Greek Notation

ΔH_i	change in H of pure component i between two states, Btu/lb
ΔH_P	change in H between two temperatures at constant pressure, Btu/lb
ΔH_T	change in H between two pressures at constant temperature, Btu/lb
ΔH_{vap}	specific enthalpy of vaporization, Btu/lb
μ	Joule–Thomson coefficient $\equiv (\partial T/\partial P)_H$, °F/psia
ϕ	isothermal throttling coefficient $\equiv (\partial H/\partial P)_T$, Btu/lb-psia
ϕ(A)	values of ϕ adjusted to ensure thermodynamic consistency
ϕ(S)	smoothed ϕ values before thermodynamic consistency checks

Subscripts

i	component in a mixture
j, k	identify specific experimental values of temperature or pressure
l	saturated liquid
M	mixture
P	property at pressure P, psia
T	property at temperature T, °F
1,2	component number in a mixture

Superscripts

E	excess property
°	designates ideal gas property
	mean property

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Received for review May 26, 1976. Resubmitted June 5, 1978. Accepted June 26, 1978. The experimental investigation was funded by the National Science Foundation. The interpretation of the data was made under a grant from the Gas Processor Association.

Supplementary Material Available: Tables of isobaric, isothermal, and isenthalpic data (8 pages). Ordering information is given on any current masthead page.

A Refractometric Study of Trialkyl Borates†

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Refractive indices at wavelengths of 5893, 5461, and 4358 Å have been observed for the following trialkyl borates: methyl, ethyl, propyl, isopropyl, butyl, and isobutyl. The measurements, which were made at temperatures between 5 and 60 °C for methyl borate and from 5 to 90 °C for the remaining homologues, were then correlated with temperature and wavelength. Thermal coefficients of the refractive indices and of the Lorentz–Lorenz molar refractions were calculated, and structural interpretations were offered whenever possible.

Since the amount of physical data for the trialkyl borates is somewhat meager and scattered throughout the literature, studies have been undertaken in this laboratory in order to obtain systematic and extensive measurements for the following series of homologues: methyl, ethyl, propyl, isopropyl, butyl, and isobutyl. These studies have thus far yielded data on the vapor pressures (*1*), densities and absolute viscosities (*2*), and surface tensions (*3*), as functions of temperature up to the normal boiling point. A further search of the literature has revealed a paucity of information with regard to the refractometric properties of this class of compounds. Individual refractive indices have been reported (for the D line), at a few different temperatures (*4*, *5*), and one reference (*6*) offered a temperature correlation of the form, $n_D^t = A - Bt$, with constants A and B being given for the D line at temperature t °C; since the data which served as the

† This work was abstracted from the M.Eng. thesis of Stephen Frimpong, University of Louisville, Louisville, Ky., 1977.

