Physical Property Correlations for Conjugated Aliphatic Nitro-olefins

Viscosity

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The viscosities of 21 conjugated linear nitro-olefins were measured at 30°, 40° and 60° C. The measured values for each compound were fitted by log η = $A + B/(C + t)$. C varied from 123.8 to 149.6 with an average value of 137.0. The series, as a whole, was fitted by the equations: log $\eta = 2.0110 + 0.0267N + 0.00192N^2 + (145.7 + 18.4N)/(t + 137.0) - \log M + GCF$, and $\log \eta = \log d^{1/3} + \log(1.4406 - 0.0579N + 0.00248N^2) + (117.4 + 20.0N)d/(t + 137.0) + GCF$, where η is the viscosity in millipoises, N is the number of carbons minus four, t is the temperature in °C., d is the density in grams per milliliter, M is the molecular weight, and GCF is the sum of the appropriate "Group Correction Factors." Values of ΔE_{vis} and $\Delta E_{vap}/\Delta E_{vis}$ for the different values of N were compared at 25° C.

THE VISCOSITIES at 30°, 40°, and 60° C. were measured for a series of 21 conjugated linear nitro-olefins having straight-chain alkyl groups, ranging from methyl to hexyl, substituted on each carbon of nitroethylene $R_ACH = C(NO_2)R_B$. These measurements were performed at the same time and on the same samples for which the methods of preparation and purification and the boiling point have been reported (*2*). The viscosities were measured with two Cannon-Fenske viscometers which were calibrated for the two-constant equation, $\eta = A\rho t - B\rho/t$, with NBS viscometer calibrating oils D and H. Appropriate corrections were applied (*1*), and the calibrations checked, at the lower end of the range, to within ±0.01 mp. against water, benzene, and carbon tetrachloride. The experimental results are given in Table I.

The measured viscosities of each compound were fitted by the three-constant equation

$$\log \eta = A + B/(C + t) \qquad (1)$$

where η is the viscosity in milliposes and t is the temperature in °C. The values of the constants are shown in Table II. The constant, C, ranges between 123.8 and 149.6, with an average value of 137.0, whereas a value of 273.2 would correspond to the equation, $\log \eta = A + B/T$. The average value of 137.0 is used in Equations 4 and 5.

The energy of viscous flow, ΔE_{vis}, was calculated by using the relation, $\Delta E_{vis} - 2.303RT^2 (d \log \eta/dT)$. Applying this to Equation 1 gives

$$\Delta E_{vis} = 2.303RBT^2/(C + t)^2 \qquad (2)$$

and

$$d(\Delta E_{vis})/dT = 2\,\Delta E_{vis}(C - 273.2)/T(C + t) \qquad (3)$$

The results (at 25° C.) are shown in Table II.

The viscosities of all 21 compounds were fitted by the two equations:

Table I. Experimental Viscosities

Compd. No.	Compd. Name	η_t, Millipoises 30°	40°	60°
1	2-Nitro-2-butene	8.12	7.19	5.85
2	2-Nitro-2-pentene	8.71	7.68	6.19
3	3-Nitro-2-pentene	9.25	8.10	6.46
4	2-Nitro-2-hexene	11.44	9.93	7.80
5	3-Nitro-2-hexene	10.91	9.43	7.37
6	3-Nitro-3-hexene	9.96	8.69	6.90
7	2-Nitro-2-heptene	13.36	11.47	8.88
8	3-Nitro-2-heptene	13.55	11.54	8.77
9	3-Nitro-3-heptene	12.92	11.07	8.49
10	4-Nitro-3-heptene	12.35	10.63	8.21
11	2-Nitro-2-octene	16.80	14.19	10.64
12	3-Nitro-2-octene	16.73	14.02	10.40
13	3-Nitro-3-octene	15.36	13.01	9.84
14	4-Nitro-3-octene	14.99	12.68	9.55
15	4-Nitro-4-octene	16.03	13.47	10.05
16	2-Nitro-2-nonene	20.19	16.83	12.41
17	3-Nitro-2-nonene	20.38	16.80	12.15
18	3-Nitro-3-nonene	19.15	15.95	11.68
19	4-Nitro-3-nonene	18.99	15.76	11.51
20	4-Nitro-4-nonene	18.72	15.60	11.46
21	5-Nitro-4-nonene	19.27	15.95	11.62

