

concluded that less deviation from the *trans* position occurs in the bromide than in the chloride and chlorobromide. Therefore, to obtain equilibrium in the liquid state of the recently thawed bromide, fewer of the *trans* molecules need isomerize and the effect upon the heat capacity would be considerably less.

The transition in the bromide has been observed by White and Morgan.³ They explain it as being due to the setting in of rotation about the zigzag Br-C-C-Br axis rather than a rotation about the carbon-carbon bond, since the dielectric constant through the transition was only minutely affected. Raman spectra measurements show that upon solidification, rotation of one halogen with respect to the other is greatly restricted. Since the heat of transition is small, compared to the heat of fusion, this is a plausible explanation of the transition.

However, the transition is of the sharp or fusion type, rather than the gradual or rotational type, and may be just a phase transition. The transitions in the chloride and the chlorobromide are of the hump or rotational type, and may well be attributed to zigzag rotation about the X-C-C-X

axis, since the dielectric constant of the chloride was unaffected in the region of the hump. Further information upon these transitions is necessary to establish this point.

While heating through the transition in the bromide, it was noticed that the sample superheated, sometimes as much as 0.35°. The same effect was noticed by White and Morgan.³

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Summary

1. The heat capacities of 1,2-dibromoethane, 1,2-dichloroethane, and 1,2-bromochloroethane have been measured over the range 90–320°K.

2. Heats of fusion and transition have been measured for these compounds.

3. Certain phenomena in connection with the thermal history of these compounds and its effect upon the specific heat have been interpreted in the light of restricted intramolecular rotation in these compounds.

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The Viscosity of Solutions of Sulfur Dioxide in Organic Liquids

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This paper is a continuation of the work begun by Lewis¹ and Adams and Rogers² on the viscosity of solutions of sulfur dioxide in organic liquids. The present paper includes data concerning the effect of dissolved sulfur dioxide on the viscosity of *n*-propyl bromide, *i*-propyl bromide and *n*-butyl bromide.

Experimental Part

n-Propyl bromide, *i*-propyl bromide and *n*-butyl bromide were each washed four to six times with concentrated sulfuric acid, followed by a solution of sodium carbonate, dried over calcium chloride and distilled.

	B. p., °C.	d_{25}^4	n_{25}^D
<i>n</i> -Propyl bromide	70.9	1.3430	1.4313
<i>i</i> -Propyl bromide	59.6	1.3060	1.4220
<i>n</i> -Butyl bromide	101.6	1.2689	1.4373

The apparatus and procedure were the same as described in the earlier paper.²

(1) J. R. Lewis, *THIS JOURNAL*, **47**, 626 (1925).

(2) H. E. Adams and H. E. Rogers, *ibid.*, **61**, 112 (1939).

Discussion

Density data for solutions of sulfur dioxide in *n*-propyl bromide, *i*-propyl bromide, and *n*-butyl bromide are found in Table I. Each liquid shows an expansion, in volume, when sulfur dioxide is dissolved in it. In the case of the *n*-propyl bromide solutions, mixtures from 0 to 60% sulfur dioxide have almost the same density as the pure *n*-propyl bromide.

In Fig. 1, the viscosity data in Table II are plotted. The viscosity is plotted against weight % and each curve is concave upward. Similar curves are obtained when the viscosity is plotted against volume %. The viscosity curves in Fig. 1 appear to be typical. The *n*-butyl bromide shows the greatest sag, as is to be expected. The difference between the viscosities of the pure sulfur dioxide and the pure *n*-butyl bromide is greater than it is for the other two liquids; consequently

