

Densities and Viscosities of Trialkyl Borates

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The temperature-dependence of density and absolute viscosity has been established for the following trialkyl borates: methyl, ethyl, propyl, isopropyl, butyl, and isobutyl. Experimental densities were fitted into the equation, $\rho = a + b(t - 25) + c(t - 25)^2 + d(t - 25)^3$, $t = ^\circ\text{C.}$, and viscosities were correlated by the expression, $\ln \eta = A + B/T + C/T^2$, $T = ^\circ\text{K.}$; the constants were evaluated on the IBM 1800 computer. Energies of activation for viscous flow and molar volumes at the boiling point were discussed in terms of molecular structure.

THE RATHER limited amount of available physical data for trialkyl borates has prompted the systematic experimental investigation of several representative homologs. The results of one work, involving vapor pressure-temperature correlations, have already been reported (1). The present study is concerned with temperature-dependence of density and absolute viscosity for the same series of borates—i.e., methyl, ethyl, propyl, isopropyl, butyl, and isobutyl.

EXPERIMENTAL

The borates were purified, assayed, and handled in the same manner as previously described (1). Reagent grade *o*-dichlorobenzene (b.p. 180.3°C. at 760 mm. of Hg) was used as the reference liquid for the viscosity determinations. Densities were observed in a 4.5-ml. bicapillary Lipkin pycnometer (Ace Glass Co., Vineland, N.J.), which was calibrated with triply-distilled reagent grade mercury. Flow times were measured to ± 0.2 second in a Cannon-Fenske modification of the Ostwald viscometer. The temperature in the water bath that was used up to 90°C. was controlled to $\pm 0.1^\circ\text{C.}$ For the higher temperatures, which were regulated to $\pm 0.3^\circ\text{C.}$, the heat transfer liquid, Therminol 77, was employed (Monsanto Co., Cincinnati, Ohio). Water bath and Therminol 77 bath temperatures were read on 0.1° and 1° graduated thermometers, respectively, each thermometer having been calibrated against the freezing and normal boiling points of water.

RESULTS AND DISCUSSION

The observed borate densities were fitted into the equation

$$\rho = a + b(t - 25) + c(t - 25)^2 + d(t - 25)^3 \quad (1)$$

where a , b , c , and d are constants, and $t = ^\circ\text{C.}$ The data indicated the usual trends, whereby the methyl borate showed the highest density, and the ρ 's of the remaining unbranched homologs increased with molecular weight above 40°C., the branched isomers having correspondingly lower values. The rather abnormal amount of curvature shown by the ρ - t plot of ethyl borate above 90°C. must be ascribed to partial decomposition, a peculiarity unique for this member of the series, and one that has been previously cited (7).

Absolute viscosities were deduced from the relationship

$$\eta = \eta_0 \rho t / \rho_0 t_0 \quad (2)$$

where η is in centipoises and t the flow time. Reliable values of ρ_0 and η_0 have been reported for *o*-dichloroben-

zene up to 140°C. (2), and accordingly, this compound was selected as the reference liquid.

The temperature-dependence of liquid viscosities is little understood, so that a variety of different functions were tested. Of these, the best reproducibility of the experimental input data was given by the expression

$$\ln \eta = A + B/T + C/T^2 \quad (3)$$

where A , B , and C are constants and $T = ^\circ\text{K.}$ The data showed an increase in η with molecular weight for the straight-chain homologs, and correspondingly lower viscosities for the branched isomers. Below 80°C., however, the isobutyl borate had higher η 's than those of the butyl isomer.

