Results

V^E_{ijk} and H^E_{ijk} data for the present ternary mixtures as a function of composition at 298.15 K are recorded in Tables II and III.

Discussion

A comparison of the V^E and H^E data at 298.15 K (*14*) for benzene + OCTE mixtures with the corresponding V^E_{ijk} and H^E_{ijk} data for benzene (i) + toluene or *o*-xylene or *p*-xylene (*j*) + OCTE mixtures, however, reveals that while the addition of toluene (j) to benzene + OCTE mixtures decreases both the V^E_{ijk} and H^E_{ijk} values for benzene (i) + toluene (j) + OCTE (k) mixtures, the addition of *o*-xylene (j) or *p*-xylene (j) to benzene + OCTE mixtures increases the V^E_{ijk} values but decreases the H^E_{ijk} values for the resulting (i + j + k) mixtures. On the other hand while the addition of *o*-xylene to toluene + OCTE mixtures increases the V^E_{ijk} values, it decreases the H^E_{ijk} values for the resulting (i + j + k) mixtures.

Registry No. Benzene, 71-43-2; toluene, 108-88-3; *o*-chlorotoluene, 95-49-8; *o*-xylene, 95-47-6; *p*-xylene, 106-42-3.

Literature Cited

(1) Mahl, B. S.; Bhardwaj, S. S.; Dhanda, S.; Kaur, S. *Thermochim. Acta* **1983**, *67*, 9.
(2) Singh, J.; Pflug, H. C.; Benson, G. C. *J. Phys. Chem.* **1968**, *72*, 1939.
(3) Otin, S.; Munoj, J.; Toledo, M. J.; Velasco, I.; Gutierrezosa, C. *J. Chem. Thermodyn.* **1985**, *17*, 419.
(4) Vogel, A. I. *A Text Book of Practical Organic Chemistry*; Longmans: London 1983; p 172.
(5) Weissberger, A. *Physical Methods of Organic Chemistry, Part I*; Interscience: 1965; p 148.
(6) Nyvlt, J.; Erdos, E. *Collect. Czech. Chem. Commun.* **1961**, *26*, 500.
(7) Kyle, B. G.; Reed, T. M. *J. Am. Chem. Soc.* **1958**, *80*, 6170.
(8) Forziati, A. F.; Rossini, F. D. *J. Res. Natl. Bur. Stand.* **1943**, *43*, 473.
(9) Timmermans, J. *Physico Chemical Constants of Pure Organic Compounds*; Elsevier: Amsterdam, 1950.
(10) Singh, P. P.; Sharma, S. P. *J. Chem. Eng. Data* **1985**, *30*, 477.
(11) Monk, P.; Wadso, I. *Acta Chem. Scand.* **1968**, *22*, 1842.
(12) Dahiya, H. P.; Singh, P. P.; Dagar, S. *Fluid Phase Equilib.* **1987**, *33*, 191.
(13) Stokes, R. H.; Marsh, K. N.; Tomlins, R. P. *J. Chem. Thermodyn.* **1969**, *1*, 211.
(14) Dahiya, H. P.; Dagar, S.; Singh, P. P. *J. Chem. Eng. Data* **1987**, *32*, 342.

Received for review September 21, 1987. Revised January 4, 1988. Accepted May 23, 1988. We thank the authorities of Maharshi Dayanand University for providing all the necessary research facilities and research fellowship to S.D.

Mutual Diffusion Coefficients for Several Dilute Solutes in *n*-Octacosane and the Solvent Density at 371–534 K

John B. Rodden, Can Erkey, and Aydin Akgerman*

Department of Chemical Engineering, Texas A&M University, College Station, Texas 77843

The Taylor dispersion technique was used to measure mutual diffusion coefficients at infinite dilution for six solutes (H_2, CO, CO_2, *n*-C_8H_{18}, *n*-$C_{12}H_{26}$, and *n*-$C_{16}H_{34}$) in liquid *n*-octacosane (*n*-$C_{28}H_{58}$) over the temperature range 371–534 K at 1.38 MPa pressure. The density of liquid *n*-octacosane was also measured at the same conditions. Using the rough hard-sphere theory, a correlation was developed which correctly represents the data.

