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Mutual Diffusivity, Thermal Conductivity, and Heat of Transport in Binary Liquid Mixtures of Alkanes in Chloroform

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Thermal conductivities, mutual diffusivities, and heats of transport have been measured as a function of composition in six binary systems of six- to eight-carbon alkanes in chloroform at 30 °C and ambient pressure. The measurement methods and the accuracy of the measured values are (a) Taylor dispersion method for diffusivities with 2% accuracy, (b) transient hot-wire method for thermal conductivities with 2% accuracy, and (c) Dufour effect method for heats of transport with about 4% accuracy. Results indicate that increased chain length decreases the diffusivity and heat of transport but has only a small increasing effect on thermal conductivity. Higher branching of the alkane chain tends to increase the diffusivity, slightly lower the heat of transport, and significantly lower the thermal conductivity.

Introduction

In a binary system, the heat and mass flux equations may be written as

$$-\mathbf{q} = k\nabla T + \rho D Q_1^* \nabla w_1 \qquad (1)$$

$$-\mathbf{j}_1 = \rho D_T \nabla \ln T + \rho D \nabla w_1 \qquad (2)$$

where $\mathbf{q}$ is heat flux, $\mathbf{j}_1$ is mass flux relative to the center of mass, k is thermal conductivity, ρ is density, D is mutual diffusivity, Q_1^* is heat of transport, D_T is the thermal diffusion coefficient, T is temperature, and w_1 is mass fraction of component 1. Onsager (*1*) derived a relationship between the cross transport coefficients D_T and Q_1^* which has been verified experimentally by Rowley and Horne (*2*). Thus, only three independent transport coefficients need to be measured in a binary nonelectrolyte mixture.

Because transport properties are often studied separately in different laboratories, there are few binary systems for which all three coefficients have been measured. Often engineering calculations require combinations of these coefficients in dimensionless groups, making data gaps bothersome. More importantly, most theories of transport properties employ analogous mechanisms and/or the same parameters for more than one transport coefficient. For example, all three properties depend upon the intermolecular potential parameters in the Enskog theory. If the model is consistent, values of the potential parameters fitted from one property could be used to predict the others.

For these reasons, and others, measurement of a complete set of transport properties for binary mixtures is important. In this paper we report measurements made in this laboratory for the diffusion coefficient, thermal conductivity, and the heat of transport on binary mixtures of *n*-hexane, *n*-heptane, *n*-octane, 3-methylpentane, 2,3-dimethylpentane, and 2,2,4-trimethylpentane in chloroform. This not only provides new experimental data for the purposes described above, but also permits qualitative examination of chain length, solute, and branching effects upon these properties. Similar studies were reported recently for the same alkanes with carbon tetrachloride (*3*).

Diffusion Coefficient Measurements

Diffusion coefficients were measured in a Taylor dispersion apparatus. Construction of the apparatus was made in accordance with well-known design parameters (*4-7*) to allow determination of diffusivities with an accuracy of better than 2.0%. Details of the theory and analysis techniques of the Taylor dispersion method are readily available, and our apparatus (*3*) was similar in design to that used by others (*7-10*). Specific details unique to this apparatus are described below. The diffusion tube, manufactured by Accu Tube Corp., consisted of a 16.684-m length of 0.052 ± 0.001-in.-o.d. and 0.031 ± 0.001-in.-i.d., 316-stainless steel tubing, tempered in a 9-in. coil. This design is consistent with the criteria derived by Aris (*4*) and Nunge et al. (*11*) for a coiled-tube dispersion apparatus. The injection valve was a Valco 6-way, zero-dead-volume valve which allowed replacement of 85 μL of carrier fluid with an equal volume of test fluid. The tubing, valve body, and injection sample loop were immersed in a Neslab-Tamson (Model TCV 70) 70-L visibility bath maintained at 30.00 ± 0.01 °C for these experiments. Temperatures were monitored with an HP 2804A quartz thermometer.

