Specific Volumes, Thermal Pressure Coefficients, and Derived Quantities of Five Dimethylsiloxane Oligomers from 25 to 140 °C

Ian A. McLure,* Alastair J. Pretty, and Paul A. Sadler
Department of Chemistry, The University, Sheffield S3 7HF, United Kingdom

The specific volumes of the first five members of the linear dimethylsiloxane series are reported in the temperature range 5–140 °C along with the thermal pressure coefficients in the range 25–160 °C. From the results thermal expansion coefficients and isothermal compressibilities have been calculated.

The principle of corresponding states is widely used in the study of pure chain-molecule liquids and polymers and of their mixtures. It is therefore important firstly to establish for a given homologous series that a principle of corresponding states exists and, secondly, to assess the extent of conformity with it of the behavior both of individual members of that series and of members of other homologous series. A convenient and sensitive test of these matters can be obtained from an analysis of liquid-state pVT data over a wide range of temperatures and homologue chain lengths (*5, 14, 17*).

In order to carry this analysis on the linear dimethylsiloxane (Me_2SiO) series, whose general formula is $(CH_3)_3Si[OSi(CH_3)_2]_{n-1}CH_3$, the following properties of the first five oligomeric members of the series, having $n = 2$ to $n = 6$, have been measured: (a) specific volume v at essentially 1 atm of pressure in the temperature range 5–140 °C and (b) isochoric thermal pressure coefficient γ_v over the temperature range 25–160 °C.

From the results of the measurements the following quantities have been calculated: (c) isobaric expansivity α_p in the temperature range 5–140 °C and (d) isothermal compressibility β_T over the temperature range 25–140 °C.

Experimental Section

Materials. The Me_2SiO oligomers were drawn from the Dow Corning Ltd. DC/200 series. They are identified here using the nomenclature of Wilcock whereby M_2D_{x-2} is the linear oligomer containing x silicon atoms (*24*). Oligomers M_2, M_2D, and M_2D_2 were purified by fractional distillation; M_2D_3 and M_2D_4, being insufficiently volatile to be purified in this way, were purified by vapor-phase chromotography using a 7-ft Carbowax 20M packed column and nitrogen carrier gas. The purity of all oligomers was checked using a 6-ft SE30 silicone rubber packed column and a hydrogen/nitrogen carrier gas; in no case was more than 1% impurity detected. The *n*-heptane used as a standard substance was purchased from British Drug Houses Ltd.; it was found to contain less than 0.5% impurity. All samples were dried over anhydrous calcium chloride and thoroughly degassed under vacuum before use.

Apparatus. The Pyrex dilatometers used to measure the specific volume were similar in design and method of operation to that described by Orwoll and Flory (*13*). The sample was confined by mercury, and changes in its volume were monitored by weighing the amount of mercury expelled from or drawn into the dilatometer. Calibration was carried out using water which had been distilled once and degassed before use. The physical properties of water were taken from the work of Kell and Whalley (*10*). The density of mercury was taken from the tables of Brombacher, Johnson, and Cross (*3*). The thermal expansivity of Pyrex glass was taken from ref 13.

All weighings were carried out in an air-conditioned room and normal buoyancy corrections were applied; the weighings are believed accurate to ±50 mg. The dilatometers were placed in a thermostat which showed temperature variations, as measured using a platinum resistance thermometer, of ±2 mK in the range 5–70 °C and ±4 mK in the range 70–160 °C. The absolute temperature was measured using a platinum resistance thermometer calibrated by the makers (Rosemount Engineering Co. Ltd.) to ±5 mK at 0 °C and to ±10 mK at 100 °C.

Details of the method of filling of the dilatometer and other manipulations are available elsewhere (*16*).

