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## Diffusion Coefficients in Binary Liquid *n*-Alkane Systems

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**Binary diffusion coefficients were measured for four *n*-alkane systems, *n*-heptane-*n*-decane, *n*-heptane-*n*-dodecane, *n*-heptane-*n*-tetradecane, and *n*-octane-*n*-tetradecane over the full range of concentrations at 25°C. The diaphragm diffusion cell method was employed. Experimental data obtained followed the relationship shown by Shieh and Lyons. Equations were developed for correlating the limiting diffusion coefficients in binary *n*-alkane systems in terms of the number of carbon atoms in the system and values of the self-diffusion coefficients of the solvent.**

Diffusion coefficients in hydrocarbon systems are fundamental data in a number of engineering applications and in the study of mass transfer. In the recovery of oil from a petroleum reservoir utilizing a bank of solvent followed by dry gas, diffusion coefficients of the components involved, oil (liquid hydrocarbons), solvent (mixture of methane and propane), and dry gas (mainly methane), are some of the data required for estimating the amount of solvent to be injected to displace the oil under miscible conditions to achieve high recovery.

The objective of this study was to supplement the meager data available for binary diffusion coefficients in liquid *n*-alkanes. A number of empirical and semiempirical equations, each subject to some limitations, have been proposed for estimating diffusion coefficients. For *n*-alkanes the application of these equations is not satisfactory. Lulis and Ratcliff (9) have indicated that large errors may be expected when the equation they developed was applied to the diffusion of long straight-chain solutes in a similar type of solvents of greater chain length.

Leffler and Cullinan (8) found that their modified Vignes equation correlates experimental data of a large number of substances well, except for liquid *n*-alkanes. From consideration of activation energy, van Geet and Adamson (27) have pointed out that long straight-chain hydrocarbons may flow and diffuse in segments of a few

carbons. Hence, the number of carbon atoms involved in the elementary displacement would be the same for both components in the binary system. A separate study of diffusion in liquid *n*-alkanes has been conducted by Shieh and Lyons (16). They showed that the diffusion coefficient is a function of the density of the mixture and is related to the average number of carbon atoms in the system. However, more data are needed to further confirm these relationships and to establish the accuracy of these correlations.

### Experimental

**Diaphragm cell method.** The diaphragm cell method was developed based on the pseudo-steady state diffusion through a porous diaphragm. A nearly steady concentration gradient is established across the porous diaphragm separating two miscible solutions of different composition. After a known period of diffusion, the concentrations of the two solutions are analyzed. The diffusion coefficient is calculated from the following equation:

$$\bar{D}_{12} = \frac{1}{\beta t} \ln \frac{c_1 - c_2}{c_3 - c_4} \quad (1)$$

Derivations of Equation 1 can be found in a number of publications such as van Geet and Adamson (21). The diffusion coefficient obtained from the diaphragm cell measurements is actually a double average over concentration and time termed the integral diffusion coefficient

$$\bar{D} = \frac{1}{t} \int dt \frac{1}{c_1 - c_2} \int_{c_2}^{c_1} D dc \quad (2)$$

Gordon (4) has shown that Equation 2 can be treated without any serious error as the ordinary integral diffusion coefficient taken over the initial concentration range.

$$\bar{D} = \frac{1}{c_1 - c_2} \int_{c_2}^{c_1} D dc \quad (3)$$

To establish a concentration gradient in the diaphragm and to attain steady state conditions, a period of prediffu-

sion is allowed, and the length of time is estimated from the expression suggested by Tham et al. (19):

$$\frac{Dt_p}{L^2} = 1.2 \quad (4)$$

The optimum diffusion time for an experiment found by Robinson et al. (14) is

$$t_{op} = 1.2/\beta D \quad (5)$$

The same equation was derived by van Geet and Adamson (21).