Introduction

Mutual diffusion coefficients, density, and viscosity are the thermophysical properties needed to evaluate mass-transfer phenomena and to design equipment for mass-transfer operations. However, relatively few data are available for these properties at conditions far from ambient. At high temperatures, diffusion data are especially scarce for liquid solvents, and do not exist for high-boiling substances. Our objective has been to measure mutual diffusion, density, and viscosity in the homologous series of *n*-alkanes at conditions where data are not available. We have previously reported measurements in heptane, dodecane, hexadecane, and eicosane over a wide temperature range (*1*–*3*). This work extends our existing data base to include mutual diffusivity and density data for liquid *n*-octacosane.

Previous work (*1*, *2*) demonstrated that the diffusion coefficient was only weakly dependent on pressure over the modest pressure range of 0.10–3.40 MPa (15–500 psia). In most cases, the effect of pressure was within the error of the experiment. Since our equipment operated best near the middle of this pressure range, all data for this study were collected at 1.38 MPa (200 psia).

Experimental Techniques

Infinite dilution diffusion coefficients of three gaseous solutes (hydrogen, carbon monoxide, and carbon dioxide) and three *n*-alkane solutes (octane, dodecane, and hexadecane) in liquid *n*-octacosane were measured by using the Taylor dispersion technique (*4*, *5*). In this method, a narrow pulse of solute with mass M, diluted in the solvent, is injected into a tube in which the pure solvent is moving in slow laminar flow. The pulse quickly assumes a Gaussian distribution which is dependent on the average solvent velocity $\bar{u}$, residence time in the tube $\bar{t}$, tube radius r, and molecular diffusivity D_{12}. The concentration at the end of the diffusion tube, distance L from the injection point, is given by the following equations:

$$C = \frac{M}{\pi r^2 (4\pi K t)^{1/2}} \exp\left(\frac{-(L - \bar{u}t)^2}{4Kt}\right) \tag{1}$$

where

$$K = D_{12} + \frac{r^2 \bar{u}^2}{48 D_{12}} \tag{2}$$

Details of the Taylor dispersion apparatus used in our previous studies were given by Matthews and Akgerman (*6*). For this study, the original apparatus was modified extensively so that data could be collected in solvents which melt at temperatures well above ambient.

---

* Author to whom inquiries should be addressed.

0021-9568/88/1733-0450$01.50/0 © 1988 American Chemical Society

Table I. Diffusion Coefficients of Gases in *n*-Octacosane at 1.38 MPa ($D_{12} \times 10^9$ m²/s)

solute	temp, K	D_{12} expt	D_{12} pred by eq 7
H_2	371	13.4 ± 0.06	13.0
	414	20.5 ± 0.29	19.9
	455	29.3 ± 0.25	30.0
	495	41.0	41.7
	534	51.5 ± 0.27	52.3
CO	371	4.36 ± 0.16	4.64
	414	6.98 ± 0.05	7.12
	455	10.7 ± 0.01	10.7
	495	15.7 ± 0.50	14.9
	534	18.8 ± 0.19	18.7
CO_2	371	3.80 ± 0.07	3.87
	414	6.12 ± 0.20	5.94
	455	8.99 ± 0.20	8.96
	495	12.7 ± 0.09	12.5
	534	15.5 ± 0.36	15.6

The solvent, *n*-octacosane, which melts at 61 °C, was maintained at approximately 90 °C in a heated reservoir where it was continuously sparged with helium. The solvent was pumped through heat-traced lines by an externally heated chromatographic pump. Solvent flow rates were chosen which met the operating criteria recommended in the literature (*5*, *7*, *8*). The solvent was first pumped through the reference side of a refractive index detector (LDC/Milton Roy Refractomonitor). The temperature of the refractive index detector cell was controlled at 100 °C by means of a constant temperature bath which recirculated ethylene glycol through a jacket surrounding the cell. Following the refractive index detector, the solvent entered a heated enclosure which was maintained to within ±0.5 K of each reported temperature. The solute pulse was then injected via a switching valve contained within the enclosure. The injected pulse was carried by the flowing solvent stream through approximately 50 m of 0.001 m i.d. stainless steel tubing before eluting through the sample side of the detector.

The detector output voltage, which is proportional to concentration, was recorded by computer every 5 s. For each eluting dispersion peak, these data were used to determine the unknown parameters K and $\bar{u}$ of eq 1. These parameters were obtained using a nonlinear least-squares model which fit the data to eq 1. Additional terms were included in the model to account for detector offset voltage and baseline drift. Once K and $\bar{u}$ were determined from the model, D_{12} was calculated from eq 2 using the quadratic formula.