The densities and absolute viscosities of the *o*-dichlorobenzene (2) obtained quite satisfactory fits with Equations 1 and 3, respectively. The flow times of this compound, which were determined by the present writers up to within a few degrees of the boiling point, also showed good concordance with Equation 3. With such equations on hand, ρ_0 , η_0 , and t_0 could be deduced readily above the 140°C. values reported (2). The excellent agreement between the observed borate densities and values calculated from Equation 1 and the fact that all flow times had been observed up to almost the boiling point made it unnecessary to determine the ρ 's for these compounds above 150°C. The maintenance of precise temperature control was difficult beyond this reading. The physical data are listed in Table I, along with values of ρ and η as calculated from Equations 1 and 3, respectively. The last temperature for each borate is the normal boiling point (1). The figures for the ethyl borate are for the undecomposed compound—i.e., one measurement, made at 110°C., has been omitted. Finally, the per cent deviation is given by $(y_{\text{obsd.}} - y_{\text{calcd.}}) \times 100 / y_{\text{obsd.}}$, where y represents either ρ or η .

The over-all Table I average deviations for densities and absolute viscosities are ± 0.0180 and $\pm 0.225\%$, respectively. Although extensive and systematic physical data for this class of compounds are somewhat lacking, some of the observed ρ 's may be compared with a few previous findings (4, 5, 6). A search of the literature disclosed one observation of the kinematic viscosities of propyl and butyl borates at 28°C. (3), and another (6) which reports the kinematic viscosities of methyl, ethyl, propyl, isopropyl, and butyl borates at three different temperatures. No temperature correlations were attempted.

The constants for Equations 1 and 3, which were evaluated on the IBM 1800 computer, are given in Table II, along with the corresponding standard error of estimate, S , for n observations, where $S = [\sum (y_{\text{obsd.}} - y_{\text{calcd.}})^2 / n]^{1/2}$.

For a relationship of the type shown by Equation 3, the energy of activation for viscous flow, E^* (kcal. per