An ISCO high-pressure pump was used to provide constant, pulse-free, laminar flow at a rate of 7.937 mL/h. The pump was calibrated with water by using a measuring buret at 22 °C. All of the measurements performed in this study were made at ambient pressure and low flow rates. Thus, the pump served

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Table I. Mutual Diffusion Coefficients as a Function of Mole Fraction for Binary Mixtures of Selected Alkanes in Chloroform at 30 °C and Ambient Pressure

solute (comp. 1)	x_1	D, 10^{-9} m^2/s	σ, 10^{-9} m^2/s
n-hexane	0.00413	2.43	0.02
	0.2034	2.42	0.04
	0.4028	2.59	0.11
	0.6000	3.18	0.04
	0.8009	3.75	0.01
	0.9894	4.44	0.07
n-heptane	0.00543	2.23	0.03
	0.2007	2.21	0.01
	0.4003	2.38	0.04
	0.6006	2.85	0.03
	0.7995	3.27	0.03
	0.9895	3.52	0.05
n-octane	0.00811	2.03	0.07
	0.2016	1.94	0.01
	0.4000	2.13	0.02
	0.6024	2.44	0.02
	0.7847	2.83	0.07
	0.9870	3.08	0.02
3-methylpentane	0.00814	2.28	0.01
	0.2019	2.35	0.02
	0.3998	2.53	0.006
	0.6000	3.00	0.14
	0.8009	3.60	0.02
	0.9906	4.53	0.05
2,3-dimethylpentane	0.00733	2.08	0.02
	0.1507	2.09	0.01
	0.3024	2.20	0.04
	0.5015	2.54	0.03
	0.7003	2.80	0.04
	0.9883	3.55	0.07
2,2,4-trimethylpentane	0.00641	1.95	0.06
	0.2009	1.92	0.01
	0.4005	2.03	0.05
	0.6000	2.29	0.05
	0.8012	2.67	0.03
	0.9866	3.06	0.08

only as a metering pump and no pressure effects nor other sample injection disturbances were seen by the detector. The detector was an HP 1037A differential refractometer equipped with thermostated prisms and 7-μL detector cells and is extremely sensitive to pressure effects and sampling problems. The instrument has a resolution and noise level of about 5 × 10^{-9} refractive index units. Both an analog and a digital output were available from the refractometer. The analog output was recorded on a strip chart recorder and was used to monitor the base line and qualitative aspects of the run. The digital output was transferred to a 16-bit, Model 7000 MDAS, data acquisition system, manufactured by Transera Corp. Data analysis was performed on an IBM PC. Rather than use a numerical calculation of the first and second moments of the output peak, the data were fitted to a normal distribution by using a nonlinear least-squares regression program. This procedure provides directly the first and second moments required to determine the mutual diffusion coefficient. Well-known corrections (*8*), although small, were made to the first and second moments for deviations due to the injected sample loop volume, the detector cell volume, and the connection tube in the detector.

Fluid mixtures were prepared volumetrically at known temperatures with reagent grade chemicals which had been processed through a Shodex filter/degasser. All runs in this work were made at 30 °C and ambient pressure. Results are shown in Table I. Also shown in this table are standard deviations determined from replicate experiments, generally four to six in number.

Thermal Conductivity Measurements

The thermal conductivity cell used in this work was a single-wire cell, machined from 316 stainless steel and sealed with Viton O-rings. The platinum measurement wire, 0.0005 in. in diameter, was obtained from American Fine Wire Co. with specifications of 99.95% purity and 266.8 (±5%) Ω/ft. A special cell insert, machined from thin-walled (0.04 in.), 0.50-in.-o.d., stainless-steel tubing, was employed to secure and align the wire in its axial position. This secured wire prohibits use of the cell over a wide range of temperatures because of the difference in thermal expansivity of the wire and the insert in which the wire is held. Nevertheless, the cell is assembled at 25 °C, and the wire should be slightly tauter at 30 °C. Calculations using the linear thermal expansivity of stainless steel and platinum indicate that the cell will expand 0.007 mm more than the measurement wire. This is less than the tolerance of the original wire positioning.

Details of the cell, its design, operation, and methods of data analysis have been previously published and discussed elsewhere (*3*, *12*–*14*). The cell was calibrated by using toluene as a reference. The value of 131.1 mW/(m·K) at 298.15 K was used as suggested by Nieto de Castro et al. (*15*). Ten additional pure liquid thermal conductivities were measured and values consistently agreed with published data to better than 2.0%. Those comparison results (*14*) indicate an accuracy of 2.0% for this instrument.