The density of *n*-octacosane was measured by using a technique we recently developed which relates solvent density to the Taylor dispersion peak retention time and solvent mass flow rate (*9*). The accuracy of the technique has been estimated at 0.1% (*9*). First, a calibration experiment is performed with a solvent of known density, such as water. The mass flow rate and peak retention time from this calibration experiment are used to determine the density of other solvents at different conditions from

$$\rho_2 = \rho_1 \frac{\dot{m}^{(2)}\bar{t}^{(2)}\,V_t^{(1)}}{\dot{m}^{(1)}\bar{t}^{(1)}\,V_t^{(2)}} \tag{3}$$

where the retention time is given by

$$\bar{t} = L/\bar{u} \tag{4}$$

The ratio of volumes in eq 3 is easily calculated by using the thermal expansion coefficient for the tube material. The actual tube volume does not need to be calculated.

n-Octacosane, hexadecane, and octane were obtained from Alfa Chemicals, and dodecane from Phillips Petroleum. All *n*-alkane purities were stated as at least 99 mol %. Bottled gases were used as received.

Table II. Diffusion Coefficients of *n*-Alkanes in *n*-Octacosane at 1.38 MPa ($D_{12} \times 10^9$ m²/s)

solute	temp, K	D_{12} expt	D_{12} pred by eq 7
$n\text{-}C_8H_{18}$	373	1.21 ± 0.03	1.18
	413	2.16 ± 0.01	2.05
	454	3.20 ± 0.09	3.34
	495	4.70 ± 0.07	4.90
	534	6.33 ± 0.08	6.36
$n\text{-}C_{12}H_{26}$	373	0.89	0.87
	413	1.56 ± 0.05	1.52
	454	2.37 ± 0.01	2.48
	495	3.59 ± 0.04	3.63
	534	4.82 ± 0.09	4.71
$n\text{-}C_{16}H_{34}$	373	0.71 ± 0.01	0.70
	413	1.25 ± 0.01	1.22
	454	1.89 ± 0.02	1.99
	495	2.84 ± 0.10	2.92
	534	3.91 ± 0.04	3.79

Table III. Multiplier β and V_D for Solutes

solute	$\beta \times 10^{-6}$ (g mol)/(s m $K^{1/2}$)	V_D, mL/(g mol)
H_2	0.0179	482.5
CO	0.0071	489.2
CO_2	0.0056	484.9
$n\text{-}C_8H_{18}$	0.0024	496.5
$n\text{-}C_{12}H_{26}$	0.0019	498.7
$n\text{-}C_{16}H_{34}$	0.0015	499.5

Results and Discussion

For most diffusivity measurements, three repeat experiments were performed and the results averaged. The average diffusion coefficients, together with the standard deviations of replicate experiments where applicable, are given in Table I and II. The standard deviations range between 0.1 and 3.7% of the mean.

We have previously applied the rough hard-sphere theory (RHS) to predict and correlate diffusion in alkane/alkane systems (*10*). According to this theory (*11*, *12*), the diffusion coefficient is given by

$$D_{12}/T^{1/2} = \beta(V - V_D) \tag{5}$$

where V is the solvent molar volume, V_D is the solvent molar volume where diffusion ceases, and β is a constant which is a function of molecular interactions. According to eq 5 $D_{12}/T^{1/2}$ should vary linearly with the molar volume of the solvent. Table III summarizes the β and V_D values for each solute obtained through linear regression. The V_D values for the alkane solutes were averaged separately from the values for the smaller gaseous solutes. There is justification for averaging separately since the intercept V_D has been found to be a weak function of solute size (*10*). For *n*-octacosane, the β's for each solute can be correlated with the hard-sphere diameter σ_1.

$$\beta = a\sigma_1^{\,b} \tag{6}$$

In this equation, σ_1 is the hard-sphere diameter of the solute and a and b are constants. Therefore, the high-temperature behavior of the diffusion coefficients in *n*-octacosane can be summarized as

$$\frac{10^9 D_{12}}{T^{1/2}} = a\sigma_1^{\,b}(V - V_D) \tag{7}$$

where for *n*-alkane solutes

$$V_D = 498.2,\ a = 0.22,\ b = -2.38 \tag{7a}$$

and for dissolved gas solutes

$$V_D = 485.5,\ a = 0.26,\ b = -2.79 \tag{7b}$$

Table IV. Core Diameters from Procedure of Bondi (*13*)