0021-9568/79/1724-0067$01.00/0

Table I. Refractive Indices

borate	t, °C	λ, Å 5893	5461	4358	borate	t, °C	λ, Å 5893	5461	4358
methyl	5	1.364 82	1.365 87	1.371 65	isopropyl	75	1.350 20	1.351 99	1.357 47
	10	1.362 38	1.363 48	1.369 10		80	1.347 86	1.349 43	1.355 09
	15	1.359 92	1.361 01	1.366 68		85	1.345 43	1.346 75	1.352 19
	20	1.357 39	1.358 66	1.364 20		90	1.342 93	1.344 18	1.349 45
	25	1.354 92	1.356 19	1.361 90		100	1.337 91	1.338 85	1.343 88
	30	1.352 44	1.353 78	1.359 33		110	1.332 90	1.333 43	1.338 18
	35	1.349 89	1.351 29	1.356 83		120	1.327 87	1.327 92	1.332 35
	40	1.347 35	1.348 86	1.354 40		130	1.322 81	1.322 31	1.326 40
	45	1.344 79	1.346 24	1.351 92		139.4	1.318 03	1.316 94	1.320 68
	50	1.342 23	1.343 60	1.349 45	butyl	5	1.414 74	1.416 13	1.423 58
	55	1.339 79	1.341 09	1.346 97		10	1.412 98	1.414 08	1.421 48
	60	1.337 27	1.338 51	1.344 49		15	1.410 98	1.412 31	1.419 33
	67.4	1.333 42	1.334 59	1.340 82		20	1.409 10	1.409 76	1.417 28
ethyl	5	1.380 96	1.381 82	1.387 84		25	1.407 14	1.408 21	1.415 29
	10	1.378 57	1.379 41	1.385 58		30	1.405 24	1.406 42	1.413 30
	15	1.376 09	1.377 18	1.383 14		35	1.403 15	1.404 51	1.411 30
	20	1.373 80	1.374 87	1.380 82		40	1.401 06	1.402 36	1.408 98
	25	1.371 51	1.372 76	1.378 80		45	1.398 90	1.400 49	1.407 03
	30	1.369 01	1.370 51	1.376 65		50	1.396 87	1.398 37	1.404 84
	35	1.366 58	1.368 19	1.374 18		55	1.394 88	1.396 44	1.403 00
	40	1.364 07	1.365 87	1.371 65		60	1.392 81	1.394 44	1.400 84
	45	1.361 56	1.363 41	1.369 23		65	1.390 75	1.392 43	1.398 76
	50	1.358 28	1.361 01	1.366 88		70	1.388 56	1.390 41	1.396 66
	55	1.356 57	1.358 66	1.364 39		75	1.386 61	1.388 27	1.394 74
	60	1.354 02	1.356 12	1.361 77		80	1.384 59	1.386 25	1.392 57
	65	1.351 55	1.353 58	1.359 14		85	1.382 45	1.384 28	1.390 33
	70	1.349 00	1.351 16	1.356 70		90	1.380 36	1.392 19	1.388 21
	75	1.346 51	1.348 67	1.354 02		100	1.376 02	1.378 05	1.384 11
	80	1.344 40	1.346 36	1.351 36		110	1.371 70	1.373 87	1.379 89
	85	1.342 10	1.343 86	1.348 66		120	1.367 34	1.369 66	1.375 67
	90	1.339 39	1.341 61	1.345 93		130	1.362 94	1.365 41	1.371 43
	100	1.334 51	1.336 29	1.340 37		140	1.358 50	1.361 12	1.367 18
	110	1.329 63	1.331 15	1.334 68		150	1.354 01	1.356 80	1.362 92
	118.3	1.325 60	1.326 83	1.329 84		160	1.349 49	1.352 45	1.358 65
propyl	5	1.401 54	1.403 02	1.409 65		170	1.344 92	1.348 06	1.354 36
	10	1.399 44	1.400 84	1.407 40		180	1.340 31	1.343 64	1.350 06
