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THERMAL EXPANSION OF COAL-DERIVED LIQUIDS

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ABSTRACT

The thermal expansion of two coal-derived liquids in the pressure range 1–4 kBar at temperatures up to 450 K has been measured calorimetrically. The high-temperature isotherms demonstrate a crossing point on the diagram of thermal expansion vs. pressure. The low-temperature isotherms demonstrate unusual behavior caused probably by the precipitation of high-melting components.

INTRODUCTION

Thermal expansion of coal-derived liquids as function of pressure and temperature is interesting for two reasons. First, from the point of view of basic knowledge it would be interesting to know, whether such complicated liquids have high-pressure–temperature behavior similar to the behavior of simple pure organic liquids, namely whether they demonstrate a clear crossing point of isotherms on the pressure diagram. Second, the thermal expansion data at the large temperature and pressure intervals can be used as a basis for calculation of other thermodynamic data of the liquids under investigation. The need of such data is evident, because the design of processes for the liquefaction of coal and upgrading of coal liquefaction products require a knowledge of thermodynamic properties of coal liquids at large pressure and temperature intervals.

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EXPERIMENTAL

The calorimetric method of determination of thermal expansion applied in this study was similar to that described previously [1] with some minor changes in the pressure transmission system. A sketch diagram of the system used in this study is presented in Fig. 1. The main difference in comparison to previously described devices is that the liquid under investigation is filled by a vacuum suction into the whole system including the extensiometric pressure sensor and the pressure generator. The calorimetric vessel consisted of a stainless steel tubing with two sleeves on it. The bottom stainless steel sleeve acted as a part of the Bridgman closure of the tubing and as a heat exchanger inside the calorimetric detector. The upper copper sleeve acted as a heat exchanger between the tubing and the calorimetric block. The method of calorimetric determination of thermal expansion and its thermodynamic basis have been described elsewere [1–3]. Here only the final equation used to determine the thermal expansion from directly measured parameters is given

$$\alpha - \alpha_r = -\frac{Q}{V_E T \Delta p} = \frac{kI}{T\Delta p} \tag{1}$$

where Δp is the stepwise pressure change in the liquid under investigation, Q is the heat effect caused by this pressure change, V_E is the volume of the liquid contained in the calorimetric vessel and surrounded by the calorimetric detector, α_r is a corrective term arising from the contribution of the vessel to the overall thermal effect; it is identified with the expansivity of the vessel material, in the present case that of the stainless steel; I is the integral

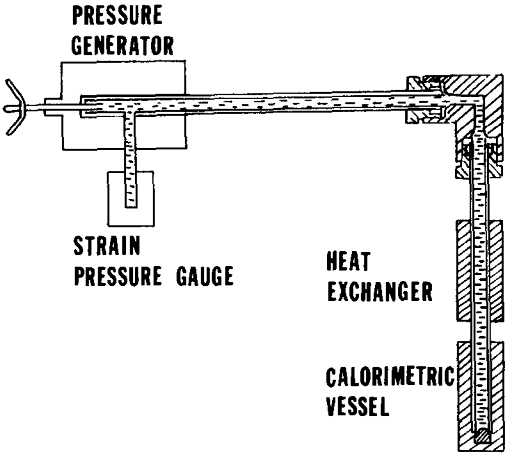

Fig. 1. A sketch diagram of the pressure transmission system and the calorimetric vessel arrangement.

TABLE 1

Physicochemical parameters of the liquids under investigation (C/H is the carbon to hydrogen ratio, $\bar{M}$ is the mean molecular weight, $\bar{T}_b$ is the mean boiling temperature, d is the density)

Liquid	C/H	$\bar{M}$	$\bar{T}_b$ (K)	d (g cm^{-3})
1	12.04	156	603	1.061
2	11.62	158	605	1.068

of the thermogram and k is the calibration constant. The calibration constant k was determined with decompression of nitrogen in the whole temperature range. The absolute temperature T was measured with a calibrated Pt resistance thermometer.

MATERIALS

The two oily liquids under investigation were derived from coal in a hydrogenation plant. Some of their physicochemical parameters are listed in Table 1 [4]. Unfortunately no exact chemical analysis was yet available. A thin chromatography test showed that the liquid No. 1 had some significant traces of dispersed carbon powder, while no such traces have been observed in the liquid No. 2.

