

Table I. *K*-Values, Vapor Pressures, and Activity Coefficients

Compound	100 °C			120 °C			130 °C			140 °C		
	<i>K</i>	<i>p</i> ^o , atm	γ_{∞}	<i>K</i>	<i>p</i> ^o , atm	γ_{∞}	<i>K</i>	<i>p</i> ^o , atm	γ_{∞}	<i>K</i>	<i>p</i> ^o , atm	γ_{∞}
Ethyl mercaptan ^a	3.65	6.29	0.877	5.41	9.65	0.857	6.20	11.76	0.856	7.06	14.16	0.865
<i>n</i> -Propyl mercaptan ^a	1.56	2.52	0.899	2.43	4.11	0.879	2.85	5.14	0.845	3.44	6.35	0.829
<i>sec</i> -Butyl mercaptan ^a	0.939	1.54	0.862	1.53	2.57	0.861	1.83	3.25	0.841	2.24	4.06	0.824
Isobutyl mercaptan ^a	0.860	1.39	0.878	1.39	2.35	0.866	1.68	3.14	0.842	2.06	3.74	0.817
<i>n</i> -Butyl mercaptan ^a	0.670	1.05	0.904	1.145	1.81	0.905	1.38	2.33	0.875	1.73	2.95	0.859
Dimethyl sulfide ^b	3.07	5.950	0.933	4.45	9.080	0.953	5.30	11.067	0.964	6.32	13.346	0.976
Methyl ethyl sulfide ^b	1.25	2.610	0.831	2.14	4.244	0.903	2.70	5.302	0.931	3.38	6.544	0.965
Diethyl sulfide ^b	0.625	1.258	0.854	1.14	2.154	0.928	1.50	2.754	0.955	1.925	3.472	0.982
Dimethyl disulfide ^b				0.74	1.330	0.956	0.95	1.729	0.973	1.2	2.215	0.991

^a*K*-values are given at 1.36 atm. ^b*K*-values are given at 1.70 atm.

Nomenclature

F_a = volumetric flow rate of elution gas at ambient conditions

K_i = equilibrium y_i/x_i for component *i*

n = mol of stationary liquid phase on column packing

p = column pressure

p_a = ambient pressure

p^o = vapor pressure

R = gas constant

t_{R_i} = retention time of solute *i*

t_g = retention time of hypothetical "nonabsorbed" gas

T = absolute temperature

T_a = absolute ambient temperature

V_{R_i} = retention volume of component *i*

V_g = free gas volume

V_i = liquid molal volume of component *i*

y = mol fraction in gas phase

z_m = compressibility factor of elution gas at column operating conditions

z_a = compressibility factor of elution gas at ambient conditions

γ_i = activity coefficient of component *i* in the liquid phase at *T*

ϕ_i = fugacity coefficient of component *i* in the elution gas at *T* and *p*

ϕ_i^o = fugacity coefficient of pure vapor *i* at *T* and p_i^o

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Vapor-Liquid Equilibria of Methyl Borate–Carbon Tetrachloride and Methyl Borate–Benzene Systems

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Vapor-liquid equilibrium measurements at 760 torr are reported for the methyl borate–carbon tetrachloride and methyl borate–benzene systems. Analysis of the data shows both of these systems to approach ideality. Equilibrium relations may be represented by the relative volatility equation with $\alpha_{MB-CCl_4} = 1.280$ and $\alpha_{MB-BZ} = 1.431$.

As a continuation of a systematic study of borate compounds initiated by one of the authors, the vapor-liquid equilibria have been measured for the two binary systems, methyl borate–carbon tetrachloride and methyl borate–benzene at a pressure of 760 ± 1 torr. An Altsheler (circulation type) still

was used and is described in detail by Hala et al. (3). The methyl borate was purchased from Apache Chemicals, Inc. (98%), and was purified by successive fractional distillations to 99.9+ % purity, giving a measured normal boiling point of 68.6 °C as compared with 68.7 °C (6). Analysis of the borate was by the standard mannitol–sodium hydroxide titration (5). Eastman Kodak spectrograde benzene and carbon tetrachloride were used. The benzene was "ACS certified" with a reported normal boiling point of 80.1 ± 0.1 °C as compared with an API-44 value of 80.1 °C (1). The carbon tetrachloride had a reported boiling point of 76.7 ± 0.1 °C as compared with 76.54 °C (4). Both the benzene and carbon tetrachloride were used as purchased.

