Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Van Lenten, Frank J. , Conaway, James E. and Rogers, L. B.(1977) 'Gas Chromatographic Retention Characteristics of Different Polysiloxane Oligomers', Separation Science and Technology, 12: 1, 1 — 28
To link to this Article: DOI: 10.1080/00372367708058062
URL: http://dx.doi.org/10.1080/00372367708058062

SEPARATION SCIENCE, 12(1), pp. 1–28, 1977

Gas Chromatographic Retention Characteristics of Different Polysiloxane Oligomers

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Abstract

The effects on the Kovats and McReynolds indices for a modified set of Rohrschneider solutes have been examined using two different batches of a commercial polysiloxane stationary phase, Dow-Corning DC-710, and five pure oligomers isolated from the mixture. The significant differences that were found between batches appear to be due primarily to changes in the percentage of one oligomer, the cyclic pentamer. This finding emphasizes the desirability of using a pure stationary phase as well as carefully specifying the column temperature in order to improve intra- and interlaboratory comparisons of retention indices.

INTRODUCTION

Polysiloxanes have been mentioned by various authors as a class of preferred stationary phases (*1–3*). Among these is DC-710, a 50% phenyl methyl siloxane polymer having a molecular weight of approximately 2600. The phenyl-substituted silicones are more thermally stable than the methyl species—usually up to 250 °C.

Silicone polymer stationary phases are produced by polymerizing a cyclosiloxane in the presence of a hexamethyldisiloxane as a chain stopper

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(*3*). The basic catalyst used must be neutralized or removed to prevent depolymerization; incomplete removal may result in column bleed. The OV-series of methylphenyl silicones (OV-17 is comparable to DC-710) are reported to have no residual catalysts and no volatile low molecular weight oligomers. The Dow-Corning fluids originally have relatively large amounts of volatiles which are later removed by vacuum stripping; a water wash is used to remove residual catalyst (*3*).

The need for standard stationary phases has been discussed by many authors (*4–6*) with the idea that many redundant stationary phases might be eliminated. A number of standard phases has been proposed along with the requirements for a standard stationary phase (*4*). The standard phases would be defined in terms of McReynolds constants (*6*). Only retention data for those standards would then be compiled, and the data would be reported in the form of Kovats retention indices. The ultimate goal is to improve interlaboratory comparisons of retention data and to reduce the uncertainty of identification by means of retention for components of complex multicomponent samples.

There have been several problems encountered in determining and using indices, especially when polymeric stationary phases were involved. These include the variability of the composition of the stationary phase between different batches (*7*), changes in composition of the stationary phase with age of the column (*8*), support (*9*, *10*) and sample size effects (*11*, *12*), accuracy of the measurement of column temperature (*13*, *14*) and flow rate (*15*), and accurate timing during data acquisition (*12*).

The major concern of the present study was the variability of stationary phase composition which we attempted to minimize by isolating a pure species of the desired stationary phase from the original mixture and then storing the columns in a nonreactive environment. In addition, support effects were minimized by derivatization of the column support by an appropriate silanization so that differences in column loading did not produce significantly different data. Furthermore, sample sizes were carefully controlled so as to minimize variability from that source.

In order to obtain accurate retention data, high-precision gas chromatography is a necessity. The first automated high-precision work was accomplished independently by Oberholtzer and Rogers (*16*) and by Guiochon and Goedert (*15*). Using such equipment, Lorenz and Rogers (*11*) determined retention retention indices for synthesized oligomers of polyethylene glycol. They related retention to oligomer chain-length, and they demonstrated the significance of sample-size effects and mixed retention mechanisms, especially for very small samples. A comparison of retention based on calculation of the first moment (peak mean) and peak maxima was made by Lorenz and other authors (*11*, *17–19*). Their conclusions were that although the peak mean was more meaningful thermodynamically, its value was very difficult to obtain accurately under any one of the following conditions: bad tailing, very large or very small sample sizes, and low signal-to-noise ratio.

