

Viscosity of Isomeric Octyl Alcohols as a Function of Temperature and Pressure*

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The viscosity of 2- and 3-octanol and 6-methyl-3-, 5-methyl-3-, and 2-methyl-3-heptanol has been measured as a function of temperature (-20° – 80°C) and pressure (0–4 kbar). Specific structural differences exist in the temperature and pressure coefficients of isobaric viscosity; these differences are minimized, but still exist, when isochoric viscosities are compared. Viscous flow and dielectric relaxation of these liquids are compared, and it is concluded that the rate-determining steps are dissimilar. A previously proposed pressure-induced liquid structure transformation in these liquids could not be verified viscometrically.

INTRODUCTION

Because the viscosity of molecular liquids is not yet amenable to theoretical analysis and prediction, and empirical approximation schemes¹ must depend on experimental results for their basis, the determination of viscosity as a function of a wide variety of experimental variables remains an interesting and valid task of the experimentalist. We report the results of such a study.

There were two reasons why we chose these isomeric octanols as test liquids. In the first place, we have studied the equilibrium^{2,3} and dynamic^{4,5} dielectric behavior of the same liquids and find it to be a sensitive function of molecular geometry. In particular, dielectric relaxation times and their temperature and pressure coefficients are structurally dependent.^{4,5} The molecular theory of dielectric relaxation is little better advanced than that of viscous flow and there is no satisfactory explanation for the often observed similarity of dielectric and viscous behavior, e.g., the dielectric relaxation time is often directly proportional to the shear viscosity.⁶ Thus, we were primarily interested to see whether the temperature and pressure coefficients of viscosity exhibited a dependence on isomer structure parallel to that of the dielectric relaxation times. If so, an essential similarity of the molecular mechanisms is strongly indicated.

Our second reason for studying the pressure dependence of viscosity of these liquids was that such experiments might confirm a suspected intermolecular structural transformation induced by hydrostatic

pressure. *PVT* studies⁷ show that the isochoric pressure vs temperature loci of 2- and 3-octanol exhibit inflections which we believe to be characteristic of the transition from relatively bulky, low-entropy species to more compact, higher-entropy forms. The only other liquid that shows similar behavior is water, where, presumably, application of pressure induces a transition from the "icelike" to the "normal liquid" form. This pressure-induced transition in water also manifests itself as an initial decrease of η with pressure.^{8,9} Pre-

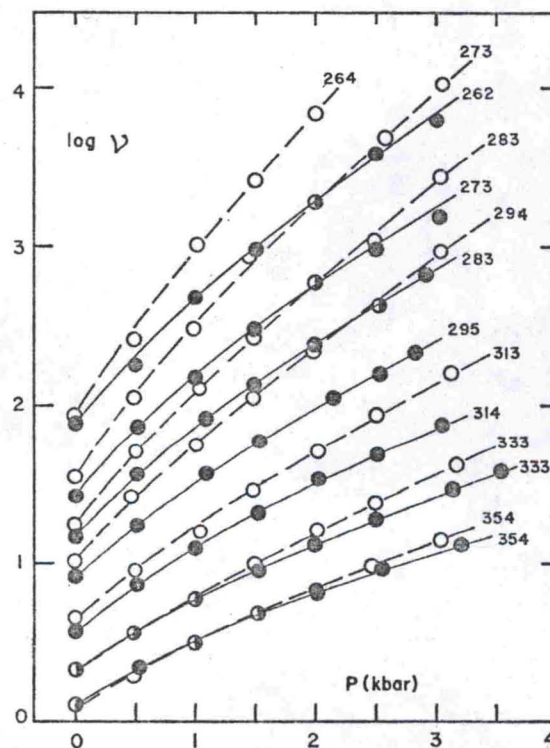


FIG. 1. Logarithm of kinematic viscosity (centistokes) as a function of pressure. Open circles refer to 2-methyl-3-heptanol, filled circles to 7-methyl-3-heptanol. Numbers to the right of each curve indicate Kelvin temperature.

