As seen from the distribution diagram acetonitrile prefers solvent phase in all three systems. With regard to the distribution, the order of solvents studied is toluene, methyl isobutyl ketone, and isoamyl acetate.

In this study the order of solvents for selectivity is toluene > isoamyl acetate > methyl isobutyl ketone.

Because toluene is more available and at a cheaper rate when compared to the other solvents, toluene can be used for the extraction of acetonitrile. However, this should be ascertained by experimentation in conventional extraction equipment.

Glossary

C	solute
K, K'	constants in Othmer–Tobias and Hand correlations
n, n'	constants in Othmer–Tobias and Hand correlations
S	solvent
W	water
X_{CS}	weight fraction of solute in solvent layer
X_{CW}	weight fraction of solute in water layer
X_{SS}	weight fraction of solvent in solvent layer
X_{WW}	weight fraction of water in water layer

Literature Cited

(1) Hand, D. B., *J. Phys. Chem.*, **34**, 1961 (1930).
(2) Othmer, D. F., Tobias, P. S., *Ind. Eng. Chem.*, **34**, 693 (1942).
(3) Othmer, D. F., White, R. W., Trueger, E., *Ind. Eng. Chem.*, **33**, 1240 (1941).
(4) Siva Rama Rao, C. V., Venkateswara Rao, K., Ravi prasad, A., Chiranjivi, C., *J. Chem. Eng. Data*, **23**, 23 (1978).
(5) Treybal, R. E., Weber, L. D., Daley, J. F., *Ind. Eng. Chem.*, **38**, 817 (1946).

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Thermal Conductivity of Liquids

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A new equation is presented which correlates thermal conductivity data as a function of both temperature and chemical structure. This enables values to be estimated for other liquids with a similar chemical structure.

1 Introduction

When process equipment is designed, accurate thermal conductivity data are required over a wide range of temperatures. Thermal conductivity is however a difficult property to measure and since there are many thousands of possible liquids it is not possible to supply industries' needs over the entire range experimentally. The necessary data may be obtained in various ways and the following broadly divides these methods in order of preference: (a) careful assessment of extensive experimental data, (b) a combination of limited experimental data and theoretical or empirical procedures, (c) derivation from experimental data for structurally similar chemicals, (d) prediction methods. Prediction methods are important and in some instances essential, but in this paper only the first three methods are considered with the emphasis being on (b) and (c).

2 Correlation of Data as a Function of Temperature

The initial task was to collect all the available literature data and make an assessment of accuracy. This has been completed[1] and, while there are much data, compared with all the possible liquids and temperature ranges there are relatively few available. In addition relatively few authors provide enough information for an objective assessment to be made of their work. Most claim accuracies of a few percent or better but these are seen to be grossly optimistic when the data for a common liquid are plotted as in Figure 1. Detailed references to the individual authors are in ref 1. It might be thought that the scatter is due to the age of some of the work but Figure 2 shows that while this may be partially true it is by no means the entire explanation.

When the assessed accuracies are also considered it is, however, often possible to sketch a line showing how thermal conductivity varies with temperature. The next task was therefore to develop an equation which fitted the experimental data adequately. Relatively simple equations were found suitable for certain liquids over limited temperature ranges but it was found that close to the critical temperature, thermal conductivity increased very rapidly, possibly approaching infinity at the critical point. It was therefore apparent that an equation with a small number of constants could only be found if the critical region is ignored and if a "pseudocritical thermal conductivity" value is used. The latter is obtained by extrapolating data from lower temperatures to the critical temperature and the difference between the pseudovalue and the real value being dealt with as a "critical enhancement".

The simplest equation found to be suitable for all organic liquids was

$$\lambda = A(1 + B\tau^{1/3} + C\tau^{2/3} + D\tau) \qquad (1)$$

where $\tau = 1 - T/T_c$, where T_c is the critical temperature, B, C, and D are constants, and A is the pseudocritical thermal conductivity.

With eq 1 it is possible to represent carefully assessed experimental data to within their estimated accuracy over the approximate temperature range from melting point to $0.9T_c$. Above $0.9T_c$ there are very few experimental values but it is believed that eq 1 will remain accurate until within a few degrees of the critical temperature at which point the "critical enhancement" becomes large.

