ELSEVIER

Thermochimica Acta 265 (1995) 119–128

thermochimica acta

Thermal conductivity measurements of *cis*- and *trans*-decahydronaphthalene isomers using a steady-state coaxial cylinders method

D. Frezzotti *, G. Goffredi, E. Bencini

EniChem S.P.A., Mantua Research Centre, Via G. Taliercio 14, 46100 Mantova, Italy

Received 24 October 1994; accepted 1 April 1995

Abstract

The thermal conductivity coefficient λ has been measured in the temperature (T K) range 302.55–391.95 K for the cis and trans isomers of decahydronaphthalene and their commercial Fluka mixture (32.15% cis/67.85% trans)w/w. The experimental Setaram C80 D calorimetric device, equipped with a suitable vessel set-up, using the steady-state coaxial cylinders method, was calibrated and then tested on pure liquid toluene. The repeatability of the measurements is better than 1% [1], and the agreement with the values given in the literature enabled us to apply this method on the conformational cis-trans isomers of decahydronaphthalene. Thermal diffusion coefficients α_D were calculated for each isomer from the conductivity results and the difference in their thermal properties is explained in compliance with the theoretical approach to organic liquid conductivity. Finally, a comparison between our experimental results and the data correlated by the Robbins and Kingrea equation confirms that experimental determinations are essential for conformational isomer structures.

Keywords: Calorimetry; *cis-trans*-Decahydronaphthalene; Liquid thermal conductivity; Steady-state cylinders conductivity method; Thermal diffusivity; Toluene

List of symbols

T	temperature/K
T_b	normal boiling point temperature/K
T_c	critical temperature of liquid/K

---

* Corresponding author.

SSDI 0040-6031(95)02416-6

T_r	reduced temperature of liquids, $T_r = T/T_c$
C_p	molar heat capacity of liquid/cal mol^{-1} K^{-1}
ρ	density/mol cm^{-3}
ΔH_{vb}	molar heat of vaporization at the normal boiling point T_b
λ	thermal conductivity coefficient: rate of heat flow per unit area per unit temperature gradient/mW cm^{-1} K^{-1}
α_D	thermal diffusivity coefficient, $\lambda/(\rho\ C_p)$/cm^2 s^{-1}
$\alpha_{D_{ref}}$	thermal iffusivity coefficient, $\lambda/(\rho\ C_p)$/cm^2 s^{-1}, obtained from mixture literature data
λ_c	thermal conductivity/mW cm^{-1} K^{-1} for *cis*-decahydronaphthalene isomer
λ_t	thermal conductivity/mW cm^{-1} K^{-1} for *trans*-decahydronaphthalene isomer
λ_{mix}	thermal conductivity/mW cm^{-1} K^{-1} for *cis-trans*-decahydronaphthalene isomer mixture, Fluka (32.15/67.85) w/w% (purity > 98%)
λ_{tol}	thermal conductivity/mW cm^{-1} K^{-1} for pure toluene
λ_{est}	estimated liquid thermal conductivity coefficient based on the Robbins and Kingrea method/cal cm^{-1} s^{-1} K^{-1}
$\lambda_{lit(n)}$	literature thermal conductivity coefficient data for different methods
λ^*	thermal conductivity coefficient data for the mixture/mW cm^{-1} K^{-1} (32.15% cis/67.85% trans) (w/w) obtained by calculation from experimental cis-trans isomer data.

1. Introduction

Thermal conductivity is an important thermo-physical property, values of which are required in almost all heat transfer calculations especially when dealing with the convective heat transfer process of fluids and lubricants. Accurate measurements of this property are very difficult, principally because of natural convection caused by the imposed temperature difference, which makes the experimental values too high, and in some cases, exceeding 10–20% of the usual engineering tolerance.

For fluids showing the same kinematic viscosity, e.g. mineral and synthetic oils [2], differences in thermal conductivity within 30% can generally lead to deviations in global thermal exchange coefficients corresponding to 15–20%.