Thermal pressure coefficients were measured in Pyrex cells similar to that shown on Figure 1. The sample was confined by mercury and the total liquid volume was maintained essentially constant at a series of increasing temperatures by automatically applying sufficient pressure to maintain the outer mercury meniscus in close proximity to the tungsten tip. The cell was placed within a steel pressure vessel which in turn was placed in an oil- or water-filled thermostat. The pressurizing system was based on nitrogen supplied by a cylinder and the control of pressure was arranged by a combination of a constant leak and a solenoid valve regulated by the mercury–tungsten contact. The pressure was measured on a Budenberg Bourdon-type standard test gauge which had been calibrated by the manufacturer to within ±2 lb $in.^{-2}$ over its range of 0–1000 lb $in.^{-2}$ and was recalibrated by us using a dead weight tester to ±1 lb $in.^{-2}$. The temperature was measured using a 100-Ω Degussa Hartglass platinum resistance element which was calibrated by us at atmospheric pressure against the R.E.C. thermometer already mentioned. The thermometer element was pressure sensitive and this was checked by careful measurement; it was found that the variation of resistance with pressure was -7.03×10^{-6} Ω atm^{-1}.

Some of the early results were obtained using a similar cell but in which the temperature was raised to regain essentially constant volume following an increase in pressure. This procedure required longer equilibration times due to the lag in the thermostat temperature increase reaching the cell through the pressure vessel and the nitrogen pressurizing gas. Apart from the delay in measurement the results are in full agreement with those obtained in the later way and are not distinguished in the tables of results.

The crude isochore slopes dp/dT were corrected to γ_V using the following expression which incorporates the effects of the thermal expansion and the compression of both quartz and mercury

$$\gamma_V = (dP/dT)(1 + \{[(1 + (V_m/V_s))(\alpha_g - \beta_g(dP/dT)) - (V_m/V_s)(\alpha_m - \beta_m(dP/dT))]/\alpha_s\})$$

where the subscripts s, m, and g refer to sample, mercury, and glass, respectively, α and β are the thermal expansivity and

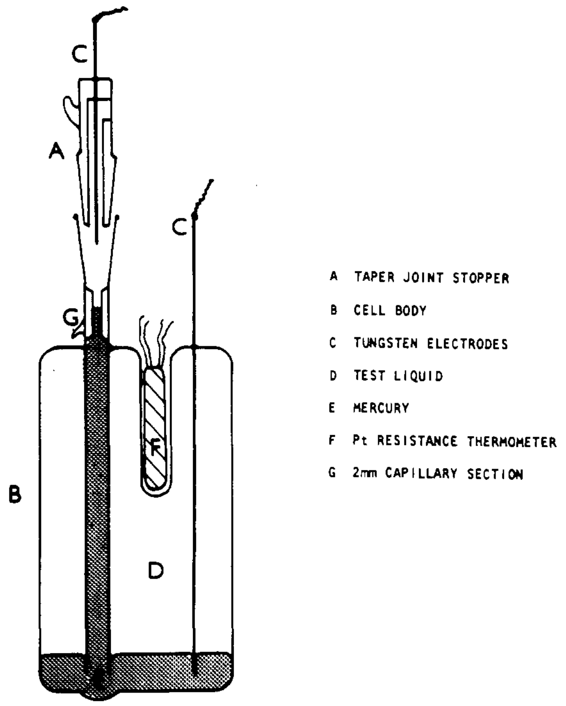

Figure 1. Thermal pressure coefficient cell: A, taper joint stopper; B, main cell body; C, tungsten electrodes; D, test liquid; E, mercury; F, platinum resistance thermometer; G, 2-mm capillary section.

Table I. Specific Volumes for Me_2SiO and *n*-Heptane

M_2		M_2D		M_2D_2	
$t/°C$	$v/cm^3\ g^{-1}$	$t/°C$	$v/cm^3\ g^{-1}$	$t/°C$	$v/cm^3\ g^{-1}$
5.351	1.277 45	26.320	1.227 13	26.319	1.179 78
26.318	1.314 50	29.394	1.231 87	29.394	1.184 04
29.394	1.320 17	31.920	1.235 81	31.920	1.187 57
31.920	1.324 87	37.236	1.244 19	37.236	1.195 08
37.236	1.334 95	42.203	1.252 15	42.205	1.202 19
42.205	1.344 56	47.208	1.260 30	47.208	1.209 44
47.208	1.354 44	52.210	1.268 57	52.210	1.216 77
57.327	1.375 14	57.327	1.277 20	57.328	1.224 41
61.834	1.384 63	61.832	1.284 92	61.833	1.231 22
66.339	1.394 37	66.339	1.292 78	66.339	1.238 14
72.833	1.408 79	72.836	1.304 44	72.837	1.248 29
78.843	1.422 56	78.843	1.315 29	78.843	1.257 83
84.807	1.436 72	84.807	1.326 44	84.807	1.267 50
		93.859	1.343 94	93.859	1.282 62
		107.255	1.371 25	107.255	1.305 95
		119.100	1.397 00	139.024	1.366 49
		139.024	1.443 96		

