Influence of Temperature on Viscosity of Nonassociated Liquids

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AN INSIGHT into the structure of liquids may be gained by investigating the extent to which full development of kinetic motion is restricted in the liquid state. This can be achieved in several ways—for instance, by measuring the energy required to vaporize a molecule or the energy content of the surface of a liquid. Again, the energy required to transfer a molecule in a liquid from one equilibrium position to another is a measure of the forces to which the molecule is subjected. This energy can be deduced from the variation of the coefficient of viscosity with temperature. As part of a more general investigation aimed at a better understanding of the liquid state, through a study of the effect of temperature on certain physical properties of liquids, the viscosity and density of 32 nonassociated liquids have been measured between 20° C. and temperatures close to their normal boiling points.

EXPERIMENTAL

The all-glass Ostwald type viscometer used was constructed according to the British Engineering Standards Association (*3*) specifications with the recommendations made by Barr (*2*) incorporated in its design. It was calibrated by means of liquids of accurately known kinematic viscosities, using the following modified form of Ostwald's equation:

$$\eta = \rho(A \times t - B/t)$$

where η is the viscosity in poises, ρ is the density of the liquids in grams per milliliter, t is the time of flow in seconds, and A and B are constants for the instrument. The calibrating liquids—benzene, water, ether, and chloroform—had been carefully purified until their densities and refractive indices checked against the accepted values given by the International Critical Tables.

After thorough cleaning and drying, the viscometer was charged with an accurately measured volume of the liquid under investigation (15 ml. at 20° C.). Intrusion of moisture and dust from the atmosphere was prevented by attaching to the limbs of the instrument guard tubes containing calcium chloride and plugs of glass wool.

Because the working volume of liquid should be the same in all experiments, an expansion correction must be applied when viscosity measurements are made at temperatures higher than those at which the viscometer has been charged. This correction was estimated from the dimensions of the instrument. If the cross section of the lower cylindrical storage bulb is α and the working colume is V, the reduction of the head due to the expansion of the liquid is

$$[V/\alpha](\rho/\rho_1 - 1)$$

where ρ and ρ_1 are the densities of the liquid at the temperatures considered. If the head, h, is taken as the mean of the initial and final heads, the correcting factor by which the time of flow has to be multiplied is

$$[1 - Vh/\alpha](\rho/\rho_1 - 1)$$

The stop-watch used was checked against a standard chronometer at regular intervals. It was fully wound before each measurement and was always used in the same position.

The densities were measured in a carefully calibrated 5-ml. pycnometer.

MATERIALS

The anhydrides and the carbonates were obtained from British Drug Houses, Ltd.; all the other materials were supplied by Light and Co., Ltd. Diallyl ether and allyl chloride were dried over anhydrous calcium sulfate for several days. Similarly the ketones were allowed to stand over anhydrous potassium carbonate, and the nitriles over phosphoric anhydride which had previously been freed from phosphorous anhydride. Acetic anhydride was dried by standing over sodium wire, while propionic and butyl anhydrides were shaken for a few minutes with phosphoric anhydride just prior to distillation.

Immediately before their introduction into the viscometer, all materials were subjected to repeated fractional distillation until the fraction collected had a constant point boiling point, density, and refractive index.

The viscosity measurements are listed in Table I.

DISCUSSION

The literature contains few experimental data concerning the viscosities of the compounds investigated in this study. Those determined previously are compared in Table II with those obtained in the present work.

Variation of Density with Temperature. The variation of density with temperature can be represented by a general equation

$$\rho_4^t = \rho_4^0 - \alpha t \times 10^{-4} - \beta t^2 \times 10^{-7}$$

where ρ_4^t is the density in grams per milliliter, t is the temperature in ° C., and ρ_4^0, α, and β are parameters whose values are listed in Table III. The values of these constants were calculated by the method of least squares from the experimental data recorded in Table I.

Andrade's Equation. The experimental data given in Table I were used to ascertain the applicability of Andrade's modified equation (*1*)

$$\eta v^{1/3} = A \exp (c/Tv)$$

to represent the variation of viscosity with temperature. In this equation, η is the viscosity, T is the absolute temperature, A and c are constants, and v is the molecular volume as given by the relationship $v = M/\rho$ where M is the molecular weight of the liquid and ρ is its density.

For each substance investigated, $\log_{10}\eta v^{1/3}$ was plotted against $1/Tv$. In most cases straight lines were obtained and from these constants A and c were calculated by the method of the least squares. Listed in Table III are the values of A and c for those compounds for which Andrade's equation was found to apply. Using these constants, viscosities were computed and compared with the experimentally obtained values.