The thermal conductivity λ characterizes the capability of a compound to transmit heat and since this phenomenon operates at a molecular level [3], it strongly depends on the chemical nature of the materials and, as we show in this paper, also on the structures for conformational isomers. So it is of primary importance to perform good measurements, both for chemical engineering applications and, especially, for scientific comprehension of the thermo-physical transport properties of substances, e.g. the thermal diffusivity coefficient α_D.

In studying the thermal conductivity of pure organic liquids, some aspects have first to be considered. Usually, measurements of thermal conductivity of a liquid performed in different laboratories are characterized by a poor reproducibility [4–7], and the repeatability standard deviation σ [1] is generally larger than 5% of the magnitude of the difference [2, 8, 9] between two values measured using the same experimental device.

Several investigators have reported the measurement of the thermal conductivity of organic liquids using different equipment based on steady-state or transient methods but, depending on the experimental apparatus used, the results were affected by discrepancies [4, 10, 11–14].

In steady-state methods, the partial derivation of the temperature T versus time is zero, while for transient methods, the prinicpal measurement is the temporal behaviour of the temperature field in the fluid.

Among all the transient and steady-state methods employed, four have given the most reliable results: the flat plate [14], the hot wire or filament [5, 15, 16], the concentric (coaxial) cylinders [4, 6, 9], and the concentric spheres [7].

Therefore, it is unequivocal that the main difficulty in the acquisition of reliable data arises from the technical apparatus employed, which should assure negligible convection heat transfer and temperature differences during experiments. In this experimental work, therefore, we performed our measurements using a Setaram C-80D calorimeter equipped with calorimetric vessels suitable for obtaining the thermal conductivity λ according to the steady-state coaxial (concentric) cylinders method [17].

In the concentric cylinders method, the liquid is located in the annular gap between two vertical coaxial cylinders, heat is supplied along the axis of the inner cylinder and the temperature difference across the thin liquid layer is measured. As transmission of heat has to be measured, the inner cylinder is made of copper, which has a high thermal conductivity, and the outer one is the wall of the vessel. Around it a suitable heating coil is would and the whole device is set in a stainless steel cylinder, fixed at the top of the calorimetric block. Using this instrument it is possible to measure the thermal conductivity of a fluid which is poured between the two walls of the reference and measurement vessels using a tube.

During the course of this experimental work, the apparatus was first checked for the limit of the repeatability standard deviation of the measurements, which was better than 1% within a confidence interval of 95% [1]. Then its usefulness and reliability were compared with all the main methods reported in the literature. The latter evaluation was performed by testing the method and the technical device on standard liquid toluene for temperatures between 302.15 and 391.15 K.

Our main aim was to obtain the thermal conductivity λ and the thermal diffusivity coefficient α_D, between 302.15 and 391.15 K, for the cis and trans isomers of decahydronaphthalene, whose thermal transport properties are not known: only their mixture, of poorly specified composition, has been investigated [18].

In addition, we will compare our results on the commercial mixture λ_{mix} with the experimental literature data [18].

The theoretical correlation of Robbins and Kingrea [9], which gives an estimate of the thermal conductivity coefficient λ for the most common organic liquids, is expressed by the relation

$$\lambda_{\mathrm{est}} = \frac{[(88.0 - 4.94H) \times 10^{-3}]}{(\Delta S^*)} \left[\frac{0.55}{T_r}\right]^N [C_p \rho^{4/3}] \qquad (1)$$

$$\Delta S^* = \Delta H_{\mathrm{vb}}/T_b + R \ln(273.15/T_b) \qquad (2)$$

where the term H is a structural parameter, while N, which can vary from 0 to 1, depends on the liquid density of the studied compound.

The above relationship (1) has been applied to the isomers of decahydronaphthalene and the thermal conductivity coefficient values compared with the experimental ones in the allowed range ($T_r = 0.5–0.7$).