3 Correlation of Data as a Function of T and of Chemical Structure

When the best available experimental data are collected, for a single class of liquids such as the *n*-alkanes, an inconsistent set of values is generally found.[2] When this was investigated it was found that, for each liquid, the experimental values were such that four or five different lines could be used to plot the variation with temperature and the difference between each line could be well within the experimental uncertainty of the data. It was therefore thought that greater reliability would be achieved if lines could be selected such that the constants in eq 1 varied smoothly as a function of the chemical structure.

For this approach eq 1 must be considered as an equation with four disposable parameters. It is however unlikely that all four of these constants can be related to structure and so an

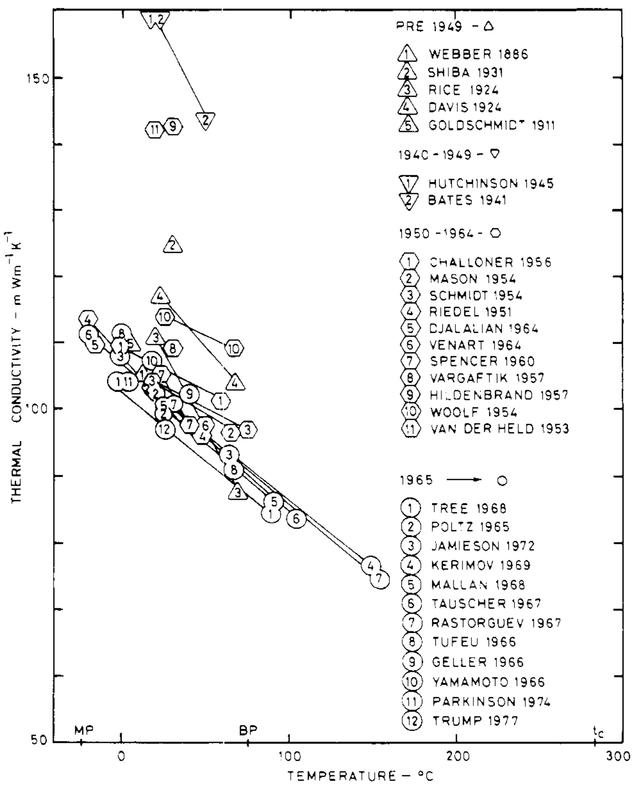

Figure 1. Carbon tetrachloride, λ as a function of T.

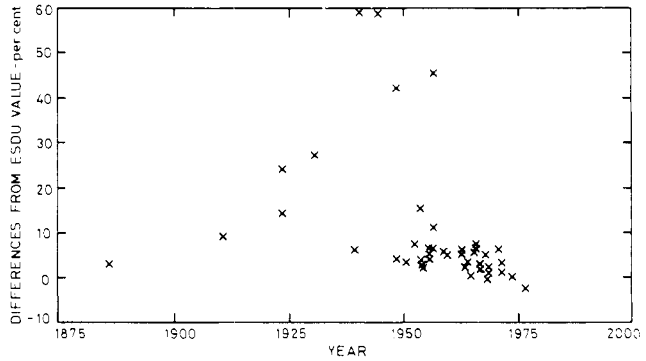

Figure 2. Carbon tetrachloride, λ error as a function of date of publication.

empirical attempt to simplify eq 1 was made and the following equation was developed

$$\lambda = A(1 + B\tau^{1/3} + C\tau^{2/3} + D\tau) \qquad (2)$$

where $C = 1 - 3B$, and $D = 3B$.

Equation 2 has only two disposable parameters and it should be possible to relate these to chemical structure. However, eq 2 cannot be used with all organic liquids but it has been tested and found satisfactory with all alkanes, alkenes and dienes, aromatic hydrocarbons, naphthenes, aliphatic and aromatic esters, aliphatic and aromatic ethers, and halogenated aliphatic and aromatic hydrocarbons.

In general, it has been found that the temperature coefficient, constant B in eq 2, varies less with structure than the pseudocritical conductivity, A, and can be plotted as shown in Figure 3. The quality or accuracy of fit is more dependent on the value of A and, while for simple structures a similar graph can be drawn, Figure 4, for more complicated structures a more detailed "carpet plot" must be prepared. Figure 5 shows such a plot for the n-alkyl esters where it can be seen that the ester is described as a molecule with varying numbers of carbon atoms but in addition the location of the ester group within the chain is allowed for. It can be seen that, for a given molecular weight, the thermal conductivity is at a minimum when the ester group is located in the center of the ester molecule.

