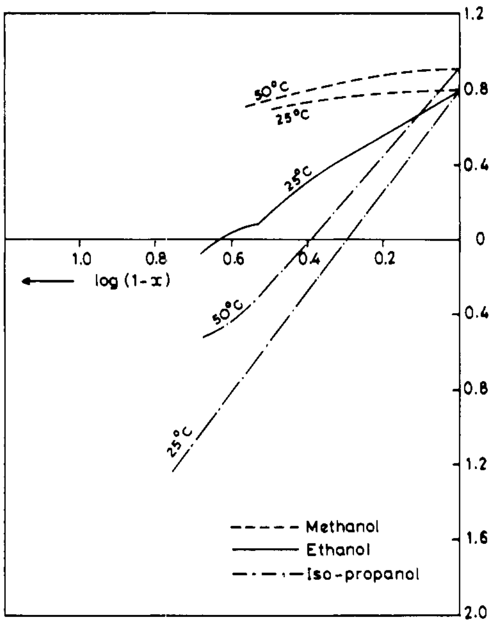

Figure 3. Logarithmic representation of solubility against mole fraction of water for the system strontium chloride–alcohol–water.

$Cl_2 \cdot 2H_2O$ even at 25 °C, in the presence of all six solvents under consideration. Further, dehydration from $SrCl_2 \cdot 2H_2O \rightarrow SrCl_2 \cdot H_2O$ takes place at 70 °C, in the presence of both formic acid and acetic acid. In fact with acetic acid, the second step can be achieved even at 50 °C. In some cases at very high concentrations of solvents, solid phase in equilibrium with solutions contained a few moles of solvent. These results show that the drop in phase transition temperatures obtained in the presence of solvents is considerable; i.e., by use of organic solvents, hydrated salts can be partially or completely dehydrated at much lower temperatures compared to those involved in the presence of air or pure aqueous systems.

Correlation of Solubility Data in the Form of Achumow's Equation[2]

It is difficult to predict solubility of electrolytes in solvents, as the solubility of a salt depends upon many factors, such as, dielectric constant, dissociation constant of the solvent, size and charge of ions, temperature, solvent–solute interaction, etc. In some cases, where a salt is insoluble in pure organic liquids, the solubility of salt in organic liquid–water mixtures can be extrapolated or interpolated at a given temperature to limited degree by Achumow's equation

$$y = y_1(1 - x)^n$$

or

$$\log y = \log y_1 + n \log (1 - x)$$

where y = solubility of salt in solvent–water mixture (mol of salt/100 mol of solvent mixture), y_1 = solubility of salt in pure water (mol of salt/100 mol of water), and $(1 - x)$ = mole fraction of water in solvent–water mixture.

The value of n in the equation is to be found from a few sets of experimental data and plotting $\log y$ against $\log (1 - x)$. The slope of this line gives the value of n. The data are plotted in Figure 3. The values of the n have been found from the linear portion of the curve. The typical equations from which the solubility data can be predicted are as follows for $SrCl_2$–2-propanol–water.

$$y = 6.35(1 - x)^{2.7} \text{ for 25 °C isotherm} \quad (1)$$

$$y = 8.23(1 - x)^{2.3} \text{ for 50 °C isotherm} \quad (2)$$

Similar equations were obtained for other systems with limitations earlier expressed.

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Pressure–Volume–Temperature Relationships of $CH_3COOC_2H_5$ and Generalized Tait Equation for Liquids at High Pressures

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Experimental P–V–T data of $CH_3COOC_2H_5$ have been determined for temperatures from −20 to +40 °C and pressures up to 1500 atm with an accuracy better than 0.13%. The Tait equation parameters were correlated by use of 321 P–V–T data points of ten compounds including $CH_3COOC_2H_5$. The average deviations are 0.5% in the specific volumes calculated by the Tait equation with the correlated parameters.

P–V–T relationships of liquids at high pressures are often unavailable for desired pressures, temperatures, and compounds in engineering calculations. Various methods have been studied in predicting liquid volumes at high pressures (*1–6, 12–17*). However, most of these methods are not always possible to estimate with reasonable accuracy the volumetric properties of liquids.