Temperatures were sampled at equal 2-ms intervals over a 800-ms period and the thermal conductivity obtained from a linear least-squares analysis of the slope of ΔT vs ln t. The first six data points ($\leq$12 ms) were never included in the regression because the finite heat capacity of the wire causes a noticeable error at short times. A wire heat capacity correction (*16*) was applied and found to be as large as 10% for times under 10 ms, but it rapidly dropped to insignificant levels by 40 ms. As mentioned, points corresponding to the first 12 ms were not included in the analysis and so the overall correction due to the finite heat capacity of the wire was small. Values of other standard corrections (*16*, *17*) for the transient hot-wire method were found to be insignificant because of the analysis procedure and experimental design. Axial heat conduction is often corrected for by using a two-wire apparatus such that the difference between the measurement and the shorter reference wires approximates an ideal infinite line source. In this apparatus, axial conduction corrections were found to be small and were further subtracted out in the analysis by imposing the same temperature rise for the runs as in the calibration. By running several trial drive voltages, the voltage required to induce the same temperature rise in each fluid was determined. Calibration of the cell against known thermal conductivities with this same voltage accomplishes the same effect as using a reference wire.

Mixtures were prepared volumetrically, mixed in closed flasks at room temperature, and immediately infused into the bottom of the cell until fluid appeared in the waste lines. Measurements were repeated between five and ten times from which a standard deviation was determined. Results of these measurements are shown in Table II. The pure-component values compared favorably with values reported in the literature; i.e., our value of 120.41 mW/(m·K) for pure *n*-heptane is 0.77% below the value of 121.34 mW/(m·K) obtained from the reference equation recommended by Nieto de Castro et al. (*15*) as a secondary standard (the suggested primary standard, toluene, was used in the equipment calibration).

Heats of Transport Measurements

Heats of transport were measured, as before, via the diffusion thermoeffect (*2*, *18*–*20*). The cell and experimental technique were the same as those used previously and are adequately described in previous publications (*3*, *19*, *20*). The method consists of creating a rough interface between two mixtures of the same two components at slightly different

Table II. Thermal Conductivities of Binary Mixtures as a Function of Mole Fraction of Selected Alkanes in Chloroform at 30 °C and Ambient Pressure

solute (comp. 1)	x_1	k, mW/(m·K)	σ, mW/(m·K)
n-hexane	0	110.79	0.07
	0.2572	104.28	0.10
	0.4801	104.90	0.12
	0.5808	105.51	0.02
	0.6751	107.25	0.07
	0.8471	112.06	0.05
	1	115.19	0.02
n-heptane	0	110.79	0.07
	0.2295	105.50	0.01
	0.4427	106.68	0.03
	0.5437	108.75	0.04
	0.6412	110.62	0.02
	0.8266	115.55	0.05
	1	120.41	0.10
n-octane	0	110.79	0.07
	0.2071	106.79	0.01
	0.4106	108.74	0.02
	0.5110	110.60	0.04
	0.6105	113.71	0.08
	0.8070	117.92	0.02
	1	123.81	0.02
3-methylpentane	0	110.79	0.07
	0.2572	99.66	0.06
	0.4801	97.83	0.05
	0.5808	99.40	0.05
	0.6751	100.36	0.02
	0.8471	104.01	0.02
	1	106.94	0.13
2,3-dimethylpentane	0	110.79	0.07
	0.2295	103.99	0.03
	0.4427	101.32	0.07
	0.5437	100.93	0.01
	0.6412	102.11	0.04
	0.8266	103.04	0.02
	1	105.26	0.05
2,2,4-trimethylpentane	0	110.79	0.07
	0.2071	102.77	0.06
	0.4106	97.27	0.06
	0.5110	96.21	0.06
	0.6105	95.67	0.05
	0.8070	95.69	0.10
	1	96.02	0.08

Table III. Heats of Transport of Chloroform in Binary Mixtures with Selected Alkanes at 30 °C and Ambient Pressure

solute (comp. 1)	x_1	$-Q_1^*$, kJ/kg	α
n-hexane	0.1334	60.0	2.10
	0.3725	49.5	2.29
	0.5808	46.3	2.40
	0.7637	40.0	2.26
	0.9257	34.1	2.13
n-heptane	0.1169	56.5	2.30
	0.3380	45.8	2.33
	0.5437	41.1	2.27
	0.7354	35.2	1.99
	0.9147	31.9	1.80
n-octane	0.1040	54.3	2.92[a]
	0.3093	45.0	2.82[a]
	0.5110	40.3	2.46[a]
	0.7092	34.2	1.91[a]
	0.9039	25.7	1.32[a]
3-methylpentane	0.1334	58.3	1.91[a]
	0.3725	48.5	2.26[a]
	0.5808	44.3	2.43[a]
	0.7637	40.1	2.40[a]
	0.9257	36.3	2.31[a]
2,3-dimethylpentane	0.1169	55.0	2.34[a]
	0.3380	45.0	2.44[a]
	0.5437	39.9	2.31[a]
	0.7354	33.5	1.92[a]
	0.9147	27.4	1.55[a]
2,2,4-trimethylpentane	0.1040	53.1	2.87[a]
	0.3093	42.6	2.69[a]
	0.5110	39.7	2.43[a]
	0.7092	31.0	1.73[a]
	0.9039	23.7	1.22[a]