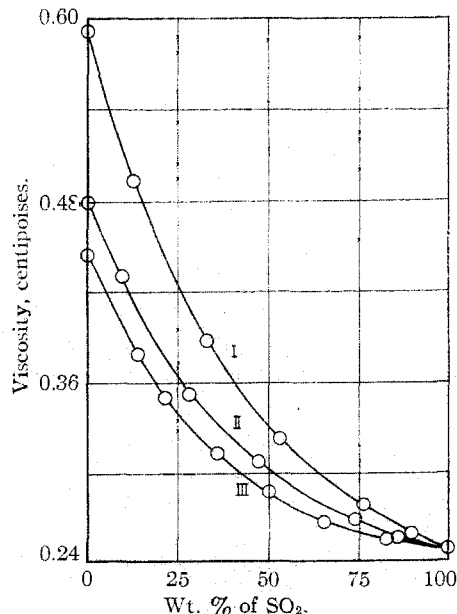
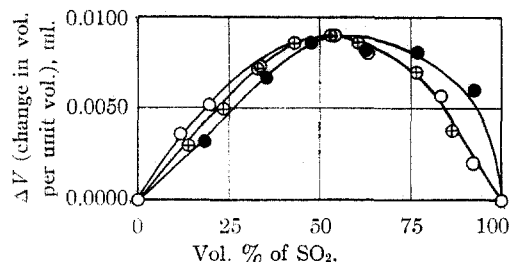
TABLE I
 DENSITY DATA AT 25°

<i>n</i> -Propyl bromide		<i>i</i> -Propyl bromide		<i>n</i> -Butyl bromide	
Wt. % of SO ₂	D. of soln.	Wt. % of SO ₂	D. of soln.	Wt. % of SO ₂	D. of soln.
0.00	1.3430	0.00	1.3060	0.00	1.2689
18.50	1.3430	11.71	1.3083	13.98	1.2780
35.61	1.3436	19.46	1.3107	23.37	1.2843
47.90	1.3436	33.33	1.3163	33.01	1.2906
62.83	1.3470	53.77	1.3266	43.00	1.2986
77.27	1.3513	63.29	1.3338	52.87	1.3076
93.51	1.3587	83.16	1.3491	60.44	1.3155
100.00	1.3680	91.75	1.3599	76.73	1.3342
		100.00	1.3680	86.38	1.3483
				100.00	1.3680

VISCOSITY DATA AT 25°

<i>n</i> -Propyl bromide		<i>i</i> -Propyl bromide		<i>n</i> -Butyl bromide	
Wt. % of SO ₂	Viscosity in centipoises	Wt. % of SO ₂	Viscosity in centipoises	Wt. % of SO ₂	Viscosity in centipoises
0.00	0.4797	0.00	0.4438	0.00	0.5914
9.46	.4311	13.79	.3789	12.44	.4942
28.00	.3527	21.72	.3499	33.24	.3877
47.13	.3076	36.13	.3183	53.14	.3237
73.97	.2679	50.18	.2870	76.06	.2786
85.75	.2569	65.24	.2664	89.53	.2592
100.00	.2472	82.68	.2555	100.00	.2472
		100.00	.2472		

the sag is not so great for the *i*-propyl bromide and *n*-propyl bromide curves.


 Fig. 1.—I, *n*-Butyl bromide; II, *n*-propyl bromide; III, *i*-propyl bromide.

 Fig. 2.—○, *n*-Butyl bromide; ●, *n*-propyl bromide; ○, *i*-propyl bromide.

Change in volume per unit volume (ΔV) has been plotted against volume per cent. in Fig. 2. ΔV was calculated using the expression in the earlier paper.² An expansion, on mixing, was found for each liquid. In the earlier work,² it was observed that ΔV was greatest for carbon tetrachloride, chloroform being next and bromoform the least. This was the same order as observed for the density-volume % curves for these three liquids. In this work, the maximum value for ΔV is practically the same for *n*-propyl bromide, *i*-propyl bromide, and *n*-butyl bromide. However, Fig. 1 and Fig. 2 give further evidence for the well-known fact that when liquids show an expansion in volume, on mixing, the fluidity of the mixture is greater than the fluidity calculated from the fluidities of the pure liquids. It is difficult to obtain an exact order for the fluidity and ΔV curves as was done in the earlier paper² because the expansion, on mixing, in each case, is almost identical.

Summary

1. The viscosities and densities of many solutions of sulfur dioxide in *n*-propyl bromide, *i*-propyl bromide, and *n*-butyl bromide were measured at 25°.
2. Expansion in volume, on mixing, was found in each case.
3. The results support the well-known fact that when liquids show an expansion, on mixing, the fluidity of the solution is greater than the fluidity calculated from the fluidities of the pure liquids.