**Apparatus and procedure.** The diaphragm cell method has gained wide acceptance as an experimental technique for measurement of diffusion coefficients, because it requires a simple apparatus and gives high accuracy. Since its original introduction in 1928 by Northrup and Anson (11), the diaphragm cell method has been considerably refined and improved upon by later workers such as McBain and Liu (10), Hartley and Runnicles (6), Stokes (18), and Robinson et al. (14). A detailed description of the diaphragm cell method is given by Gubbins and Bhatia (5).

The diaphragm cell used in this experiment is similar to the one described by Gubbins and Bhatia which is a modified Stokes' cell. The cell consists of two compartments separated by a horizontal porous diaphragm. The diaphragm is a fritted glass disc, 30 mm in diameter and 2 mm thick and has pore size in the range of 5–10  $\mu$ . The volumes of the compartments are 30 cm<sup>3</sup>. Stoppers were machined from Teflon rods. The top stopper has a small hole for expelling excess liquid when it is inserted into the cell. Each compartment contains a stirrer consisting of a thin iron wire encased in a plastic tubing. The weights of the stirrers were adjusted so that the one in the lower compartment floats and the other sinks (Figure 1). The stirrers are rotated at a constant speed by means of a U-shaped magnet driven by a synchronous electric motor. A rotating speed of 60 rpm was sufficient to mix the content in each compartment. The cell is held in a constant temperature water bath whose temperature is maintained stable to better than 0.01°C.

To fill the cell for a diffusion experiment, the diffusion cell is mounted invertedly in the filling apparatus (Figure 2). The denser solution which has been deaerated in the round flask is drawn by suction to fill the entire cell. With temporary stoppers the cell is removed from the filling apparatus. The temporary stopper to compartment I is replaced with the bottom Teflon stopper. The diffusion cell is then held in the constant temperature water bath the right end up, compartment I being the lower section.

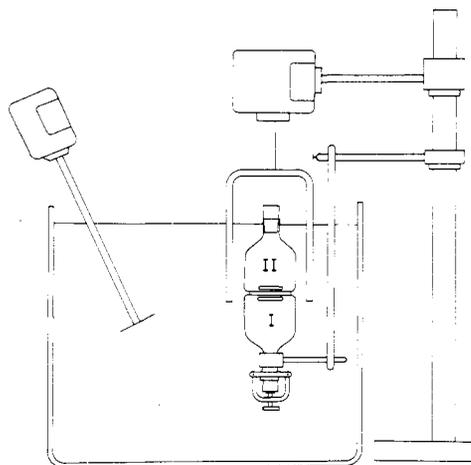


Figure 1. Experimental apparatus

After thermal equilibrium has been attained, compartment II is emptied and refilled with the lighter test solution. After a period of prediffusion has elapsed, the solution in the upper compartment is again replaced with fresh solution to begin the actual diffusion experiment.

After a time period of diffusion, estimated from Equation 5 ranging from three to six days, the experiment is terminated by withdrawing the solution from compartment II, about 10 cc being kept in a screw cap test tube for concentration analysis. The cell is removed from the water bath, and a sample is quickly collected from compartment I for concentration determination. Samples taken from compartments I and II and a sample saved from the solution used to fill compartment II at the beginning of the experiment are analyzed by the use of a differential refractometer. The initial concentration in the lower compartment is calculated from the material balance by the following equation:

$$c_1 = c_3 + (c_4 - c_2) \left[ \frac{V_{II} + \frac{V'}{2}}{V_I + \frac{V'}{2}} \right] \quad (6)$$

The diffusion cells were calibrated by use of the system of 0.1N potassium chloride solution diffusing into water at 25°C. The cell constants were calculated with diffusion data listed by Stokes (18).