Table I. Observed and Calculated Densities and Viscosities

	$T, ^\circ\text{C.}$	$\rho, \text{G./ML.}$			$\eta, \text{Cp.}$		
		Obsd.	Calcd.	Deviation, %	Obsd.	Calcd.	Deviation, %
Borate							
Methyl	25	0.9273	0.92726	0.00397	0.3750	0.37502	-0.00585
	30	0.9203	0.92038	-0.00875	0.3568	0.35677	0.00920
	40	0.9066	0.90652	0.00888	0.3245	0.32450	0.00000
	50	0.8925	0.89255	-0.00541	0.2969	0.29692	-0.00725
	60	0.8785	0.87849	0.00131	0.2733	0.27329	0.00391
	67.4		0.86804			0.25797	
Ethyl	25	0.8576	0.85767	-0.00758	0.5178	0.51713	0.130
	30	0.8519	0.85182	0.00909	0.4875	0.48857	-0.219
	40	0.8402	0.84011	0.0104	0.4392	0.43821	0.225
	50	0.8282	0.82838	-0.0220	0.3945	0.39536	-0.217
	60	0.8167	0.81665	0.00617	0.3586	0.35880	-0.0568
	70	0.8050	0.80493	0.00869	0.3278	0.32758	0.0665
	80	0.7932	0.79324	-0.00509	0.3010	0.30025	0.248
	90	0.7816	0.78160	0.00000	0.2761	0.27659	-0.178
	118.3		0.74904			0.22410	
Propyl	25	0.8546	0.85454	0.00699	1.0220	1.01396	0.786
	30	0.8497	0.84977	-0.00840	0.9393	0.94320	-0.416
	40	0.8400	0.84016	-0.0187	0.8165	0.82130	-0.587
	50	0.8305	0.83044	0.00715	0.7142	0.72057	-0.892
	60	0.8209	0.82062	0.0339	0.6405	0.63704	0.541
	70	0.8110	0.81070	0.0371	0.5718	0.56753	0.747
	80	0.8000	0.80067	-0.0842	0.5066	0.50817	-0.310
	90	0.7907	0.79054	0.0196	0.4619	0.45796	0.852
	110	0.7699	0.76998	-0.00987	0.3757	0.37824	-0.676
	130	0.7492	0.74899	0.0280	0.3169	0.31768	-0.246
	150	0.7275	0.72759	-0.0117	0.2716	0.27138	0.0823
	170		0.70576		0.2351	0.23487	0.0987
	178.6		0.69624			0.22159	
Isopropyl	25	0.8126	0.81251	0.0105	0.8049	0.80399	0.114
	30	0.8073	0.80732	-0.00258	0.7502	0.74826	0.259
	40	0.7968	0.79688	-0.0103	0.6490	0.65211	-0.479
	60	0.7756	0.77573	-0.0172	0.5048	0.50641	-0.319
	70	0.7649	0.76498	-0.0110	0.4516	0.45132	0.0611
	80	0.7544	0.75409	0.0409	0.4059	0.40423	0.411
	90	0.7432	0.74304	0.0222	0.3647	0.36435	0.0955
	110	0.7200	0.72035	-0.0492	0.3009	0.30095	-0.0169
	130	0.6969	0.69678	0.0167	0.2524	0.25273	-0.129
	139.4		0.68535			0.23435	
Butyl	25	0.8538	0.85366	0.0165	1.6434	1.64437	-0.0592
	30	0.8494	0.84938	0.00181	1.5182	1.51033	0.518
	40	0.8407	0.84078	-0.00910	1.2814	1.28503	-0.283
	50	0.8318	0.83209	-0.0351	1.1029	1.10452	-0.147
	60	0.8231	0.82333	-0.0285	0.9582	0.95891	-0.0742
	70	0.8147	0.81451	0.0238	0.8393	0.84074	-0.171
	80	0.8060	0.80561	0.0483	0.7413	0.74209	-0.106
	90	0.7970	0.79665	0.0439	0.6607	0.66034	0.0539
	110	0.7778	0.77855	-0.0964	0.5334	0.53393	-0.0996
	130	0.7605	0.76023	0.0358	0.4421	0.44087	0.279
	150	0.7417	0.74171	-0.00126	0.3728	0.37156	0.331
	170		0.72302		0.3183	0.31812	0.0560
	190		0.70418		0.2764	0.27660	-0.0731
	200		0.69471		0.2587	0.25893	-0.0896
	220		0.67569		0.2290	0.22932	-0.138
	233.5		0.66281			0.21236	
Isobutyl	25	0.8402	0.83992	0.0330	1.8218	1.81039	0.626
	30	0.8355	0.83562	-0.0146	1.6426	1.63940	0.195
	40	0.8265	0.82690	-0.0487	1.3498	1.36020	-0.770
	50	0.8181	0.81804	0.00759	1.1374	1.14438	-0.614
	60	0.8091	0.80904	0.00717	0.9771	0.97575	0.138
	70	0.8000	0.79993	0.00891	0.8405	0.84270	-0.262
	80	0.7910	0.79071	0.0364	0.7356	0.73439	0.165
	90	0.7813	0.78141	-0.0136	0.6496	0.64664	0.456
	110	0.7624	0.76258	-0.0239	0.5145	0.51470	-0.0393
	130	0.7436	0.74357	0.00430	0.4217	0.42068	0.242
	150	0.7245	0.72448	0.00334	0.3529	0.35248	0.118
	170		0.70542		0.3011	0.30100	0.0321
	190		0.68650		0.2612	0.26170	-0.191
	200		0.67714		0.2449	0.24516	-0.105
	210.4		0.66748			0.23014	