The Tait equation has had considerable success in describing P–V–T data, but this use has been limited to compounds for which the Tait parameters are available. Hence the development of the correlation of the Tait parameters may be useful in the prediction of P–V–T data for a wide range of liquids. It has been previously shown that an approximately linear relationship exists between the reduced Tait parameter, B_T/P_c, and the

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Table I. Specific Volumes of Ethyl Acetate

pressure, atm	specific vol, cm³/g			
	−20 °C	0 °C	20 °C	40 °C
P_0	1.0556 (–)[a]	1.0821 (–)[a]	1.1110 (0.1)[a]	1.1420 (0.2)[a]
194	1.0395	1.0625	1.0878	1.1143
388	1.0268	1.0474	1.0701	1.0941
581	1.0152	1.0335	1.0550	1.0776
774	1.0047	1.0221	1.0417	1.0629
968	0.9956	1.0122	1.0304	1.0493
1161	0.9873	1.0028	1.0192	1.0371
1354	0.9795	0.9938	1.0095	1.0267
1547	0.9726	0.9865	1.0012	1.0166

[a] Saturated vapor pressure, P_0 (atm).

Table II. Tait Equation Parameters for Ethyl Acetate

temp, °C	B_T, atm	C
−20	1064	0.0878
0	885	
20	744	
40	632	

reciprocal of the reduced temperature for several liquids (*10*), but this correlation fails for CH_3COOCH_3, which has a large value for the ratio of T_b/T_c, compared with those for other liquids.

The purpose of this investigation is to determine $P-V-T$ data of $CH_3COOC_2H_5$ with the large temperature ratio of T_b against T_c and to develop a new correlation for various liquids including $CH_3COOC_2H_5$.

$P-V-T$ Relationships of $CH_3COOC_2H_5$

The apparatus and the experimental procedure were the same as those described previously (*9*, *11*). The sample of $CH_3COOC_2H_5$ was obtained from Nakarai Chemicals, Ltd. (Japan), of purity stated to be better than 99%, and no further purification was attempted. Table I presents the experimental specific volumes for $CH_3COOC_2H_5$. All measured points lie on a smooth curve with deviations less than 0.13% at each isotherm. The largest deviation of the fit of the specific volumes at saturated vapor pressures was 0.06% from the previous literature (*7*). The Tait equation is written as

$$(V_0 - V)/V_0 = C \ln((B_T + P)/(B_T + P_0)) \qquad (1)$$

The Tait parameters B_T and C were evaluated from the experimental $P-V-T$ data for each of the four isotherms by a least-squares method. Table II is a summary of the results. In this evaluation, the specific volume at the saturated vapor pressure, P_0, was chosen as V_0. The Tait equation with the parameters listed in Table II reproduces the experimental specific volumes with a deviation not exceeding 0.13%.

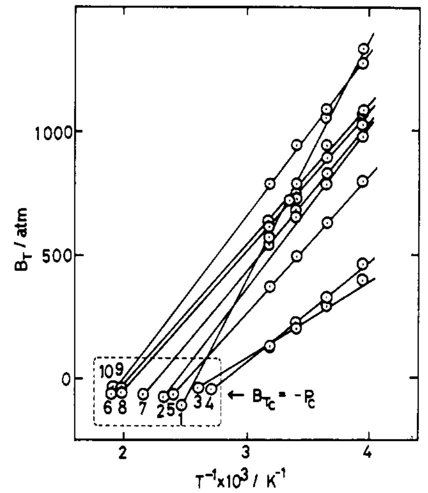

Figure 1. Tait parameter B_T as function of reciprocal of temperature. (Numbers refer to compounds in Table III.)

Correlation for Tait Parameters B_T and C

The Tait parameter B_T (*8*, *9*, *11*) is inversely proportional to temperature for several liquids including $CH_3COOC_2H_5$ as shown in Figure 1.

$$B_T \propto T^{-1} \qquad (2)$$

In this figure, the parameter B_T can be reasonably extrapolated to the value of $-P_c$ at the critical temperature for each liquid.

$$B_{T_c} = -P_c \qquad (3)$$

The parameter B_{T_c} at the critical temperature should be equal to $-P_c$ from eq 1 and the critical condition $(\partial P/\partial V)_{T_c} = 0$. Consequently, the B_T/B_{T_b} ratio is represented by a straight line against T_b/T, which passes through $-P_c/B_{T_b}$ at T_b/T_c and B_{T_b}/B_{T_b} (=1) at T_b/T_b (=1), respectively, for any liquid as the following equation.

$$B_T/B_{T_b} = (-P_c/B_{T_b}) + ((1 + P_c/B_{T_b})/(1 - T_b/T_c))(T_b/T - T_b/T_c) \qquad (4)$$

If the B_{T_b} value of a given compound is not available, the value is further correlated by P_c as shown in Figure 2. The parameter C can be obtained from the temperature ratio T_b/T_c presented in Figure 3.