M_2D_3		M_2D_4		*n*-Heptane	
$t/°C$	$v/cm^3\ g^{-1}$	$t/°C$	$v/cm^3\ g^{-1}$	$t/°C$	$v/cm^3\ g^{-1}$
23.963	1.147 77	20.215	1.123 79	24.325	1.470 29
29.178	1.154 50	24.945	1.129 55	29.999	1.480 76
34.268	1.161 12	29.942	1.135 69	40.156	1.499 80
39.146	1.167 57	34.939	1.141 92	45.023	1.509 38
44.093	1.174 17	39.817	1.148 05	50.026	1.519 42
50.114	1.182 30	44.919	1.154 52	54.819	1.529 22
56.791	1.191 47	49.953	1.160 99	59.277	1.538 54
61.650	1.198 23	54.660	1.167 04	65.087	1.551 06
66.450	1.205 01	60.731	1.175 01		
71.466	1.212 18	64.876	1.180 51		
81.577	1.226 92	69.987	1.187 37		
91.054	1.241 10	74.610	1.193 63		
101.831	1.257 86	79.750	1.200 69		
111.346	1.273 11	89.901	1.214 93		
120.741	1.288 67	99.773	1.229 12		
135.161	1.313 63	109.017	1.242 86		
		119.202	1.258 39		
		129.440	1.274 57		
		138.753	1.289 80		

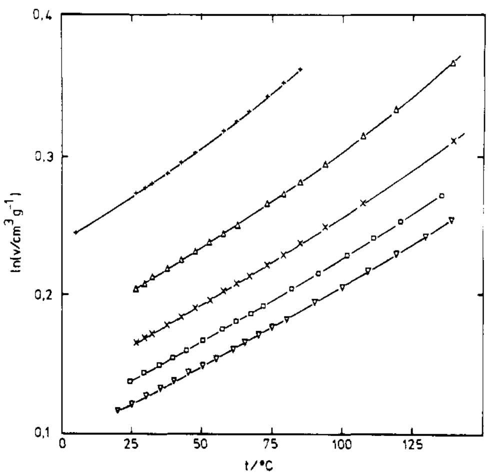

Figure 2. Specific volumes of dimethylsiloxane oligomers: +, M_2; △, M_2D; ×, M_2D_2; □, M_2D_3; ▽, M_2D_4.

Table II. Specific Volume Coefficients for Me_2SiO and *n*-Heptane

Substance	$10a_0$	10^3a_1	10^7a_2	10^9a_3	$10^5\sigma$
M_2	2.3774	1.3253	9.7833	8.468	0.8
M_2D	1.7197	1.2304	2.3618	7.366	2.0
M_2D_2	1.3480	1.1485	2.9225	4.513	0.4
M_2D_3	1.1114	1.1065	1.6239	3.692	1.0
M_2D_4	0.9487	1.0763	0.8736	3.211	0.9
n-Heptane	3.5716	1.1105	22.376		4.0

isothermal compressibility, respectively, and V is the volume. The values of β_g, β_m, α_g, and α_m were taken from ref 2 and the value of α_s was measured in this study. Full details of the methods employed are available elsewhere (*16*, *19*).

Results of Measurements

Specific Volume. The results of our measurements of specific volume v are listed in Table I and shown graphically in Figure 2. As a check on technique, the specific volume of *n*-heptane was measured over the temperature range 25–65 °C, and the results are also given in Table I. Since one of the principal aims of the investigation was a knowledge of the thermal expansivity $\alpha_p = [\partial \ln v/\partial T]_p$, the data were fitted to a smoothing equation in which $\ln v$, rather than the more common v, was expressed as a power series in temperature t

$$\ln(v/cm^3\ g^{-1}) = a_0 + a_1(t/°C) + a_2(t/°C)^2 + a_3(t/°C)^3 \quad (1)$$

The coefficients a_i are listed in Table II along with the standard deviation σ.