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¹ A. Bondi, *Physical Properties of Molecular Crystals, Liquids, and Glasses*. (John Wiley & Sons, Inc., New York, 1968), Chap. 12.

² W. Dannhauser, *J. Chem. Phys.* **48**, 1911 (1968).

³ G. P. Johari and W. Dannhauser, *J. Chem. Phys.* **48**, 5114 (1968).

⁴ W. Dannhauser, *J. Chem. Phys.* **48**, 1918 (1968).

⁵ G. P. Johari and W. Dannhauser, *J. Chem. Phys.* **50**, 1862 (1969).

⁶ This is a direct consequence of the assumed viscous-damped rotating-sphere model of dielectric relaxation originally introduced by Debye. For a discussion see, for example, C. P. Smyth, *Dielectric Behavior and Structure* (McGraw-Hill Book Co., New York, 1955), p. 114ff.

⁷ G. P. Johari and W. Dannhauser, *J. Chem. Phys.* **48**, 3407 (1968).

⁸ P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons Ltd., London, 1958), Chap. XII.

⁹ R. A. Horne and D. S. Johnson, *J. Phys. Chem.* **70**, 2182 (1966).

TABLE I. Parameters for the equation $(\rho_t)_P = (\rho_0)_P - APl$.

Pressure (kbar)	7;2		7;3		6;3		5;3		2;3	
	ρ_0	$10^4 A$	ρ_0	$10^4 A$	ρ_0	$10^4 A$	ρ_0	$10^4 A$	ρ_0	$10^4 A$
0	0.835	7.66	0.838	8.20	0.835	7.20	0.835	8.30	0.841	8.04
1	0.882	5.50	0.881	6.60	0.883	5.34	0.881	6.69	0.887	6.83
2	0.914	4.85	0.912	5.81	0.914	4.54	0.913	5.90	0.919	6.54
3	0.938	4.44	0.936	5.20	0.937	4.02	0.935	5.81	0.943	5.80
4	0.959	3.98	0.953	5.00	0.952	3.36	0.952	5.75	0.962	5.10

TABLE II. Kinematic viscosity (centistokes) of 2-octanol as a function of temperature and pressure.

Temp (°K)	Pressure (kbar)								
	0.001	0.5	1.0	1.5	2.0	2.5	3.0	3.5 ^a	4.0 ^a
263.1	42.7	105.	215.	410.	780.	1190.	2300.
273.6	21.5	47.5	95.0	170.	300.	510.	848.	1300.	2000.
283.3	14.0	30.0	56.0	92.0	156.0	250.	380.	580.	870.
293.4	9.0	17.5	31.2	52.0	82.0	127.	192.0	280.	430.
313.4	4.92	8.4	12.8	19.8	30.0	44.0	60.0	84.0	115.
333.4	2.18	3.80	5.80	8.90	12.5	16.9	24.0	33.1	44.0
354.1	1.42	2.25	3.35	4.70	6.50	8.80	11.8	15.5	20.5

^a Extrapolated values.

TABLE III. Kinematic viscosity (centistokes) of 3-octanol as a function of temperature and pressure.

Temp (°K)	Pressure (kbar)								
	0.001	0.5	1.0	1.5	2.0	2.5	3.0	3.5 ^a	4.0 ^a
262.4	79.2	210.	485.	980.	1950.	3750.	7100.	13 000.	24 000.
273.1	27.60	72.	158.	310.	580.	1000.	1800.	3 100.	5 300.
282.4	14.98	37.	74.	140.	248.	430.	730.	1 230.	2 030.
294.9	8.35	17.5	33.2	58.	98.	160.	255.	420.	640.
313.9	3.76	7.3	12.7	21.	33.	49.	73.	106.	155.
333.2	2.15	3.7	6.0	9.2	13.5	19.	27.	37.5	42.
353.1	1.30	2.15	3.25	4.70	6.5	8.8	11.8	15.8	21.9

^a Extrapolated values.