Table II. Constants for Equations 1 and 3

R in B(OR) ₃	Equation 1				
	a	-b	-c	d	S
CH ₃	0.92726	1.3731 × 10 ⁻³	7.0987 × 10 ⁻⁷	3.5502 × 10 ⁻¹⁰	5.80 × 10 ⁻⁴
C ₂ H ₅	0.85767	1.1675 × 10 ⁻³	2.2279 × 10 ⁻⁷	2.7603 × 10 ⁻¹⁰	8.68 × 10 ⁻⁵
C ₃ H ₇	0.85454	9.5121 × 10 ⁻⁴	5.0998 × 10 ⁻⁷	-4.3784 × 10 ⁻¹¹	2.59 × 10 ⁻⁴
iso-C ₃ H ₇	0.81251	1.0374 × 10 ⁻³	2.7087 × 10 ⁻⁷	-3.3009 × 10 ⁻¹⁰	1.83 × 10 ⁻⁴
C ₄ H ₉	0.85366	8.5287 × 10 ⁻⁴	4.0483 × 10 ⁻⁷	5.0421 × 10 ⁻¹⁰	3.18 × 10 ⁻⁴
iso-C ₄ H ₉	0.83992	8.5608 × 10 ⁻⁴	8.3089 × 10 ⁻⁷	2.3275 × 10 ⁻¹⁰	1.89 × 10 ⁻⁴
	Equation 3				
	-A	B	C	S	
CH ₃	3.71465	7.21879 × 10 ⁻²	2.78780 × 10 ⁻⁴	2.07 × 10 ⁻³	
C ₂ H ₅	4.32480	1.15434 × 10 ⁻¹	-1.82476 × 10 ⁻⁴	7.23 × 10 ⁻⁴	
C ₃ H ₇	4.58674	1.42978 × 10 ⁻¹	-1.72043 × 10 ⁻⁴	4.07 × 10 ⁻³	
iso-C ₃ H ₇	4.86188	1.46513 × 10 ⁻¹	-2.39146 × 10 ⁻⁴	1.49 × 10 ⁻³	
C ₄ H ₉	4.17103	1.23605 × 10 ⁻¹	4.65993 × 10 ⁻⁴	2.39 × 10 ⁻³	
iso-C ₄ H ₉	3.66779	7.28965 × 10 ⁻²	1.61627 × 10 ⁻³	4.75 × 10 ⁻³	

mole), should have the following temperature-dependence

$$E^* = R(B + 2C/T) \quad (4)$$

where R is the gas constant. Equation 4 predicts that E^* should decrease with increasing T , but the Table II data indicate that this is true only for methyl, butyl, and isobutyl borates. The opposite effect displayed by the remaining borates would suggest that the mechanism for activation is complex in these instances. For the unbranched homologs, E^* at the boiling point is related to n , the number of carbon atoms in a single alkyl group, by the expression

$$E^* = 377n + 1403 \quad (5)$$

Equation 5 gives an average error of $\pm 3.1\%$. The molar volume at the boiling point, V_b (ml. per mole), can also be correlated to n , by the relationship

$$V_b = 75.77n + 43.55 \quad (6)$$

which obtains an average error of $\pm 0.23\%$.

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Isothermal Vapor-Liquid Equilibrium Data for the System Heptane-Ethyl Butyrate at 74.7° and 100° C.

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Isothermal equilibrium vapor and liquid composition measurements have been made for the heptane-ethyl butyrate system at 74.7° and 100° C., using equilibrium samples produced with the aid of a vapor recirculation equilibrium still. Vaporization equilibrium constants (K -values) were calculated from the equilibrium compositions, and the thermodynamic consistency was checked by the method of Redlich and Kister. Composition and liquid specific volume data were obtained for this binary system at 20° C.

ISOOTHERMAL vapor-liquid equilibrium data at low pressures are useful for studying the thermodynamics of nonideal solutions and desirable for establishing the vaporization equilibrium constants— K -values—used for the design of equilibrium stage processes.

A survey of the literature indicates that no such isothermal data have been published for the system heptane-ethyl butyrate in the vicinity of 75° and 100° C. Because of this, the determinations of equilibrium composition reported here were made.

EXPERIMENTAL

A detailed description of the experimental equipment, calibrations, procedures, and methods has been given by Lodi and Scheller (4), and by the authors in an earlier paper (6).

Briefly, a modification of the vapor recirculation equilibrium still described by Hipkin and Myers (2) was used in this work. Pressure in the still was controlled by a Cartesian manostat of the type described by Gilmont