Although others have chosen to work with commercial mixtures (*20*, *21*) or to synthesize pure oligomers (*11*), we have elected to isolate pure species from a complex mixture using supercritical fluid chromatography (SFC). Early work by Jentoft and Gouw established that a monodisperse polystyrene could be fractionated by pressure-programmed SFC into approximately 18 discrete oligomeric species (*22*). Similarly, Nieman and Rogers (*23*) have recently shown that DC-710 could be fractionated by pressure-programmed SFC into more than 20 oligomers. Thus SFC seems to be a viable technique for the separation of pure oligomers for characterization as stationary phases.

In the present study, pressure-programmed SFC has been used to separate DC-710 into individual oligomers which had been previously analyzed by mass spectral analysis and found to be >95% pure cyclic (D_x) and linear (MD_xM) species up to peak number 9 (*23*). Under appropriate conditions the resolution of individual oligomers desired for collection as pure stationary phases (peaks 3 through 6 and 9) could be maximized.

One purpose of the present study was to determine if there were differences in retention indices between batches of commercially obtained DC-710. If so, the differences between oligomers would be of interest, especially if one (or more) oligomer(s) could be purified to give a standard stationary phase. The differences in retention characteristics of each oligomer should also be manifested by thermodynamic quantities such as the enthalpy of solution for each solute on a given stationary phase.

Because of the small amount of each oligomer fractionated by SFC, capillary, rather than packed, columns were used. Furthermore, static coating was selected in preference to the dynamic coating technique because it required only about 10% of the amount of stationary phase in order to give the same effective loading.

In order to accomplish the characterization of the polymeric and oligomeric stationary phase, the following steps were taken. First, columns were coated using two different batches of DC-710 in order to determine the differences, if any, between batches. Second, the effects of loading were studied using one batch so as to rule out that effect from the differences between batches. Then, five different oligomers were isolated by SFC in order to determine both the differences between cyclic and linear species having the same number of siloxane units and also to determine differences between oligomers having the same type of structure. For each stationary phase the McReynolds constants were determined using a modified list of Rohrschneider solutes (*24*). Finally, differential thermodynamic enthalpies corresponding to structural differences were estimated on the basis of measurements at two temperatures.

EXPERIMENTAL

Reagents and Column Packings

For the supercritical experiments, technical grade *n*-pentane (Eastman Kodak, Rochester, New York), purified by the method described in the literature (*25*), was used as the mobile phase. Batches of DC-710 polymer were purchased from Alltech Associates, Inc. (Arlington Heights, Illinois). *n*-Decane (99% mole pure, Phillips Petroleum Co., Bartlesville, Oklahoma) was used 1:1 v/v to decrease the viscosity of the DC-710 so as to make it compatible with our injection system. Porasil C, 100/150 mesh, was purchased from Waters Associates (Milford, Massachusetts).

In the experiments used for characterizing liquid phases, hexamethyldisilazane and trimethylchlorosilane (Pierce Chemical Co., Rockford, Illinois) were used as silanizing reagents for capillary columns. The solute standards used were *n*-hexane, *n*-heptane, *n*-octane, and *n*-nonane (99% mole pure, Phillips Petroleum Co., Bartlesville, Oklahoma). Methane was used as the nonretained solute (CP grade, Matheson Gas Products, E. Rutherford, New Jersey). The primary functional probes were benzene, chloroform, nitropropane, dioxane, 2-pentanone, and ethyl acetate (Baker Analyzed Reagent Grade, J. T. Baker Co., Phillipsburg, New Jersey). Squalane stationary phase was purchased from Eastman Organic Chemicals.

The carrier gas was 99.9% pure Selox nitrogen. Selox hydrogen was used for the flame ionization detector. Gases were passed through 4A molecular sieve traps.

Apparatus

The SFC apparatus used for polymer fractionation was the same as previously described (*23*) with the following exceptions: a Model 8500 Liquid Chromatograph (Varian Associates, Walnut Creek, California) was used as the pumping system, obviating the need for a depulsification network. A pneumatically actuated 5 μl sampling valve (Valco Instruments, Houston, Texas) was used as the injection system. The sample was supplied to the valve through a pressurized reservoir containing the bulk DC-710 polymer diluted 1:1 with *n*-decane so that it could flow into the injection loop. Fractions of the eluate were collected using a Model T fraction collector (Isco, Lincoln, Nebraska).