TABLE 2

Thermal expansion of coal liquid 1 (pressure p in bar, thermal expansion α in 10^4 K^{-1})

447.76 K		414.31 K		378.21 K		345.84 K		314.88 K	
p	α	p	α	p	α	p	α	p	α
3599	3.29	3572	3.43	3591	3.64	3328	3.84	3516	3.75
3394	3.36	3372	3.54	3381	3.71	3073	3.93	3352	3.83
3128	3.48	3111	3.64	3117	3.75	2820	3.94	3186	3.85
2852	3.61	2847	3.77	2878	3.80	2576	4.06	3026	3.94
2558	3.78	2579	3.92	2632	3.94	2329	4.18	2868	4.00
2279	3.92	2316	3.97	2374	4.03	2075	4.32	2708	4.09
2022	4.10	2065	4.10	2114	4.22	1826	4.50	2462	4.26
1771	4.33	1827	4.28	1863	4.39	1587	4.69	2155	4.22
1530	4.55	1582	4.49	1615	4.60	1345	4.85	1869	4.77
1283	4.76	1331	4.71	1364	4.80	1106	5.12	1572	4.89
1036	5.11	1091	5.00	1112	5.08	868	5.40	1272	4.92
804	5.43	864	5.33	872	5.39	626	5.74	990	5.16
596	5.80	649	5.68	653	5.69	380	6.18	740	5.25
403	6.31	446	6.09	446	6.29	127	6.72	485	5.79
223	6.45	258	6.62	246	6.68			267	6.13
117	7.47	92	7.15	75	7.07			94	6.49

TABLE 3

Thermal expansion of coal liquid 2 (pressure p in bar, thermal expansion α in 10^4 K^{-1})

447.80 K		400.28 K		368.98 K		339.30 K		312.80 K	
p	α	p	α	p	α	p	α	p	α
3534	3.34	3515	3.56	3473	3.76	3443	3.90	3490	3.56
3338	3.40	3306	3.67	3192	3.81	3182	3.93	3266	3.77
3069	3.48	3040	3.72	2910	3.92	2907	4.05	3207	3.87
2803	3.54	2781	3.85	2632	4.04	2636	4.19	2992	4.18
2549	3.70	2271	4.17	2359	4.20	2363	4.43	2925	4.03
2293	3.92	1995	4.39	2090	4.38	2090	4.65	2710	4.41
2026	4.06	1725	4.59	1823	4.55	1816	4.87	2412	4.77
1765	4.29	1470	4.75	1566	4.76	1562	4.95	2134	5.05
1510	4.53	1221	5.04	1310	5.01	1317	5.07	1876	5.53
1257	4.78	974	5.37	1054	5.30	1063	5.30	1613	5.90
1013	5.14	733	5.73	807	5.69	816	5.60	1359	6.26
781	5.51	505	6.20	568	6.11	561	5.96	1107	6.41
554	5.99	301	6.64	337	6.52	325	6.43	850	6.42
365	6.49	119	7.25	125	7.03			585	6.34
212	7.11							331	6.31
								121	6.66

RESULTS AND DISCUSSION

The results of calorimetric measurements of thermal expansion of the two liquids are listed in Tables 2 and 3. Graphic representations of pressure dependence of thermal expansion at different temperatures are given in Figs.

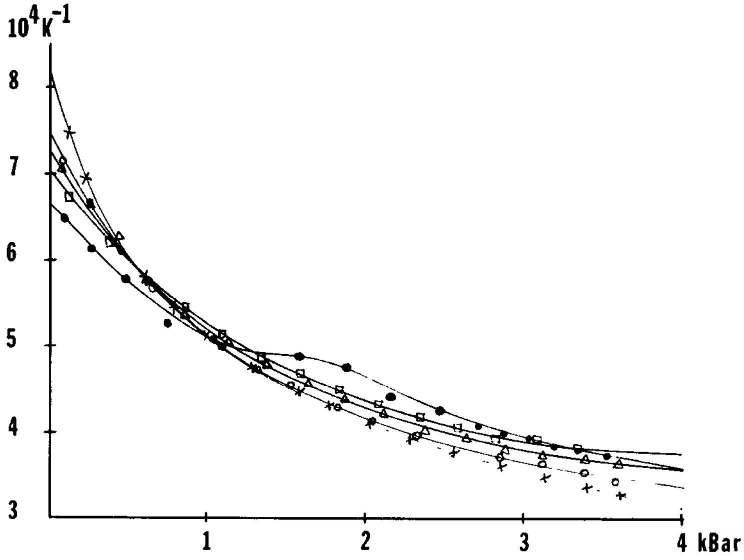

Fig. 2. Thermal expansion of coal liquid 1: (●) − 314.88 K, (□) − 345.84 K, (△) − 378.21 K (○) − 414.31 K, (×) − 447.76 K.