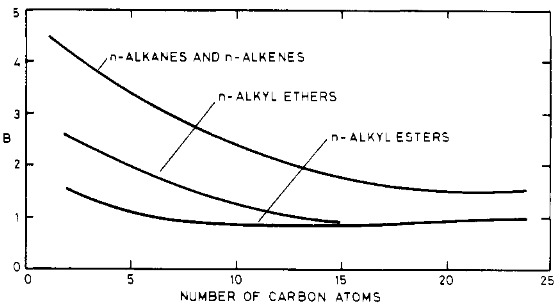

Figure 3. B as a function of number of carbon atoms.

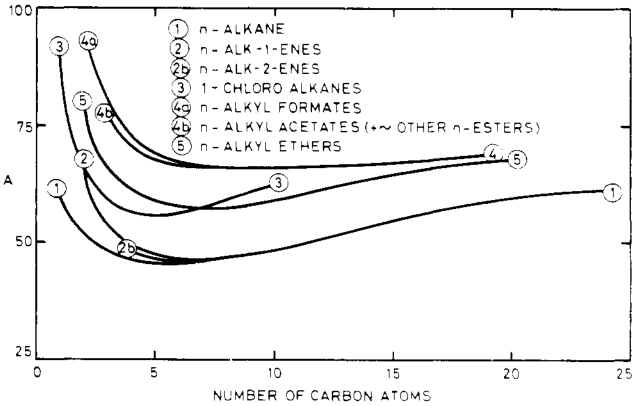

Figure 4. A as a function of number of carbon atoms.

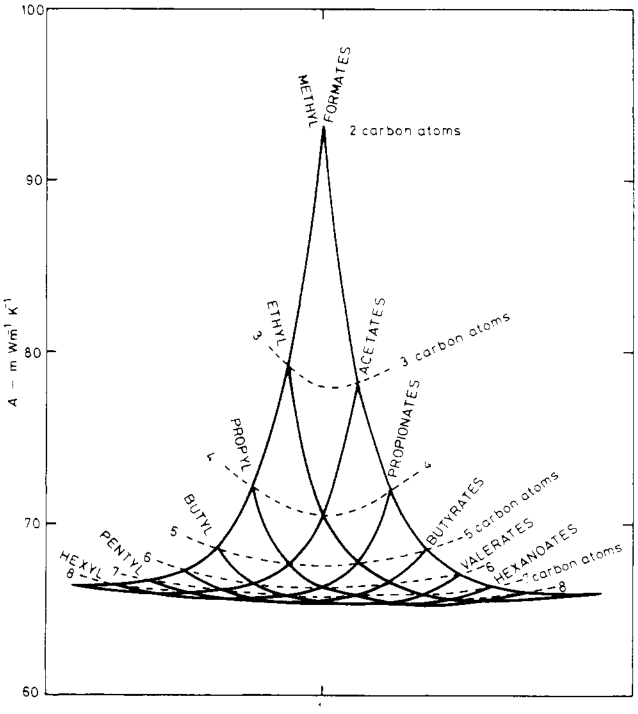

Figure 5. A as a function of number of carbon atoms and location of ester group.

When eq 2 is used with the values of A and B taken from Figures 3, 4, and 5, the values of thermal conductivity fit the experimental data for individual compounds to within their experimental accuracy and also have values which vary smoothly from one member to another within a single chemical series. This procedure is believed to give more confidence in smoothing the experimental values where extensive data exist but its greatest value is in the ability to extend limited experimental data to much wider temperature ranges and in the prediction of values for structurally similar chemicals for which no experimental values exist. Detailed tabulations with eq 2 have been prepared by the author under the sponsorship of ESDU and may be found in ref 3-6 for 58 alkanes, 27 alkenes and dienes, 166 halogenated aliphatic hydrocarbons, and 146 *n*-alkyl esters. New experimental measurements have also been made with 6 aliphatic ethers and a more detailed description is given in ref 7 of the quality of fit of eq 2 to the experimental values.