Comparison of Calculated Results

The specific volumes of ten compounds for temperatures from −20 to +40 °C and pressures up to 1500 atm were evaluated by using the generalized Tait parameters B_T by eq 4 and C estimated from T_b/T_c in Figure 3, where B_{T_b} was determined

Table III. Deviation of Calculated Specific Volumes from Experimental Values[a]

no.	compd	P range, atm	no. of points	av dev, %	max dev, %	data source	T_b/T_c
1	NH_3	95-1774	37	0.3	−0.7	9	0.591
2	SO_2	283-1587	24	0.6	−0.9	8	0.611
3	CCl_2F_2	95-1587	34	0.4	−1.1	11	0.632
4	$CHClF_2$	95-1575	34	0.8	1.4		0.603
5	CH_3Cl	283-1574	32	0.4	0.7		0.599
6	CH_3I	283-1574	32	0.7	1.2		0.597
7	CH_3Br	283-1574	32	0.2	−0.5		0.607
8	C_2H_5Br	194-1547	32	0.6	−1.0		0.613
9	CH_3COOCH_3	194-1547	32	0.4	0.7		0.651
10	$CH_3COOC_2H_5$	194-1547	32	0.7	1.0	b	0.669

[a] Temperature range is from +40 to −20 °C except for SO_2. The range for SO_2 is from +20 to −20 °C. [b] Present work.

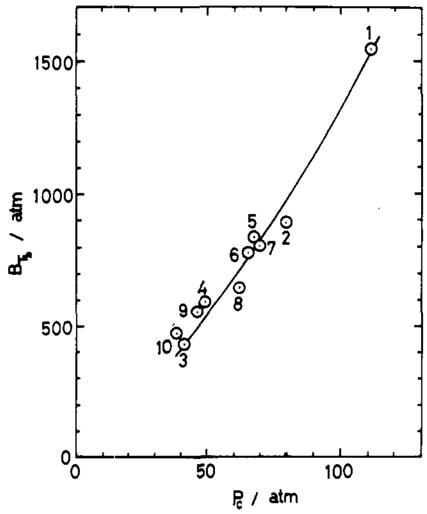

Figure 2. Tait parameter B_{T_b} at boiling point vs. critical pressure. (Numbers refer to compounds in Table III.)

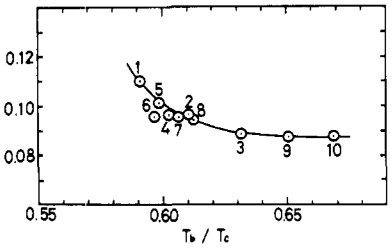

Figure 3. Tait parameter C vs. ratio T_b/T_c. (Numbers refer to compounds in Table III.)

from the curve presented in Figure 2, and were compared with the literature values. The result of this comparison is presented in Table III, in which the percentage deviation is defined by $100(V_{\text{exptl}} - V_{\text{calcd}})/V_{\text{exptl}}$. The specific volumes calculated by eq 1 by using the generalized eq 4 and C obtained from Figure 3 reproduce the literature data within 1.4%.

Glossary

B_T, C	Tait equation parameters, atm and dimensionless, respectively
P	pressure, atm
T	temperature, K
V	specific volume, cm^3/g

Subscripts

b	normal boiling point
c	critical point
0	reference state

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Thermal Conductivities of Trialkyl Borates[†]

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This paper reports the thermal conductivities of the following trialkyl borate homologues as functions of temperature: methyl, ethyl, propyl, isopropyl, butyl, and isobutyl. A concentric sphere apparatus was used for the measurements. The close agreement between observed and reported literature values for benzene seemed to justify the use of this apparatus for the measurement of thermal conductivities.

This paper is the latest in the series of papers dealing with the systematic measurements of physicochemical properties of several homologous trialkyl borates. The previous studies have reported data on vapor pressures (*2*), densities and absolute viscosities (*3*), surface tensions (*4*), and refractive indices (*5*) as functions of temperature up to the normal boiling point. The object of the present investigation has been to measure the thermal conductivities of the following trialkyl borates over the same range of temperatures: methyl, ethyl, propyl, isopropyl, butyl, and isobutyl. A review of literature has revealed no information with regard to the thermal conductivities of these compounds. This, coupled with the importance of this property in the design of heat exchange equipment involving these compounds, has provided the impetus to undertake this work.

Apparatus

The defining equation for thermal conductivity is the Fourier law of conduction, which can be stated as

$$q = -kA\frac{dT}{dr} \tag{1}$$

where q = rate of heat flow by conduction (J/s), k = thermal conductivity, (J/(m s K)), A = area normal to the direction of heat flow (m^2), T = temperature (K), and r = radial distance over which heat flows by conduction (m).

[†] This work was abstracted from the M. Eng. thesis of L.D.T., University of Louisville, Louisville, KY, 1978.

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