TABLE IV. Kinematic viscosity (centistokes) of 6-methyl-3-heptanol as a function of temperature and pressure.

Temp (°K)	Pressure (kbar)								
	0.001	0.5	1.0	1.5	2.0	2.5	3.0	3.5 ^a	4.0 ^a
262.6	65.95	250.	760.	2100.	5500.	14 200.	35 000.	86 000.	...
272.4	31.14	108.	300.	740.	1680.	3 750.	8 400.	17 500.	38 000.
282.4	16.81	47.5	115.	245.	485.	1 000.	1 940.	3 700.	7 000.
293.1	9.63	23.0	49.0	98.0	188.	360.	670.	1 180.	2 100.
313.4	4.75	9.30	16.6	28.0	47.0	77.0	124.	198.	310.
332.7	2.19	4.01	6.90	11.0	17.0	26.5	38.5	56.1	81.0
353.5	1.31	2.19	3.40	5.10	7.40	10.80	15.50	22.0	30.5

^a Extrapolated values.

TABLE V. Kinematic viscosity (centistokes) of 5-methyl-3-heptanol as a function of temperature and pressure.

Temp (°K)	Pressure (kbar)								
	0.001	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0 ^a
260.6	80.5	280.	860.	2600.	7300.	20 700.	55 000.
263.2	64.5	215.	650.	1900.	5300.	13 500.	31 000.
270.2	43.88	123.	320.	850.	2080.	5 000.	11 900.	28 000. ^a	62 000.
277.1	24.52	65.	160.	358.	800.	1 910.	4 000.	8 400. ^a	17 300.
288.6	12.95	30.5	65.	135.	275.	541.	1 000.	1 950. ^a	3 730.
298.2	7.84	17.3	34.5	65.0	115.	200.	340.	540. ^a	950.
313.5	4.13	8.11	15.0	26.0	43.5	72.0	116.	178. ^a	300.
331.8	2.15	3.84	6.50	10.5	16.1	24.3	36.5	54.1	78.0
359.8	1.159	1.83	2.72	3.95	5.50	7.80	10.6	14.8	20.0

^a Extrapolated values.

sumably the "icelike" form is less susceptible to shear stress because of the H-bond network than the collapsed, "normal," form. We hoped that the transition in the alcohols, which we postulated to be from a dimer ring to an open *n*-mer structure, would also be apparent in the viscosity.

Finally, there is very little systematic data available on the structural dependence of the pressure coefficient of viscosity of relatively simple liquids other than hydrocarbons.^{10,11} Regarding alcohols, a class of liquids much used in hydraulic apparatus, we are aware only of Kuss¹² study of isomeric butanols. Our results essentially confirm his qualitative conclusions regarding the structural dependence of the pressure coefficient of viscosity and provide further data over a wide range of temperature and pressure as the basis for, and test of, theories of viscous flow.

EXPERIMENTAL

Materials

The alcohols, their source and methods of purification and identification, the notation used to describe them, and pertinent physical properties have been reported elsewhere.⁴

Viscometer

The rolling-ball viscometer is essentially that described by Horne and Johnson⁹ with some modifications.

The viscometer is jacketed so that thermostated silicone oil can be circulated around the tube. The temperature was controlled to $\pm 0.5^\circ$ during a run. The viscometer assembly is mounted on a pivot so that it can be tilted in either direction from the horizontal. A free-floating piston is attached to one end of the

viscometer to isolate the test liquid from the pressurizing oil. The high-pressure pump and gauges are similar to those described before³; the pressure is estimated to ± 5 bar.