The high precision gas chromatograph previously described (*19*) was modified to provide more automated operation. A Valco gas sampling valve with a 5.0-μl internal sampling loop was used for on-column injection.

A multisolute capability was implemented for the system by the use of a multiport rotary valve which routed carrier gas through one of up to ten saturators containing solutes for chromatographic experiments. Helium flowing into the common port of a pneumatically actuated 22-port rotary gas valve (Model ACST-10-HTa, Valco Instruments) was routed into a glass saturator system.

An automatic temperature-setting capability involved a stepper motor coupled with a Thermotrol proportional temperature controller (Hallakainen Instruments, Richmond, California). It operated in a feedback mode from an amplified thermocouple signal which was monitored by an analog-to-digital converter (Anscan, Beckman Instruments, Fullerton, California). A stepping motor (Model 31616, Haydon Switch and Instrument, Inc., Waterbury, Connecticut) was linked to the Thermotrol temperature controller by a 100-tooth gear which had been slipped onto the shaft of the coarse control potentiometer of the temperature controller.

Barometric pressure measurements were made using a Model 538–12 Barocell differential transducer and a 1014-A electronic manometer (Datametrics Inc., Wilmington, Massachusetts). A full-scale reading of 1000 Torr resulted in an output of 10 V. The output of the transducer was referenced to vacuum using a vacuum pump.

Measurements of barometric and column-head pressures, of temperatures, and of detector outputs were accomplished using an Anscan analog-to-digital converter interfaced to a PDP-11/20 computer (Digital Equipment Corp., Maynard, Massachusetts). Programs were written in BASIC modified by a real-time assembly-language patch.

Procedures

All capillary columns were prepared from borosilicate glass. After cleaning with several solvents, the tubing was drawn into 11 to 12 m lengths of 0.2 mm i.d. by the apparatus previously described (*26*). The columns were silanized using a 5: 1 mixture of hexamethyldisilazane and trimethylchlorosilane. The mixture was rapidly flushed from the column and the ends sealed. After heating the column for 12 hr at 200°C, the residual silylating mixture was removed using a flow of pure nitrogen for 1 hr at 200°C (*27*).

The columns were statically coated by a modification of an existing procedure (*28*). A solution of stationary phase (in chloroform) was used to fill the column, one end of which was then filled with waterglass (sodium silicate) and allowed to dry. A vacuum pump was attached to the free end of the column and the solvent was removed over a period of about 2 days.

Dynamic coating was accomplished in the usual manner. Loading was estimated on the basis of comparison of capacity ratios for a 15%w/v dynamically coated column of Batch 2 of DC-710.

All columns were conditioned for 8 hr under a flow of 5 ml/min of helium up to about 20 to 25°C above its maximum operating temperature. Thus the bulk DC-710 polymer and fractionated oligomers were conditioned at 100°C. However, in the case of the squalane stationary phase, the maximum conditioning temperature used was 75°C. Columns were plumbed into the system using shrinkable Teflon tubing and were mounted directly over the oven fan. Before use, the ends of the columns were sealed to prevent aging.

In the supercritical fluid experiments the conditions for maximum resolution of oligomers in the DC-710 bulk polymer were determined by holding the column at a temperature above the critical point at 400 psi and observing the resulting resolution at a fairly rapid pressure programming rate (10 psi/min). After a satisfactory temperature had been found, the pressure programming rate for subsequent runs was slowed to about 5 psi/min so as to obtain adequate resolution. The pressure program was produced by the manual operation of the syringe at a constant rate combined with the manual decrease of the opening of the exit metering valve. The final conditions selected for fractionation and collection were 222°C and 5 psi/min.

