Surface Tensions of Trialkyl Borates

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Experimental surface tensions, obtained at atmospheric pressure by the capillary rise method, were established for the following trialkyl borates: methyl, ethyl, propyl, isopropyl, butyl, and isobutyl. The observed values were correlated with temperature by means of polynomial regression analysis.

The amount of physical data for trialkyl borates is somewhat limited and scattered throughout the literature. To provide systematic and extensive experimental measurements of several physicochemical properties for this class of compounds, two investigations have thus far been carried out on the following series of representative homologs: methyl, ethyl, propyl, isopropyl, butyl, and isobutyl borates. One of the studies gives the results of vapor pressure-temperature correlations (*2*), and the other reports the temperature dependence of density and absolute viscosity (*3*). The present work is concerned with the measurement of surface tensions and their correlation with temperature.

EXPERIMENTAL

The borates were purified, assayed, and stored in the manner previously described (*2*). Following an earlier procedure (*3*), the same bath fluids, thermometers, and thermometer calibrations were employed. Bath temperatures were maintained by means of a Model 2155 Versa-Therm Electronic Temperature Controller (Cole-Palmer Instrument Co., Chicago, Ill. 60648).

Surface tensions were observed at atmospheric pressure by the capillary rise technique, and the tube radii were found by using deionized water and spectroquality benzene as calibrating liquids. Two capillaries, having different radii, were simultaneously immersed in the liquid under observation, and

Table I. Observed and Calculated Surface Tensions

		γ, Dyn/cm		
Borate	T, °C	Obsd	Calcd	Deviation, %
Methyl	25	19.45	19.447	0.0138
	30	18.85	18.858	−0.0429
	40	17.68	17.667	0.0716
	50	16.45	16.460	−0.0626
	60	15.24	15.237	0.0203
	67.4		14.321	
Ethyl	25	19.27	19.268	0.00856
	30	18.80	18.782	0.0938
	40	17.76	17.802	−0.237
	50	16.82	16.811	0.0555
	60	15.82	15.808	0.0748
	70	14.83	14.795	0.239
	80	13.72	13.770	−0.360
	90	12.75	12.734	0.126
	100		11.687	
	110		10.629	
	118.3		9.743	
Propyl	25	21.51	21.470	0.184
	30	21.05	21.076	−0.124
	40	20.24	20.262	−0.129
	50	19.43	19.432	−0.0112
	60	18.56	18.579	−0.102
	70	17.74	17.711	0.162
	80	16.83	16.834	−0.0264
	90	16.02	15.953	0.418
	100	15.07	15.072	−0.0151
	110	14.15	14.197	−0.332
	130	12.44	12.482	−0.341
	150	10.90	10.849	0.468
	170	9.32	9.336	−0.175
	178.6		8.733	
Isopropyl	25	17.53	17.502	0.157
	30	17.02	17.038	−0.105
	40	16.10	16.118	−0.111
	50	15.24	15.210	0.195
	60	14.30	14.315	−0.105
Isopropyl, *contd.*	70	13.41	13.432	−0.164
	80	12.53	12.561	−0.250
	90	11.70	11.703	−0.0260
	100	10.93	10.857	0.667
	130	8.37	8.393	−0.275
	139.4		7.644	
Butyl	25	23.00	23.017	−0.0740
	30	22.63	22.660	−0.134
	40	21.94	21.947	−0.0299
	50	21.26	21.232	0.132
	60	20.55	20.517	0.162
	70	19.86	19.801	0.298
	80	19.09	19.084	0.0305
	90	18.27	18.367	−0.530
	100	17.69	17.649	0.233
	110	16.89	16.930	−0.236
	130	15.58	15.490	0.577
	150	13.99	14.048	−0.411
	170	12.60	12.602	−0.0166
	190	11.09	11.154	−0.575
	210	9.76	9.703	0.588
	233.5		8.304	
Isobutyl	25	21.31	21.362	−0.242
	30	20.98	20.959	0.0992
	40	20.18	20.156	0.119
	50	19.38	19.355	0.130
	60	18.55	18.556	−0.0302
	70	17.78	17.758	0.122
	80	16.94	16.963	−0.135
	90	16.14	16.169	−0.182
	100	15.40	15.378	0.144
	110	14.55	14.588	−0.263
	130	13.11	13.015	0.726
	150	11.42	11.449	−0.255
	170	9.80	9.891	−0.930
	190	8.40	8.341	0.704
	210.4		6.768	