Because of the wide range of viscosity encountered in this study, several ball¹³ sizes were used, ranging from 0.0937 to 0.1562 in. in diameter rolling in a liner tube of 0.163 in. i.d. The viscometer was calibrated for the viscosity range 0.2–5000 cP at atmospheric pressure by using various liquids as standards. In addition, for the test alcohols, data obtained with the rolling-ball viscometer at 1 atm were checked at several temperatures against those obtained with a Cannon-Fenske capillary viscometer. The agreement was generally better than 1%. We found that our data for 7;2 and 2;3 at atmospheric pressure agree well with Bingham and Darrall's,¹⁴ but our results for 5;3 and 6;3 differ greatly. This is in accord with our previous observation² that literature dielectric results for 5;3 and 6;3, obtained on the same samples that Bingham used, are apparently incorrect and this substantiates our suspicion that these samples were impure.

The roll times, ranging from 5 to >1500 sec, were reproducible to 0.1%. We estimate that errors due to dimensional changes of the viscometer or the ball in our experimental range of temperature and pressure are less than 0.5%. The greatest source of error is undoubtedly due to the uncertainty of the viscosity of the calibrating fluids, and we assign a maximum uncertainty of $\pm 3\%$ to our data.

The measured roll times and the viscometer constants yield the kinematic viscosity. In order to convert these results to shear viscosity, the temperature and pressure dependence of the liquid density may be estimated to $\pm 1\%$ by the relation³

$$(\rho_t)_P = (\rho_0)_P - A_P t.$$

The parameters $(\rho_0)_P$ and A_P are listed in Table I.

¹³ M-50 steel balls obtained from Industrial Tectonics, Inc., Ann Arbor, Mich.

¹⁴ E. C. Bingham and L. B. Darrall, *J. Rheol.* **1**, 174 (1930).

¹⁰ W. A. Steel and W. Webb, "Transport Properties of Liquids," in *High Pressure Physics and Chemistry*, R. S. Bradley, Ed. (Academic Press Inc., New York, 1963), Vol. 1, p. 163.

¹¹ D. L. Hogenboom, W. Webb, and J. A. Dixon, *J. Chem. Phys.* **46**, 2586 (1967).

¹² E. Kuss, *Z. Angew. Phys.* **7**, 372 (1955).

TABLE VI. Kinematic viscosity (centistokes) of 2-methyl-3-heptanol as a function of temperature and pressure.

Temp (°K)	Pressure (kbar)								
	0.001	0.5	1.0	1.5	2.0	2.5	3.0	3.5 ^a	4.0 ^a
263.7	81.42	310.	905.	2500.	6800.	17 500.	44 000.	98 000.	...
273.4	35.67	115.0	310.	860.	1930.	4 300.	9 500.	21 000.	44 000.
283.4	17.77	50.0	120.	265.	600.	1 250.	2 500.	5 000.	9 700.
293.5	10.51	26.0	55.0	110.	225.	440.	860.	1 650.	3 000.
312.8	4.66	9.20	16.8	29.5	50.0	86.0	140.	230.	370.
332.9	1.962	3.65	6.40	10.0	15.6	24.0	36.5	55.	80.5
354.4	1.187	1.95	3.05	4.55	6.70	9.60	13.6	19.3	26.

^a Extrapolated values.

RESULTS

For each compound, the logarithm of the kinematic viscosity was plotted as a function of pressure at each temperature. Typical results are shown in Fig. 1 which illustrates the effect of isomer structure on viscous behavior. The resulting curves were smoothed by a least-squares fit of $\ln \nu$ to a third-order polynomial in P . Interpolated values of the kinematic viscosity of 2-octanol (7;2), 3-octanol (7;3), 6-methyl-3-heptanol

(6;3), 5-methyl-3-heptanol (5;3), and 2-methyl-3-heptanol (2;3) are listed as a function of temperature and pressure in Tables II-VI.