Thermal Pressure Coefficient. The total pressure p experienced by the sample was obtained by adding the measured atmospheric pressure to the gauge pressure. The pressure conversion factor used was 1 lbf in.$^{-2}$ = 6.895 kPa. Rather than obtain the slope of the uncorrected isochore from the p–t graph the slope of the p–R graph, where R is the platinum resistance thermometer reading, was obtained before introducing the thermometer conversion factors for pressure and temperature dependence. The corrected values of γ_v are listed in Table III and shown graphically in Figure 3 for the Me_2SiO oligomers. The temperatures listed are those at which each isochore passed through $p = 0$; thus perhaps the values of γ_v might strictly be designated γ_v ($p = 0$). However, for simplicity we prefer to use γ_v, implying the zero pressure limit. The third column shows the values of γ_v obtained at the stated temperature from the smoothing equation

$$\gamma_v/kPa\ K^{-1} = b_0 + b_1(t/°C) + b_2(t/°C)^2 + b_3(t/°C)^3 \quad (2)$$

The coefficients b_i are listed in Table IV along with the standard

Table III

t/°C	γ_v/ kPa K^{-1}	γ_c (calcd)/ kPa K^{-1}	No. of p–R points
	M_2		
22.780	698	696	6
31.904	647	650	5
34.822	635	636	6
39.366	617	616	5
45.822	589	588	5
56.719	545	545	5
66.227	509	509	5
73.388	484	483	5
83.371	445	447	5
86.810	435	435	5
89.284	428	426	5
	M_2D		
23.098	711	712	5
23.493	713	711	5
30.042	676	679	5
33.061	667	666	5
42.354	623	624	5
43.115	624	621	5
48.001	600	600	5
54.101	573	575	5
63.353	539	539	6
70.465	516	513	5
88.781	449	449	5
96.163	430	426	5
106.759	390	393	5
119.768	354	357	5
137.344	315	313	5
	M_2D_2		
24.410	718	719	5
33.774	678	677	5
46.806	622	622	6
62.815	559	559	5
78.567	502	503	6
88.703	470	470	6
104.526	423	422	6
115.777	389	389	5
127.992	358	356	6
138.385	328	330	6
142.394	319	320	6
161.417	276	275	5
	M_2D_3		
23.767	727	726	6
33.354	682	684	5
53.235	602	603	5
64.126	564	562	5
73.654	524	528	5
74.190	530	526	5
103.501	434	432	4
109.713	412	414	5
128.458	366	365	5
142.775	332	332	5
	M_2D_4		
23.864	740	743	5
32.491	706	702	5
53.377	616	611	4
64.043	564	568	6
77.605	517	519	4
88.350	482	483	4
102.358	440	440	4
112.869	414	411	4
134.640	357	358	4

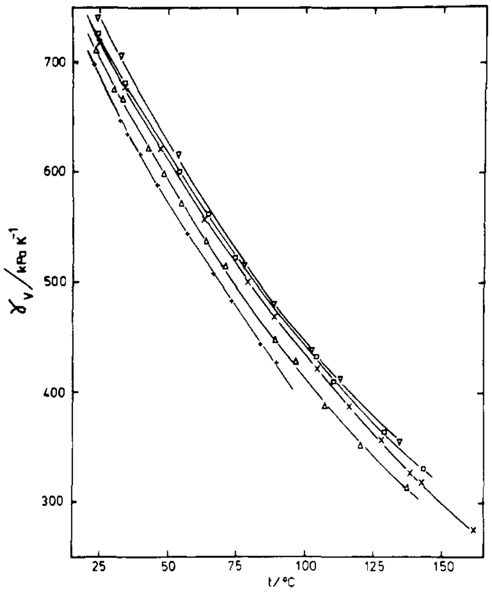

Figure 3. Thermal pressure coefficients of dimethylsiloxane oligomers: +, M_2; Δ, M_2D; ×, M_2D_2; □, M_2D_3; ∇, M_2D_4.

