

sion based on variance about the model equation. We believe these data will provide a basis for comparison of the thermodynamics of solution for these solid hydrocarbons, with that of the much more studied gaseous and liquid hydrocarbons.

ACKNOWLEDGMENT

We are indebted to Thomas M. Ward for the use of the equipment used in this study, and for much valuable advice and discussion.

LITERATURE CITED

- (1) Arnold, D. S., Planck, C. A., Erickson, E. E., Pike, F. P., *J. Chem. Eng. Data*, **3**, 253 (1958).
- (2) Bohon, R. L., Claussen, W. F., *J. Amer. Chem. Soc.*, **73**, 1571 (1951).
- (3) Dreisbach, R. R., "Physical Properties of Chemical Compounds," p 137, *Advances in Chemistry Series*, Vol. 15, American Chemical Society, Washington, D.C.

- (4) Getzen, F. W., in Johnson, J. F., Porter, R. S., "Proceedings of the American Chemical Society Symposium on Ordered Fluids and Liquid Crystals," p 53, Plenum, New York, N.Y., 1970.
- (5) Hodgman, C. D., "Handbook of Chemistry and Physics," 44th ed., p 2409, Chemical Rubber, New York, N.Y., 1962.
- (6) Inscoc, M. N., *Nature*, **211**, 1083 (1966).
- (7) Mortimer, F. S., *J. Amer. Chem. Soc.*, **45**, 633 (1923).
- (8) Parks, G. S., Huffman, H. M., *Ind. Eng. Chem.*, **23**, 1138 (1931).
- (9) Sadowska, H. W., Stepniwska, G. B., Recko, R. M., *Przem. Chem.*, **48**, 282 (1969); *CA*, **71**, 64915.
- (10) Skau, E. L., *J. Phys. Chem.*, **39**, 761 (1935).
- (11) Spaght, M. E., Thomas, S. B., Parks, G. S., *ibid.*, **36**, 882 (1932).
- (12) Ward, H. L., *ibid.*, **38**, 761 (1934).
- (13) Zarella, W. M., Mousseau, R. J., Coggeshall, N. D., Morris, M. S., Schroyer, G. S., *Geochim. Cosmochim. Acta*, **31**, 1155 (1967).

RECEIVED for review October 19, 1970. Accepted September 24, 1971. This work supported in part by a National Science Foundation Summer Traineeship (R. D. W.). Submitted by R. D. W. in partial fulfillment of the requirements for the PhD degree at North Carolina State University, Raleigh, N.C., 1970.

Some Properties of Binary Systems of Hexane and Normal Chloroalkanes

E. L. HERIC¹ and B. M. COURSEY²

Department of Chemistry, University of Georgia, Athens, Ga. 30601

Viscosities, densities, refractive indices, and refractivity intercepts at 25°C are presented for nine binary liquid systems of *n*-hexane with 1-chloroalkanes from 1-chlorobutane through 1-chlorooctadecane. These, and the derived properties excess molar Gibbs free energy of activation for flow and excess molar volume, are related to halide chain length and composition. Behavior in the present systems is compared with that reported previously for those systems containing the same halides with *n*-hexadecane as the *n*-alkane component.

The viscometric (2), volumetric (9), and refractometric (11) properties at 25°C have been reported previously for mixtures in nine binary liquid systems of *n*-hexadecane (C₁₆) with 1-chloroalkanes from 1-chlorobutane (C₄Cl) through 1-chlorooctadecane (C₁₈Cl). (For convenience *n*-alkanes will generally be abbreviated in the text as C_{*n*} and 1-chloroalkanes as C_{*n*}Cl.) In the present paper the work is extended by the substitution of C₆ as the *n*-alkane, with the same halide components. C₁₆ is of greater chain length than most of the present 1-chloroalkanes, and C₆ is of shorter chain length than most of them. The purpose is to establish the effect of this alteration of the relative chain lengths of the *n*-alkane and the 1-chloroalkanes.

EXPERIMENTAL

Equipment. The equipment and techniques parallel that of earlier work (7, 8). A water bath thermostatically controlled to ±0.01°C was used. Bath temperature was monitored with a Beckman thermometer set with a calibrated

thermometer. The calibration of the latter was against an NBS certified standard. Times were measured with an electric stopclock which had been calibrated against an electronic time standard. The cathetometer used in density determinations indicated height to ±0.05 mm. Weighings were made with a Mettler 300-gram-capacity precision balance with certified balance weights.