DISCUSSION

In order to provide a common basis for intercomparison of the isomers and to facilitate comparison of our viscometric results with those of the dielectric investigations, we adopt the activated complex model of viscosity due to Eyring¹⁵ as the basis for discussion. The basic equation is

$$\eta V / N h = \nu M / N h = \exp(\Delta G^\ddagger / RT), \quad (1)$$

where η is the shear viscosity (poise), ν is the kinematic viscosity (stokes), N is Avogadro's number, V is the molar volume, M is the molecular weight, and ΔG^\ddagger is the Gibbs free energy of activation for viscous flow. With the usual assumptions of transition state theory¹⁵ we have

$$\left(\frac{\partial \ln \nu}{\partial P} \right)_T = \frac{\Delta V^\ddagger}{RT} \quad (2)$$

and

$$\left(\frac{\partial \ln \nu}{\partial T^{-1}} \right)_P = \frac{\Delta H^\ddagger}{R}, \quad (3)$$

where ΔV^\ddagger , and ΔH^\ddagger , the volume and enthalpy of activation, respectively, are convenient measures of the pressure and temperature dependence of the kinematic viscosity. The question of what the molecular significance of the activation parameters might be in such complicated systems remains intriguing and unanswered.

ΔV^\ddagger 's were evaluated from the least-squares polynomials according to Eq. (2) and the results are listed in Table VII. An inspection of the data reveals that the activation volume (i.e., the pressure coefficient of viscosity) is greatest for those isomers whose hydroxyl group is most sterically hindered because of the

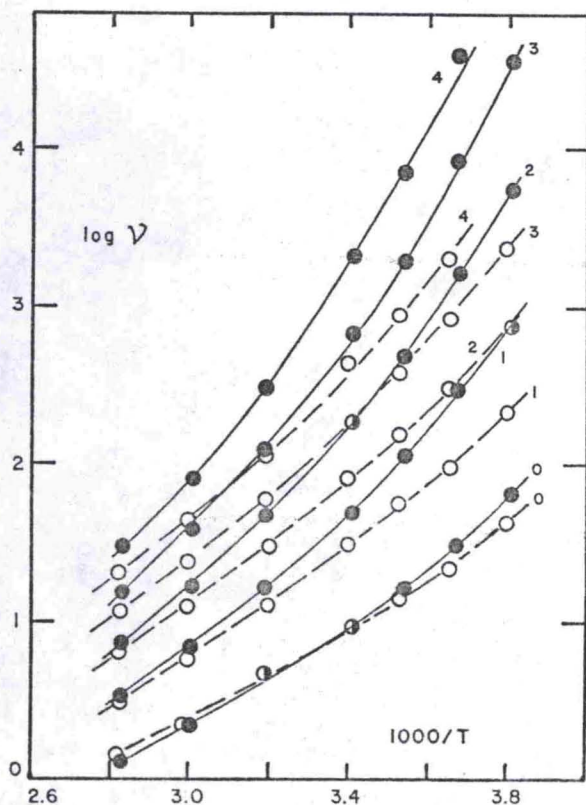


FIG. 2. Logarithm of kinematic viscosity (centistokes) as a function of reciprocal Kelvin temperature. Open circles refer to 7-methyl-2-heptanol, filled circles to 6-methyl-3-heptanol. Numbers to the right of each curve indicate the pressure in kilobar.

¹⁵ S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Co., New York, 1941).