A 50-μl diluted sample was introduced to the column at 400 psi and the pressure program commenced. Discrete fractions were collected for 2-min intervals. Oligomer peaks 3 through 6 and 9 (*23*) were collected and used as pure stationary phases to be characterized by high precision gas chromatography. The components have been previously characterized by mass spectral analysis as the cyclic tetramer (D_4), the linear tetramer (MD_4M), cyclic pentamer (D_5), the linear pentamer (MD_5M), and the linear

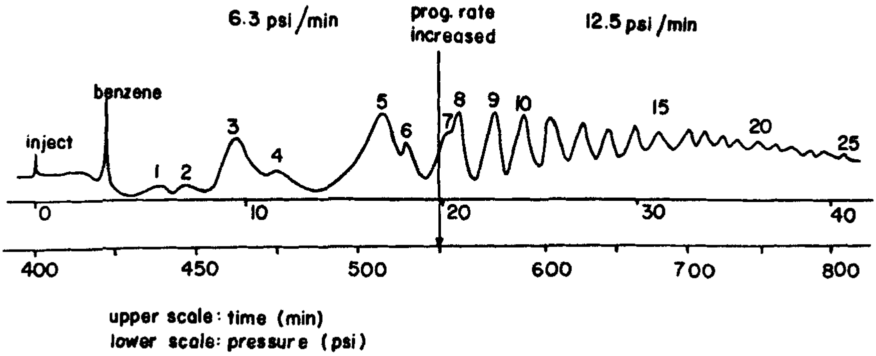

FIG. 1A. SFC separation of DC-710 at 223 °C.

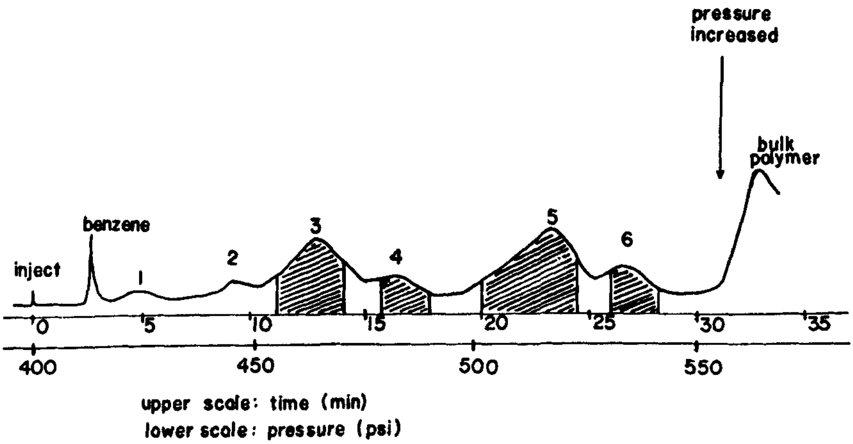

FIG. 1B. Preparative separation of DC-710 at 223 °C.

heptamer (MD_7M) for peaks 3 through 6 and 9, respectively. The cyclic species are those remaining from incomplete conversion of the starting materials, while the linear species are the products. Figures 1A and 1B show the results of such an experiment.

Description of the procedures for sampling and flow control for the high precision gas chromatographic analysis have been previously described (*19*). The temperature of the saturator chamber was limited to about 40°C so as to minimize evaporation of some of the highly volatile solutes. Conditions for maximum peak responses were determined by systematically varying saturator charge-up times and delay times from charge-up until injection using a multiparameter computer program. Conditions for each solute could be varied by means of software changes in the BASIC language program.

As previously stated, a multisolute sampling capability was devised using a 22-port rotary valve in which a portion of the gas was routed through a common input port to one of up to ten saturators. The saturated carrier gas was routed back through its paired port in the valve and out of the common output port to an exponential dilution flask and sampling valve. A rotary switch mechanically connected to the valve was used to indicate valve position through a device interface panel (*29*). An earlier attempt using an 11-port valve in which the saturator output was fed into a gas manifold system as a common output "port" was abandoned because of cross-contamination between solutes.