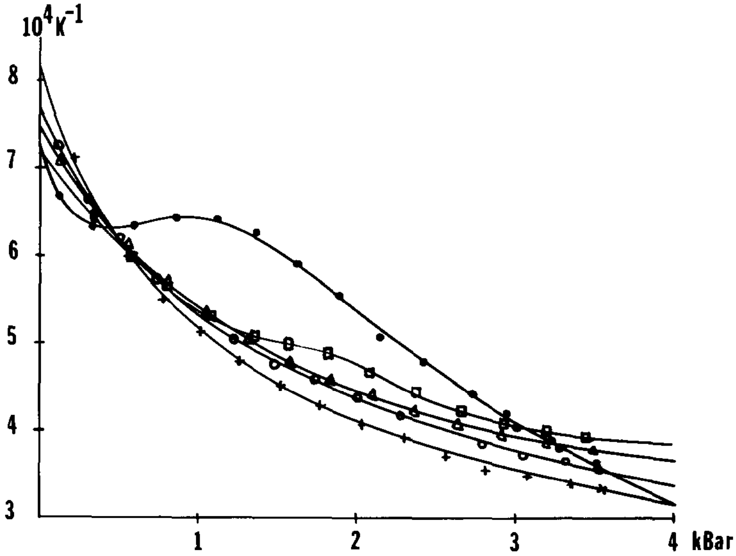

Fig. 3. Thermal expansion of coal liquid 2: (●) – 312.80 K, (□) – 339.30 K, (△) – 368.98 K, (○) – 400.28 K, (×) – 447.80 K.

2 and 3. The most interesting result of these investigations is the existance of an unequivocal crossing point of isotherms at higher temperatures. It is a very similar behavior to that of pure simple organic liquids [5,6]. At lower

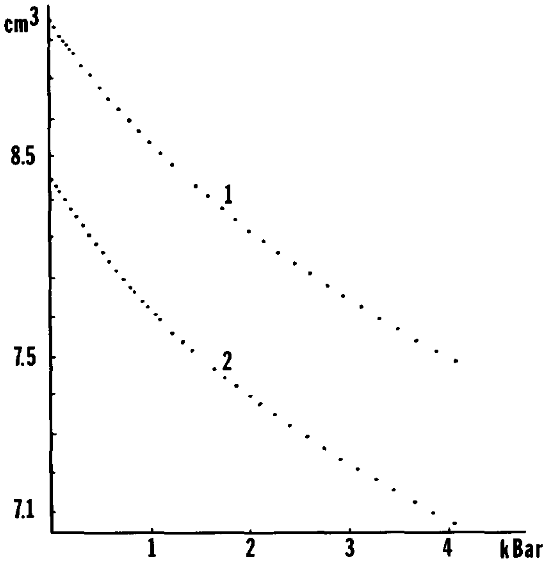

Fig. 4. Volumes vs. pressure diagram at 298 K for two samples of the coal liquids under investigation.

temperatures both liquids demonstrate unusual behavior. At first glance one would assume that irregularities on the low-temperature isotherms are connected with the solidification of the liquids at high pressures. However, such changes should also be accompanied by drastic volume changes. We have measured separately the volumes of both liquids as a function of pressure at 298 K, so that data are available at temperatures even lower than those at which the calorimetric measurements have been done. The results of measurements are presented in Fig. 4. One can see that there are no observable drastic changes of volumes as functions of pressure. However this result does not exclude the possibility of a partial precipitation of certain components with high melting points. It is very likely that the volumetric method is not sensitive enough to detect such changes in a multicomponent mixture. Further studies with pure model liquids could be helpful in elucidation of this problem.

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