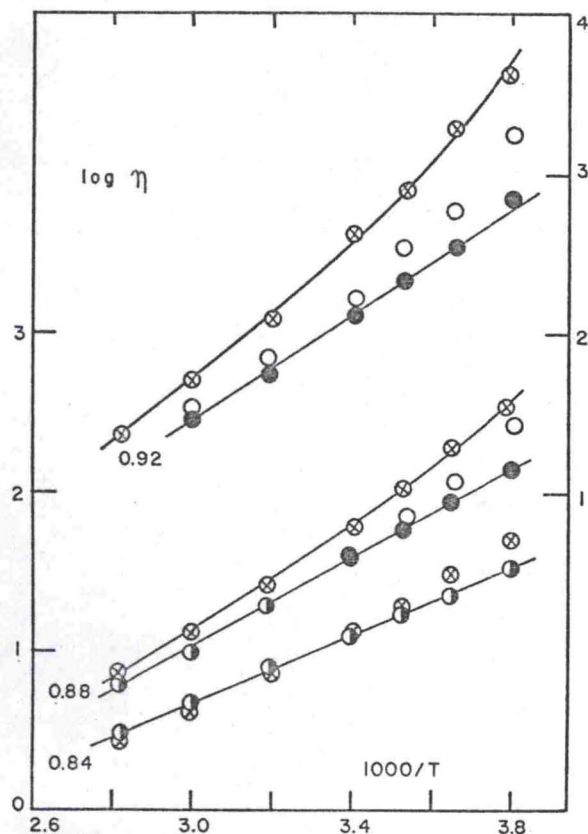


Fig. 3. Logarithm of isochoric shear viscosity (centipoise) as a function of reciprocal Kelvin temperature. Open circles refer to 7-methyl-3-heptanol; filled circles to 7-methyl-2-heptanol; crossed circles to 2-methyl-3-heptanol, 5-methyl-3-heptanol, and 6-methyl-3-heptanol. Left ordinate for data at 0.84 and 0.88 g/ml, right ordinate for data at 0.92 g/ml.

proximity of neighboring groups. This effect is most pronounced at low temperatures and becomes negligible at higher temperatures, the general trend being similar to that reported by Kuss¹² for isomeric butanols.

The viscous and dielectric relaxation results are parallel in that the most hindered species, in the sense discussed above, are most pressure sensitive although we note that for all five isomers $\Delta V^\ddagger_v > \Delta V^\ddagger_e$ at temperatures where the experiments overlap. In virtually all other respects, however, the viscous and dielectric results differ. For each isomer at every temperature, $\ln \nu$ (or $\ln \eta$) is concave to the pressure axis as indicated by the monotonic decrease of the ΔV^\ddagger_v 's with pressure. In contrast, ΔV^\ddagger_e is essentially independent of pressure for 2;3 and 5;3, decreases slightly with pressure for 6;3, and is very pressure-dependent for 7;3.⁵

We find no evidence at the highest pressures for an inflection of the $\ln \eta$ - P curves as noted by Hogenboom *et al.*¹¹ for some hydrocarbons.

We also found no viscometric indication for the presumed pressure-induced liquid structure transition in 7;2 or 7;3 but this may be due to the extremely large pressure dependence of the viscosity which would tend to mask expected small changes. (At 30°C, application

of 3 kbar increases the viscosity of water^{8,9} by 30% while the viscosity of 7;3 increase by about a factor of 30.)

Another significant difference between the dielectric and viscometric results is shown by the temperature coefficients and their pressure dependence. The dielectric studies were done at low temperatures where the viscosity of the liquids is very much greater than those reported here. In fact, because of the very long dielectric relaxation times encountered in the previous study, we surmised that the liquids were close to their glass transition region. Thus the linearity of the $\log \nu$ vs $1/T$ plots was both unexpected and puzzling. By contrast, as Fig. 2 illustrates, the temperature dependence of the isobaric viscosity is not defined by the Arrhenius equation even at relatively high temperatures. Such

TABLE VII. Volume of activation^a for viscous flow.

$T(^{\circ}\text{K})$	Pressure (kbar)				
	0	0.5	1	2	3
2-octanol					
263.1	42.7	35.1	29.4	23.9	26.2
283.3	35.9	31.3	27.4	22.0	19.5
313.4	27.0	24.9	22.9	19.7	17.2
354.1	26.0	23.5	21.3	18.1	16.4
3-octanol					
262.0	43.2	38.1	33.9	28.3	26.3
282.4	42.1	36.4	31.8	25.7	23.6
313.9	36.0	31.3	27.4	21.9	19.5
353.1	31.2	26.5	22.7	18.0	16.9
6-methyl-3-heptanol					
262.6	57.5	50.9	45.6	39.2	...
282.4	50.1	44.1	39.1	32.5	30.3
313.4	35.1	32.1	29.5	25.9	24.3
353.5	30.3	27.6	25.3	22.0	20.4
5-methyl-3-heptanol					
260.6	54.2	50.7	47.9	44.0	...
288.6	41.4	38.3	35.7	32.1	30.6
313.5	36.9	33.1	29.9	25.7	24.2
359.8	27.5	24.9	22.8	19.9	18.2
2-methyl-3-heptanol					
263.7	56.5	51.5	47.2	41.0	...
283.4	48.0	43.9	40.3	35.0	32.1
312.8	35.3	32.6	30.3	27.0	25.3
354.4	29.3	27.0	24.9	21.7	19.6