	15	1.397 35	1.398 74	1.405 32		190	1.335 66	1.339 18	1.345 75
	20	1.395 23	1.396 50	1.403 18		200	1.330 96	1.334 69	1.341 43
	25	1.393 12	1.394 62	1.401 22		210	1.326 22	1.330 16	1.337 09
	30	1.390 93	1.392 43	1.398 94		220	1.321 44	1.325 60	1.332 74
	35	1.388 07	1.390 29	1.396 72		230	1.316 62	1.321 00	1.328 38
	40	1.386 67	1.388 21	1.394 55		233.5	1.314 92	1.319 38	1.326 85
	45	1.384 53	1.386 12	1.392 39	isobutyl	5	1.409 16	1.410 47	1.417 47
	50	1.382 39	1.383 79	1.390 46		10	1.407 32	1.408 39	1.415 35
	55	1.380 30	1.381 63	1.387 97		15	1.405 30	1.406 36	1.413 42
	60	1.377 46	1.379 47	1.385 77		20	1.403 27	1.404 45	1.411 36
	65	1.375 29	1.377 36	1.383 58		25	1.401 12	1.402 48	1.409 65
	70	1.373 12	1.375 12	1.381 45		30	1.399 03	1.400 61	1.407 58
	75	1.371 00	1.373 07	1.379 05		35	1.396 92	1.398 61	1.405 38
	80	1.368 70	1.370 57	1.376 65		40	1.394 82	1.396 62	1.403 18
	85	1.366 52	1.368 51	1.374 44		45	1.392 69	1.394 62	1.400 91
	90	1.364 13	1.366 43	1.372 03		50	1.390 57	1.392 61	1.398 88
	100	1.359 52	1.361 87	1.367 41		55	1.388 10	1.390 48	1.396 48
	110	1.354 86	1.357 38	1.362 67		60	1.386 42	1.388 45	1.394 55
	120	1.350 16	1.352 87	1.357 86		65	1.384 23	1.386 43	1.392 27
	130	1.345 41	1.348 32	1.353 00		70	1.382 01	1.384 35	1.390 40
	140	1.340 61	1.343 74	1.348 08		75	1.379 87	1.382 00	1.388 16
	150	1.335 77	1.339 13	1.343 09		80	1.377 77	1.379 84	1.386 15
	160	1.330 89	1.334 49	1.338 05		85	1.375 54	1.377 80	1.384 02
	170	1.325 96	1.329 81	1.332 95		90	1.373 74	1.375 56	1.381 95
	178.6	1.321 68	1.325 77	1.328 52		100	1.369 20	1.371 18	1.377 45
isopropyl	5	1.383 97	1.385 39	1.391 65		110	1.364 88	1.366 69	1.373 08
	10	1.381 77	1.382 99	1.389 33		120	1.360 53	1.362 13	1.368 68
	15	1.379 43	1.380 77	1.386 96		130	1.356 17	1.357 50	1.364 26
	20	1.377 02	1.378 60	1.384 71		140	1.351 79	1.352 80	1.359 80
	25	1.374 67	1.376 50	1.382 70		150	1.347 39	1.348 04	1.355 32
	30	1.372 25	1.374 07	1.380 38		160	1.342 98	1.343 20	1.350 82
	35	1.369 89	1.371 57	1.377 91		170	1.338 54	1.338 29	1.346 28
	40	1.367 33	1.369 14	1.375 38		180	1.334 09	1.333 31	1.341 72
	45	1.364 89	1.366 81	1.372 92		190	1.329 62	1.328 25	1.337 13
	50	1.362 50	1.364 48	1.370 26		200	1.325 12	1.323 13	1.332 51
	55	1.360 11	1.362 03	1.367 89		210	1.320 62	1.317 94	1.327 87
	60	1.357 64	1.359 43	1.365 42		210.4	1.320 43	1.317 73	1.327 68
	65	1.355 17	1.357 02	1.362 79					
	70	1.352 75	1.354 41	1.360 10					