[a] Thermodynamic factors determined from modified UNIFAC equation (ref *22*).

compositions. This is done in a thermostated boundary-sharpening cell similar in principle to Tselius diffusion cells. A syringe pump is used to withdraw solution from the interfacial plane of the cell at a rate faster than the diffusional dissipation while fresh mixtures of the upper and lower phases are infused at the top and bottom, respectively, of the cell. In this manner, the initially rough interface is sharpened and stabilized, creating an initial step function in composition until the pumps are turned off at the start of the experiment.

Platt et al. (*19*) have shown that accurate values of the heat of transport are obtained when measured temperature profiles are used to regress Q_1^* from a numerical solution of the diffusion thermoeffect boundary-value problem with isothermal initial conditions, and the same technique was used in this work. This is possible because a steady state is established between heat transported by the more rapid thermal conduction mode and that transported by the slower molecular diffusion mode. Simulation of the process shows that temperature profiles always relax back to the appropriate temperature profiles obtained from the numerical solution of the isothermal initial-condition problem, regardless of small initial temperature nonuniformities due to the boundary creation technique (*19*).

Temperatures were monitored in the cell using two (one above and one below the initial interface) 40 gauge copper–constantan thermocouples of bead diameter less than 0.2 mm, referenced to each other. The thermocouples were positioned equidistant from the plane of the initial interface formation by using micrometers located external to the cell and calibrated to zero at the interface. For all the runs reported in this work, the cell location of the temperature probes was 3.0 ± 0.1 mm from the interface, corresponding to reduced cell coordinates from bottom to top of $z = 0.4$ and $z = 0.6$. Experimental data were recorded from 900 to 7200 s and analyzed as described by Rowley and Hall (*20*).

A Monte Carlo error propagation and a worst-possible-case error analysis were performed using the uncertainties of the input thermophysical properties, the uncertainties in independent variables (time and position), and the uncertainty in the measured dependent variable, temperature difference. Thermal conductivities and mutual diffusivities reported herein were used in the data error analysis, and other properties were obtained from the literature. The worst-case analysis indicated the uncertainty in fitted Q_1^* values to be 10% and the Monte Carlo technique indicated an uncertainty of 4% at the 95% confidence level. Measured heats of transport are reported in Table III. Also shown in this table are calculated values of the thermal diffusion ratio, α, which were determined, using Onsager reciprocity, from the relationship

$$\alpha = \frac{D_T}{D x_1 x_2} = \frac{Q_1^* M_1^2 M_2^2}{[RTM^3(1 + \Gamma_{11})]} \qquad (3)$$

where M_i is molecular weight of component i, M is mean molecular weight of the mixture, R is the gas constant, and $\Gamma_{11} = (\partial \ln \gamma_1/\partial \ln x_1)_{T,P}$ is the so-called thermodynamic factor. This latter quantity was determined from the NRTL model for the activity coefficient, γ_1, using parameters compiled and reported by Gmehling and Onken (*21*).

Discussion

It is of interest to plot the diffusion coefficient as a function of composition. Figure 1 shows the mutual diffusivity data and

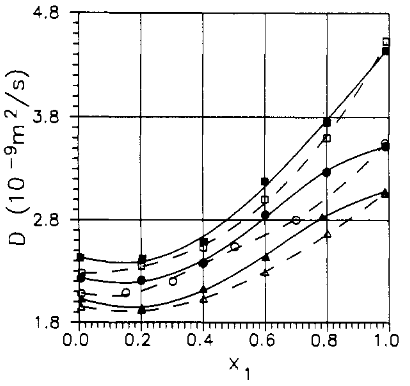

Figure 1. Experimental points and smoothed curves (solid lines for straight chain, dashed for branched alkane) for mutual diffusion coefficients of alkanes in chloforom at 30 °C and ambient pressure as a function of alkane mole fraction: (■) *n*-hexane; (●) *n*-heptane; (▲) *n*-octane; (□) 3-methylpentane; (○) 2,3-dimethylpentane; and (△) 2,2,4-trimethylpentane.