Table IV. Thermal Pressure Coefficient Equation Coefficients

Substance	b_0	b_1	10^2b_2	10^4b_3	σ
M_2	837.2	−7.137	4.605	−1.98	2
M_2D	826.3	−5.211	1.079		3
M_2D_2	839.6	−5.298	1.477	−0.224	1
M_2D_3	836.2	−4.882	0.947		2
M_2D_4	865.2	−5.410	1.223		3

Table V. Comparison of the Specific Volume of *n*-Heptane with Previous Values

	Specific volume of *n*-heptane, v/cm^3 g^{-1}		
t/°C	This work	Ref 25	Ref 1
20.0	1.462 67	1.462 84	1.462 42
30.0	1.480 66	1.481 26	1.480 82
40.0	1.499 54	1.500 38	1.499 48
50.0	1.519 34	1.519 99	1.519 06
60.0	1.540 10	1.540 59	1.540 12

deviation σ. The precision of the values of γ_v is believed to be close to 0.6% and the accuracy close to 1%.

Discussion

Specific Volume v. As a check on our method and technique we have measured the specific volume of *n*-heptane. A comparison of our results at five rounded temperatures with those of Young (*25*) and from the API-44 (*1*) compilation is given in Table V; the agreement is satisfactory.

The specific volumes of several cyclic and linear Me_2SiO oligomers have been measured by Hurd (*9*). Our principal reason for repeating his work was to extend his temperature range, 20–80 °C, to permit a more searching test of the principle of corresponding states. Table VI contains a comparison at three rounded temperatures of Hurd's results with ours in the form $\Delta v = v_{(\mathrm{Hurd})} - v_{(\mathrm{this\ work})}$. The agreement is satisfactory at this stage and the regularity of the discrepancies suggests that some part of these arises from the use of a different smoothing equation in our work. We carefully checked one possible source of error—thermal degradation—by a combination of GLC and other analytical techniques and failed to find evidence of decomposition in any one of the oligomers following thermal cycling. Similar checks on one oligomer containing about 25 $-OSi(CH_3)_2-$ units did produce refractive index evidence of decomposition following cycling between 25 and 160 °C and we discontinued our measurements on this material. Since our measurements were completed Shih and Flory have reported pVT measurements on a polymer containing about 1300 $-OSi(CH_3)_2-$ units from 20 to 207 °C apparently without thermal degradation

Table VI. Comparison of the Specific Volumes of Me_2SiO

	Specific Volume of This Work-Hurd = Δv/cm^3 g^{-1}		
	t/°C		
	25.0	50.0	75.0
M_2	−0.005 22	−0.003 67	−0.000 30
M_2D	−0.002 24	−0.002 19	−0.002 06
M_2D_2	−0.000 46	−0.000 69	−0.000 62
M_2D_3	+0.000 58	+0.000 25	+0.000 16
M_2D_4	+0.001 22	+0.000 83	+0.000 25

Table VII. Molar Masses, Molar Volumes, and Molar Volume Increments of Me_2SiO at 25 °C

Substance	M/g	V_m/cm^3 mol^{-1}	ΔV_m/cm^3 mol^{-1}
M_2	162.382	213.059	
M_2D	236.537	289.773	76.714
M_2D_2	310.693	365.977	76.204
M_2D_3	384.848	442.221	76.244
M_2D_4	459.004	518.499	76.278

Table VIII. Thermal Expansion Coefficients at 30 °C for Me_2SiO

Substance	Thermal expansion coeff, $10^3\alpha_P$/K^{-1}	
	This work	Lit. values
M_2	1.407	1.311 (*9*), 1.491 (*7*), 1.42 (*15*)
M_2D	1.265	1.276 (*9*)
M_2D_2	1.178	1.191 (*9*)
M_2D_3	1.126	1.128 (*9*)
M_2D_4	1.090	1.102 (*9*), 1.103 (*7*)

Table IX. Isothermal Compressibility for Me_2SiO at 30 °C

Substance	Isothermal compressibility $10^9\beta_T$/Pa^{-1}	
	This work	Weissler (*22*)
M_2	2.13	2.28
M_2D	1.86	1.96
M_2D_2	1.70	1.77
M_2D_3	1.61	1.66
M_2D_4	1.53	1.56

Table X. Comparison with the 25 °C Data of Chang for M_2

	This work	Chang (*4*)
v/cm^3 g^{-1}	1.31208	1.3167
$10^3\alpha_P$/K^{-1}	1.390	1.398
γ_v/kPa K^{-1}	684	685
$10^9\beta_T$/Pa^{-1}	2.03	2.012

problems (*21*). From a consideration of all sources of error in our work we believe that our precision is of the order ±0.00005 cm^3 g^{-1} and that our accuracy may be little more.