An automatic temperature-setting capability was devised for the chromatographic column oven. The feedback control concept was related to the number of steps that a stepping motor turned in order to adjust the potentiometer of a proportional temperature controller to a desired set-point temperature. A calibration experiment indicated that 100 steps caused a change of 4.8°C in the temperature. In practice, the temperature of the system was determined by an iron–constantan thermocouple whose output passed through an amplifier having a very high common mode rejection ratio ($G = 113.4$). The difference between the system temperature and desired temperature was converted into the number of steps required. Then the stepping motor was activated by the computer through a driver circuit constructed in this laboratory. After an appropriate equilibration time (1 min/°C for a cooling cycle and 0.2 min/°C for a heating cycle), the temperature was again measured. If the system temperature was less than ± 0.1°C from the desired temperature and remained within those tolerances for 1 min, the temperature setting procedure was considered to be completed. If the temperature was outside of the specified tolerances or if it was unstable, appropriate calculations for a heating or cooling adjustment were made, and the stepping motor was again activated to bring the temperature within the specifications. Temperatures were rechecked for deviations after each experiment. Time needed for going from ambient to any desired temperature ranged from 30 to 50 min. The time required to go from 60 to 70°C was generally of the order of 10 to 15 min.

The temperatures used in this study were 60 and 70 ± 0.1 °C for all columns. The upper temperature was limited by bleed from the squalane column and possibly from the smaller oligomers. The temperature control of the oven was better than ±0.05 °C.

A constant sample size (5 μl of solute-saturated carrier gas) was used for all determinations. The linear flow rate was varied from 20 to 50 cm/sec to maintain a retention time for methane of approximately 45 sec. After the temperature had stabilized, the stability of the flow was checked, the sample injected, and data acquisition begun. Data acquisition was carried out as previously described (*19*) using a total of 230 points for solutes and 200 points for the nonretained peak. Acquisition rates varied from 2.5 to 10 Hz. Delay times from injection to the beginning of data acquisition were adjusted to get points for at least ±5 standard deviation units from the maximum. In general, retention times were reproducible to better than 200 msec.

Calculations

There are advantages and disadvantages to calculating retention indices by either peak maxima or peak means. Peak maxima are less influenced by peak shape, noise, and sample size than are peak means. However, the retention indices based on peak means are more susceptible to baseline noise and adsorption effects, which depend on relative sample size but they are more thermodynamically meaningful (*30–32*) than peak maxima.

The zeroth through second moments were calculated using the appropriate summations. The second central moment was calculated by adjusting the second moment with respect to the first moment. The accuracy of the moments was severely limited by the signal-to-noise ratio, becoming unsatisfactory at S/N ratios less than 20.

Gram polynomials were used to find the peak maximum on the basis of the inflection point of a second degree polynomial fit to seven points across the top of a peak (*33*).

The average linear velocity of the carrier gas was calculated on the basis of the time of a nonretained peak as

$$F = L/t_0 \qquad (1)$$

where L is the column length (in centimeters) and t_0 is the time for methane in seconds. The typical relative standard deviation of the linear flow was 0.2%.

The capacity ratio, k, was calculated on the basis of both the retention time at the center of gravity, t_c, and the retention time at peak maximum, t_m. The capacity ratio based on the retention time at peak maximum was given by

$$k_m = (t_m - t_0)/t_0 \tag{2}$$

where t_0 is peak maximum retention time for a nonretained methane peak. The capacity ratio based on the center of gravity was calculated by substituting t_c for t_m and the center of gravity retention time of methane for t_0.

Since capacity ratios calculated on the basis of retention times can vary because of slight changes of flow rate, it was necessary to normalize the k values to a common flow. This normalized capacity ratio is the equivalent of a net retention volume.

The Kovats retention index system was the basis on which the stationary phase characteristics were calculated (*34*). Under all conditions the retention index of *n*-alkanes is arbitrarily fixed at $100z$, where z is the number of carbons present in the *n*-alkane standards. If a solute with net retention volume V_{N_x} is eluted between alkanes containing z and $z + 1$ carbons, then its retention index is

$$I_x = 100\left[z + \frac{\log V_{N_x} - \log V_{N_z}}{\log V_{N_{(z+1)}} - \log V_{N_z}}\right] \tag{3}$$

It can be shown that $(1 + k)$ may be substituted for V_N to give the same value for I_x. The Kovats indices where calculated on the basis of peak maximum (I_{max}) and first moment (I_{mean}).

