Properties of Aliphatic and Aromatic Aldehydes under High Pressure

Compressibility and Viscosity Determination

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Compressibility and viscosity measurements have been made on seven aliphatic and three aromatic aldehydes at pressures up to 20,000 p.s.i.g. The viscosity data have been correlated by means of an empirical equation. Experimental data are presented in graphical form for the pressure range investigated.

DATA on the viscosity and compressibility of liquids are generally scarce. Previous investigations have concentrated mainly on organic compounds. The work on high pressure physical properties was pioneered by Bridgman (*1*).

Almost no work has so far been reported on aldehydes, possibly because they are difficult to work with. The aliphatic aldehydes are low boiling liquids with a disagreeable smell and are harmful to the human system. The aromatic aldehydes have a tendency to be oxidized to their corresponding acids.

EXPERIMENTAL

Concurrent measurements of the physical properties were conducted in a compact apparatus (*3*). Compressibility was measured by a piston displacement device (*2*) in conjunction with viscosity measurement, which was performed by a falling cylinder method (*4*, *5*).

Pressure was generated in the equipment by means of a manually operated hydraulic pump. The pressure was measured by a Bourdon gage. The precision of pressure measurement was within $\pm 0.2\%$. The temperature was measured by calibrated thermometers to an accuracy of $\frac{1}{2}$° F.

The compressibility meter consisted of a 16-inch long, $\frac{1}{4}$-inch I.D. stainless steel tube with cap-collar-gland assembly at both ends. Inside the tube there was a piston-magnet assembly soldered together. Outside the compressibility meter was a magnet-pointer assembly. The pointer indicated the position of the piston to one tenth of a millimeter.

The viscometer consisted of a fall tube, 152.5294 cm. long with 0.4710 cm. inside diameter. The tube was of stainless steel. The plummet used was a thin hollow cylinder of a uniform outside diameter of 0.43688 cm. with hemispherical ends. Bridgman had used plummets with three projecting lugs to keep the plummet coaxial during its fall. The lugs introduced some error in the measurements and were omitted in the present setup. Modified electrical contacts, with specially designed plugs, made the use of lugs unnecessary. The coaxial fall of the plummet through the viscometer tube was confirmed by means of a stethoscope.

METHOD OF OPERATION

Before starting experiments with the aldehydes, several test runs were made with various liquids of known viscosity to examine the accuracy of the apparatus. Plummets of different dimensions were tried to find the optimum plummet size. The authors discovered that plummets with

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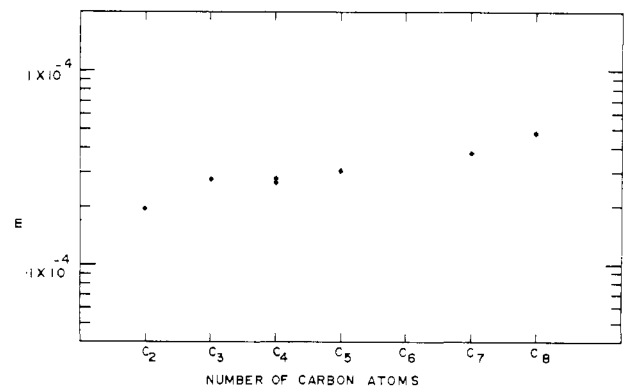

