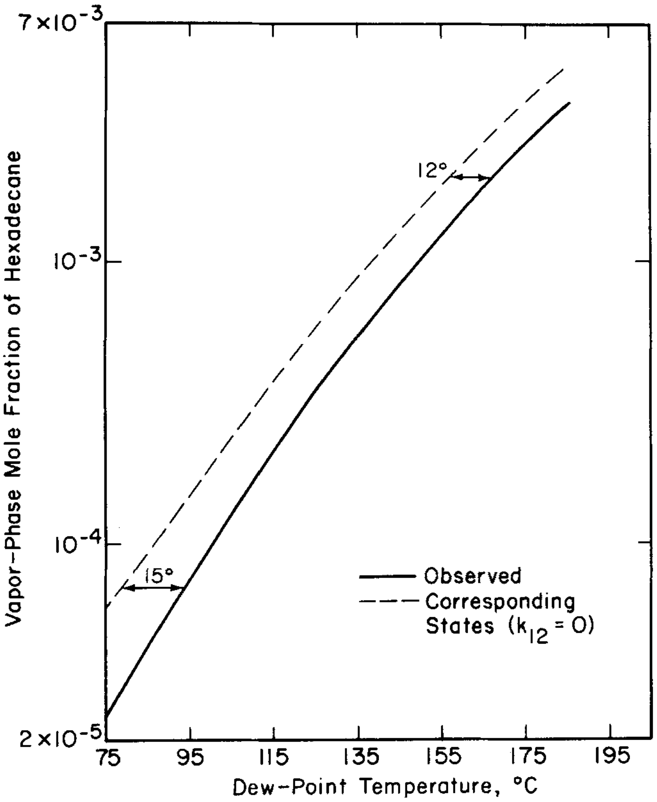

Fig. 10. Dew-point temperature for ethane-hexadecane mixture at 25 atm.

DEW-POINT TEMPERATURE

Equation (4) represents the dew-point conditions. The fugacity of component i in the pure liquid phase is essentially equal to the vapor pressure. However, corrections for the effect of pressure and for solubility of the light component can be introduced as in Equation (6). The fugacity in the gas phase is obtained from the virial equation, Equation (3). In a typical dew-point temperature calculation, pressure and mole fraction of the gas mixture are known, and the temperature is to be found. For binary systems, Equations (3) and (6), together with the correlation (Figures 6 and 7), determine the dew-point temperature. Figures 9 and 10 show dew-point temperatures for the systems ethane-diphenylmethane and ethane-hexadecane. Also shown in these figures are dew-point temperatures predicted by a corresponding states correlation using uncorrected mixing rules to determine B_{12}.

Extension of the virial equation to multicomponent mixtures is straightforward (Prausnitz, 1969); therefore, dew-point temperatures for multicomopent mixtures can also be predicted with confidence. The fugacity coefficient of a component i in a multicomponent mixture is given by Equation (3).

Figure 11 shows dew-point temperatures for 1-methyl naphthalene in an equimolar mixture of carbon dioxide and methane. Experimental solubility data for carbon dioxide and methane in 1-methyl naphthalene (Chappelow and Prausnitz, 1974; Tremper and Prausnitz, 1976) were used to obtain liquid-phase fugacities [Equation (6)]. Figure 11 also shows dew-point temperatures calculated assuming that the vapor is an ideal gas $({}^{\phi}c_{11}H_{10} = 1)$.

Figure 12 shows dew-point temperatures for eicosane and bicyclohexyl saturated in an equimolar mixture of hydrogen and methane. There are two dew-point temperatures for such a mixture, one for eicosane and the

