[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR AND COMPANY]

Refractive Indices of the Normal Saturated Aliphatic Nitriles

BY A. DORINSON AND A. W. RALSTON

The aliphatic nitriles constitute an excellent series of compounds with which to test the hypothesis regarding the temperature dependence of the refractive indices of polar organic molecules advanced in a previous communication from this Laboratory.[1] There it was found that the refractive index of a straight chain fatty acid in the liquid state, plotted as a function of temperature, exhibited a sharp change of slope in the vicinity of 40°. This was ascribed to the influence of temperature on the orientation of the dipoles in the body of the liquid: at temperatures sufficiently elevated the thermal agitation of the molecules overcomes the restraint imposed by dipole interaction. A more extensive study of this effect is possible with the normal aliphatic nitriles because the members of this series up to pentadecylonitrile are liquids throughout the range necessary to demonstrate the effect.

The even carbon numbered nitriles used in this study were prepared by the catalyzed action of ammonia on the corresponding highly purified acids; the odd nitriles were prepared from the next lower fatty acids by the well-known sequence: ester → alcohol → halide → nitrile. The final purification consisted of a careful fractional distillation. Some of the nitriles, available from a previous investigation,[2] were treated with a few pellets of potassium hydroxide to remove fatty acids and water before distillation. Judged by the observation that the refractive indices of the entire series at 25°, from capronitrile to stearonitrile, fell on a smooth curve, the nitriles used were quite pure. Butyronitrile and valeronitrile were slightly less pure by this criterion. The freezing points[3] of several of the nitriles are: caprinitrile, −14.46°; lauronitrile +4.02°; myristonitrile 19.25°; palmitonitrile 31.40°; stearonitrile 40.88°.

The refractive indices were read on an Abbe type refractometer with jacketed prisms through which water from a thermostat was circulated. Temperatures were read on a calibrated thermometer.

The refractive indices of the nitriles are listed in Table I. These are the data as read directly on the refractometer, uncorrected for the effect of temperature on the prism of the instrument. A graphical representation is given in Fig. 1; here a correction whose magnitude amounts to 0.000006 $(t - 20)$ has been added to the original data for temperatures above 20°. The range of the graph has been extended by using the data of Merckx, Verhulst and Bruylants[4] at 15°. A definite change of slope occurs in the vicinity of 40–45°. In view of the fact that the dipole moment of the nitrile group is larger than that of the carboxyl group, some significance might be attributed to the occurrence of this change at a slightly higher temperature than was noted for the fatty acids.

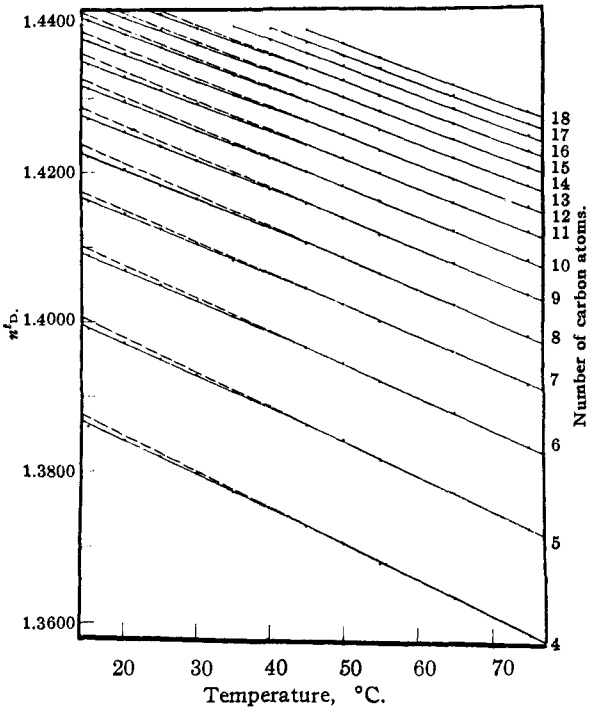

Fig. 1.—The variation of refractive index with temperature. Extrapolation is represented by the dotted line. The points at 15° are from the data of Merckx, Verhulst and Bruylants.[4]

The availability of reliable data on the densities of the nitriles[4,5] makes it possible to calculate their molecular refractivities. Several of these are plotted as a function of temperature in Fig. 2. Change of slope is more pronounced for the molecular refractivities than for the refractive indices themselves. The value of the molecular refractivity does not become constant above the inflection point, which indicates that other factors besides orientation of the dipoles affect its magnitude. It is also seen that the slope of molecular refractivity *vs.* temperature becomes steeper for higher members in the series. Careful examina-

(1) Dorinson, McCorkle and Ralston, THIS JOURNAL, **64**, 2739 (1942).

(2) Ralston, Selby and Pool, *Ind. Eng. Chem.*, **33**, 682 (1941).

(3) These freezing points were determined by Mr. C. W. Hoerr of his Laboratory.

(4) Merckx, Verhulst and Bruylants, *Bull. soc. chim. Belg.*, **42**, 177 (1933).

(5) Daragan, *ibid.*, **44**, 602 (1935).

TABLE I

REFRACTIVE INDICES (n^tD) OF NORMAL ALIPHATIC NITRILES (UNCOR.)