Figure 1. *m* against number of carbon atoms

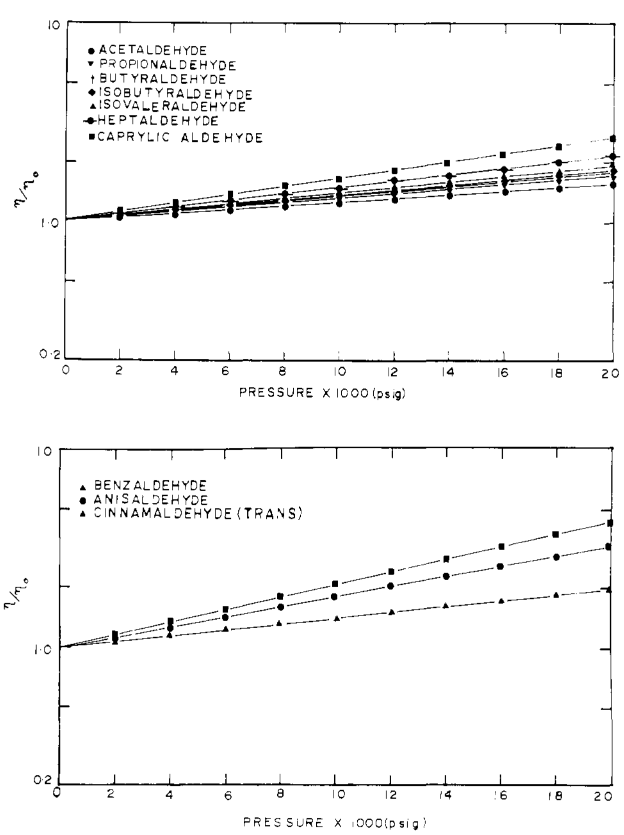

Figure 2. Viscosity-pressure diagrams

Table I. Viscosity and Compressibility Data

Press., P.S.I.G.	Relative Viscosity, η/η_0	Volume Change, $-\Delta V$, cc.	Compressibility, $-\Delta V/V_0 \times 100$	Press., P.S.I.G.	Relative Viscosity, η/η_0	Volume Change, $-\Delta V$, cc.	Compressibility, $-\Delta V/V_0 \times 100$
Acetaldehyde, 71.6° F., η_0 = 0.3468 cp.				Heptaldehyde, 71.7° F., η_0 = 0.9543 cp.			
2,000	1.0835	0.6774	1.86	2,000	1.0883	0.4210	1.16
4,000	1.1462	1.2725	3.49	4,000	1.1736	0.8103	2.24
6,000	1.2030	1.7789	4.87	6,000	1.2778	1.1490	3.18
8,000	1.2598	2.2252	6.10	8,000	1.3619	1.4687	4.06
10,000	1.3091	2.6145	7.16	10,000	1.4611	1.7631	4.87
12,000	1.3620	2.9880	8.19	12,000	1.5746	2.0321	5.62
14,000	1.4098	3.3267	9.11	14,000	1.6933	2.2853	6.32
16,000	1.4568	3.6306	9.99	16,000	1.8264	2.5164	6.95
18,000	1.5068	3.9186	10.74	18,000	1.9720	2.7380	7.57
20,000	1.5478	4.1877	11.47	20,000	2.1209	2.9501	8.15
Propionaldehyde, 74.3° F., η_0 = 0.4293 cp.				Caprylic Aldehyde, 69.3° F., η_0 = 1.2527 cp.			
2,000	1.0485	0.5064	1.40	2,000	1.1078	0.4052	1.12
4,000	1.0919	0.9812	2.71	4,000	1.2227	0.7597	2.10
6,000	1.1390	1.3896	3.83	6,000	1.3497	1.0794	2.98
8,000	1.1944	1.7726	4.89	8,000	1.4806	1.3927	3.84
10,000	1.2593	2.1113	5.82	10,000	1.6231	1.6713	4.61
12,000	1.3550	2.4373	6.72	12,000	1.7913	1.9340	5.34
14,000	1.4506	2.7475	7.58	14,000	1.9780	2.1777	6.01
16,000	1.5367	3.0260	8.35	16,000	2.1684	2.3993	6.62
18,000	1.6469	3.2856	9.06	18,000	2.3779	2.6177	7.22
20,000	1.7256	3.5388	9.76	20,000	2.6071	2.8171	7.78
Butyraldehyde, 84.0° F., η_0 = 0.5486 cp.				Benzaldehyde, 71.7° F., η_0 = 1.386 cp.			
2,000	1.0839	0.5666	1.57	2,000	1.0689	0.3070	0.84
4,000	1.1603	1.0540	2.92	4,000	1.1456	0.5761	1.58
6,000	1.2352	1.4750	4.09	6,000	1.2321	0.8135	2.23
8,000	1.3025	1.8359	5.09	8,000	1.3141	1.0477	2.87
10,000	1.3816	2.1746	6.02	10,000	1.4199	1.2630	3.46
12,000	1.4554	2.4943	6.91	12,000	1.5169	1.4719	4.03
14,000	1.5316	2.7855	7.72	14,000	1.6240	1.6681	4.57
16,000	1.6057	3.0640	8.49	16,000	1.7369	1.8549	5.08
18,000	1.6889	3.3109	9.17	18,000	1.8716	2.0226	5.54
20,000	1.7568	3.5420	9.81	20,000	2.0088	2.2030	6.03
Isobutyraldehyde, 82.8° F., η_0 = 0.5382 cp.				Anisaldehyde, 76.7° F., η_0 = 3.3716 cp.			
2,000	1.0753	0.5698	1.58	2,000	1.1217	0.2374	0.66
4,000	1.1589	1.0984	3.04	4,000	1.2064	0.4495	1.24
6,000	1.2411	1.5542	4.31	6,000	1.3531	0.6679	1.85
8,000	1.3170	1.9435	5.39	8,000	1.5103	0.8578	2.37
10,000	1.3970	2.3170	6.42	10,000	1.7141	1.0414	2.88
12,000	1.4771	2.6589	7.37	12,000	2.1277	1.2345	3.41
14,000	1.5528	2.9469	8.17	14,000	2.1511	1.3896	3.84
16,00	1.6289	3.2349	8.96	16,000	2.4274	1.5605	4.31
18,000	1.7021	3.4787	9.64	18,000	2.8247	1.7188	4.75
20,000	1.7801	3.7161	10.30	20,000	3.2857	1.8675	5.16
Isovaleraldehyde, 81.0° F., η_0 = 0.6823 cp.				*trans*-Cinnamaldehyde, 84.3° F., η_0 = 3.6054 cp.			
2,000	1.1009	0.7913	2.17	2,000	1.1813	0.3324	0.92
4,000	1.1788	1.2598	3.45	4,000	1.3540	0.6172	1.70
6,000	1.2703	1.6776	4.59	6,000	1.5731	0.8388	2.31
8,000	1.3462	2.0448	5.60	8,000	1.8286	1.0445	2.88
10,000	1.4235	2.3803	6.52	10,000	2.1453	1.2281	3.39
12,000	1.5459	2.6968	7.38	12,000	2.5460	1.4244	3.93
14,000	1.6207	3.0039	8.32	14,000	2.9569	1.5827	4.36
16,000	1.7141	3.2761	8.97	16,000	3.4255	1.7409	4.80
18,000	1.8033	3.5198	9.64	18,000	3.9394	1.8992	5.24
20,000	1.9109	3.7509	10.27	20,000	4.3505	2.0290	5.59