	σ, Å		σ, Å
H_2	2.572	n-C_8H_{18}	6.552
CO	3.718	n-$C_{12}H_{26}$	7.436
CO_2	3.968	n-$C_{16}H_{34}$	8.148
		n-$C_{28}H_{58}$	9.761

Table V. Density of *n*-Octacosane at 1.38 MPa

temp, K	density, g/mL	temp, K	density, g/mL
373	0.756	495	0.675
413	0.734	534	0.651
454	0.705		

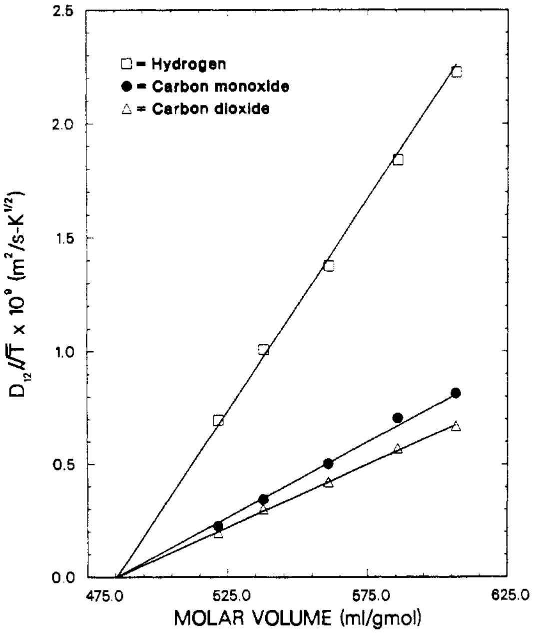

Figure 1. $D_{12}/T^{1/2}$ as a function of solvent molar volume for gaseous solutes in the solvent *n*-octacosane over the temperature range 371–534 K. Straight lines represent predictions of eq 7.

In eq 7, D_{12} is in m^2/s, V is in mL/(g mol), T is in K, and σ_1 is in angstroms. Table IV gives the solute hard-sphere diameters calculated by using the procedure of Bondi (*13*). The diameter of the solvent *n*-octacosane is also included for reference. Figures 1 and 2 show the data and the corresponding plots of eq 7. Predicted diffusion coefficients are also summarized in Tables I and II.

As seen in Figures 1 and 2, there is some deviation from linearity. Large deviations from RHS theory may be expected for long-chain hydrocarbons such as *n*-octacosane since spherical symmetry is highly unlikely. However, the fit to the theoretical equation is surprisingly good considering the size of the *n*-octacosane molecule. In addition, the deviations from linearity for all the solutes have the same trend which might also be explained in terms of the temperature dependency of the hard-sphere diameters. Since the necessary data to evaluate this temperature dependency is not available, the hard spheres were treated as constants in this analysis.

Density data for *n*-octacosane measured at the operated temperatures and pressure are given in Table V. These values were used to calculate the solvent molar volumes for the RHS analysis. Figure 3 is a plot of density versus temperature for the data. The density varies linearly with temperature over the temperature range 371–534 K at 1.38 MPa pressure. Density data were not available in the literature at these conditions.

By a development analogous to that for diffusion, the RHS theory predicts (*11*, *12*)

$$T^{1/2}/\eta = \beta'(V - V_\eta) \tag{8}$$

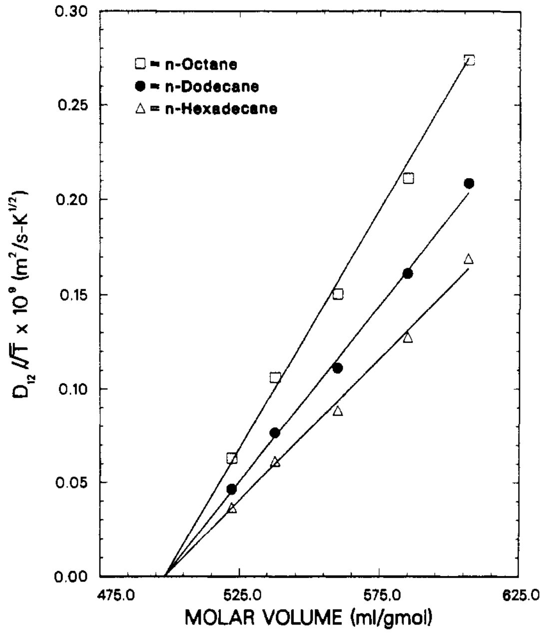

Figure 2. $D_{12}/T^{1/2}$ as a function of solvent molar volume for *n*-alkane solutes in the solvent *n*-octacosane over the temperature range 373–534 K. Straight lines represent predictions of eq 7.