Table II. Fits of Individual Compounds

Compd. No.	Eq. 1 Constants A	B	C	ΔE_{vis}(25° C.), Kcal./Mole Eq. 2	$\left(\frac{d\Delta E_{vis}}{dT}\right)_{25°}$ Eq. 3
1	−0.0257	156.2	137.0	2.42	−0.0137
2	−0.0958	186.0	149.6	2.48	−0.0118
3	−0.0888	182.5	143.0	2.63	−0.0137
4	−0.0716	196.4	143.8	2.80	−0.0144
5	−0.0638	180.7	134.0	2.91	−0.0171
6	−0.0333	169.3	134.1	2.72	−0.0160
7	+0.0253	171.9	126.2	3.06	−0.0200
8	−0.1694	229.8	146.6	3.18	−0.0157
9	−0.1781	234.8	152.1	3.05	−0.0140
10	−0.1851	237.6	156.1	2.95	−0.0128
11	−0.1205	233.5	143.5	3.35	−0.0173
12	−0.1096	218.1	133.6	3.53	−0.0208
13	−0.0299	192.9	128.6	3.33	−0.0210
14	−0.1035	212.5	136.1	3.33	−0.0190
15	−0.0766	204.4	129.5	3.48	−0.0217
16	+0.0106	199.1	123.8	3.66	−0.0246
17	−0.0835	217.4	126.1	3.88	−0.0253
18	+0.1695	250.7	142.7	3.63	−0.0189
19	−0.1056	222.7	130.9	3.73	−0.0228
20	−0.1091	227.1	134.4	3.64	−0.0212
21	−0.0670	209.0	124.6	3.80	−0.0253