**Analysis.** Concentrations of mixtures of hydrocarbons were measured by the use of a differential refractometer. The Rayleigh interference differential refractometer was developed based on the principle of light interference. Light passing through a medium experiences a phase retardation related to the pathlength and refractive index of the medium. Two beams of light, derived from the same small source and each passing through a different liquid, are arranged to produce an interference pattern, the position of which is related to the difference in phase retardation between the two beams. In this instrument a second interference pattern is formed under conditions where there is no difference in phase retardation between the two interference beams. The relative position of the two interference patterns is then a measure of the refractive index difference between the two solutions.

This type of instrument is extremely sensitive and is capable of measuring a difference of only 0.000002 in the refractive index between two liquids. Calibration curves were established between refractometer readings and solution concentrations for every 10 vol % from 0 to 100 taking 0, 10, 20, and so forth as reference concentrations. Concentration of a sample was determined by

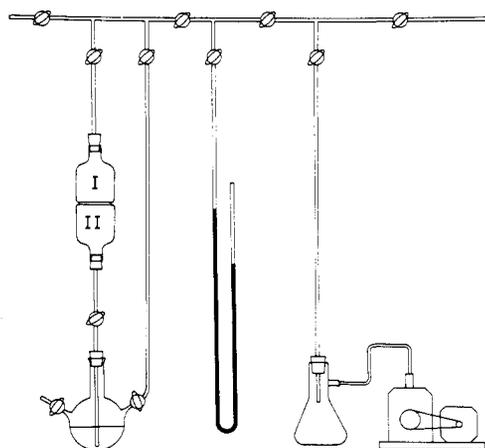


Figure 2. Filling apparatus

comparing it with one of the reference solutions within the 10% range of the sample.

Concentrations of the potassium chloride solutions from all calibrations were determined by the mercurimetric titration method. The chloride ions were titrated with mercuric nitrate standard. A mixed indicator of diphenylcarbazone and bromophenol blue was used. It was yellow in color in the presence of chloride ions. The end point of the titration was the formation of the blue-violet mercury diphenylcarbazone complex.

**Chemicals and materials.** The paraffin hydrocarbons were purchased from Phillips Petroleum Co. Pure grade hydrocarbons were used in all diffusion experiments without further purifications. Mixtures of hydrocarbons were prepared in volumetric flasks and stored in Teflon-lined screw cap bottles. Potassium chloride and mercuric nitrate were all reagent grade chemicals. Distilled water was used in all solution preparations and in volume calibrations of the diffusion cell.

**Error analysis.** The effect of errors in analyzing the concentrations on the calculated value of  $\bar{D}$  is given as follows. The diffusion equation is

$$\bar{D} = \frac{1}{\beta t} \ln \frac{c_1 - c_2}{c_3 - c_4} \quad (7)$$

where

$$c_1 = c_3 + (c_4 - c_2) \frac{V_{II} + \frac{V'}{2}}{V_I + \frac{V'}{2}} \quad (8)$$

For simplification it is assumed that

$$V_I = V_{II} \quad (9)$$

then

$$c_1 = c_3 + c_4 - c_2 \quad (10)$$

and

$$\bar{D} = \frac{1}{\beta t} \ln \frac{c_3 + c_4 - 2c_2}{c_3 - c_4} \quad (11)$$

For a given experimental diffusion time

$$\bar{D} = \bar{D}(c_2, c_3, \text{ and } c_4) \quad (12)$$

$$d\bar{D} = \frac{\partial \bar{D}}{\partial c_2} dc_2 + \frac{\partial \bar{D}}{\partial c_3} dc_3 + \frac{\partial \bar{D}}{\partial c_4} dc_4 \quad (13)$$

or

$$d\bar{D} = \frac{1}{\beta t} \frac{2}{(c_3 + c_4 - 2c_2)(c_3 - c_4)} [(c_4 - c_3)dc_2 + (c_2 - c_4)dc_3 + (c_3 - c_2)dc_4] \quad (14)$$