Furthermore, as follows from the theoretical treatment for the thermal conductivity of liquids, it is interesting to observe that this property decreases with temperature and depends on chemical structure changes, in terms of the nature, position and molecular weight of the substituents. This behaviour, due to the relationship between λ and the vibrational molecular motions [3], was also observed in the past, in progressive substitutions within a homologous series for several compounds [19].

In the present case, it is noteworthy that a conformational cis-trans change in a complex structure such as decahydronaphthalene varies the thermal conductivity λ of one of its conformational isomer with respect to the other.

2. Experimental

2.1. Apparatus and procedure

In view of the above description of the coaxial cylinders method, both the measurement and reference vessels were filled with three different liquids, in order to obtain the calibration curve drawn approximately between 303.15 and 393.15 K. An illustration of the cells, together with the principle of the thermal conductivity set-up, is given in Fig. 1.

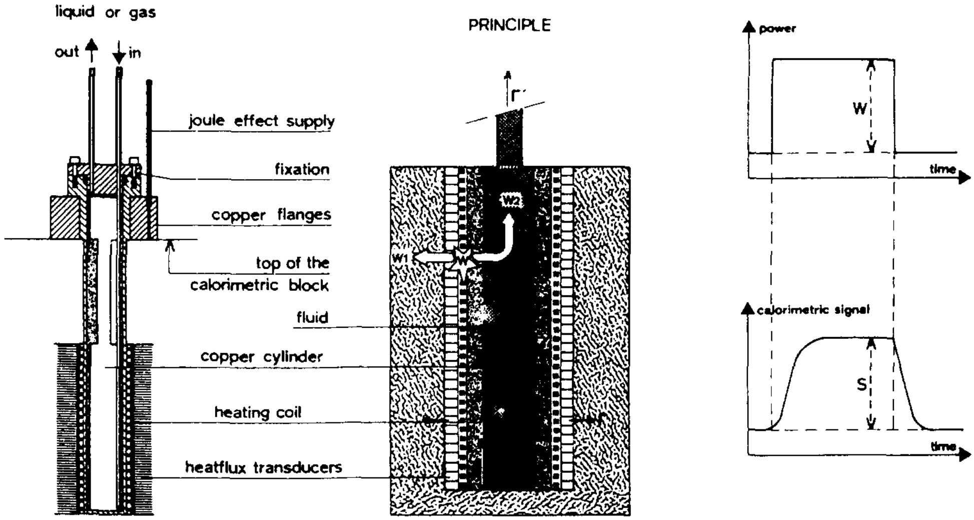

Fig. 1. Thermal conductivity set-up of the Setaram coaxial cylinders vessel.

When equilibrium is attained, i.e. the difference in power w between the reference and measurement vessels is controlled, an impulse of current is sent only to the measurement cell through the heating coil for a discrete period of time, in order to obtain a constant power W dissipated by the Joule effect. The dissipated power goes through both the detector, W_1, and the liquid, W_2, which transmits the heat to the copper cylinder and then to the environment.

At this point, depending on the thermal conductivity of the fluid, an exothermic deviation of the calorimetric signal will be recorded.

The following relations, in conformity to the steady-state principle, determine the power dissipated through the calorimetric detector [17]

$$W_1 = w\frac{[l/\pi' + l/\gamma]}{[l/\pi' + l/\pi + l/\gamma]} \tag{3}$$

$$\gamma = \frac{[2l\lambda]}{[\log r'/r]} \tag{4}$$

where w is the power generated by the Joule effect in the heating coil, π' and π represent, respectively, the thermal conductances due to heat leak created by the copper cylinder and by the detection zone expressed in mW K^{-1}, l is the length of the annular space (cm), r' the radius of the outer cylinder (vessel), r the radius of the inner cylinder (copper), γ(mW K^{-1}) the thermal conductance of the annular volume of fluid, and λ the thermal conductivity coefficient (mW $cm^{-1} K^{-1}$).