Table III. Fits of Viscosity Equations

						η_{30° Millipoises					η_{40° Millipoises					η_{60° Millipoises			
Compd. No.	R_A	R_B	*GCF* Eq. 4	*GCF* Eq. 5	$d_4^{30\,a}$	Eq. 4	Eq. 4-obsd.	Eq. 5	Eq. 5-obsd.	$d_4^{40\,a}$	Eq. 4	Eq. 4-obsd.	Eq. 5	Eq. 5-obsd.	$d_4^{60\,a}$	Eq. 4	Eq. 4-obsd.	Eq. 5	Eq. 5-obsd.
1	Me	Me	+0.023	+0.010	1.0374	7.97	−0.15	8.00	−0.12	1.0263	7.12	−0.07	7.13	−0.06	1.0057	5.87	+0.02	5.87	+0.02
2	Et	Me	−0.010	−0.013	0.9972	8.86	+0.15	8.88	+0.17	0.9872	7.79	+0.11	7.81	+0.13	0.9672	6.28	+0.09	6.28	+0.09
3	Me	Et	−0.001	−0.010	1.0031	9.04	−0.21	9.06	−0.19	0.9932	7.96	−0.14	7.97	−0.13	0.9734	6.41	−0.05	6.40	−0.06
4	Pr	Me	+0.017	+0.012	0.9798	11.36	−0.08	11.42	−0.02	0.9700	9.86	−0.07	9.89	−0.04	0.9518	7.74	−0.06	7.77	−0.03
5	Me	Pr	+0.003	−0.005	0.9797	11.00	+0.09	10.98	+0.07	0.9701	9.54	+0.11	9.52	+0.09	0.9518	7.50	+0.13	7.47	+0.10
6	Et	Et	−0.034	−0.033	0.9739	10.10	+0.14	10.14	+0.18	0.9651	8.76	+0.07	8.81	+0.12	0.9458	6.89	−0.01	6.91	+0.01
7	Bu	Me	+0.008	+0.002	0.9598	13.46	+0.10	13.35	−0.01	0.9509	11.51	+0.04	11.42	−0.05	0.9334	8.82	−0.06	8.76	−0.12
8	Me	Bu	+0.006	−0.001	0.9631	13.39	−0.16	13.38	−0.17	0.9539	11.45	−0.09	11.43	−0.11	0.9363	8.78	+0.01	8.76	−0.01
9	Pr	Et	−0.007	−0.008	0.9568	13.00	+0.08	12.94	+0.02	0.9473	11.11	+0.04	11.05	−0.02	0.9293	8.53	+0.04	8.48	−0.01
10	Et	Pr	−0.030	−0.028	0.9572	12.33	−0.02	12.37	+0.02	0.9480	10.54	−0.09	10.58	−0.05	0.9300	8.09	−0.12	8.11	−0.10
11	Am	Me	+0.022	+0.020	0.9449	16.82	+0.02	16.77	−0.03	0.9363	14.18	−0.01	14.14	−0.05	0.9189	10.61	−0.03	10.58	−0.06
12	Me	Am	+0.021	+0.019	0.9452	16.78	+0.05	16.75	+0.02	0.9366	14.14	+0.12	14.12	+0.10	0.9196	10.59	+0.19	10.57	+0.17
13	Bu	Et	−0.016	−0.018	0.9460	15.41	+0.05	15.42	+0.06	0.9370	12.99	−0.02	12.99	+0.02	0.9198	9.72	−0.12	9.72	−0.12
14	Et	Bu	−0.027	−0.024	0.9412	15.02	+0.03	14.98	−0.01	0.9324	12.66	−0.02	12.64	−0.04	0.9155	9.48	−0.07	9.47	−0.08
15	Pr	Pr	−0.003	−0.003	0.9451	15.88	−0.15	15.92	−0.11	0.9363	13.38	−0.09	13.41	−0.06	0.9188	10.02	−0.03	10.03	−0.02
16	Hx	Me	+0.021	+0.023	0.9298	20.29	+0.10	20.23	+0.04	0.9214	16.86	+0.03	16.83	0.00	0.9050	12.32	−0.09	12.32	−0.09
17	Me	Hx	+0.020	+0.015	0.9357	20.24	−0.14	20.26	−0.12	0.9271	16.82	+0.02	16.82	+0.02	0.9110	12.29	+0.14	12.30	+0.15
18	Am	Et	−0.002	0.000	0.9303	19.24	+0.09	19.22	+0.07	0.9220	15.99	+0.04	15.99	+0.04	0.9056	11.68	0.00	11.70	+0.02
19	Et	Am	−0.012	−0.004	0.9269	18.81	−0.18	18.83	−0.16	0.9186	15.62	−0.14	15.67	−0.09	0.9018	11.42	−0.09	11.47	−0.04
20	Bu	Pr	−0.012	−0.012	0.9338	18.81	+0.09	18.87	+0.15	0.9251	15.62	+0.02	15.67	+0.07	0.9082	11.42	−0.04	11.44	−0.02
21	Pr	Bu	0.000	+0.001	0.9305	19.33	+0.06	19.28	+0.01	0.9220	16.06	+0.11	16.03	+0.08	0.9053	11.74	+0.12	11.72	+0.10

[a] See ref. (2).

Table IV. Group Correction Factors (GCF)

	Equation 4		Equation 5	
R	R_A	R_B	R_A	R_B
Me	+0.008	+0.015	+0.003	+0.007
Et	−0.025	−0.009	−0.020	−0.013
Pr	+0.002	−0.005	+0.005	−0.008
Bu	−0.007	−0.002	−0.005	−0.004
Am	+0.007	+0.013	+0.013	+0.016
Hx	+0.006	+0.012	+0.016	+0.012