Viscosities were determined with Cannon-Fenske ASTM viscometers with different capillary diameters because of the 20-fold increase in viscosity in the 1-chloroalkane series. Three freshly obtained NBS oils of certified viscosity were employed as primary calibration standards for the ASTM 50 and 100 viscometers. Kinetic energy corrections compared favorably with those predicted for the given capillary diameters (17).

Densities were determined with a 4.5-ml. Lipkin pycnometer with precision capillary arms of 1-mm i.d. The pycnometer was calibrated with air-free distilled water, with heights of the liquid in the capillary arms measured relative to a single etched mark on each arm. The calibration was rechecked periodically. The precision of the results obtained with the pycnometer was dependent upon precautions previously described (10).

The viscometers and pycnometer were maintained in the bath until constant flow time or liquid volume, respectively, was obtained. As room temperature was only slightly lower than

¹ To whom correspondence should be addressed.

² Present address, U.S. Army Engineer Reactors Group, Fort Belvoir, Va. 22060.

Table I. Properties of Purified Components at 25°C

	Density, g/ml		Kinematic viscosity, cS		Refractive index, n_D		Refractivity intercept, $n_D - d/2$
	Exptl $\pm 10^6$ std. error	Lit. ^a	Exptl $\pm 10^3$ std. error	Lit. ^b	Exptl	Lit. ^c	Exptl
<i>n</i> -Hexane	0.65509 \pm 3	0.65481 - 0.65518	0.4529 \pm 0.0	0.4464 - 0.4559	1.37244	1.3720 - 1.37230	1.04490
1-Chlorobutane	0.88095 \pm 3	0.8797 - 0.8812	0.4837 \pm 0.3	0.476 - 0.494	1.39996	1.39953 - 1.4001	0.95948
1-Chloropentane	0.87700 \pm 3	0.8769 - 0.8795	0.6227 \pm 0.6	0.622	1.41000	1.4100 - 1.41026	0.97150
1-Chlorohexane	0.87338 \pm 2	0.8733 - 0.8745	0.7952 \pm 0.1	0.783 - 0.796	1.41762	1.4177	0.98093
1-Chlorooctane	0.86922 \pm 3	0.8695 - 0.8706	1.298 \pm 1	1.305 - 1.32	1.42850	1.4286	0.99389
1-Chlorodecane	0.86586 \pm 4	0.8666	2.046 \pm 1		1.43603	1.4360	1.00310
1-Chlorododecane	0.86363 \pm 5	0.8634 - 0.8644	3.089 \pm 1	3.07	1.44151	1.4414	1.00969
1-Chlorotetradecane	0.86190 \pm 3	0.8628	4.496 \pm 0		1.44479	1.4455	1.01384
1-Chlorohexadecane	0.86065 \pm 1	0.8615 - 0.8616	6.299 \pm 2	6.40	1.44815	1.4487	1.01782
1-Chlorooctadecane ^d	0.85968 \pm 5	0.8605	8.590 \pm 0		1.45062	1.4513	1.02078

^a From 6 sources identified in Reference (2) for halides; for *n*-hexane (1, 3, 5, 7, 12, 15, 16). ^b From 5 sources identified in Reference (2) for halides; for *n*-hexane (1, 3, 7, 15, 16). ^c From 5 sources identified in Reference (2) for halides; for *n*-hexane (1, 3, 7, 14, 15, 16). ^d Supercooled liquid.

25°C, temperature equilibrium was established rapidly. Evaporation losses were negligible, both from pycnometer and viscometers.

Liquids were mixed in a 50-ml modified glass syringe sealed by glass at the needle end. Again evaporation rates were negligible. Transfer to the viscometers and pycnometer was by overpressure through capillary tubing installed within the syringe plunger. The glass equipment contained ball and socket joints to reduce evaporation on transfer. Joints were treated with hexane to remove traces of nonvolatile components.

Refractive indices were measured with a Bausch and Lomb precision refractometer, thermostated at $25.00 \pm 0.01^\circ\text{C}$, and using the sodium-D line, 5893 Å. The refractometer was calibrated, and frequently rechecked, with air-free distilled water.

Replication of measurements on the pure components indicate an estimated precision of $\pm 0.1\%$ in viscosity, ± 0.00005 gram/ml in density, and ± 0.00003 unit in refractive index.