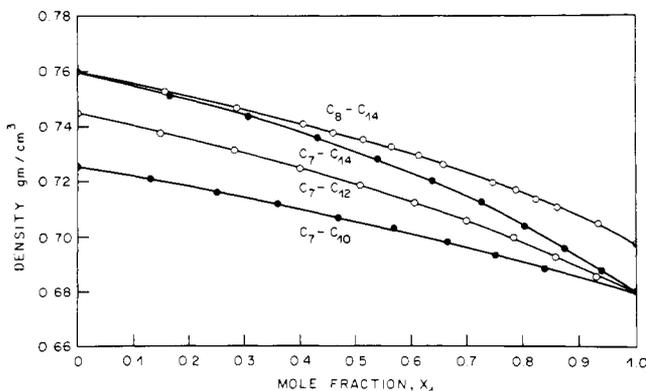


Figure 3. Density in binary *n*-alkane systems at 25°C

and

$$\frac{d\bar{D}}{\bar{D}} = 2 \frac{\frac{dc_2}{c_2}(c_4 - c_3)c_2 + \frac{dc_3}{c_3}(c_2 - c_4)c_3 + \frac{dc_4}{c_4}(c_3 - c_2)c_4}{(c_3 - c_4)(c_3 + c_4 - 2c_2) \ln \left[ \frac{c_3 + c_4 - 2c_2}{c_3 - c_4} \right]} \quad (15)$$

The relative errors in concentration may be assumed to be roughly equal for a set of measurements

$$\frac{dc_2}{c_2} \approx \frac{dc_3}{c_3} \approx \frac{dc_4}{c_4} = \frac{dc}{c_{ave}} \quad (16)$$

Since the experimental conditions are so that  $c_3 > c_4 > c_2$ , the errors will accumulate if the errors in  $c_2$  and  $c_3$  both have signs opposite to that of the error in  $c_4$ . The maximum error in  $\bar{D}$  is

$$\frac{d\bar{D}}{\bar{D}} = 4 \frac{dc}{c_{ave}} \frac{c_4(c_3 - c_2)}{(c_3 - c_4)(c_3 + c_4 - 2c_2) \ln \left[ \frac{c_3 + c_4 - 2c_2}{c_3 - c_4} \right]} \quad (17)$$

The sensitivity of the Rayleigh interference differential refractometer is so that the absolute value of  $dc$  is approximately equal to 0.01 in concentration of volume percent. The relative error in concentration  $dc/c_{ave}$  is calculated to be 0.20 and 0.01% at 5 and 95 vol % concentration level, respectively. The maximum relative error in  $d\bar{D}/\bar{D}$  is then estimated to be less than 1%.

## Results and Discussion

Experimental results of density are shown in Figure 3. Experimental data of diffusion coefficients are presented in Table I. Values reported are the integral diffusion coefficients. It was assumed that the integral diffusion coefficient equals the differential diffusion coefficient at the average concentration in view of the near linear behavior of the experimental diffusion coefficient with volume fraction over a short range of concentration and the small concentration differences between the two compartments used in the experiments. Mutual diffusion coefficients at 50 mol % of several *n*-alkanes were previously measured by Trevoy and Drickamer (20). Values of  $1.57 \times 10^{-5}$  cm<sup>2</sup>/sec and  $1.28 \times 10^{-5}$  cm<sup>2</sup>/sec were obtained by Trevoy and Drickamer for the systems *n*-heptane-*n*-dodecane and *n*-heptane-*n*-tetradecane, respectively. These values are compared to those obtained in the present measurement of  $1.59 \times 10^{-5}$  cm<sup>2</sup>/sec and  $1.35 \times 10^{-5}$  cm<sup>2</sup>/sec with percentage differences of 1.3 and 5.2.