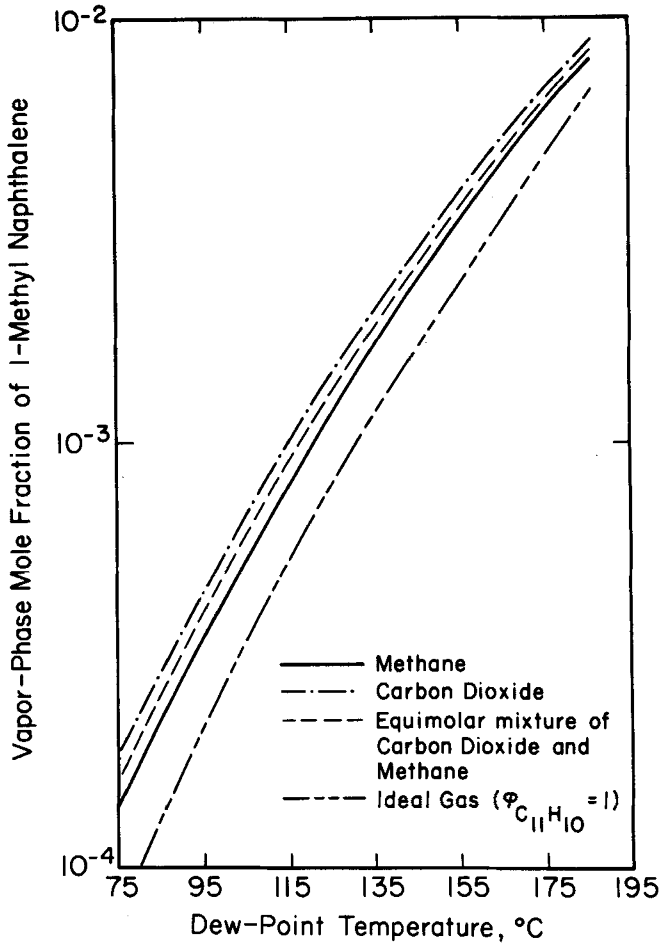

Fig. 11. Dew-point temperature for 1-methyl naphthalene in carbon dioxide and methane at 35 atm.

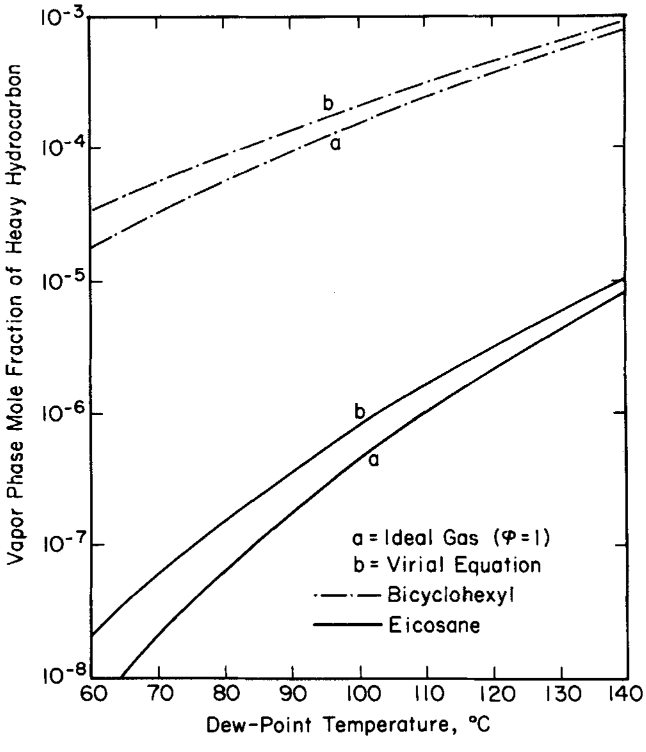

Fig. 12. Dew-point temperature for eicosane and bicyclohexyl in an equimolar mixture of hydrogen and methane at 75 atm.

other for bicyclohexyl. It is assumed that these two heavy hydrocarbons condense separately; this assumption is reasonable because the normal boiling point difference between eicosane and bicyclohexyl is about 150°C.

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NOTATION

B = second virial coefficient
f = fugacity
k = Boltzmann's constant
N = Avogadro's number
n = number of chain linkages
P = total pressure
$\bar{R}$ = radius of gyration of a molecule
T = absolute temperature
v = molar volume
x = liquid-phase mole fraction
y = vapor-phase mole fraction
z = compressibility factor
γ = activity coefficient
ϵ = intermolecular potential energy
σ = diameter of molecule as defined by Equation (9)
ϕ = fugacity coefficient

Subscripts

$1,2,i,j$ = components
m = mixture
d = dew point

Superscripts

V = vapor phase
L = liquid phase
s = saturation

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APPENDIX: CALCULATION OF MEAN RADIUS OF GYRATION

The mean radius of gyration $\bar{R}$ is defined by

$$\bar{R}^2 = \frac{(\text{Product of } q \text{ Principal Moments of Inertia})^{1/q}}{\text{Mass}} \qquad \text{(A1)}$$

For a linear molecule, $q = 2$; for others $q = 3$.

For methane, $q = 3$. The three moments of inertia (Moelwyn-Hughes, 1961) are

$$I_x = I_y = I_z = 5.298 \times 10^{-40} \text{ g-cm}^2$$

Substituting in Equation (A1) we get

$$\bar{R} = \sqrt{\frac{5.298 \times 10^{-40} \times 6.02 \times 10^{23}}{16.0426}} = 0.443\text{Å}$$

This result differs from that calculated by Thompson (1966) and quoted by Reid et al. (1977) because Thompson's definition of $\bar{R}^2$ for nonlinear molecules arbitrarily includes a factor 2π to facilitate correlation of $\bar{R}$ with Pitzer's acentric factor.

Thompson's radius of gyration for methane is $\bar{R} = 1.1234$Å. When this is divided by $\sqrt{2\pi}$, we obtain 0.448, in essential agreement with our value for $\bar{R}$.

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