The complete experimental results and discussion of the work plus a nomenclature and Tables II through IV have been deposited with the ACS Microfilm Depository Service.

Materials. Purification of the halides has been described in detail (2). In brief summary, all halide starting material was Eastman Grade except C_4Cl (Eastman Technical) and C_{16}Cl (Eastman Practical). C_4Cl , C_5Cl , C_6Cl , and C_{12}Cl were each twice fractionally distilled. C_{10}Cl , C_{14}Cl , C_{16}Cl , and C_{18}Cl were purified chromatographically. C_8Cl was not further purified because several analytical chromatographs on different columns revealed no impurity peaks. All purified halides were also examined chromatographically for impurity peaks.

n-Hexane was Matheson, Coleman and Bell chromatographic quality. It was used without further purification after analytical chromatographs showed no impurity peaks.

Comparison of experimental and literature values of the kinematic viscosities, densities, and refractive indices is given in Table I. Experimental values represent the mean of at least three determinations. Stated uncertainties are in terms of standard deviation.

RESULTS AND DISCUSSION

As noted previously (2), the difference between experimental and literature values, Table I, is considerable for some of the halides. This is true even for the viscosity, which is generally the property among those listed here which is least significantly affected by small amounts of impurities.

The limited number of literature values for some of the halides makes it difficult to conclude whether they are more dependable than those reported here. However, the analytical chromatographs do not indicate impurities are a source of large error in the present work.

The systematic behavior described below indicates that present results for mixtures are of acceptable quality.

Kinematic viscosities, densities, refractive indices, and refractivity intercepts were obtained for six to ten mixtures in each of the nine systems. The molar excess Gibbs free energies of activation for flow and the molar excess volumes were also calculated. The refractivity intercept is defined (13) as $n_D - d/2$. The molar excess Gibbs free energy of activation for flow is defined through the Eyring viscosity equation (4) as

$$\nu = \frac{hN}{M} \exp(\Delta^*G/RT) \quad (1)$$

By definition $\Delta^*G^E = \Delta^*G - \Delta^*G^i$, and for an ideal binary mixture $\Delta^*G^i = x_1\Delta^*G_1 + x_2\Delta^*G_2$. Thus for a binary mixture,

$$\Delta^*G^E = RT[\ln(\nu M) - x_1 \ln(\nu_1 M_1) - x_2 \ln(\nu_2 M_2)] \quad (2)$$

and if $\Delta^*G^E > 0$, the viscosity is greater than that of an ideal mixture. The molar excess volume is defined as

$$\Delta V^E = V - x_1 V_1 - x_2 V_2 \quad (3)$$

with V , V_1 , and V_2 obtained as the ratio of molecular weight to density.

Viscometric Behavior. The kinematic viscosity of C_6 is less than that of any of the present halides. In all systems but one, the kinematic viscosity shows monotonic decrease with decreasing halide concentration. The exception is $\text{C}_6\text{-C}_4\text{Cl}$, which exhibits a minimum at low halide concentration. The kinematic viscosities of these two components differ by only 0.03 cS.

Δ^*G^E from Equation 2 is plotted vs. mole fraction C_6 in Figure 1 for the nine systems. The behavior is similar to that of the $\text{C}_{16}\text{-C}_n\text{Cl}$ systems (2) in that the curves are broadly parabolic in form. For each *n*-alkane with the halide, Δ^*G^E values are positive except for the range of halide chain lengths approaching that of the *n*-alkane. The systematic behavior is evident from Figure 2, where for both C_6 and C_{16} with these halides the extreme Δ^*G^E in each system is plotted vs. the halide chain length.

Three effects may influence flow behavior in mixtures in the present type of systems. Disruption of dipole-dipole forces enhances flow, and impedance of segmental flow impedes it. It is evident from the combination of generally positive values of Δ^*G^E with expansion upon mixing in the $\text{C}_{16}\text{-C}_n\text{Cl}$ systems (2, 9), that volume change is not the major factor in flow behavior in these systems.

