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Note

Isobaric heat capacities of five dimethylsiloxane oligomers at 303.15 and 323.85 K from sound velocity and pVT data

IAN A. McLURE
Department of Chemistry, The University, Sheffield S3 7HF (England)
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The isothermal compressibilities β_T derived from recent measurements in this laboratory of the specific volumes V and isochoric thermal expansion coefficients γ_V of the first five members of the dimethylsiloxane (DMSO) oligomeric series differ from values calculated by Weissler[1] from his velocity of sound data using the equation

$$\beta_T = (V/W^2) + (TV\alpha_p^2/c_p) \tag{1}$$

where W is the velocity of sound, T is temperature, and α_p and c_p are the isobaric thermal expansivity and specific isochoric heat capacity, respectively. Subsequent study has revealed that the discrepancy arises, at least in the case of the first member of the series — hexamethyldisiloxane, from errors in the c_p and α_p data used by Weissler. A comparison showing the quantities involved at 303.15 K is given in Table 1 where (V/W^2) is shown more conventionally as the isentropic compressibility β_S. Weissler quoted his c_p results for no substances other than hexamethyldisiloxane and so the analysis given in Table 1 cannot be repeated for the other four DMSO oligomers discussed here. However, it seems likely that similar weaknesses beset all his β_T values. Nevertheless, his W values appear accurate and, together with more recent DMSO pVT data, they permit the calculation of c_p at the two

TABLE 1

COMPARISON OF THERMODYNAMIC DATA ON HEXAMETHYLDISILOXANE AT 303.15 K

	Weissler	*Recent data*
c_p (J K^{-1} g^{-1})	1.88	1.930^a
v (cm^3 g^{-1})	1.3271	1.3212^b
α_p (mK^{-1})	1.60	1.407^b
β_S (GPa^{-1})	1.741	1.73^c
β_T (GPa^{-1})	2.287	2.134^b

[a] According to D. W. Scott et al.[2]. [b] From ref. 3. [c] Obtained from Weissler's W and V from ref. 3.

TABLE 2

COMPRESSIBILITIES AND HEAT CAPACITIES FOR DIMETHYLSILOXANE OLIGOMERS

Substance	β_S *(GPa^{-1})*	β_S *(GPa^{-1}) (ref. 1)*	β_T *(GPa^{-1})*	β_T *(GPa^{-1}) (ref. 1)*	c_p *(J K^{-1} g^{-1})*	C_p *(J K^{-1} mol^{-1})*
T = 303.15 K						
M_2	1.73_3	1.741	2.13_4	2.287	1.97_6	32_1
M_2D	1.51_8	1.517	1.80_6	1.964	1.74_4	41_2
M_2D_2	1.40_3	1.404	1.69_9	1.766	1.68_2	52_3
M_2D_3	1.33_2	1.333	1.61_3	1.659	1.58_4	61_0
M_2D_4	1.27_9	1.264	1.52_7	1.555	1.65_1	75_8
T = 323.85 K						
M_2	2.15_3	2.195	2.62_3		2.07_8	33_8
M_2D	1.84_5	1.864	2.22_3		1.86_2	44_0
M_2D_2	1.68_2	1.697	2.00_2		1.81_0	56_2
M_2D_3	1.58_9	1.600	1.87_8		1.75_3	67_5
M_2D_4	1.51_7	1.512	1.78_3		1.74_0	79_9

temperatures — 303.15 and 323.85 K — at which W has been measured. Although c_p is much better obtained calorimetrically, no such data appear to exist and it is to fill this gap that the present report is made.

Table 2 contains the results and some of the intermediate quantities. The different DMSO oligomers are denominated in column 1 by Wilcock's notation whereby M_2D_{x-2} is the open-chain DMSO oligomer containing x silicon atom[4]; x can be regarded as a measure of the chain-length of the oligomer. Columns 2 and 4 contain the β_S and β_T calculated from the pVT data from this laboratory ($\beta_T = \alpha_p/\gamma_V$). All of the coefficients refer effectively to zero pressure. Columns 3 and 5 contain the analogous quantities reported by Weissler; his measurements of c_p were carried out at 303.15 K only and thus he records only β_T(303.15 K). Column 6 contains c_p calculated via eqn (1). Finally column 7 contains molar isobaric heat capacities C_p calculated using molar masses based on H = 1.008_0, C = 12.011, O = 15.999_4, and Si = 28.08_6. It is difficult to assess the effect of the accumulated errors of all the quantities appearing in the expression for c_p but taking the uncertainty in the accuracy of β_T and β_S, the least well determined of the set, as around ±1–2% it seems safe to take the error in c_p to be around ±5%. The difference ($\beta_T - \beta_S$) diminishes with chain-length and thus the inaccuracy in c_p increases with chain-length. The materials used in the pVT studies were all pure single substances but in Weissler's work M_2D_4 was a viscosity-characterised cut containing M_2D_4 as a principal component only. Although this does not noticeably affect the trend of W or β_S with chain-length, it should be borne in mind as representing the limit of the calculation of c_p from Weissler's data.