Table II. Constants for Equation 1

borate	a	$-b \times 10^4$	$-c \times 10^7$	$S \times 10^4$
methyl	1.367 33	4.938 90	1.311 19	0.4193
	1.368 18	4.663 08	4.744 28	0.4997
	1.374 05	4.886 15	0.668 480	0.7299
ethyl	1.383 60	4.942 36	−0.331 820	2.466
	1.383 99	4.432 40	3.377 91	1.294
	1.389 87	4.270 09	6.797 04	1.277
propyl	1.403 65	4.187 82	2.249 80	2.299
	1.405 04	4.163 14	1.542 70	0.9030
	1.411 61	4.122 98	2.962 94	0.9650
isopropyl	1.386 49	4.723 89	1.339 37	0.7077
	1.387 53	4.373 37	4.952 73	0.8967
	1.393 79	4.347 28	6.438 61	1.351
butyl	1.416 86	3.873 77	2.106 19	1.014
	1.417 92	3.812 67	1.744 13	1.438
	1.425 54	4.082 03	0.619 044	0.9269
isobutyl	1.411 45	4.132 66	0.917 606	1.377
	1.412 17	3.747 21	3.523 79	0.8806
	1.419 63	4.080 09	1.377 92	1.833

Table III. Thermal Coefficients

borate	$-(dn/dt) \times 10^4$	$(d \ln R/dt) \times 10^4$
methyl	5.024	2.160
	4.971	2.340
	4.930	2.686
ethyl	4.911	1.808
	4.753	2.248
	4.916	2.041
propyl	4.402	1.479
	4.310	1.748
	4.404	1.714
isopropyl	4.851	1.497
	4.844	1.559
	4.959	1.492
butyl	4.074	1.364
	3.978	1.631
	4.141	1.435
isobutyl	4.220	1.249
	4.082	1.601
	4.211	1.497

basis for this correlation were taken from a rather large number of works, and over only a small temperature range, the resulting calculated values of n are not in accord with the findings of the present investigation, particularly at the higher temperatures. In the light of these limitations, it was decided to experimentally observe n at three wavelengths, 5893, 5461, and 4358 Å, at 5 °C intervals from 5 to 60 °C for methyl borate and from 5 to 90 °C for the other homologues and then to correlate the measurements with temperature and wavelength.

Experimental Section

The borates were purified, assayed, and stored in the manner previously described (*1*). Refractive indices were measured with a Bausch and Lomb Model 33-45-03 refractometer, capable of a precision of ±0.000 03 RI units. Prism temperatures were maintained to within ±0.02 °C by means of a water circulating bath unit (Catalog No. 3052, Labline Inc., Chicago, Ill.). A General Electric Sodium Lab-Arc was used as the source of the D line, 5893 Å, whereas a Bausch and Lomb mercury arc illuminator provided the green and blue lines, i.e., 5461 and 4358 Å, respectively.

Results and Discussion

Table I lists the observed refractive index measurements, which were made at 5 °C intervals from 5 to 60 °C for the methyl borate and from 5 to 90 °C for the other homologues. In view of the appearance of the plots of n vs. t, values of n above 60 °C (or above 90 °C) were calculated at 10 °C intervals from the following equation

$$n = a + bt + ct^2 \qquad t = °C \tag{1}$$

(Constants a, b, and c, which were evaluated by means of polynomial regression analysis on a Hewlett-Packard Model 2000C computer, are given in Table II, along with the standard error of estimate, as previously defined (*1*); they are reported in the wavelength order 5893, 5461, and 4358 Å.) An examination of the Table I data shows the expected increase in n with molecular weight, and the lower values of the branched isomers in relation to the corresponding unbranched homologues. Too, the inverse variation of n with wavelength λ and temperature t is clearly evident.

As shown in Table I, it is apparent that n changes with t only to a very slight extent. From a structural standpoint, it is important that the Lorentz–Lorenz molar refraction, R, which is of an additive and constitutive nature, should be essentially temperature independent. In order to test the thermal dependence of R, the basic relationship

$$R = M(n^2 - 1)/\rho(n^2 + 2) \tag{2}$$

where M is the molecular weight and ρ the density may be differentiated to give

$$d \ln R/dt = [6n(\partial n/\partial t)/(n^2 - 1)(n^2 + 2) - \partial \ln \rho/\partial t] \tag{3}$$

Table III lists average values for dn/dt (deduced from eq 1) and for $d \ln R/dt$, where the data for the evaluation of $\partial \ln \rho/\partial t$ were taken from ref 2; the results are tabulated in the same order of wavelengths as in Table II.

The low thermal coefficients of the Lorentz–Lorenz molar refraction shown by the Table III data, and which amount to less than 0.03%/deg, would seem to justify the use of R in structure studies (at least for this class of compounds).

A correlation between n and λ may clearly be demonstrated by means of the following dispersion equation

$$n = A + B/\lambda^2 + C/\lambda^4 \qquad \lambda = Å \tag{4}$$

Constants A, B, and C, are given in Table IV, and they were calculated at 20 °C (this being the most common temperature at which refractive indices are generally reported).

Table IV. Constants for Equation 4

borate	A	$B \times 10^{-4}$	$C \times 10^{-12}$
methyl	1.350 54	21.186 7	0.903 317
ethyl	1.370 74	0.326 256	3.572 58
propyl	1.390 80	5.591 74	3.404 61
isopropyl	1.366 84	37.036 4	−0.589 662
butyl	1.415 36	−52.402 9	10.643 4
isobutyl	1.400 64	−4.407 61	4.704 44

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Received for review May 26, 1978. Accepted October 7, 1978.