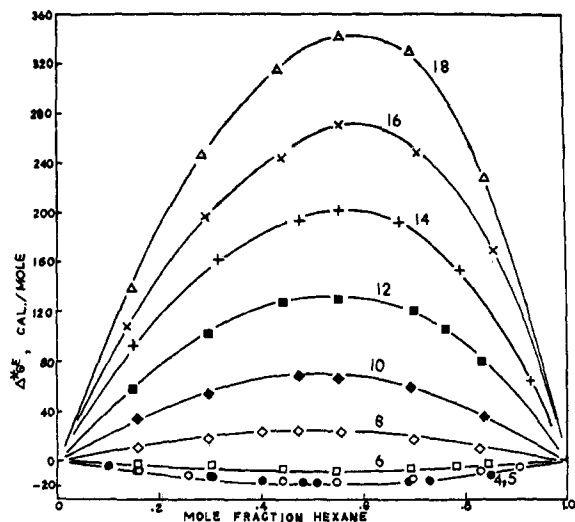


Figure 1. Excess molar Gibbs free energy of activation for flow

Number indicates chain length of the 1-chloroalkane

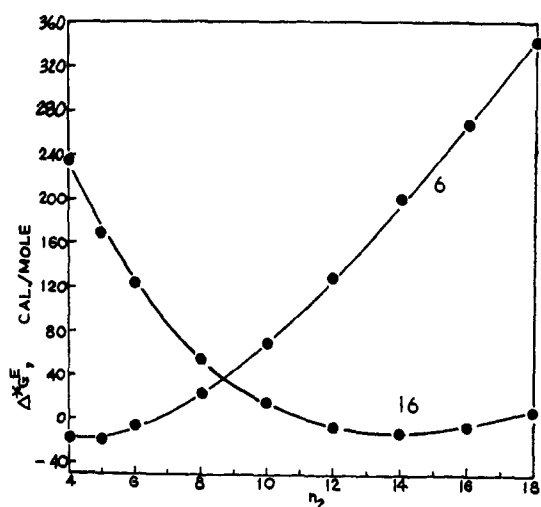


Figure 2. Extreme values of the excess Gibbs free energy of activation for flow as a function of the 1-chloroalkane chain length

6. *n*-Hexane as alkane
16. *n*-Hexadecane as alkane

The extent of the asymmetry in the curves of Figure 1 may be shown with the coefficients of the fitting equation

$$\Delta^*G^E = x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \dots] \quad (4)$$

All orders of Equation 4 through the sixth were examined with the aid of a digital computer. The data were weighted according to the uncertainty in mole fraction (6). That order was selected for a system beyond which additional terms did not significantly improve the fit. (Similar procedures were followed in applying additional fitting equations, described below.) All C_6 - C_n Cl systems except those containing C_6 Cl and C_8 Cl are asymmetrical, with the asymmetry varying systematically with halide chain length.

Δ^*G^E has been resolved into partial molar properties,

$$\Delta^*G^E = x_1\overline{\Delta^*G_1^E} + x_2\overline{\Delta^*G_2^E} \quad (5)$$

through $\overline{\Delta^*G_i^E} = \Delta^*G^E - x_i(d\Delta^*G^E/dx_i)$, with Δ^*G^E from Equation 4. As with C_{16} and the present halides, the variation

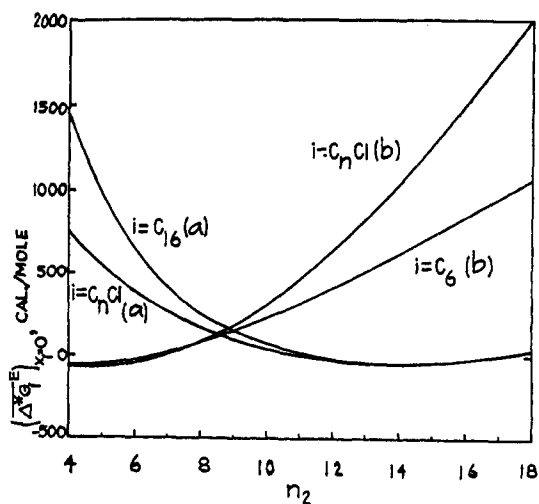


Figure 3. Limiting values of the partial molar excess Gibbs free energy of activation for flow as a function of the 1-chloroalkane chain length

a. $C_{16} + C_n$ Cl systems
b. $C_6 + C_n$ Cl systems

of $\overline{\Delta^*G_i^E}$ with composition in each of the present systems shows a smooth trend from zero at $x_i = 1$ to the largest value at $x_i = 0$.