McReynolds constants (*35*) for the solutes on a given stationary phase may be calculated as $\Delta I_P = I_P{}^X - I_S{}^X$, where $I_P{}^X$ is the Kovats index for compound X on stationary phase, P, and I_S is its index on squalane (a nonpolar reference stationary phase). Again, McReynolds constants where calculated both on the basis of peak maxima and peak means.

Experimental values of ΔH_{soln} were calculated by the slope of the plot of the change in capacity ratio from 60 to 70°C against the reciprocal of the absolute temperature. All computer programs used for these calculations were written in BASIC.

RESULTS

Comparisons of Two Different Batches of DC-710

Table 1 shows the Kovats indexes and McReynolds constants (ΔI) for the solute probes at 60 and 70°C. Standard deviations, based upon three measurements, are shown in parentheses following the index value. Indices based upon peak maxima usually gave a more sensitive indication of differences between the batches than did indices based upon peak means. Each solute, except nitropropane, exhibited significantly larger differences in Kovats indices for the different batches of DC-710 bulk stationary phase (as purchased from the supplier) than for different loadings of the same batch of DC-710, which usually gave values within the experimental error for replicates on a given column (±2 i.u. for maxima-based data). Thus, in most cases, there was better agreement between the heavily coated column of Batch 2 and the lightly coated column of Batch 2 than between the lightly coated columns of Batches 1 and 2.

The index differences between batches were larger at 60°C than at 70°C. The largest difference in index units was 32 i.u. (mean value, 22 i.u.) for *n*-propanol at 60°C, whereas benzene and nitropropane exhibited only small differences between batches. The order of differences between batches (from largest to smallest) was *n*-propanol, dioxane, 2-pentanone, ethyl acetate, benzene, and nitropropane.

Comparisons of the Same Oligomer from Different Batches of DC-710

Agreement between the same oligomer isolated from different batches of DC-710, calculated on the basis of peak maxima, was usually better than ±2 i.u., while indices calculated on the basis of peak means were usually better than ±4 i.u. (Table 2). Subscripts *1* and *2* indicate different batches, and the values in parentheses are, once again, standard deviations. The better precision for peak maxima was due to the fact that the maximum was usually less influenced by baseline noise than the mean. Poorer precision occurred when column coatings were very low and when relatively nonvolatile solutes were used, thereby giving small peaks having a signal-to-noise ratio (S/N) less than 20. Thus the worst precision for calculating mean-based indices occurred with a highly polar solute (i.e., *n*-propanol) on a lightly coated column.

Comparisons of Oligomers

The ranges of index values for oligomeric stationary phases for the same solute are shown in Table 3. The decreasing order of effect of oligomers on the range of solute indices was: *n*-propanol > ethyl acetate > dioxane > 2-pentanone ~ benzene ~ nitropropane (Figs. 2A and 2B). The corresponding indices on squalane are given in Table 4.

TABLE 1
Effects of Changing the Batch of DC-710 and the Liquid Loading on the Kovats and McReynolds Indices at Two Different Temperatures

	DC-710(1)	DC-710(2-light)	DC-710(2-heavy)
Ethyl Acetate, 60 °C			
I_{max}	702.0(2.7)	713.0(1.5)	710.0(4.7)
ΔI_{max}	130.0	141.0	138.0
I_{mean}	702.6(1.3)	710.0(4.7)	705.1(0.7)
ΔI_{mean}	124.4	131.8	126.9
Ethyl Acetate, 70 °C			
I_{max}	701.9(0.2)	704.7(2.6)	703.0(0.1)
ΔI_{max}	126.3	129.1	127.4
I_{mean}	701.6(0.9)	713.1(2.8)	718.8(4.5)
ΔI_{mean}	120.0	131.5	137.2
Dioxane 60 °C			
I_{max}	820.7(0.3)	836.2(1.7)	836.0(1.9)
ΔI_{max}	171.6	187.1	186.9
I_{mean}	822.0(1.4)	842.5(1.8)	840.7(1.6)
ΔI_{mean}	150.9	171.4	169.6
Dioxane, 70 °C			
I_{max}	822.6(0.4)	837.0(2.0)	834.0(1.0)
ΔI_{max}	169.0	183.4	180.6
I_{mean}	823.4(0.3)	831.7(3.9)	826.7(1.2)
ΔI_{mean}	170.1	178.4	173.4
Benzene, 60 °C			
I_{max}	741.3(0.1)	735.1(2.1)	732.7(0.1)
ΔI_{max}	103.5	97.3	94.9
I_{mean}	737.1(2.4)	743.2(3.0)	736.8(8.0)
ΔI_{mean}	96.6	102.7	96.3
Benzene, 70 °C			
I_{max}	747.2(0.9)	741.1(1.6)	742.9(0.2)
ΔI_{max}	106.3	100.2	102.0
I_{mean}	747.3(1.5)	747.3(1.5)	746.4(2.1)
ΔI_{mean}	100.8	100.8	99.9