Shieh and Lyons (16) have shown that in binary *n*-alkane mixtures  $D_{12}/\alpha_{12}$  is a linear function of the mixture density,  $\rho$ . All these lines extrapolate to zero mobility at  $\rho = 0.84$ , and the slope of these lines is a linear function of  $\sqrt{n_1 n_2}$ . These linear relationships are shown along with the experimental data obtained for the four pairs of hydrocarbons in Figures 4 and 5. The differences between experimental and predicted values were 7.77, 1.82, 3.95, and 3.94% for *n*-heptane-*n*-decane, *n*-heptane-*n*-dodecane, *n*-heptane-*n*-tetradecane, and *n*-octane-*n*-tetradecane, respectively. The average for the four systems is 4.35%.

Values of the nonideality correction factor were calculated with the empirical equations obtained by van Geet (22),

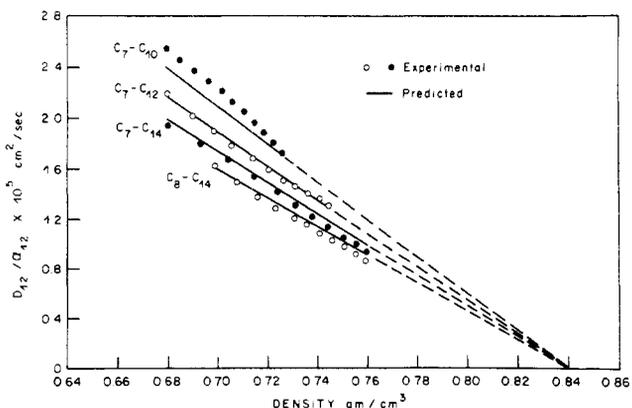
$$\alpha_{12} = 1 + \frac{\partial \ln f_1}{\partial \ln x_1} = 1 - 2ax_1x_2 \quad (18)$$

$$a = b(n_1 - n_2)^2 \quad (19)$$

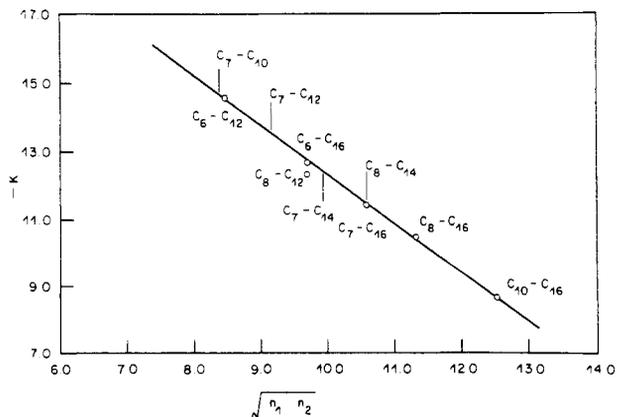
**Table I. Experimental Diffusion Coefficients at 25°C**

Mole fraction of <i>n</i> -heptane	$D_{12}$ , $10^{-5}$ cm <sup>2</sup> /sec
<b><i>n</i>-Heptane-<i>n</i>-decane</b>	
0.0395	1.748
0.0654	1.836
0.0654	1.829
0.1286	1.904
0.1899	1.859
0.2496	1.968
0.3069	2.027
0.3628	2.082
0.4170	2.119
0.4696	2.153
0.5208	2.148
0.5705	2.264
0.6188	2.230
0.6658	2.273
0.7115	2.291
0.7561	2.376
0.7994	2.438
0.8827	2.452
0.9228	2.507
0.9618	2.525
0.9618	2.535
<b><i>n</i>-Heptane-<i>n</i>-dodecane</b>	
0.0772	1.352
0.0772	1.367
0.2146	1.432
0.2146	1.406
0.2158	1.423
0.3390	1.475
0.3400	1.460
0.3407	1.507
0.3992	1.540
0.4526	1.525
0.5563	1.692
0.5575	1.660
0.6520	1.705
0.6993	1.820
0.7416	1.815
0.8225	1.975
0.8231	1.933
0.8971	2.060
0.9665	2.140
0.9668	2.148
<b><i>n</i>-Heptane-<i>n</i>-tetradecane</b>	
0.0526	0.974
0.0868	0.976
0.0868	0.969