Molar Volume V. The molar volume V at 25 °C was obtained from v using molecular weights based on H = 1.008 0, C = 12.011 1, O = 15.999 4, and Si = 28.086 (11). V is very linear in the number of silicon atoms in the oligomer as Table VII shows. This linearity accounts qualitatively for the very small excess volume of mixing observed in binary mixtures of Me_2SiO oligomers (*20*).

Isobaric Thermal Expansivity α_p. α_p is easily evaluated from eq 1 using the coefficients a_i of Table II. In the phenomenological form of corresponding states which we have used (*5*) the quantity α_pT is used as the basic measure of reduced temperature and so it was one of the secondary aims of this investigation to reconcile the slight inconsistency of the value of α_p of M_2 derived from Hurd's work which was first pointed out by Patterson, Bhattacharya, and Picker (*15*). In Table VIII we list our values of α_p at 30 °C with those reported by Hurd, Patterson et al. and by Gee. Although the agreement between ourselves and the others save Hurd is not perfect, the disagreement between Hurd's value and all the others is very marked thus supporting the view that Hurd's values for M_2 bear a certain imprecision which perhaps can be associated with the opportunity for unaccountable evaporation of M_2 from his dilatometer. With the other oligomers diminishing volatility readily accounts for the increasing concordance of our results.

Thermal Pressure Coefficient γ_V. As a check on the performance of our equipment we measured γ_V for pure dry benzene and carbon tetrachloride. For benzene at 30.83 °C we obtained γ_V/kPa K^{-1} = 121_4 to be compared with an interpolated value of 120_7 from ref 18. Our result for carbon tetrachloride at 31.25 °C was 109_8 to be compared with values of 109_2, 108_9, 108_4, and 108_5 to be found in ref 2, 23, 8, and 6, respectively. We believe that the agreement is satisfactory and supports our claim that our precision in determining γ_V is about 0.6% and our accuracy little more than 1%.

Isothermal Compressibility β_T. It is generally recognized that it is difficult to obtain accurate isothermal compressibilities, $\beta_T = -[\partial \ln v/\partial p]_T$, from low-pressure compression experiments. In fact it has been observed (*18*) that many reported values of β_T obtained in this way are close to the subsequently reported values of the isentropic compressibility β_S. A better way of arriving at β_T involves the relation $\beta_T = \alpha_p/\gamma_V$. From the coefficients given in Tables II and IV for eq 1 and 2 values of β_T can readily be calculated for the Me_2SiO series at any temperature within the range of the measurements. The values obtained at 30 °C are shown in Table IX. Weissler also obtained β_T from his measurements of the velocity of sound and some rather crude heat capacity data (*22*). His results are also shown in Table IX. The agreement between the two sets of estimates of β_T is no more than fair although it does improve with increasing chain length. The discord arises chiefly from the values of α_p and, in particular, heat capacity which were available to Weissler. Our pVT data and Weissler's velocity of sound data are better combined to obtain the heat capacities of the Me_2SiO oligomers studied here and the results of this calculation are available elsewhere (*12*).

A final useful comparison is given in Table X wherein are listed our values for various quantities at 25 °C and the corresponding values obtained by Chang (*4*). There is some internal inconsistency in Chang's results in that $\beta_T \neq \alpha_p/\gamma_v$, but for α_p and γ_v, which are probably the quantities actually measured, the agreement is excellent.

We are engaged at present in extending all of the program of measurement described above to lower temperatures close to the nearly uniform freezing points of these oligomers in the vicinity of −80 °C.