(continued)

TABLE 1 (continued)

	DC-710(1)	DC-710(2-light)	DC-710(2-heavy)
2-Pentanone, 60 °C			
l_{max}	785.1(1.3)	800.5(1.0)	798.7(0.4)
Δl_{max}	153.6	169.0	167.2
l_{mean}	784.5(0.3)	792.2(3.1)	793.3(3.1)
Δl_{mean}	145.6	153.3	154.4
2-Pentanone, 70 °C			
l_{max}	785.0(1.4)	794.9(3.7)	796.2(1.4)
Δl_{max}	151.9	161.8	163.1
l_{mean}	789.3(4.9)	790.6(6.0)	789.4(2.2)
Δl_{mean}	156.6	157.9	156.7
n-Propanol, 60 °C			
l_{max}	677.8(0.6)	712.1(0.6)	707.7(2.7)
Δl_{max}	187.5	221.8	217.4
l_{mean}	688.9(2.2)	706.8(3.4)	710.6(2.6)
Δl_{mean}	200.8	218.7	222.5
n-Propanol, 70 °C			
l_{max}	676.5(3.2)	707.5(2.4)	705.0(1.4)
Δl_{max}	187.0	218.0	215.5
l_{mean}	685.8(2.7)	711.4(3.7)	685.8(2.7)
Δl_{mean}	194.2	219.8	194.2
Nitropropane, 60 °C			
l_{max}	878.9(0.1)	878.6(0.3)	877.6(1.2)
Δl_{max}	219.2	218.9	217.9
l_{mean}	877.9(3.2)	875.5(6.2)	874.5(1.6)
Δl_{mean}	218.8	216.4	215.4
Nitropropane, 70 °C			
l_{max}	879.8(0.6)	876.8(1.8)	875.9(2.6)
Δl_{max}	215.2	212.2	211.3
l_{mean}	877.0(0.9)	874.9(6.6)	871.8(6.9)
Δl_{mean}	214.2	212.1	209.0

TABLE 2

Effects of Oligomer Source, Size, and Structure on the Kovats and McReynolds Indices at Two Different Temperatures