Table I. Viscosity in 10^{-5} Poise

t, ° C.	2-Pentene	2-Methyl-1-pentene	4-Methyl-2-pentene	1-Hexene	2-Ethyl-1-hexene	1-Hexyne	Diallyl Ether	Allyl Chloride
20.0	214	290	265	283	472	373	441	330
25.0	201	277	250	269	...	...	417	313
30.0	189	263	238	254	423	333	392	302
35.0	180	249	224	243	...	...	...	286
40.0	...	237	213	231	381	298	350	273
50.0	...	212	193	210	345	268	315	...
60.0	...	...	...	193	313	242	285	...
80.0	...	...	...	...	263	...	234	...
100.0	...	...	...	...	225	...	...	...
	1-Octene	2-Octene	*n*-Decene	Cyclohexene	1-Vinyl-2-cyclohexene	Methyl *n*-Propyl Ketone	Methyl *n*-Amyl Ketone	Methyl *n*-Nonyl Ketone
20.0	506	506	828	650	690	489	815	2065
30.0	450	451	725	571	608	438	709	1689
40.0	406	406	636	504	543	394	623	1415
50.0	365	366	560	450	486	357	553	1195
60.0	333	333	504	403	439	324	495	1030
80.0	276	277	406	...	363	271	405	790
100.0	233	234	338	...	304	...	337	628
120.0	...	...	288	...	258	...	285	516
140.0	...	...	243	...	...	...	...	430
	Pinacolone	Diisopropyl Ketone	Acetic Anhydride	Propionic Anhydride	Butyric Anhydride	Dimethyl Carbonate	Diethyl Carbonate	Dibutyl Carbonate
20.0	713	632	901	1127	1571	625	813	1920
30.0	625	559	786	967	1337	549	707	1580
40.0	552	500	691	839	1140	487	623	1326
50.0	492	448	615	733	983	435	553	1132
60.0	440	404	550	653	861	392	495	982
80.0	360	333	448	524	680	355	445	858
100.0	...	279	374	431	553	323	403	756
120.0	...	...	...	360	453	...	334	602
140.0	...	...	...	306	376	...	...	492
	...	...	...	...	...	...	...	410
	Propionitrile	*n*-Capronitrile	Isocapronitrile	Benzonitrile	Benzyl Cyanide	*o*-Tolunitrile	*m*-Tolunitrile	*p*-Tolunitrile
20.0	431	975	980	1346	2161	1755	1653	...
30.0	387	842	843	1140	1779	1456	1370	1437
40.0	351	733	734	991	1505	1233	1160	1220
50.0	318	648	646	869	1293	1063	999	1050
60.0	292	576	573	772	1125	928	873	916
80.0	243	465	460	633	880	727	691	722
100.0	...	385	381	523	712	594	564	588
120.0	...	324	319	440	586	497	468	491
140.0	...	274	270	374	512	421	399	415

Table II. Comparison with Previous Work

		Viscosity, Poise	
Compound	t, ° C.	Present work	Other work (*4*)
Allyl chloride	15.0	0.003475	0.00347
	20.0	0.003300	0.003295
	30.0	0.003019	0.00300
	40.0	0.002732	0.002735
Acetic anhydride	15.0	0.009681	0.00971
	30.0	0.007863	0.00783
Dimethyl carbonate	25.0	0.005853	0.005845
Diethyl carbonate	25.0	0.007550	0.007476
	30.0	0.007071	0.00698
Di-*n*-butyl carbonate	25.0	0.01760	0.01763
Propionitrile	15.0	0.004532	0.00454
	30.0	0.003874	0.00389
Benzonitrile	15.0	0.01463	0.01447
	30.0	0.01140	0.01111
	100.0	0.005171	0.005151
Benzyl cyanide	25.0	0.01956	0.0198

The fit between observed and calculated values of the viscosities is in general very good, if the range of viscosities—i.e., the ratio of the lowest to the highest viscosity in the set of observations—is not too large. This is the case of the hydrocarbons studied, where the range of viscosities varied from 1.16 for 2-pentene to 3.19 for *n*-decene. For these, Andrade's equation was found to represent the experimental data with accuracy, the deviation between observed and calculated values being at most 1% and generally much less. In the case of *p*-, *m*-, and *o*-tolunitrile, benzyl cyanide, and di-*n*-butyl carbonate, where the viscosity ranges are 3.74, 4.15, 4.17, 4.49, and 4.68, respectively, the plots of $\log_{10}\eta v^{1/3}$ against $1/Tv$ show slight but definite curvatures, being concave towards the $\log_{10}\eta v^{1/3}$ axis. The degree of curvature increases from *p*-tolunitrile to di-*n*-butyl carbonate, indicating that the deviation from Andrade's relationship increases as the viscosity ranges get larger. Examination of Table IV reveals that structure affects the magnitude of *c*.

Qualitative Trends. In any homologous series, the value of *c* increases with increasing chain length. For instance, *c* increases from 3.334×10^4 for 2-pentene to 7.408×10^4 for *n*-decene, from 3.306×10^4 for methyl *n*-propyl ketone to 10.960×10^4 for methyl *n*-nonyl ketone, and from 3.582×10^4 for acetic anhydride to 7.695×10^4 for butyric anhydride.