smaller clearances and larger lengths gave more accurate results than plummets of larger clearances and smaller lengths. Eventually, a plummet with outside diameter 0.43688 cm. and 2.5400 cm. long was selected. Test run data of benzene and carbon tetrachloride agreed to three decimal places with the previously reported values (*4, 6*).

The loading of the equipment was done with the help of a secondary pump. The sample liquid was pumped into the apparatus from the secondary pump and allowed to flow out for a couple of minutes. All the joints were tightened slightly at this time and the liquid entrance valve from the secondary pump was closed tightly. The main pump was closed to the atmosphere and a pressure of 2000 p.s.i. was built up in the apparatus. All the joints were now tightened and pressure brought back to atmosphere. The loading procedure took about 30 minutes.

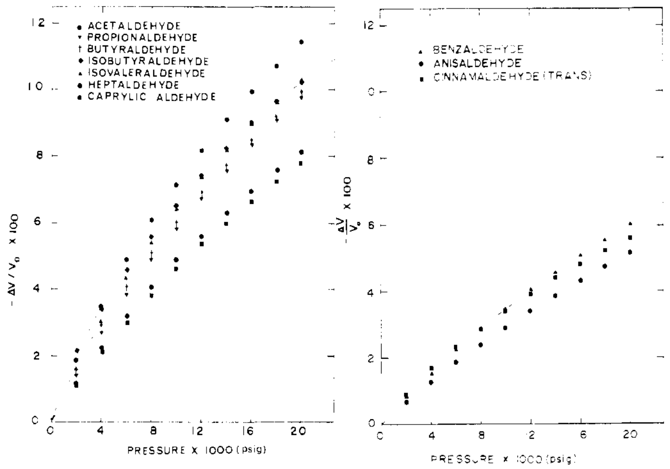

Figure 3. Compressibility diagrams

In case of highly volatile and poisonous liquids, the secondary pump was replaced by a stainless steel and aluminum bomb. The sample was forced into the system by the use of high pressure nitrogen.

RESULTS

Viscosity data are given in Table I with the compressibility data for all the aldehydes studied. The viscosity data are estimated to be correct within ±1%. The errors associated with the compressibility data are below ±0.4%.

The equation which correlated the viscosity data with pressure is:

$$\eta = \eta_o \exp mP \qquad (1)$$

where η_o represents viscosity under atmospheric conditions and m is a constant specific to each substance. m is plotted against a number of carbon atoms in Figure 1. Equation 1 correlates aldehyde data to a confidence level of 95%.

Graphical representation of viscosity data is given in Figure 2. The slopes of the straight lines indicate the magnitude of m. Compressibility diagrams for aliphatic and aromatic aldehydes are presented in Figure 3.

NOMENCLATURE

η = viscosity, cp.
η_o = viscosity under atmospheric conditions, cp.
m = constant, Equation 1
P = pressure, p.s.i.

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Densities, Refractive Indices, Molar Refractions, Viscosities, and Dielectric Constants of Triethylene Glycol Dimethyl Ether–Water Solutions at 25° C.

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Densities, refractive indices, viscosities, and dielectric constants of mixtures of water and triethylene glycol dimethyl ether have been determined at 25° C. Molar refractions are also presented. The refractive indices of the solutions increase sharply from pure water to 0.2 mole fraction ether and then increase slowly to the value for the pure ether. The partial molal volume of the ether passes through a minimum which is about 8% less than the ideal molal volume at 0.03 mole fraction ether. The viscosity exhibits a pronounced maximum at 0.14 mole fraction ether. The dielectric constant increases smoothly with water content.

DENSITIES, refractive indices, viscosities, and dielectric constants of mixtures of triethylene glycol dimethyl ether and water have been determined at 25° C. as part of a study of polyether and polyether-water systems. These data as well as the molar refractions of these solutions are presented.

EXPERIMENTAL

Technical triethylene glycol dimethyl ether (Ansul Chemical Co., Ansul E-161) was distilled over sodium under a pressure of 1.5 mm. of Hg at 79° C. A controlled amount of nitrogen was allowed to bubble through the boiling ether. Ether distilled under these conditions contains less than 0.01% water as measured by the Karl Fischer reagent. At 25° C., the ether has a refractive index of 1.4209 and density of 0.9795 compared with the respective values of 1.4233 at 20° C. and 0.974 at 24° C. reported by Zellhoefer (*8*). Water used for the solutions was distilled from dilute potassium permanganate solution in a seasoned all borosilicate glass assembly. Solutions were prepared as described earlier (*6*).