4 Conclusions

An equation has been developed which fits the experimental thermal conductivity data from the melting point to approximately 0.9 of the critical temperature. The constants of this equation were correlated not only as individual compounds but also as members of their chemical series, and the values tabulated by this procedure represent the thermal conductivity data to within their estimated experimental accuracy. The predicted data obtained by interpolation of the constants of eq 2 are claimed to have a similar accuracy which is much better than would have been obtained from any purely predictive equation of the type described in ref 8.

Acknowledgment

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Literature Cited

(1) Jamieson, D. T., Irving, J. B., Tudhope, J. S., "Liquid Thermal Conductivity: a Data Survey to 1973", HMSO, Edinburgh, 1975.
(2) Reynard, K. W., in "Symposium on Physical Properties of Liquids and Gases for Plant and Process Design", HMSO, Edinburgh, 1970.
(3) *Eng. Sci. Data Item*, **No. 75003** (1975).
(4) *Eng. Sci. Data Item*, **No. 75009** (1975).
(5) *Eng. Sci. Data Item*, **No. 76009** (1975).
(6) *Eng. Sci. Data Item*, **No. 76017** (1975).
(7) Jamieson, D. T., Cartwright, G., *Natl. Eng. Lab.* (*U.K.*), *Rep.*, **No. 651** (1978).
(8) Reid, R. C., Prausnitz, J. M., Sherwood, T. K., "The Properties of Gases and Liquids", 3rd ed., McGraw-Hill, New York, 1977.

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NEW COMPOUNDS

Synthesis of *N*-(1-Naphthyl) Hydroxamic Acids

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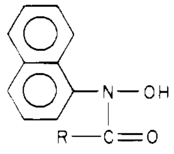
Preparation and properties of eight new crystalline *N*-aryl hydroxamic acids derived from *N*-(1-naphthyl)hydroxylamine are described.

Introduction

Synthesis of ten hydroxamic acids, of which eight are new acids, derived from *N*-(1-naphthyl)hydroxylamine with the general formula (I) (where R is acetic or substituted benzoic acid derivatives), is described.



I

Table I. Properties of *N*-(1-Naphthyl) Hydroxamic Acids[a]

compd no.	hydroxamic acid	mol formula	mp, °C	% yield	IR spectra, cm^{-1} ν_{O-H}	IR spectra, cm^{-1} $\nu_{C=O}$	IR spectra, cm^{-1} ν_{N-O}	UV spectra (λ_{max}), nm band II	UV spectra (λ_{max}), nm band I
I	*N*-(1-naphthyl)benzo-	$C_{17}H_{13}NO_2$	165	70	3222	1626	905	275	225
II	*N*-(1-naphthyl)aceto-	$C_{12}H_{11}NO_2$	120	65	3297	1626	905	284	224
III	*N*-(1-naphthyl)cinnamo-	$C_{19}H_{15}NO_2$	130	75	3190	1626	922	285	220
IV	*N*-(1-naphthyl)-*p*-chlorobenzo-	$C_{17}H_{12}NO_2Cl$	148[b]	60	3279	1653	910	282	236
V	*N*-(1-naphthyl)-*o*-chlorobenzo-	$C_{17}H_{12}NO_2Cl$	126	55	3270	1650	920	283	225
VI	*N*-(1-naphthyl)-*p*-bromobenzo-	$C_{17}H_{12}NO_2Br$	207	60	3190	1626	903	283	224
VII	*N*-(1-naphthyl)-*p*-iodobenzo-	$C_{17}H_{12}NO_2I$	175[c]	65	3248	1623	904	283	224
VIII	*N*-(1-naphthyl)-*p*-nitrobenzo-	$C_{17}H_{12}N_2O_4$	174	70	3215	1653	909	257	224
IX	*N*-(1-naphthyl)-*m*-nitrobenzo-	$C_{17}H_{12}N_2O_4$	138	65	3221	1653	909	283	226
X	*N*-(1-naphthyl)-3,5-dinitrobenzo-	$C_{17}H_{11}N_3O_6$	215	60	3248	1639	905	267	224

[a] Elemental analysis in agreement with theoretical values were obtained and submitted for review. [b] Reported mp 148 °C (*5*). [c] Reported mp 175 °C (*5*).