Acknowledgment

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Glossary

a_i	coefficients for expression 1 for ln v
b_i	coefficients for expression 2 for γ_v
p	pressure
T, t	temperature
V	molar volume
v	specific volume
α_p	isobaric thermal expansivity
β_T	isothermal compressibility
γ_v	isochoric thermal pressure coefficient
σ	standard deviation

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Dielectric Constants, Viscosities, Densities, and Refractive Indices of Some Alkylsydnones at Several Temperatures

Robert J. Lemire and Paul G. Sears*
Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506

Dielectric constants, viscosities, densities, and refractive indices of four liquid alkylsydnones were measured at two to six temperatures within the range of 25–125 °C. All experimental data (except refractive indices) for 3-methylsydnone and 3-isopropylsydnone have been fitted to appropriate equations. Kirkwood–Fröhlich correlation factors for these two sydnones also have been calculated. The dielectric constant of each alkylsydnone is high, and particularly high in the case of 3-methylsydnone (ϵ = 144.0 at 40 °C) even though the calculated Kirkwood–Fröhlich correlation factor of 1.03 for this compound implies that there is little net parallel alignment of dipoles in the liquid. Factors which might affect the use of 3-methylsydnone as a nonaqueous solvent also are discussed.

The chemistry of the sydnones (see Figure 1) has been studied extensively since the original preparation of 3-phenylsydnone by Earl and Mackney (*7*). The structure, reactions, and some physicochemical properties of these interesting compounds have been reviewed by Baker and Ollis (*1*), by Stewart (*24*), and, more recently, by Ohta and Kato (*20*). One very notable feature of the sydnones is their unusually high dipole moments; values for many sydnones are greater than 6 D (*6, 12*) and the value for 3-methylsydnone has been reported (*3, 22*) as 7.3 D. While most sydnones are relatively high-melting solids, many of the 3-alkylsydnones are liquids at or slightly above room temperature. Nevertheless, it appears that no previous study considering bulk physical properties such as dielectric constants, viscosities, densities, and refractive indices of 3-alkylsydnones has been reported.

Considering the high dipole moments, the apparently convenient liquid range and the reasonably well described syntheses of these compounds, it appeared that one or more of these compounds might be a potentially useful nonaqueous solvent provided purification were feasible and the bulk physical properties were known.

Experimental Section

Preparation and Purification of the Sydnones. 3-Methylsydnone was prepared from *N*-methylglycine, commonly known as sarcosine, by the method of Vasil'eva and Yashunskii (*25*). A liquid–liquid extractor was used (*11*) for 12–24 h to recover the *N*-nitroso-*N*-methylglycine intermediate prior to its treatment with acetic anhydride. Yields of 70–80% of crude 3-methylsydnone were routinely achieved from 200-g portions of the *N*-methylglycine. *Warning: immediate introduction of air after vacuum distillation of the product from acetic anhydride* (*while the residual material was still hot*) *was found to lead to a mild explosion* (*see also ref 11*). The 3-methylsydnone was readily purified by fractional freezing (*2*). The compound appears to exist in two distinct colorless crystalline forms: needles which have a melting point near 36 °C (in agreement with the literature (*11*) and plates which melt several degrees lower.

The preparation of 3-isopropylsydnone starting with ethyl bromoacetate and isopropylamine has been reported (*10, 15*); however, the method used to prepare 3-isopropylsydnone in quantity for the present work was similar to that used for the preparation of 3-*tert*-butylsydnone reported by Procházka and co-workers (*21*). Potassium cyanide (390 g) and isopropylamine (354 g) were dissolved together in water (360 mL). After the solution was cooled to 5 °C, concentrated aqueous HCl (575 mL) was added slowly. Formaldehyde (525 g of 37% aqueous solution) was added dropwise over 2 h at 10–15 °C. To the resulting brown solution, water (300 mL) was added followed by sodium hydroxide (270 g in 380 mL of water). The dark red solution was refluxed for 2 h. Water (1000 mL) was added and then removed by distillation together with any unreacted amine and aldehyde. The solution was acidified, the alkylamino acid was nitrosated (in portions), and the solution was allowed to stand overnight. The *N*-nitroso-*N*-isopropylglycine was then removed by filtration and dried (vacuum, 40 °C). The yield of *N*-nitroso-*N*-isopropylglycine was 65–70%. This material then was treated with an excess of acetic anhydride and the mixture was allowed to stand for several days at room temperature. The acetic anhydride and acetic acid were removed by vacuum distillation, and the crude isopropylsydnone was recovered by distillation (130 °C) under vacuum (yield 330 g). This compound also was purified by fractional freezing and was found to be colorless and to melt at approximately 57 °C (lit. (*15*), 54–55.5 °C).