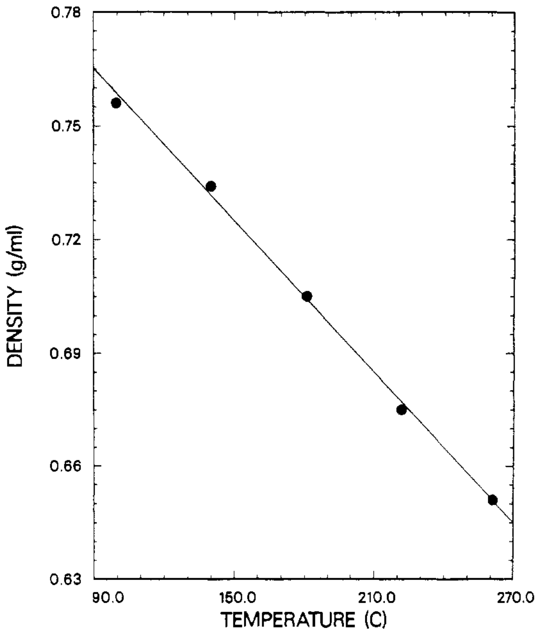

Figure 3. Density of *n*-octacosane as a function of temperature at 1.38 MPa pressure.

The above relation is plotted in Figure 4 for *n*-octacosane. Viscosity values were calculated from a literature correlation based on actual screened data for *n*-octacosane (*14*). The quantities β' and V_η are analogous to β and V_D. V_η is the molar volume at which fluidity ($1/\eta$) goes to zero and is expected to be approximately equal to V_D, the RHS intercept for diffusion. For *n*-octacosane, V_η equals 506.6 mL/(g mol), which is in close agreement with the reported V_D values for both gaseous and alkane solutes. This agreement gives further evidence that the RHS theory is applicable to alkane molecules as large as *n*-octacosane, even though these molecules are not spherical.

Glossary

D_{12}	infinite dilution diffusion coefficient of solute 1 in solvent 2
K	effective Taylor dispersion coefficient

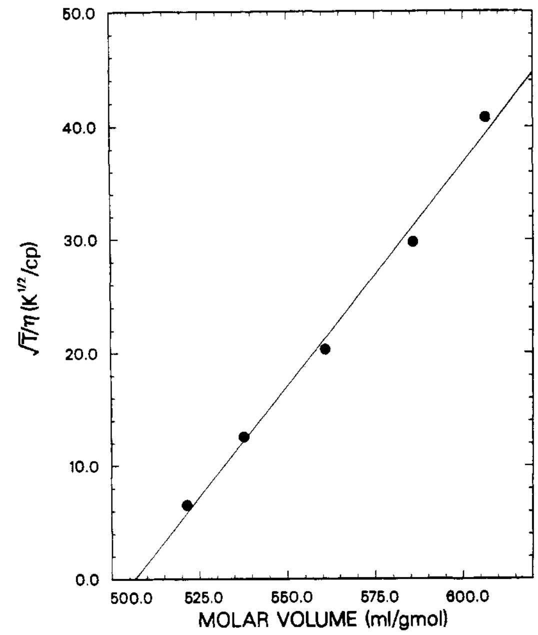

Figure 4. Dependence of $T^{1/2}/\eta$ on molar volume for *n*-octacosane.

L	dispersion tube length
$\dot{m}$	mass flow rate
M	mass of injected solute
r	dispersion tube radius
T	absolute temperature
$\bar{t}$	peak retention time
$\bar{u}$	average velocity of solvent
V	molar volume of solvent
V_t	total volume of dispersion tube
ρ	density
σ_1	solute hard-core diameter
η	viscosity

Registry No. H_2, 1333-74-0; CO, 630-08-0; CO_2, 124-38-9; n-C_8H_{18}, 111-65-9; n-$C_{12}H_{26}$, 112-40-3; n-$C_{16}H_{34}$, 544-76-3; n-$C_{28}H_{58}$, 630-02-4.