Table V. $\Delta E_{\text{vis.}} - \Delta E_{\text{vap.}}$ Relationships

N	*t*, ° C.	ΔEvis., Kcal./Mole (Eq. 6)	$\Delta E_{\text{vap.}}$, Kcal./Mole (Eq. 7)	$\dfrac{\Delta E_{\text{vap.}}}{\Delta E_{\text{vis.}}}$
0	25.0	2.26	11.3	5.0
1	25.0	2.54	12.1	4.7
2	25.0	2.83	12.7	4.5
3	25.0	3.12	13.5	4.3
4	25.0	3.40	14.3	4.2
5	25.0	3.69	15.2	4.1

$$\log \eta = 2.0110 + 0.0267N + 0.00192N^2 + (145.7 + 18.4N)/(t + 137.0) - \log M + GCF \qquad (4)$$

and

$$\log \eta = \log d^{1/3} + \log(1.4406 - 0.0579N + 0.00248N^2) + (117.4 + 20.0N)d/(t + 137.0) + GCF \qquad (5)$$

where η is the viscosity in millipoises, *N* is the number of carbons minus four, *t* is the temperature in ° C., *d* is the density in grams per ml., *M* is the molecular weight, and *GCF* is the sum of the appropriate two "Group Correction Factors" listed in Table IV.

Equation 4 fitted the measured viscosities of the 21 compounds with a 50% probable error of ±0.076. Equation 5, which involves the density, fitted with a 50% probable error of ±0.070. The results of these fits are shown in Table III.

Equations 4 and 5 were developed by adapting the basic equations, $\eta = Ae^{B/T}$ and $\eta v^{1/3} = Ae^{B/Tv}$, respectively. In both equations, *T* is replaced by $t + 137.0$, and the constants are expressed as functions of *N* and *M*.

The "Group Correction Factors" given in Table IV greatly improved the fit, particularly in the case of the ethyl group. These seem to be somehow related to the structure. They may reflect the shape of the molecule and the degree of shielding of the polar nitro group.

The ΔE_{vis} values which are reported in Table V were calculated from the equation

$$\Delta E_{\text{vis}} = 2.303RT^2(145.7 + 18.4N)/(t + 137.0)^2 \qquad (6)$$

which was derived from Equation 4. The ΔE_{vap} values were calculated from the data of Lampe (2) by the use of the equation

$$\Delta E_{\text{vap}} = RT[2.303TT_{760}\phi/(1.15T - 0.15T_{760})^2 - 1]$$

where

$$T_{760} = T_{10}/2 - 1063.0 + \tfrac{1}{2}\,[(2125.9 - T_{10})^2 + 11987T_{10}]^{1/2}$$

and $\phi = 4.31 + 0.00216T_{760}$.

The ratio $\Delta E_{\text{vap}}/\Delta E_{\text{vis}}$ was calculated at 25° C. for all six values of *N* (Table V). It decreases with increasing values of *N* and it increases with temperature; for example, it equals 5.0 for *N* = 0 at 25° C. and 5.4 for *N* = 0 at 50° C. The ratios are somewhat higher than the range normally expected (3 to 4) and would fall within this range only at temperatures corresponding to relatively low vapor pressures or high viscosities.

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LITERATURE CITED

(1) Hardy, R.C., "NBS Viscometer Calibrating Liquids and Capillary Tube Viscometers," Natl. Bur. Stds. Monograph **55**, 1962.
(2) Lampe, K.F., Mende, T.J., Mills, A.P., J. CHEM. ENG. DATA **7**, 85 (1962).

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Isothermal Compressibilities of Carbon Tetrachloride, Methanol, and Isopropyl Alcohol

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An experimental arrangement for the measurement of isothermal compressibilities of liquids is described. The compressibilities of carbon tetrachloride, methanol, and isopropyl alcohol obtained by using this experimental arrangement in the temperature range of 30° to 70° C. are reported.