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Table II. Constants for Equation 2

R in $B(OR)_3$	a	$-b$	c	d	S
CH_3	19.447	1.1743×10^{-1}	-8.1670×10^{-5}	0	8.49×10^{-3}
C_2H_5	19.268	9.6918×10^{-2}	-5.5536×10^{-5}	0	2.81×10^{-2}
C_3H_7	21.470	7.8092×10^{-2}	-1.5798×10^{-4}	8.2359×10^{-7}	3.45×10^{-2}
iso-C_3H_7	17.502	9.3226×10^{-2}	6.1617×10^{-5}	0	3.13×10^{-2}
C_4H_9	23.017	7.1310×10^{-2}	-3.5685×10^{-6}	0	5.04×10^{-2}
iso-C_4H_9	21.362	8.0506×10^{-2}	9.6590×10^{-6}	0	4.60×10^{-2}

the heights read to within ±0.02 cm with an uncalibrated precision cathetometer. At least three or four pairs of readings were taken at any given temperature. The arithmetic mean of the surface tension deduced from each capillary was regarded as the final observation. The difference between the two was in no instance greater than 1%. Densities were taken from a previous work (*3*).

RESULTS AND DISCUSSION

Observed surface tensions were deduced from the usual capillary rise equation for liquids that wet glass and therefore have essentially a zero contact angle,

$$\gamma = hg\rho r/2 \qquad (1)$$

where γ is in dyn cm^{-1}, g is the gravitational constant, ρ is the density, and r is the capillary radius.

The plot of surface tension vs. temperature showed the expected general increase in γ with molecular weight for the unbranched homologs and correspondingly lower γ's for the branched isomers (those of the isopropyl compound being even lower than observations for methyl and ethyl borates). The abnormal amount of curvature shown by the ethyl borate plot above 90°C would seem to confirm the suggestion of partial decomposition unique for this homolog (*5*); a similar anomaly was previously noted in the plot of density vs. temperature (*3*).

Experimental γ's were correlated with temperature by the relationship

$$\gamma = a + b(t - 25) + c(t - 25)^2 + d(t - 25)^3 \qquad (2)$$

where t = °C, and the constants a, b, c, and d were evaluated by polynomial regression analysis.

Observed and calculated γ's are given in Table I along with the per cent deviation as previously defined (*2*). Surface tensions for ethyl borate above 90°C are for the undecomposed compound. These values were calculated from the equation deduced for this homolog from 25–90°C. The last temperature for each borate is the normal boiling point (*2*).

The overall Table I average derivation is ±0.191%. A search of the literature disclosed one report of the γ's of methyl borate at three temperatures between 15-52°C and at four temperatures between 15-64°C for ethyl borate (*4*), and one other investigation of the γ's of propyl and butyl borates at 20°C (*1*). Temperature correlations were not given in either work.

Constants a, b, c, and d for Equation 2 are listed in Table II along with the standard error of estimate, S, as previously defined (*2*).

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Sound Velocities and Related Properties in Binary Solutions of Aniline

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In continuation of our work on thermodynamic properties of binary solutions comprising polar and associated liquids (*5–9*), we present in this paper measurements of sound velocities and densities as functions of temperature and composition for solutions of aniline in tetraline, bromobenzene, methanol, *tert*-butanol, pyridine, and tetrahydrofuran. Using Eyring's equation (*11*), we evaluated the free volume in liquids and solutions. The free volume so calculated can be utilized to explain the behavior of liquids and solutions in various ways (*3–5*).

EXPERIMENTAL

Sound Velocity Measurements. The ultrasonic velocities were measured at 3 Mc/sec frequency by using the optical interference method of Hiedemann and Bachem (*14*, *15*). The liquid, contained in an optical glass cell 30 × 30 × 20

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