The calorimetric signal S, corresponding to W, and the thermal conductivity coefficient λ are linked by the relation

$$\lambda = \frac{[-S + a]}{[bS + c]} \tag{5}$$

with a, b, c constants.

Water, n-undecane and n-tridecane, whose boiling points are, respectively, 373.15, 469.08 and 508.42 K, have been chosen as standards for the thermal conductivity of liquids [8, 20], in order to determine the constants a, b, and c in compliance with Eq. (3).

The temperature range available for good measurements is from room temperature to 473.15 K, and, for the whole set of measurements, we used an auxiliary thermostat, built on the top of the calorimetric block, which assures a better thermal stability and thus greater accuracy of results. The maximal pressure of the liquid in the two vessels is 1.5 MPa, and in order to avoid the formation of air bubbles, measurements were carried out well under the boiling point of the studied liquid.

Once the heat supply to the vessels was turned on, the whole system was permitted to reach steady state at the fixed temperature for about two hours; then, a power input of 100 mW to the measurement cell was sent for about 3600 s, in order to record the corresponding calorimetric signal due to the thermal conductivity coefficient of the considered liquid. After a suitable time gap, in which the instrument achieved the initial heat flux conditions, a subsequent current input was transmitted and the signal readings repeated several times for the same equilibrium temperature.

The investigated decahydronaphthalene isomers were obtained from the commercial mixture, 32.15% cis/67.55% trans (w/w), Fluka Chemie A.G., by fractional vacuum distillation using an Oldershaw-type column (40 perforated plates).

At 330.35–332.05 K and 1.43.10E–01 MPa, we obtained a fraction with 99.3% trans isomer, as determined by gas chromatography. The pure cis isomer (purity > 99.9%) was obtained at the same vacuum of 1.43.10E–01 MPa and 337.55–337.95 K.

3. Results and discussion

As mentioned above, the first measurements were performed on liquid toluene (purity > 99%), between 302.15 and 391.15 K, in order to evaluate the reliability of our data in comparison with the literature and the repeatability of the measurements. In Table 1, the results obtained from pure toluene are shown together with some of the most recent literature data obtained by different methods.

By observing these results, it is clear that in the range 303.15–333.15 K, our data are comparable with those obtained by three coaxial cylinders and hot-wire transient methods [6, 16]; at the same time as far as temperatures above 353.15 K are concerned, the match is closer with the hot-wire steady-state approach [6]. The repeatability of our measurements is of the order of 1% and the corresponding quadratic correlation constants are given for λ_{tol}, and for all the other properties presented here in Table 6.

The thermal conductivity coefficients λ for the two liquid cis and trans isomers of decahydronaphthalene are shown in Table 2. It is interesting to observe that the difference between λ_c and λ_t lies between 2% and 4%, with respect to the experimental error; the *trans*-decahydronaphthalene presents the larger coefficient λ, and, according to most literature experimental data, this is due to the greater flexibility and the characteristic linear structure of the trans conformation. This behaviour gives further evidence of the important role played by the cis–trans isomer transition, which modifies the thermal transport properties of the material to some extent (see our results

Table 1

Experimental data for λ_{tol} for toluene (purity > 99%) compared with literature data, λ_{lit1} measured by coaxial cylinders [6], λ_{lit2} by hot wire steady state [6], λ_{lit3} by hot wire transient [16], and λ_{lit4} by hot wire transient [6, 8]

T/K	λ_{tol}/mWcm^{-1}K^{-1}	λ_{lit1}/mWcm^{-1}K^{-1}	λ_{lit2}/mWcm^{-1}K^{-1}	λ_{lit3}/mWcm^{-1}K^{-1}	λ_{lit4}/mWcm^{-1}K^{-1}
302.55	1.286	1.310	1.343	1.320	1.317
312.55	1.273	1.283	1.319	1.296	1.288
322.45	1.260	1.256	1.295	1.272	1.259
332.45	1.247	1.230	1.272	1.248	1.230
342.35	1.231	1.203	1.248	1.225	1.201
352.25	1.216	1.177	1.225	1.201	1.172
362.25	1.200	1.150	1.201	1.177	1.143
372.15	1.182	1.124	1.177	1.154	1.114
382.05	1.165	1.097	1.154	1.130	1.085
391.95	1.146	1.071	1.130	1.106	1.056

