

Table II. Surface Tension Measurements of 6.1 Wt. % NaF-17.7 Wt. % NaCl-76.2 Wt. % NaI Eutectic

Temperature, °C.	Surface Tension, Dynes/Cm.
550	102.3
578	101.5
600	100.5
602	97.4
651	98.2
681	94.8
693	95.5
741	91.0

Table III. Viscosity Measurements of 6.1 Wt. % NaF-17.7 Wt. % NaCl-76.2 Wt. % NaI Eutectic

Temperature, °C.	Kinematic Viscosity, Centistokes	Viscosity, Centipoises
557	0.69	1.76
581	0.68	1.72
601	0.62	1.56
610	0.60	1.50
661	0.545	1.34
679	0.53	1.29
696	0.53	1.29
734	0.525	1.25
755	0.47	1.11
794	0.465	1.10

expansion. Bloom's (1) data for sodium iodide were used.

The viscosity was determined by measuring the time required for the liquid between two levels in a calibrated cup to flow through a vertical capillary (0.04458 cm. in diameter and 1.5748 cm. long) in the bottom of the cup. The two levels were determined by two pointed electrodes mounted in the cup. Movement of the liquid level surface past an electrode point was indicated by a sudden change in electrical resistance. To make a run, the cup was filled by dipping it into the crucible; it was then raised above the crucible, and the time interval during which the liquid level fell from the top to the bottom electrode points was measured.

The viscosity capillary cup was calibrated by mathematical computations based on the physical dimensions (5). These computations were checked at room temperature using water and mercury.

RESULTS

The density measurements are given in Table I. The following equation fits the data with a standard deviation of 0.020: Density, g./cc. = $3.057 - 0.0009t$ (for t from 540° to 800° C.).

The measured values of density were very nearly equal to the values of density computed using additive volumes of the pure components. As an example, at 800° C. the measured density is 2.33 grams per cc., whereas the value computed from the volumes of the pure components is 2.29 grams per cc.

The surface tension measurements are given in Table II. The following equation fits the data with a standard deviation of 1.25: Surface tension, dynes/cm. = $133.18 - 0.05578t$ (for t from 550° to 750° C.). Values of the surface tensions of the pure salt components are not available in the literature.

The viscosity measurements are given in Table III. The following equation fits the data with a standard deviation of 0.0624: Viscosity, centipoises = $3.2952 - 0.002854t$ (for t from 560° to 800° C.). The measured viscosities of the salt mixture do not vary widely from those of its components. For example, the viscosity at 800° C. is 1.0 cp., whereas, the viscosities of the sodium chloride and sodium iodide components are given (4) as 1.556 and 1.10 cp., respectively. The viscosity of sodium fluoride is not reported. The authors believe that the accuracy in the determinations are as follows: for density, $\pm 0.9\%$; for surface tension, $\pm 1.2\%$; and for viscosity, $\pm 6\%$.

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Thermal Study of the Glass-Type Transformation of 2-Methylthiophene

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The detailed trend of the heat capacity in the region of 2-methylthiophene transformation has been delineated from 110° to 195° K. by equilibrium adiabatic calorimetry. The temperature dependence is that of a glass-type transition with a continuous inflected curve without a local maximum.

SECOND-ORDER glass-type transitions, which involve no apparent isothermal adsorption of heat, have been reported for 2-methylthiophene (7) and 3-methylthiophene (6). Since the detailed trend of the heat capacity in the transition region was not delineated in these investigations, a calorimetric sample of 2-methylthiophene was borrowed for a careful investigation of the thermal properties in this region.

The 2-methylthiophene studied was a portion of the standard sample of sulfur compound API-USBM Serial No. 21. In view of the previous characterization of the sample (7), further fractional fusions were not studied; however, microchemical analysis indicated 72.9% by weight of carbon and 7.52% of hydrogen (theoretical: C = 73.2; H = 7.37). A sample massing 62.631 grams was distilled into calorimeter W-14, and measurements were made in the Mark III adi-

abatic, vacuum cryostat previously described (2, 8). The heat capacity of the sample represented about 80% of the total.