Mole fraction of <i>n</i> -heptane	$D_{12}$ , $10^{-5}$ cm <sup>2</sup> /sec
<b><i>n</i>-Heptane-<i>n</i>-tetradecane</b>	
0.1652	1.040
0.2368	1.138
0.2375	1.089
0.3047	1.152
0.3698	1.232
0.3698	1.223
0.4863	1.339
0.5397	1.416
0.5903	1.464
0.6376	1.520
0.6821	1.558
0.7254	1.628
0.7245	1.596
0.7662	1.625
0.8048	1.711
0.8407	1.736
0.8754	1.797
0.9090	1.839
0.9501	1.871
0.9718	1.888
<b><i>n</i>-Octane-<i>n</i>-tetradecane</b>	
0.0440	0.883
0.0775	0.885
0.0775	0.913
0.1507	0.974
0.2198	1.022
0.2198	1.029
0.2853	1.053
0.3474	1.067
0.4063	1.119
0.4624	1.122
0.5157	1.115
0.5665	1.210
0.6149	1.257
0.6613	1.260
0.7055	1.320
0.7478	1.331
0.7884	1.371
0.8273	1.402
0.8646	1.495
0.8646	1.509
0.9005	1.532
0.9349	1.568
0.9681	1.542
0.9810	1.626



**Figure 4.** Linear relationship between  $D_{12}/\alpha_{12}$  and density in binary *n*-alkane systems at 25°C



**Figure 5.** Slope of  $D_{12}$  and  $\rho$  relationship in binary *n*-alkane systems at 25°C

where  $b$  has been found from several binary  $n$ -alkanes to be constant and has a value of  $-0.00111$ .  $\alpha_{12}$  calculated from Equations 18 and 19 for the four binary systems is shown in Figure 6.

From available data the limiting diffusion coefficient of a solute is a linear function of the logarithm of the number of carbon atoms in the solute for a particular solvent, as shown in Figure 7. Self-diffusion coefficients of the liquids are also included. The slope of these lines, a different one for each solvent, is related to the number of carbon atoms in the solvent; this relationship is shown in

Figure 8. An analytical expression was established from these two relationships in terms of the number of carbon atoms in the solute and in the solvent and value of the self-diffusion coefficient of the solvent as follows:

$$D_{12}^{\circ} = D_{22} + \frac{1}{0.1964 - 0.06785 n_2} \times 10^{-5} \log \frac{n_1}{n_2} \quad (20)$$

Self-diffusion coefficients in  $n$ -alkanes have been measured for a large number of liquids at  $25^{\circ}\text{C}$ . These values have been summarized by van Geet (22). In Table II experimental limiting diffusion coefficients and data sources

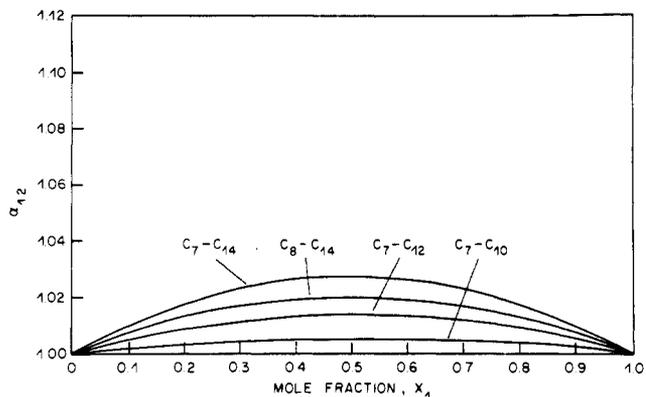


Figure 6. Nonideality correction factor in binary  $n$ -alkane systems at  $25^{\circ}\text{C}$