Table 2
Experimental data of λ for separated cis and trans isomers of decahydronaphthalene

T/K	Cis λ_c/mW cm^{-1} K^{-1}	Trans λ_t/mW cm^{-1} K^{-1}
302.55	1.365	1.381
312.55	1.346	1.364
322.45	1.327	1.346
332.45	1.307	1.328
342.35	1.287	1.310
352.25	1.267	1.292
362.25	1.246	1.274
372.15	1.226	1.256
382.05	1.205	1.237
391.95	1.183	1.223

on α_D, Table 4). So far it has been the general opinion that only progressive branching or side substitutions would alter the thermal conductivity coefficient.

Following the theoretical approach to the thermal conductivity of liquid polyatomic molecules [3], this λ dependence on molecular structure is connected to the molecular vibrational internal motions and, in general, to the rotational and translational degrees of freedom, while experimental observations led to the conclusion that λ increases with chain length, with progressive negative deviations due to the side group effect [3].

As far as the general inverse temperature relationship is concerned, for the cis–trans decalin isomers the thermal conductivity coefficient also decreases with increasing temperature, and, in agreement with the above conclusions, a more consistent dependence on T/K was found for the trans isomer (see Tables 2 and 6).

Table 3 shows the λ_{mix} results obtained from the commercial mixture (32.15% cis/67.85% trans) w/w, associated with the related λ^* values calculated from the

Table 3
Experimental data for λ_{mix} obtained for the mixture of decahydronaphthalene isomers (32.15% cis/67.85% trans) w/w: λ^*, calculated using our experimental data on separated isomers from Table 2, by application of the additivity formula Eq. (6); λ_{ref}, literature data obtained by estimation from results on mixed cis and trans isomers $(293.15 < T < 433.15)$ K [18]

T/K	Cis–trans λ_{mix}/mW cm^{-1} K^{-1}	Cis–trans λ^*/mW cm^{-1} K^{-1}	Cis–trans λ_{ref}/mW cm^{-1} K^{-1}
302.55	1.383	1.38	1.13
312.55	1.365	1.36	1.12
322.45	1.346	1.34	1.10
332.45	1.327	1.32	1.09
342.35	1.307	1.30	1.08
352.25	1.288	1.28	1.07
362.25	1.267	1.27	1.06
372.15	1.247	1.25	1.05
382.05	1.226	1.23	1.04
391.95	1.205	1.21	1.03

experimental λ_c and λ_t values of Table 2, in compliance with the additivity rule

$$\lambda^* = \frac{[(\lambda_c \times 32.15) + (\lambda_t \times 67.85)]}{100} \tag{6}$$

In addition, the λ_{ref} values [18] for a mixture of cis and trans isomers is shown in order to allow a comparison between experimental λ_{mix} and literature data. The agreement between λ_{mix} and λ^* is very close and represents, within the interval due to random error propagation [21] on λ^*, a useful checking test of the chosen model, namely the additivity rule expressed by Eq. (6).

As far as the thermal transport properties of decalin are concerned, the diffusivity coefficient α_D ($cm^2 s^{-1}$) for the cis and trans decahydronaphthalene isomers were estimated from our measurements of Table 2 and the literature heat capacity and density data [8]; they are listed in Table 4, together with the estimated literature value $\alpha_{D_{ref}}$ [18]. The thermal diffusion, as a result of the lower steric hindrance, is higher for the trans isomer than for the cis. By comparison with the previously published mixture data, our results for the two isomers represent both an up-to-date contribution and a meaningful improvement.