Mixture analyses were from refractive index measurements using a Bausch and Lomb Model 33-45-03 refractome-

Table I. Vapor-Liquid Equilibria

$t, ^\circ\text{C}$	$x,$ liquid mol fraction of methyl borate	$y,$ vapor mol fraction of methyl borate	y_i^a vapor mol fraction of methyl borate	t_i^a $^\circ\text{C}$
Methyl borate—carbon tetrachloride				
76.7	0.000	0.000
75.6	0.108	0.130	0.134	75.6
75.2	0.155	0.187	0.189	75.2
75.1	0.175	0.208	0.213	75.0
74.7	0.227	0.266	0.272	74.6
74.5	0.251	0.294	0.299	74.4
74.1	0.290	0.344	0.343	74.1
73.9	0.324	0.370	0.379	73.8
73.7	0.346	0.403	0.403	73.6
73.1	0.427	0.486	0.488	72.9
72.9	0.450	0.517	0.515	72.8
72.6	0.490	0.550	0.551	72.5
71.2	0.652	0.711	0.706	71.2
70.6	0.723	0.779	0.770	70.6
70.0	0.808	0.851	0.844	70.0
69.2	0.923	0.942	0.940	69.2
68.6	1.000	1.000
Methyl borate—benzene				
80.1	0.000	0.000
78.8	0.080	0.118	0.110	79.1
77.5	0.172	0.238	0.228	77.9
76.3	0.262	0.348	0.336	76.8
75.2	0.363	0.455	0.449	75.5
73.8	0.476	0.579	0.565	74.2
73.0	0.572	0.659	0.657	73.1
71.7	0.668	0.747	0.743	72.1
70.6	0.783	0.841	0.838	70.8
69.7	0.885	0.918	0.917	69.7

^a Values calculated assuming ideality at measured x values.

ter capable of precision to ± 0.00003 RI units. The sodium D-line at 25.0 ± 0.1 $^\circ\text{C}$ was used. Solutions for the calibrations were prepared gravimetrically from the pure components, and the refractive index vs. concentration curves showed only slight curvature. Reproducibility of sample analyses was precise through the third decimal place.

Experimental data are tabulated in Table I. Along with the experimental data are estimations of temperature and vapor compositions as calculated by assuming ideal behavior at the measured liquid compositions.

Calculations, assuming ideality, were made using the following equations for representation of the vapor pressures.

Methyl borate

$$\log_{10} P^\circ = 5.7221 - 589.399/(138.82 + t)$$

Carbon tetrachloride

$$\log_{10} P^\circ = 6.93390 - 1242.43/(230 + t)$$

Benzene

$$\log_{10} P^\circ = 7.6546 - 1686/(273.15 + t)$$

The equation for methyl borate was derived from data of Christopher and Shilman (2) and represents their experimental data with a higher degree of reproducibility than the equation reported in the original article. Equations for the other two compounds were taken from Lange's "Handbook of Chemistry" (6, 7). The estimated data give a reasonable representation of the measured values. In addition, activity coefficients were calculated from the equation

$$\gamma = \frac{yP}{xP^\circ} \tag{1}$$

and varied randomly, for both components, about a value of unity. Values of the activity coefficients ranged from 0.95 to 1.02 for the methyl borate—carbon tetrachloride system and from 0.94 to 1.08 for the methyl borate—benzene system. As a consequence of these findings, the equilibrium data for these systems may be adequately represented for most purposes by the relative volatility equation

$$y = \frac{\alpha x}{1 + x(\alpha - 1)} \tag{2}$$

with the following values of the relative volatilities

$$\alpha_{\text{MB-CCl}_4} = 1.280$$

$$\alpha_{\text{MB-C}_6\text{H}_6} = 1.431$$

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Nomenclature

P = total pressure, mm Hg

P° = vapor pressure, mm Hg

x = mol fraction, liquid

y = mol fraction, vapor

t = degrees Celsius

α = relative volatility

γ = activity coefficient, dimensionless

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