Table IV. Coefficients in the Smoothing Equation D (10^{-9} m^2/s) = $\sum_{i=0}^{4} A_i x_1^{\,i}$ for the Diffusion Coefficient

solute (comp. 1)	a_0	a_1	a_2	a_3	a_4
n-hexane	2.439	-1.024	3.993	-0.167	-0.771
n-heptane	2.237	-0.753	2.322	2.735	-3.032
n-octane	2.037	-1.092	3.212	0.647	-1.175
3-methylpentane	2.280	0.027	1.235	1.034	0
2,3-dimethylpentane	2.094	-1.193	8.456	-11.775	6.018
2,2,4-trimethylpentane	1.957	-0.707	2.530	-0.686	0

smoothed curves for the six alkanes with chloroform. The smoothing equation is a polynomial in mole fraction; it and its coefficients are contained in Table IV. As expected, the mutual diffusion coefficient decreases with increasing chain length for the straight-chain molecules. Likewise, the addition of more methyl groups onto the pentane chain decreases the mutual diffusivity. A comparison between pairs of alkanes having the same molecular weight shows that the more branched alkane has a smaller D in chloroform than the straight chain. This is consistent with the results found for these same solutes in carbon tetrachloride (*3*) although, from a hydrodynamic point of view, one would assume that the branched molecule, being more spherical, would have a higher mutual diffusivity. It has been observed experimentally (*23*), and several models and correlations for the mutual diffusion coefficient have made use of the fact, that the intradiffusion coefficient and the mutual diffusion coefficient are equal at infinite dilution. Thus, in the limit of pure alkane, the diffusion coefficients shown in Figure 1 become equal to the intradiffusion coefficient values. This plot shows that the intradiffusion of chloroform in the alkane solvent differs with molecular weight, but is apparently the same for both branched- and straight-chain molecules. On the other hand, the intradiffusion of alkane in nearly pure chloroform decreases regularly with the solute's molecular weight and its branched character.

The thermal conductivity results are shown in Figure 2. Mixtures of the straight-chain alkane with chloroform have similar behaviors with respect to composition with chain length apparently decreasing the thermal conductivity slightly. More effect is seen for branching than for chain length. This is probably due to the fact that internal vibration modes of the molecules are important in thermal conduction as well as translational modes.

The heat of transport of these alkanes in chloroform mixtures is illustrated in Figure 3. Although there is more scatter in these data than for diffusivities and thermal conductivities due to the larger experimental uncertainties, all of the systems show a rather small, but evidently real, S-shape behavior; the heats of transport are nearly linear except for this behavior between 0.2 and 0.5 mole fraction of alkane. Just as in the case of diffusion coefficients, heats of transport (or at least the absolute value) decrease with increasing molecular weight for the straight-chain alkanes. Branching also decreased the heat of transport except for large hexane mole fractions. The similarity of these trends with those observed for the diffusion coefficient is indicative of the similarity of the transport modes. It is very interesting to observe that, unlike the diffusion coefficients, the heats of transport may converge at a single value in the pure chloroform limit. Unfortunately, our Dufour effect experiments require significant composition and density differences between the two initial phases so that the pure-component limits could not be approached any closer. While an accurate extrapolation to $x_1 = 0$ is not possible from our data, the trends illustrated in Figure 3 tend to indicate a convergence of Q_1^* values toward a unique limit. Since for a binary system $Q_1^* = -Q_2^*$ (*20*), this limiting value can be taken as a pure-component value for chloroform. This suggests that it may be appropriate to compile pure-component values of heats of transport from which mixture predictions could be made. The possibilities of doing so certainly mandate additional studies to be performed closer to the pure component limits.

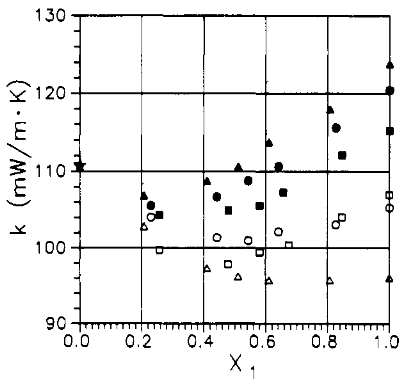

Figure 2. Thermal conductivity of alkanes + chloroform mixtures as a function of alkane mole fraction at 30 °C and ambient pressure. Points represent experimental values for (■) *n*-hexane; (●) *n*-heptane; (▲) *n*-octane; (□) 3-methylpentane; (○) 2,3-dimethylpentane; (△) 2,2,4-trimethylpentane; and (★) pure chloroform.