Literature Cited

(1) Matthews, M. A.; Rodden, J. B.; Akgerman, A. *J. Chem. Eng. Data* **1987**, *32*, 317.
(2) Matthews, M. A.; Rodden, J. B.; Akgerman, A. *J. Chem. Eng. Data* **1987**, *32*, 319.
(3) Rodden, J. B.; Erkey, C.; Akgerman, A. *J. Chem. Eng. Data* **1988**, *33*, 344.
(4) Taylor, G. *Proc. R. Soc.* **1953**, *A219*, 186.
(5) Hunt, B. *Int. J. Heat Mass Trans.* **1976**, *20*, 393.
(6) Matthews, M. A.; Akgerman, A. *AIChE J.* **1987**, *33*, 881.
(7) Alizadeh, A.; Nieto de Castro, C. A.; Wakeham, W. A. *Int. J. Thermophys.* **1980**, *1*, 243.
(8) Alizadeh, A.; Wakeham, W. A. *Int. J. Thermophys.* **1982**, *3*, 307.
(9) Matthews, M. A.; Akgerman, A. *Int. J. Thermophys.* **1987**, *8*, 363.
(10) Matthews, M. A.; Akgerman, A. *J. Chem. Phys.* **1987**, *87*, 2285.
(11) Dymond, J. H. *J. Chem. Phys.* **1974**, *60*, 969.
(12) Chen, S. H.; Davis, H. T.; Evans, D. F. *J. Chem. Phys.* **1982**, *77*, 2540.
(13) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.
(14) Engineering Sciences Data Item No. 79027; Eng. Sci. Data Unit Ltd., London, 1979.

Received for review October 8, 1987. Revised February 16, 1988. Accepted May 9, 1988. This work was partially supported by the U.S. Department of Energy under Contract DE-AC22-84PC 70032.

Measurements of VLE, v^E, and h^E for Binary Mixtures of 1-Chlorohexane with Three *n*-Alkylbenzenes: Toluene, Ethylbenzene, *n*-Propylbenzene

Hanns-Ingolf Paul,[†] **Josef Krug,**[‡] **and Helmut Knapp***

Institute of Thermodynamics and Plant Design, Technical University, Berlin (West), FRG

Results of a series of experimental investigations of three binary mixtures of 1-chlorohexane with toluene, ethylbenzene, and *n*-propylbenzene are reported: T, p, x, y data of vapor–liquid equilibria (VLE), h^E, T, x data of calorimetric measurements, and v, T, x data of volumetric measurements. VLE data are checked for thermodynamic consistency by performing the test of Fredenslund and used to fit parameters of several g^E models. UNIFAC predictions and experimental data are compared. h^E and v^E data were correlated with Redlich–Kister polynomials.

Introduction

Reliable experimental information, i.e., VLE, h^E, and v^E, is helpful to study and to understand the conditions in liquid mixtures. In addition, experimental data, particularly VLE, are of great importance for the thermodynamic design of industrial separation processes.

In continuation of the extensive experimental studies at our laboratories and in cooperation with the TOM project (*2*, *3*), mixtures of *n*-alkanes with chloroalkylbenzenes were investigated. A summary of the experimental program is given in Table I. The experimental data provide a basis to study heteroproximity effects of the functional groups of a molecule. For practical purposes experimental data can be represented by appropriate equations, i.e., VLE data by well-approved semitheoretical g^E models and h^E and v^E data with highly flexible Redlich–Kister polynomials.

Experimental Section

Apparatus and Instrumentation. (1) Vapor pressures of pure components and of mixtures were measured in a dynamic still, type Stage, with recycling liquid and vapor fractions. The temperature was determined with a platinum resistance thermometer, Pt 25 (Rosemount 162 CE), in combination with a standard resistor (25 Ω) and a six-digit voltmeter (Prema 6040,

---

* Author to whom correspondence should be addressed.
[†] Now with BASF AG, Ludwigshafen, FRG.
[‡] Now with Bayer AG, Leverkusen, FRG.

0021-9568/88/1733-0453$01.50/0 © 1988 American Chemical Society