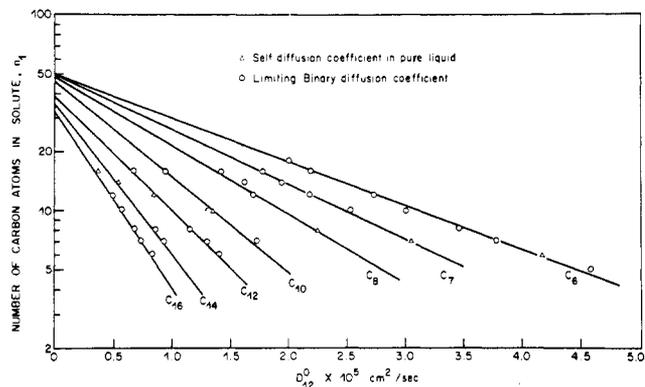


Figure 7. Limiting diffusion coefficient in  $n$ -alkane systems at  $25^{\circ}\text{C}$

Table II. Comparison of Methods of Estimating Limiting Diffusion Coefficients

Solute	Solvent	Exptl, $D_{12}^{\circ}$ $10^{-5}$ $\text{cm}^2/\text{sec}$	Percentage difference <sup>a</sup>							Equation 20	Data ref
			Wilke and Chang (23)	Schiebel (15)	Othmer and Thakar (12)	Sitara- man et al. (17)	Luis and Ratcliff (9)	Reddy and Dorais- wamy (13)			
C <sub>5</sub>	C <sub>6</sub>	4.59	14.56	0.23	36.14	29.52	4.54	18.70	3.05	3	
C <sub>7</sub>	C <sub>6</sub>	3.78	14.29	6.70	35.94	23.65	4.63	13.36	0.80	3	
C <sub>8</sub>	C <sub>6</sub>	3.47	13.53	8.31	35.37	20.56	3.64	9.56	0.30	3	
C <sub>10</sub>	C <sub>6</sub>	3.02	12.68	10.94	34.73	15.37	2.08	3.27	0.00	3	
C <sub>12</sub>	C <sub>6</sub>	2.74	13.45	14.06	35.31	12.28	2.10	0.51	3.65	3	
C <sub>16</sub>	C <sub>6</sub>	2.21	8.51	12.04	31.62	0.28	5.55	14.51	7.24	3	
C <sub>18</sub>	C <sub>6</sub>	2.01	6.99	11.42	30.48	4.56	8.40	20.05	9.95	3	
C <sub>10</sub>	C <sub>7</sub>	2.54	15.76	14.98	40.78	18.60	9.33	11.13	2.50	This work	
C <sub>12</sub>	C <sub>7</sub>	2.19	12.13	14.01	38.23	11.21	4.86	2.83	0.50	This work	
C <sub>14</sub>	C <sub>7</sub>	1.94	9.36	13.26	36.29	4.82	1.12	4.33	0.60	This work	
C <sub>16</sub>	C <sub>7</sub>	1.78	8.66	14.02	35.79	0.74	0.48	8.86	2.20	2	
C <sub>12</sub>	C <sub>8</sub>	1.71	30.87	10.32	38.23	6.64	3.37	1.95	2.88	21	
C <sub>14</sub>	C <sub>8</sub>	1.63	11.31	16.18	40.79	6.99	6.84	2.17	3.70	This work	
C <sub>16</sub>	C <sub>8</sub>	1.43	6.52	13.34	37.60	1.43	1.16	6.77	1.90	16	
C <sub>7</sub>	C <sub>10</sub>	1.73	16.62	9.26	48.72	25.96	16.83	28.40	5.05	This work	
C <sub>16</sub>	C <sub>10</sub>	0.96	7.06	15.50	42.84	0.97	7.69	1.20	6.60	16	
C <sub>6</sub>	C <sub>12</sub>	1.42	23.05	11.94	55.52	33.84	24.87	49.09	5.50	1	
C <sub>7</sub>	C <sub>12</sub>	1.30	24.11	16.84	56.14	32.38	26.73	47.78	6.30	This work	
C <sub>8</sub>	C <sub>12</sub>	1.15	20.55	16.03	54.08	26.99	23.88	33.45	2.20	21	
C <sub>16</sub>	C <sub>12</sub>	0.67	8.93	18.54	47.36	0.72	13.76	8.73	5.20	7	
C <sub>7</sub>	C <sub>14</sub>	0.93	25.24	17.38	58.83	33.10	29.57	51.07	3.61	This work	
C <sub>8</sub>	C <sub>14</sub>	0.85	24.24	19.41	58.28	30.08	29.34	48.70	4.30	This work	
C <sub>6</sub>	C <sub>16</sub>	0.85	33.37	22.16	64.69	42.25	37.45	59.85	0.0	1	
C <sub>7</sub>	C <sub>16</sub>	0.74	21.56	23.69	63.73	38.53	36.75	57.12	4.50	2	
C <sub>8</sub>	C <sub>16</sub>	0.68	31.02	26.06	63.44	36.10	37.00	55.28	4.10	16	
C <sub>10</sub>	C <sub>16</sub>	0.57	27.67	27.22	61.66	29.32	34.98	50.34	5.00	16	
C <sub>12</sub>	C <sub>16</sub>	0.49	24.34	27.48	59.90	22.68	32.60	35.93	1.90	7	
Average			17.14	15.23	45.95	18.50	14.93	23.04	3.46		