The values of $\overline{\Delta^*G_i^E}$ at $x_i = 0$ for both C_6 and C_{16} with these halides are plotted in Figure 3 vs. halide chain length. For either *n*-alkane with the halides the behavior is similar. When the two mixture components have considerably different chain lengths, $\overline{\Delta^*G_i^E}$ at $x_i = 0$ is larger for the component of longer chain length.

Volumetric Behavior. The density of C_6 is less than that of any of the present halides. For all of the present systems there is a monotonic decrease in density with increasing halide concentration. Densities are suitable for analyzing these binary mixtures, with the present uncertainty of ± 0.00005 gram/ml corresponding to about 0.02% of the density difference between C_6 and the 1-chloroalkanes.

Densities may be expressed by

$$d = \phi_1d_1 + \phi_2d_2 + \phi_1\phi_2[e + f(\phi_1 - \phi_2) + g(\phi_1 - \phi_2)^2 + \dots] \quad (6)$$

where the first two terms on the right side represent ideal density behavior. Coefficients for Equation 6 have been evaluated. No more than two coefficients are required for the present systems, with a typical standard error of ± 0.00005 g/ml.

ΔV^E from Equation 3 is plotted vs. mole fraction of C_6 in Figure 4. For comparison, results in the corresponding systems containing C_{16} (9) are also included. The two sets of curves in Figure 4 show a sharply contrasting behavior. With C_6 as the alkane component, ΔV^E tends to negative values, while with C_{16} , ΔV^E is positive. Moreover the former ΔV^E tend to be larger than the latter and more asymmetrical.

Coefficients of the fitting equation

$$\Delta V^E = x_1x_2[H + K(x_1 - x_2) + L(x_1 - x_2)^2 + \dots] \quad (7)$$

have been evaluated. From one to three coefficients are necessary, depending upon the halide chain lengths. The typical standard error is ± 0.01 ml/mol.

Refractometric Behavior. The refractive index of C_6 is less than that of any of the present halides. As with density, all of the present systems exhibit a monotonic decrease in refractive index with decreasing halide concentration. Refrac-

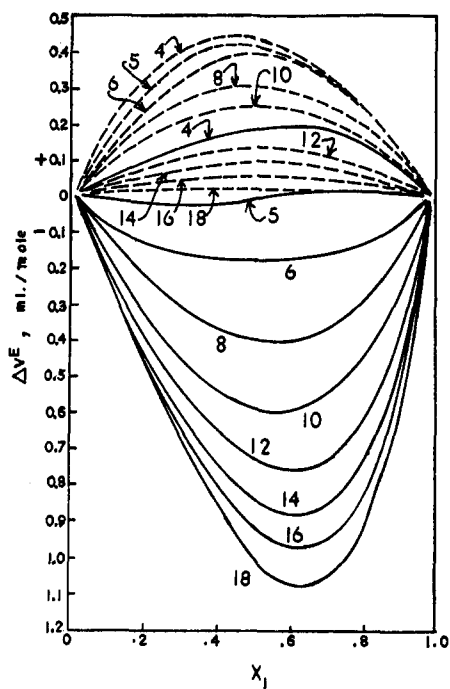


Figure 4. Excess molar volumes vs. *n*-alkane mole fraction

Number indicates chain length of the 1-chloroalkane

Dashed lines. $C_{16} + C_nCl$ systems
Solid lines. $C_8 + C_nCl$ systems

tive index is less suitable for analyzing these systems than density, however.

Refractive indices may be represented by

$$n_D = \phi_1 n_{D1} + \phi_2 n_{D2} + \phi_1 \phi_2 \times [p + q(\phi_1 - \phi_2) + r(\phi_1 - \phi_2)^2 + \dots] \quad (8)$$

where the first two terms on the right side represent ideal refractive index behavior. Coefficients for Equation 8 have been evaluated. A single coefficient is sufficient for these systems, with a typical standard error of ± 0.00006 unit.

The refractivity intercept, $n_D - d/2$, of C_8 is greater than that of any of the present halides. For all of the systems of Table II, there is a monotonic increase in refractivity intercept with decreasing halide concentration. Refractivity intercept and refractive index are about equally suitable for analyzing these systems.

Refractivity intercepts may be represented by

$$n_D - d/2 = \phi_1(n_{D1} - d_1/2) + \phi_2(n_{D2} - d_2/2) + \phi_1 \phi_2 [s + t(\phi_1 - \phi_2) + u(\phi_1 - \phi_2)^2 + \dots] \quad (9)$$

A single coefficient is sufficient for these systems, with a typical standard error of ± 0.00007 unit. The deviation from volume fraction additivity of refractivity intercepts is considerably less than that for either density or refractive index, especially at the higher chain lengths.