From the results in Table 2 a comparison can be made with the $c_p(M_2)$ studies at the Bureau of Standards[2]; the present values at 303.15 and 323.85 K are higher by

2.4 and 4.8%, respectively (Weissler's value at 303.15 K is 2.6% lower than the Bartlesville value). Despite this discrepancy, it is believed that the present results are no more than 5% inaccurate with one exception to be discussed now.

The chain-length dependence of oligomer heat capacity is better discussed in terms of the specific heat capacities c_p rather than of the molar heat capacities C_p in which the molar mass plays a distracting role. Figure 1 shows c_p as a function of chain-length x; the error bars reflect the ±5% inaccuracy limit given earlier. It is clear that the c_p–x curve is smooth save for $c_p(M_2D_3)$; the two values shown fall below the best line through the others, this is believed to be due to a slightly low $\gamma_V(M_2D_3)$ the effect of which becomes more serious at high x as already noted. Interestingly, the limiting value quoted by Weissler for material of molar mass 4000 of $c_p(303.15\ \mathrm{K}) = 1.63\ \mathrm{J\ K^{-1}g^{-1}}$ is close to the asymptotic value to which our values are tending. The drop in c_p with x is expected for an oligomeric series.

A plausible case can be made out for taking tetramethylsilane as the first member of the DMSO series. Thus on extrapolating the c_p–x curve back to $x = 1$ one might expect to obtain the value for C_p (tetramethylsilane). The value obtained by a 13 K extrapolation of the results of Aston et al.[5] is approximately 2.4 $\mathrm{J\ K^{-1}g^{-1}}$ and it can be seen on the figure that this value is not inconsistent with the trend of the $c_p(x)$ function.

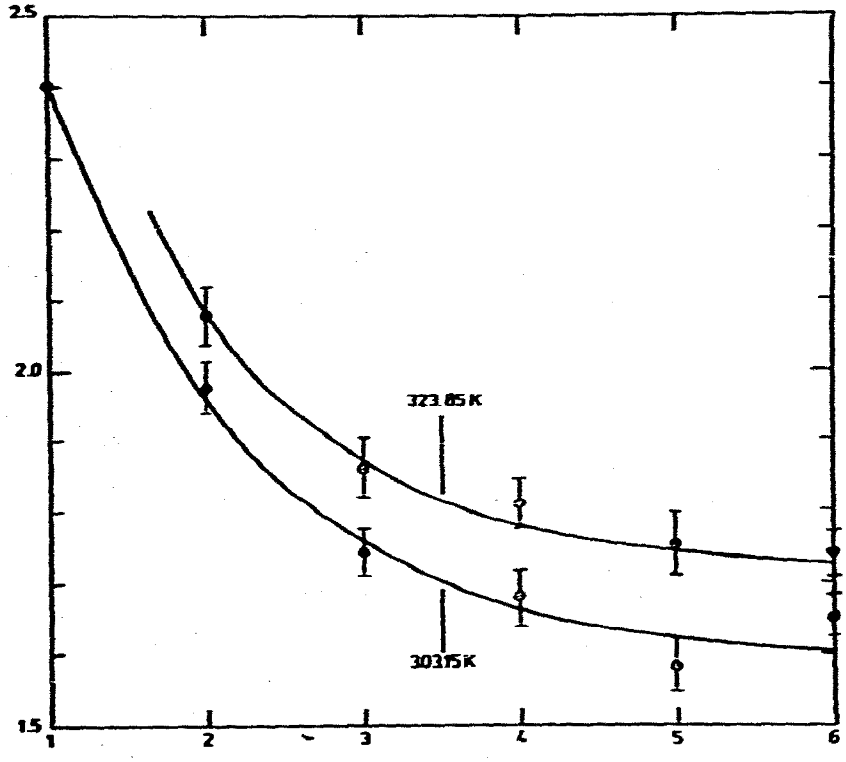

Fig. 1. Specific isobaric heat capacities for dimethylsiloxane oligomers. Ordinate, c_p ($\mathrm{J\ K^{-1}\,g^{-1}}$); abscissa, DMSO chain-length x.

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