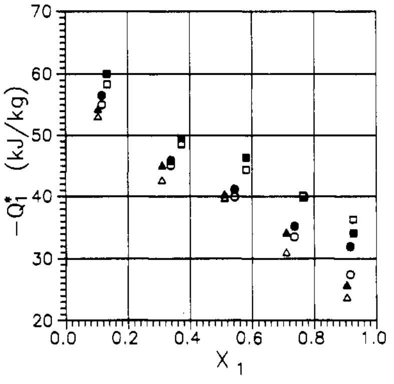

Figure 3. Heats of transport of alkanes in chloroform at 30 °C and ambient pressure as a function of alkane mole fraction: (■) *n*-hexane; (●) *n*-heptane; (▲) *n*-octane; (□) 3-methylpentane; (○) 2,3-dimethylpentane; and (△) 2,2,4-trimethylpentane.

Significantly, the above trends are all in agreement with those found for alkane + carbon tetrachloride mixtures (*3*). Even the convergence (or possibly slight cross over) behavior of the mutual diffusion coefficient in the pure alkane limit exhibited in Figure 1 was evident in the previous studies on carbon tetrachloride.

Having measured the complete set of heat-mass coefficients for these systems, we can check the assumption commonly made in hot-wire thermal conductivity measurements of mixtures that thermal diffusion effects are negligible. We do so by using the worst-case scenario developed by Rowley et al. (*3*) which assumes immediate establishment of the steady-state composition gradient in the fluid mixture. Their analysis indicates that the maximum fractional correction for thermal diffusion in binary liquids to the thermal conductivity obtained from the previous analysis is given by

$$\epsilon = \frac{k_\infty - k}{k} = \frac{\rho D Q_1^{*2} x_1 x_2 M_1^2 M_2^2}{M^3 R T^2 k (1 + \Gamma_{11})} \qquad (4)$$

where ϵ is a fractional correction between the effective and true thermal conductivities. Obviously the actual effect of thermal conduction will be much (probably orders of magnitude) less than that calculated in the worst-possible-case treatment, and ϵ obtained from eq 4 by using the values of the properties measured in this study is only on the order of −0.2%. While thermal diffusion may be a significant correction in steady-state thermal conductivity measurements, it apparently poses no problems for the transient measurements made on these systems.

Conclusions

Thermal conductivities, mutual diffusivities, and heats of transport have been measured as a function of composition in six binary systems of six- to eight-carbon alkanes in chloroform at 30 °C and ambient pressure. These results are an attempt to increase the data base for which all three transport properties are known and to provide qualitative information about structural effects upon transport properties. It was found that increasing chain length decreases the diffusivity and heat of transport but has only a small increasing effect on thermal conductivity. Higher branching of the alkane chain tends to increase the diffusivity, slightly lower the heat of transport, and significantly lower the thermal conductivity. It was found that mutual diffusion coefficients at the pure alkane limit (hence the intradiffusion coefficients of chloroform at infinite dilution) were independent of the branched nature of the molecule but decreased with molecular weight. Plots of the heat of transport as a function of composition seem to indicate that a single unique value may be obtained in the pure chloroform limit. This may be significant in developing ways of calculating mixture values from tabulated pure component values.

Glossary

D	mutual diffusion coefficient
D_T	thermal diffusion coefficient
$\mathbf{j}_i$	mass flux of component *i* relative to center of mass
k	thermal conductivity
k_∞	mixture thermal conductivity at steady-state thermal diffusion conditions
M	mixture mean molecular weight
M_i	molecular weight of component *i*
$\mathbf{q}$	heat flux
Q_i^*	heat of transport of component *i*
R	gas constant
T	temperature
w_i	mass fraction of component *i*
x_i	mole fraction of component *i*
z	reduced cell height

Greek Letters

α	thermal diffusion factor
γ_i	activity coefficient of component *i*
Γ_{11}	thermodynamic factor defined subsequent to eq 3
ϵ	fractional error in thermal conductivity due to thermal diffusion
ρ	density
σ	standard deviation

Registry No. Chloroform, 67-66-3; *n*-hexane, 110-54-3; *n*-heptane, 142-82-5; *n*-octane, 111-65-9; 3-methylpentane, 96-14-0; 2,3-dimethylpentane, 565-59-3; 2,2,4-trimethylpentane, 540-84-1.

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