NOMENCLATURE

- A, B, C = coefficients for fitting of data, Equation 4
 Δ^*G = molar Gibbs free energy of activation for flow, cal/mol
 Δ^*G_i = partial molar Gibbs free energy of activation for flow, cal/mol
 H, K, L = coefficients for fitting of data, Equation 7

M = mol wt, grams

N = Avogadro number

R = gas constant, cal/deg mol

T = absolute temperature, °K

V = molar volume, ml/mol

ΔV = volume of mixing, ml/mol

d = density, g/ml

e, f, g = coefficients for fitting of data, Equation 6

h = Planck constant, erg sec

n_D = refractive index, Na-D line

$n_D - d/2$ = refractivity intercept

p, q, r = coefficients for fitting of data, Equation 8

s, t, u = coefficients for fitting of data, Equation 9

x = mole fraction

ν = kinematic viscosity—i.e., dynamic viscosity per density, cS.

ϕ = volume fraction

SUBSCRIPTS

1 = component 1 (*n*-hexane)

2 = component 2 (1-chloroalkane)

SUPERSCRIPTS

E = excess

i = ideal

LITERATURE CITED

- (1) Bidlack, D. L., Anderson, D. K., *J. Phys. Chem.*, **68**, 3790 (1964).
- (2) Coursey, B. M., Heric, E. L., *J. Chem. Eng. Data*, **14**, 426 (1969).
- (3) Forziati, A. F., Glasgow, A. R., Willingham, C. B., Rossini, F. D., *J. Res. Natl. Bur. Stand.*, **36**, 129 (1946).
- (4) Glasstone, S., Laidler, K. J., Eyring, H., "The Theory of Rate Processes," p 484, McGraw-Hill, New York, N.Y., 1941.
- (5) Gomez-Ibanez, J. D., Liu, C., *J. Phys. Chem.*, **67**, 1388 (1963); **65**, 2148 (1961).
- (6) Heric, E. L., *J. Chem. Eng. Data*, **11**, 66 (1966).
- (7) Heric, E. L., Brewer, J. G., *ibid.*, **12**, 574 (1967).
- (8) Heric, E. L., Brewer, J. G., *ibid.*, **14**, 55 (1969).
- (9) Heric, E. L., Coursey, B. M., *Can. J. Chem.*, **48**, 3911 (1970).
- (10) Heric, E. L., Coursey, B. M., *J. Chem. Eng. Data*, **15**, 536 (1970).
- (11) Heric, E. L., Coursey, B. M., *ibid.*, **16**, 185 (1971).
- (12) Holmes, J. T., Olander, D. R., Wilke, C. R., *A.I.Ch.E. J.*, **8**, 646 (1962).
- (13) Kurtz, S. S., Ward, A. L., *J. Franklin Inst.*, **222**, 563 (1936).
- (14) Mair, B. J., *J. Res. Natl. Bur. Stand.*, **9**, 457 (1932).
- (15) Rossini, F. D., Pitzer, K. S., Arnett, R. L., Braun, R. M., Pimentel, G. C., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons," Am. Petrol. Inst. Research Project 44, Carnegie Press, Pittsburgh, Pa., 1947, 1953.
- (16) Shepard, A. F., Henne, A. L., Midgley, J., *J. Amer. Chem. Soc.*, **53**, 1948 (1931).
- (17) Willihnganz, E. A., McCluer, W. B., Fenske, M. R., McGrew, R. V., *Ind. Eng. Chem. Anal. Ed.*, **6**, 232 (1934).

RECEIVED for review November 23, 1970. Accepted August 21, 1971. Presented at the Combined Southeast-Southwest Meeting, ACS, New Orleans, La., December 1970. Work supported by the Petroleum Research Fund administered by ACS. The complete experimental results and discussion of the work plus a nomenclature and Tables II through IV will appear following these pages in the microfilm edition of this volume of the Journal. Single copies may be obtained from the Business Operations Department, American Chemical Society, 115 Sixteenth St., N.W., Washington, D.C. 20036, by referring to author, title of article, volume, and page number. Remit by check or money order \$4.00 for photocopy or \$2.00 for microfiche.