Finally in Table 5, we compare the estimated conductivity coefficients of Eq. (1), $\lambda_{est(c)}$, $\lambda_{est(t)}$, and the experimental λ_c and λ_t of Table 2, expressed in cal $cm^{-1} s^{-1} K^{-1}$.

The correlation of Robbins and Kingrea [9] allows an estimation, for most organic compounds, of the λ coefficient from the known temperature-dependent properties, C_p and ρ. Therefore, for simple organic substances, this equation permits an approximate but helpful method when no experimental data are available. In that case, it is very difficult to differentiate the two isomers because the hydrogen cis–trans isomerism does not induce a reasonable difference in the structural H parameter, therefore the estimation is based on only chemical-physical properties.

It is clear that the prediction is better for the *trans*-decahydronaphthalene, with a relative percentage deviation of about 5%, which decreases with increasing tempera-

Table 4
Thermal diffusivity coefficient α_D estimated from the experimental thermal conductivity data of cis and trans decahydronaphthalene isomers (Table 2), heat capacity and density data [8], $\alpha_{D_{ref}}$ is from the literature [18] and referred to a mixture of cis and trans isomers

T/K	Cis α_D/($cm^2 s^{-1}$)e+04	Trans α_D/($cm^2 s^{-1}$)e+04	Cis–trans α_{Dref}/($cm^2 s^{-1}$)e+04
302.55	9.06	9.55	7.66
312.55	8.79	9.27	7.47
322.55	8.51	8.99	7.27
332.45	8.24	8.73	7.09
342.35	7.98	8.48	6.90
352.25	7.72	8.23	6.71
362.25	7.47	7.99	6.51
372.15	7.22	7.76	6.33
382.05	6.98	7.54	6.14
392.05	6.75	7.35	5.95

Table 5
Comparison between $\lambda_{est(c,t)}$ calculated values following the Robbins and Kingrea method [8,9], and experimental λ_c and λ_t of Table 2 converted to cal cm^{-1} s^{-1} K^{-1}

T/K	Cis $\lambda_{est(c)}$/ cal cm^{-1} s^{-1} K^{-1} e+04	Cis λ_c cal cm^{-1} s^{-1} K^{-1} e+04	% deviation $([\lambda_{est}-\lambda_c])/\lambda_c \times 100$	Trans $\lambda_{est(t)}$ cal cm^{-1} s^{-1} K^{-1} e+04	Trans λ_t cal cm^{-1} s^{-1} K^{-1} e+04	% deviation $([\lambda_{est}-\lambda_t])/\lambda_t \times 100$
302.55	3.70	3.26	13.5	3.48	3.30	5.5
312.55	3.64	3.22	13.1	3.42	3.26	4.9
322.55	3.58	3.17	12.8	3.36	3.22	4.5
332.45	3.52	3.12	12.7	3.30	3.17	4.1
342.35	3.47	3.08	12.7	3.25	3.13	3.8
352.25	3.41	3.03	12.8	3.20	3.09	3.5
362.25	3.36	2.98	13.0	3.15	3.04	3.4
372.15	3.32	2.93	13.3	3.10	3.00	3.2
382.05	3.27	2.88	13.6	3.05	2.96	3.1
391.95	3.23	2.83	14.1	3.00	2.92	2.7

Table 6
Values of constants in the second-degree least-squares equation together with correlation coefficients r^2 (Symbol) $= a + bT + cT^2$, $302.55 < T < 391.95$ K; λ in mW cm^{-1} K^{-1}, α_D in cm^2 s^{-1}

Symbol	a	b	c	r^2
λ_c	1.816	−1.07e−03	−1.4e−06	0.99999
λ_t	1.956	−1.97e−03	2.5e−07	0.99977
λ_{mix}	1.755	−6.4e−04	−2.0e−06	0.99999
λ^*	1.91	−1.68e−03	−2.7e−07	0.99991
λ_{tol}	1.291	1.17e−03	−3.9e−06	0.99987
$\alpha_{D(cis)}$	20.03	−4.42e−02	2.6e−05	0.99999
$\alpha_{D(trans)}$	22.72	−5.81e−02	4.8e−05	0.99996

ture. In spite of the experimental evidence, $\lambda_{est(t)}$ is lower, largely, than $\lambda_{est(c)}$; this result is in contrast with the above-mentioned general considerations and is probably due to the weakness of the prediction method as applied to conformational isomers.