The observed heat capacities are presented in consecutive sequence in Table I and depicted in Figure 1. Consequently, the temperature increments employed may usually be inferred from the adjacent mean temperatures. Increments in the transformation region were typically 0.3° to 1.8° K. These data, given in terms of the defined thermochemical calorie equal to 4.1840 joules, an ice point of 273.15° K., and a mole weight equal to 98.169 grams, have not been adjusted for curvature. They are considered to have a probable error of approximately 0.3%. At cooling rates as gradual as 10° per hour, slow energy release took place over periods in excess of 20 hours on heating into the

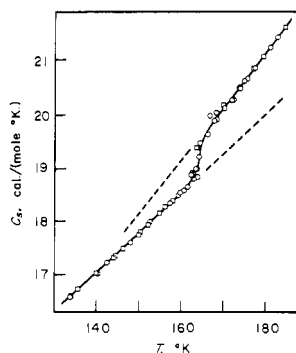


Figure 1. Heat capacity of 2-methylthiophene in the transformation region

○ This investigation
□ Pennington *et al.* (7)

Table I. Molal Heat Capacity of 2-Methylthiophene^a

T	C _p	T	C _p	T	C _p
Series I		Series IV		Series VIII	
110.15	14.87	144.65	17.37	168.52	19.99
116.36	15.31	152.84	17.98	175.07	20.65
125.02	15.93	157.84	18.40	181.23	21.27
133.86	16.56				
142.67	17.21	Series V		Series IX	
Series II		160.12	18.51	140.43	17.03
		161.60	18.69	148.17	17.60
157.56	18.35	162.28	18.62		
159.99	18.55	162.74	18.81	Series X	
160.87	18.59	163.19	18.79		
161.76	18.66	163.64	18.85	157.68	18.33
163.02	18.88	164.08	18.98	159.54	18.49
164.67	19.47	164.51	18.90	161.40	18.93
166.49	19.64	164.96	19.11	163.27	19.32
168.41	19.64			164.95	19.54
Series III		Series VI		Series XI	
		160.42	18.59		
170.40	20.14	161.94	18.99	164.90	20.16
172.27	20.30	162.94	19.23	166.37	19.64
174.10	20.51			168.09	19.92
175.91	20.70	Series VII			
177.72	20.90	163.64	18.99		
183.09	21.48	164.38	19.23		
191.70	22.39	165.10	19.24		
199.70	23.40	166.87	20.06		

^aUnits: cal., mole, ° K.

region 150° to 156° K. The energy release was independent of whether the sample was cooled previously from the melt or from temperatures between the anomaly and the melting point. Thermal equilibration in the transformation region required more than 8 hours; above and below the transformation region less than an hour was required. In view of small temperature increments and long equilibration times, a slight uncertainty in the drift introduced a significant error into the calculated heat capacity. These new data clearly define the phenomenon as a glass-type transition without isothermal adsorption of energy, as was suggested by the earlier study of Pennington *et al.* (7). The authors find a continuous inflected curve with no evidence for a maximum in the heat capacity in the transition region.

No report of the energy release noted below the transition has been made previously. Although it may be occasioned by the presence of a metastable form such as those reported for 3-methylthiophene (3) and 2-methylfuran (5), the magnitude of the energy release is comparable with that expected for the conversion of the undercooled form on the basis of the difference in the slopes of the heat capacity curves adjacent to the transition (Figure 1). The greater slope on the high temperature side is consistent with the onset of an additional degree of freedom. The barrier to rotation of the methyl group attached to the thiophene nucleus may be reasonably assumed to be lowered with increasing temperature so that a less restricted rotation takes place. Transformations of similar appearance have been noted in 3-methylthiophene (6), in *sym*-dimethylhydrazine (1), and in thiazole (4) with comparable rises in the heat capacities. If fusion did not occur so near the transition temperature, it is likely that another change in the trend of the slope would be noted after the methyl group had attained its maximum contribution to the heat capacity and the rotation had become essentially classical. The postulated change from librational to rotational motion of methyl groups obviously will not hold for thiazole. Increased librational motion of the aromatic rings (loosely packed by virtue of the protuberance) may be responsible in such cases.

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