^a cm³/mole.

curves were smoothed by a third-order polynomial in T^{-1} in order to evaluate ΔH^\ddagger , as a function of temperature and pressure.

In the temperature range where the dielectric and viscometric data overlap, $\Delta H^\ddagger_e > \Delta H^\ddagger_v$. Again, the two sets of results show a similarity insofar as ΔH^\ddagger_e and ΔH^\ddagger_v for 7;2 are less than the corresponding ΔH^\ddagger 's for 7;3 which, in turn, are slightly less than those for the more hindered isomers 6;3, 5;3, and 2;3. As with the ΔV^\ddagger_e 's, the differences in ΔH^\ddagger_v between isomers is greatest at the lowest temperatures.

Unlike the dielectric results, $(\partial \Delta H^\ddagger_v / \partial P)_T > 0$ for each isomer at every temperature, and in general ΔH^\ddagger_v is much more pressure-dependent than ΔH^\ddagger_e . Since

$$\Delta V^\ddagger = (\partial \Delta G^\ddagger / \partial P)_T = (\partial \Delta H^\ddagger / \partial P)_T - T(\partial \Delta S^\ddagger / \partial P)_T,$$

we find that ΔV^\ddagger is always the result of a compensation between the pressure dependence of ΔH^\ddagger_v and ΔS^\ddagger_v . $(\partial \Delta H^\ddagger_v / \partial P)_T$ for our test liquids range from about 150 to 350 cm³/mole, roughly constant over the pressure range and with no obvious dependence on isomer structure. This is in marked contrast to the dielectric results⁵ where there appears to be a strong dependence on molecular structure.

The simplest free-volume theories predict a constant viscosity at constant density and various empirical schemes have been devised to account for departures from this model.¹⁶ We note that the structural effects are greatly minimized when isochoric rather than isobaric viscosities are compared, as in Fig. 3, but differences persist and become increasingly important

¹⁶ See Ref. 11 for a summary of various modified free-volume models and their general inapplicability.

at the higher densities. Since the compressions of these isomeric alcohols are quite similar, one must invoke a structurally sensitive compressibility and expansibility of the "free volume" (however, one may wish to define this nebulous parameter¹⁷) to account for the remaining differences. At the present stage of theoretical development this seems a fruitless exercise in curve fitting.

Even though there are obvious differences in the viscometric behavior of these isomers, they all appear to have essentially the same value of $(\partial P / \partial T)_\eta \approx 50$ bar deg⁻¹. A similar circumstance was found in the dielectric studies where, despite large differences in the temperature and pressure coefficients of the relaxation times, $(\partial P / \partial T)_\tau$ was the same for all five isomers. We note that $(\partial P / \partial T)_\tau : (\partial P / \partial T)_\eta : (\partial P / \partial T)_v \approx 10:5:2$ for these octanol isomers but have no explanation for the observation at this time.

CONCLUSIONS

The viscous behavior of structural isomers of octyl alcohol depends markedly on the position of the hydroxyl group and the proximity of neighboring methyl groups. The pressure and temperature dependence of viscosity is superficially similar to that of dielectric relaxation, but there are significant differences which suggest that the molecular mechanisms are not closely related.

ACKNOWLEDGMENT

We thank the Office of Saline Water for their generous support for this work.

¹⁷ See Ref. 1, p. 255ff, for a discussion.