Nitrile	20.0°	25.0°	30.0°	35.0°	40.0°	45.0°	50.0°	55.0°	65.0°	75.0°
Butyro-	1.3842	1.3820	1.3798	1.3773	1.3754	1.3729	1.3706	1.3862	1.3636	1.3590
Valero-	1.3972	1.3950	1.3929	1.3908	1.3887	1.3864	1.3843	1.3820	1.3774	1.3727
Capro-	1.4069	1.4049	1.4028	1.4008	1.3986	1.3966	1.3944	1.3921	1.3878	1.3834
Enantho-	1.4144	1.4124	1.4104	1.4083	1.4064	1.4044	1.4022	1.4000	1.3960	1.3917
Caprylo-	1.4204	1.4183	1.4164	1.4145	1.4124	1.4104	1.4085	1.4063	1.4021	1.3980
Pelargono-	1.4254	1.4235	1.4216	1.4197	1.4176	1.4157	1.4137	1.4115	1.4075	1.4035
Capri-	1.4296	1.4276	1.4256	1.4237	1.4218	1.4199	1.4180	1.4159	1.4119	1.4080
Undecylo-	1.4330	1.4312	1.4293	1.4273	1.4254	1.4236	1.4217	1.4197	1.4156	1.4118
Lauro-	1.4360	1.4341	1.4322	1.4304	1.4286	1.4267	1.4248	1.4227	1.4188	1.4149
Tridecylo-	1.4387	1.4368	1.4349	1.4330	1.4312	1.4294	1.4275	1.4254	1.4216	1.4177
Myristo-	1.4410	1.4392	1.4373	1.4354	1.4335	1.4317	1.4298	1.4279	1.4240	1.4202
Pentadecylo-		1.4413	1.4395	1.4376	1.4356	1.4338	1.4320	1.4300	1.4261	1.4224
Palmito-				1.4396	1.4377	1.4358	1.4340	1.4319	1.4281	1.4244
Margaro-					1.4392	1.4373	1.4355	1.4336	1.4298	1.4260
Stearo-						1.4389	1.4370	1.4351	1.4313	1.4276

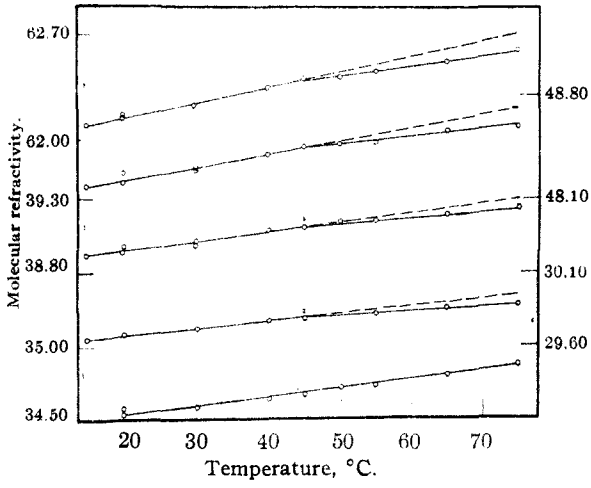

Fig. 2.—The variation of molecular refractivity with temperature: heptane (1); capronitrile (2); caprylonitrile (3); caprinitrile (4); tridecylonitrile (5).

tion of the graphs of the densities and of the refractive indices showed a distinct convergence of these curves at lower temperatures.

Highly purified specimens of *n*-heptane and *n*-octane were run as control substances. The refractive indices and the molecular refractivities of these compounds were found to be straight-line functions of temperature.

Summary

1. The refractive indices of the normal aliphatic nitriles from butyronitrile to stearonitrile inclusive were determined at a number of temperatures between 20 and 75°.

2. For each nitrile an abrupt change of slope in the refractive index *vs.* temperature curve occurs at 40–45°.

3. Corresponding graphs of the molecular refractivities also show a change of slope.

CHICAGO, ILL. RECEIVED NOVEMBER 19, 1943

[CONTRIBUTION NO. 508 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Heats of Dilution of Sodium Chloride in Ethylene Glycol at 25°[1]

BY W. E. WALLACE, L. S. MASON AND A. L. ROBINSON

The heats of dilution of electrolytes of nearly all the common valence types have been extensively studied in aqueous solution. These heats of dilution, when extrapolated to infinite dilution, have provided ample opportunity for comparison with the Debye–Hückel limiting law. Further comparison of experiment with theory could be provided by a comparable body of data in non-aqueous media. Theory requires that, in the limit, ΦL_2, the relative apparent molal heat content of the solute, be linear with respect to the square root of the concentration, regardless of the solvent medium, but that for a salt of a given valence type ΦL_2 be dependent on certain characteristics of the solvent, namely, the dielectric constant, the temperature derivative of the dielectric constant, and the volume–temperature relationships for the particular solvent.

Probably the only significant study of heats of dilution of electrolytes in strictly non-aqueous solvents is the work of Jackson, Smith, Gatty and Wolfenden[2] who determined these properties for

(1) This investigation was supported by a grant from the Buhl Foundation. This paper was presented to the Division of Physical and Inorganic Chemistry at the Pittsburgh meeting of the American Chemical Society, September, 1943.

(2) N. S. Jackson, A. E. C. Smith, O. Gatty and J. H. Wolfenden, *J. Chem. Soc.*, 1376–1379 (1934).