4. Conclusions

In conclusion, by measuring the thermal conductivity coefficient $\lambda = f[T]$, for two cis–trans conformational isomers, we found that the phenomenon of heat transmission is strictly connected with the internal molecular motions, as the theoretical approaches state. It is not the case that all the empirical correlations provided to predict the λ coefficient present a direct dependence on the density ρ of the compound, which is directly associated with the chemical structure of the fluid.

Finally we recall that for both industrial and academic applications it is of primary importance to measure the thermal conductivity coefficient using a technical device such as the coaxial cylinders. Only in this way can measurements of a high degree of sensitivity and reproducibility be generally attained for cis–trans conformational isomers of a complex structure such as decahydronaphthalene.

References

[1] DIN (Deutsches Institut Für Normung), Part III(4), 1983, 1319.
[2] M. Agnesi, V. Arrigoni, E. Polinelli and G.P. Lanza, Tribol. Lubrificazione, 11 (1976) 139.
[3] N.V. Tsederberg, Thermal Conductivity of Gases and Liquids, M.I.T. Press, Cambridge, MA, 1965.
[4] G.M. Mallan, M.S. Michaelian and F.J. Lockhart, J. Chem. Eng. Data, 17 (1972) 412.
[5] B.J. Gudzinowcz, R.H. Campbell and J.S. Adams, J. Chem. Eng. Data, 9 (1964) 79.
[6] J.E.S. Venart, J. Chem. Eng. Data, 10 (1965) 239.
[7] W.N. Vanderkooi, D.L. Hildenbrand and D.R. Stull, J. Chem. Eng. Data, 12 (1967) 377.
[8] T.E. Daubert and R.P. Danner, Physical and Thermodynamic Properties of Pure Chemicals (Data Compilation), Hemisphere Publishing Corporation, New York, USA, 1989.
[9] P.E. Liley, R.C. Reid and E. Buck, in R.H. Perry and D. Green (Eds.), Perry's Chemical Engineers Handbook, McGraw-Hill International Editions, New York, 6th edn., 1984, Sect. 3 p. 284.
[10] J.M. Lenoir and K.E. Hayworth, J. Chem. Eng. Data, 16 (1971) 129.
[11] D.J. Raal and R.L. Rijsdijk, J. Chem. Eng. Data, 26 (1981) 351.
[12] H.M. Roder and C.A. Nieto de Castro, J. Chem. Eng. Data, 27 (1982) 12.
[13] H. Ozbek and S.L. Phillips, J. Chem. Eng. Data, 25 (1980) 263.
[14] K. Ogiwara, Y. Arai and S. Saito, Ind. Eng. Chem. Fundam., 19 (1980) 295.
[15] J.D. Raal and R.L. Rijsdijk, J. Chem. Eng. Data, 26 (1981) 351.
[16] S.R. Atalla, A.A. El--Sharkawy and F.A. Gasser, Int. J. Thermo., 2(2) (1981) 155.
[17] P. Le Parlouer, M. Rouyer and F. Pithon, Thermochim. Acta, 92 (1985) 375.
[18] American Petroleum Institute, API Monograph Series, Cis and trans Decalin, API Publication 706, Washington, D.C., 1978.
[19] T.K. Slawecki and M.C. Molstad, Ind. Eng. Chem., 48(6) (1956) 1100.
[20] Y.S. Touloukian and D.P. Luley, Thermal Conductivity of Non-Metallic Liquids and Gases, ISI Plenum, New York, 1970.
[21] J.C. Miller and J.N. Miller, Statistics for Analytical Chemistry, Ellis Horwood Limited, England, 1986.