<sup>a</sup> Percentage difference =  $\frac{\text{Experimental} - \text{Calculated}}{\text{Experimental}} \times 100$ .

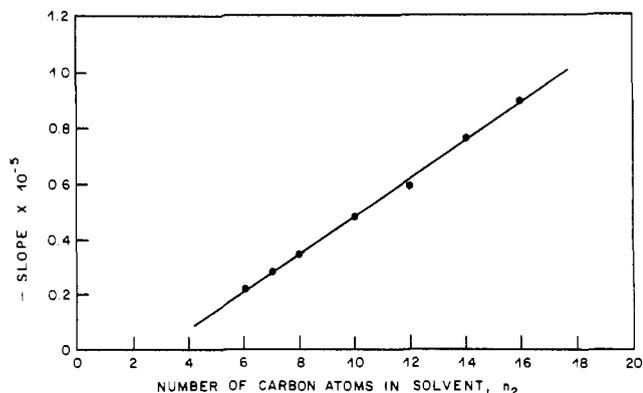


Figure 8. Slope of  $\log n_1$  and  $D_{12}^0$  relationship in  $n$ -alkane systems at  $25^\circ\text{C}$

are listed together with percentage differences between experimental values and values calculated from Equation 20 and six other methods.

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#### Nomenclature

- $a$  = constant in Equation 18  
 $b$  = constant in Equation 19  
 $c$  = concentration  
 $c_1, c_2$  = initial concentration in lower and upper compartment, respectively  
 $c_3, c_4$  = final concentration in lower and upper compartment, respectively  
 $D$  = diffusion coefficient  
 $D_{12}$  = differential diffusion coefficient  
 $\bar{D}_{12}$  = integral diffusion coefficient  
 $D_{12}^0$  = limiting diffusion coefficient  
 $D_{22}$  = self-diffusion coefficient  
 $f_i$  = activity coefficient of component  $i$   
 $L$  = effective pore length

- $n$  = number of carbon atoms in the component  
 $t$  = diffusion time  
 $t_p$  = pre-diffusion time  
 $t_{op}$  = optimum diffusion time  
 $V_I$  = volume of lower compartment  
 $V_{II}$  = volume of upper compartment  
 $V'$  = volume in porous diaphragm  
 $x_i$  = mole fraction of component  $i$

#### Greek Letters

- $\alpha_{12}$  = nonideality correction factor  
 $\beta$  = diffusion cell constant  
 $\rho$  = density

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