Table III. Densities, Density Parameters, Boiling Points, and Refractive Indices

Substance	ρ_4^0	α	β	B.P. at 760 Mm.	n^{20}_D
2-Pentene	0.6695	9.625	0.0	36.4	1.3798
2-Methyl-1-pentene	0.7083	9.975	0.0	61.7	1.3926
4-Methyl-2-pentene	0.6857	9.467	0.0	55.3	1.3878
1-Hexene	0.6949	9.650	0.0	64.1	1.3861
2-Ethyl-1-hexene	0.7432	8.204	5.833	119.4	1.4191
1-Octene	0.7321	8.023	6.333	121.5	1.4084
2-Octene	0.7365	8.412	1.917	124.2	1.4152
n-Decene	0.7567	7.733	1.458	171.7	1.4290
1-Hexyne	0.7347	9.800	0.0	71.6	1.3966
Cyclohexene	0.8299	9.750	0.0	83.1	1.4472
1-Vinyl-2-cyclohexene	0.8465	8.317	4.722	128.7	1.4625
Diallyl ether	0.8291	10.346	4.405	94.5	1.4121
Allyl chloride	0.9637	13.101	0.0	45.1	1.4230
Methyl *n*-propyl ketone	0.8261	9.810	4.810	101.9	1.3909
Methyl *n*-amyl ketone	0.8324	8.470	2.000	151.3	1.4077
Methyl *n*-nonyl ketone	0.8405	7.252	3.510	227.8	1.4290
Pinacolone	0.8262	9.538	0.0	106.2	1.3985
Diisopropyl ketone	0.8233	8.571	5.080	123.8	1.4005
Acetic anhydride	1.1054	11.983	4.261	139.4	1.3892
Propionic anhydride	1.0343	11.182	1.125	167.2	1.4050
Butyric anhydride	0.9868	9.709	1.578	198.2	1.4120
Dimethyl carbonate	1.0958	12.583	9.166	90.4	1.3659
Diethyl carbonate	0.9972	10.713	8.437	126.9	1.3818
Di-*n*-butyl carbonate	0.9435	9.284	1.947	207.4	1.4084
Propionitrile	0.8015	9.675	7.501	97.3	1.3654
n-Capronitrile	0.8215	7.843	4.632	163.1	1.4068
Isocapronitrile	0.8208	8.273	1.739	156.3	1.4057
Benzonitrile	1.0228	8.775	1.251	190.9	1.5252
o-Tolunitrile	1.0100	8.325	1.874	204.7	1.5252[a]
m-Tolunitrile	1.0028	8.466	0.332	214.1	0.9859
p-Tolunitrile	1.0010	8.233	1.851	218.1	1.5281[b]
Benzyl cyanide	1.0321	8.042	1.042	232.4	1.5198[a]

[a] Measured at 25° C. [b] Measured at 30° C.

Table IV. Values of Parameters *A* and *c* in Andrade's Equation

$$\eta v^{1/3} = A \exp (C/Tv)$$

Substance	$A \times 10^3$	$c \times 10^{-4}$
2-Pentene	0.8993	3.334
2-Methyl-1-pentene	1.438	3.603
4-Methyl-2-pentene	1.384	3.632
1-Hexene	1.662	3.393
2-Ethyl-1-hexene	2.246	4.764
1-Octene	2.213	5.069
2-Octene	2.187	5.006
n-Decene	2.205	7.408
1-Hexyne	1.628	3.526
Cyclohexene	1.772	3.662
1-Vinyl-2-cyclohexene	2.129	4.644
Diallyl ether	1.784	3.864
Allyl chloride	1.976	2.073
Methyl *n*-propyl ketone	2.046	3.306
Methyl *n*-amyl ketone	2.017	5.421
Methyl *n*-nonyl ketone	1.830	10.960
Pinacolone	1.918	4.624
Diisopropyl ketone	2.108	4.962
Acetic anhydride	2.089	3.582
Propionic anhydride	2.232	5.277
Butyric anhydride	2.137	7.695
Dimethyl carbonate	1.772	2.934
Diethyl carbonate	2.100	4.551
Propionitrile	1.838	2.036
n-Capronitrile	1.993	4.872
n-Capronitrile	1.895	4.973
Benzonitrile	2.254	4.305

Branching of the carbon chain increases the value of *c*. Whereas for 2-pentene *c* is 3.334 × 10^4, for 2-methyl-1-pentene and for 4-methyl-2-pentene it is 3.603 and 3.632 × 10^4, respectively. Introduction of an ethyl group in the molecule of 1-hexene increases the value of *c* from 3.393 × 10^4 to 4.764 × 10^4 for 2-ethyl-1-hexene. Similarly, addition of a methyl group to pinacolone to form diisopropyl ketone changes the value of *c* from 4.624 × 10^4 to 4.962 × 10^4.

The position of the side chain or of the double bond appears to have little effect. The values of *c* for 2-methyl-1-pentene and 4-methyl-1-pentene are 3.603 × 10^4 and 3.632 × 10^4, respectively; for 1-octane and 2-octene they are 5.069 × 10^4 and 5.006 × 10^4.

A comparison of the values of *c* for 1-hexene and cyclohexene indicates that *c* is larger for a cyclic compound than for the corresponding straight-chain one.

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