DURING the last few years isothermal compressibilities have been receiving increasing attention in studies of the molecular interactions and the behavior of pure liquids and binary liquid mixtures. Measurements of the compressibilities of liquids have been made earlier by Carnazzi (*3*), Dolezalek and Speidel (*6*), Drecker (*7*), Richards and Shipley (*16*), Rontgen (*17*), Tyrer (*18*), Bridgman (*2*), Philip (*14*), McKinney (*12*), and Freyer (*9*). However, accurate experimental data on the liquids and liquid mixtures in the neighborhood of the atmospheric pressure suitable for obtaining the isothermal compressibilities at zero pressure, which are required for comparison with the results of the various statistical models proposed for describing the properties of liquids and liquid mixtures, are not readily available. Recently, McGlashan and others (*5*), have made measurements of the compressibilities of binary mixtures of carbon tetrachloride and cyclohexane and have shown that if volume changes on mixing are taken into account, improved agreement between the quasicrystalline model of Guggenheim (*10*) and experiment can be obtained. Their results also agree well with the cell model proposed by Prigogine (*15*). Measurements on the molar volumes and compressibilities of biphenyl and *m*-, *o*-, and *p*- terphenyl have been made by Opdycke and others (*13*). They have compared their results with those predicted by the Eyring-Hirschfelder (*11*) free volume model adapted to polymers by Flory (*8*) and also those of corresponding state treatment of Prigogine. The measurement of isothermal compressibilities of pure liquids and binary liquid mixtures containing a polar and a nonpolar molecule is reported in this paper, and an experimental arrangement for the accurate measurement of compressibilities of carbon tetrachloride, methanol, and isopropyl alcohol in the range of temperatures 30° to 70° C. is described.

EXPERIMENTAL PROCEDURE

Purification of Materials. Best available samples of mercury, carbon tetrachloride, methanol, and isopropyl alcohol from Merck's and B.D.H. (British Drug House) used in these investigations were subjected to further purification in the laboratory by usual methods described earlier (*4*). The purity of the samples used for the experiments was checked by determining their densities with a Desmyter and Chaudhri type pycnometer (*4*). Table I shows the observed densities of liquids used.

Table I. Densities of Liquids at 40° C.

Substance	Observed Density, G./Ml.	Density Quoted in Literature, G./Ml.
Carbon tetrachloride	1.5550	1.55501
Methanol	0.77230	0.77232
Isopropyl alcohol	0.76900	0.76910

Experimental Arrangement. The experimental setup used in the present experiments is, in general, similar to that used by McGlashan (*5*) with some modifications as described below.

The pressure chamber, (Figure 1) which can be used for pressures up to 50 atm., is made of a steel cylinder *A* open at one end, 10 inches high, 4 inches in I.D., 1-inch wall thickness. The upper end could be closed by means of a lid *B* which could be screwed to the upper threaded portion of chamber *A*. Leakage of air through the sides of the lid was prevented by O ring *C* fixed between the concentric grooves on lid *B* and the top of cylinder *A*. Visual observations on the piezometer capillary inside the chamber were made through a vertical perspex window, *D*, 5 inches high, 1¼ inches wide, and 1½ inches thick fitted to the cylinder by a steel frame with nuts and bolts as shown in Figure 1,*b*. A rubber gasket between the steel frame and the perspex sheet prevented the leakage of air through the sides of the window. The piezometer was held vertical in a brass stand *E* mounted on a heavy circular steel plate resting on the bottom of the cylinder, *A*. The chamber was nickel plated both outside and inside to avoid rusting. The entire pressure chamber up to mark *L*, in Figure 1, was held under water in a thermostat. The steel chamber ensured a quicker thermal equilibrium between the thermostat and the inside of the chamber. The perspex window could stand pressures up to 50 atm. without showing any signs of strain. Pressure was applied to the chamber by connecting it through pressure leads of copper *S* to a nitrogen cylinder. The pressures were regulated through a needle valve and measured on a bourdon standard test gage with an accuracy of ±0.07 atm. Temperature control inside the chamber during the periods of measurement as observed on a 1° Beckmann thermometer divided into parts was better than 0.001° C. Temperatures were measured on