	D_4	MD_4M	D_5	MD_5M	MD_7M
Ethyl Acetate, 60°C					
$I_{\mathrm{max}1}$	689.9(0.6)	702.8(0.02)	712.7(0.7)	699.9(0.02)	698.6(0.1)
$I_{\mathrm{max}2}$	692.5(1.8)	702.0(0.02)	710.6(0.3)	697.3(0.02)	697.9(0.5)
I_{max}	692.1(1.3)	702.4(0.02)	711.7(0.6)	698.6(0.02)	698.3(0.4)
ΔI_{max}	119.2	130.4	139.7	126.6	126.3
$I_{\mathrm{mean}1}$	680.2(7.8)	701.7(1.8)	715.2(3.5)	698.3(1.1)	700.0(0.1)
$I_{\mathrm{mean}2}$	687.0(1.2)	701.0(1.8)	713.8(0.7)	696.3(1.9)	703.6(1.9)
I_{mean}	683.6(5.5)	701.4(1.8)	714.5(2.5)	697.3(1.5)	701.8(1.3)
ΔI_{mean}	105.4	123.2	136.3	119.1	123.6
Ethyl Acetate, 70°C					
$I_{\mathrm{max}1}$	688.6(0.3)	701.3(0.1)	712.8(0.7)	698.0(0.01)	697.5(0.3)
$I_{\mathrm{max}2}$	687.0(1.6)	701.8(0.1)	720.6(2.0)	696.7(0.3)	696.5(0.2)
I_{max}	687.8(1.1)	701.6(0.1)	716.7(1.5)	697.4(0.2)	697.0(0.3)
ΔI_{max}	112.3	126 0	141.1	121.8	121.4
$I_{\mathrm{mean}1}$	711.9(0.6)	701.8(0.1)	728.5(7.9)	698.6(0.5)	697.9(2.3)
$I_{\mathrm{mean}2}$	715.8(1.7)	702.3(0 5)	725 1(3.5)	697.4(0.2)	698.8(1.6)
I_{mean}	713.9(1.3)	702.1(0.5)	726.8(6.0)	698.0(0.4)	698.4(2.0)
ΔI_{mean}	132.3	120.5	145.2	116.4	116.8
Dioxane, 60°C					
$I_{\mathrm{max}1}$	812.6(1.9)	820.0(0.2)	820.9(0.8)	818.8(0.04)	816.9(0.05)
$I_{\mathrm{max}2}$	814.7(1.4)	819.6(0.2)	834.1(0.3)	816.1(0.2)	818.9(0.1)
I_{max}	813.7(1.7)	819.8(0.2)	827.6(0.6)	817.5(0.1)	817.9(0.08)
ΔI_{max}	164.6	170.7	178.5	168.4	168.8
$I_{\mathrm{mean}1}$	811.4(2.3)	820.6(0.1)	824.2(2.3)	819.5(1.5)	818.5(0.4)
$I_{\mathrm{mean}2}$	811.1(1.3)	820.2(0.1)	832.5(3.2)	816.7(0.1)	818.1(0.2)
I_{mean}	811.3(1.8)	820.4(0.1)	828.4(2.8)	818.1(1.1)	818.3(0.3)
ΔI_{mean}	140.2	149.3	157.3	147.0	147.2
Dioxane, 70°C					
$I_{\mathrm{max}1}$	810.6(0.2)	822.8(0.3)	831.4(0.9)	820.0(0.5)	819.1(0.3)
$I_{\mathrm{max}2}$	809.4(0.2)	822.4(0.3)	826.7(0.6)	819.1(0.3)	818.3(0.3)
I_{max}	810.0(0.2)	822.6(0.3)	829.1(0.8)	819.6(0.4)	818.7(0 3)
ΔI_{max}	156.4	169.0	175.5	166.0	165.1
$I_{\mathrm{mean}1}$	812.0(3.7)	822.8(0.3)	836.4(2.9)	820.0(1.6)	820.9(0.9)
$I_{\mathrm{mean}2}$	809.3(0.3)	822.5(1.5)	832.7(0.8)	819.2(1.5)	817.6(0.3)
I_{mean}	810.7(2.6)	822.7(1.1)	834.6(2.1)	819.6(1.6)	819.3(0.7)
ΔI_{mean}	157.4	169.4	181.3	166.3	166.0

(continued)

TABLE 2 (continued)

	D_4	MD_4M	D_5	MD_5M	MD_7M
Benzene, 60 °C					
l_{max1}	734.2(0.8)	739.1(0.3)	733.2(3.9)	737.3(0.5)	737.7(0.4)
l_{max2}	731.7(1.3)	738.6(0.3)	732.2(2.1)	735.4(0.4)	739.8(0.1)
l_{max}	733.0(1.1)	738.9(0.3)	732.7(3.1)	736.4(0.4)	738.8(0.3)
Δl_{max}	95.2	101.1	94.9	98.6	101.0
l_{mean1}	737.4(4.5)	741.6(0.2)	732.9(5.0)	737.8(0.6)	739.7(0.6)
l_{mean2}	741.0(0.6)	741.0(0.2)	733.6(2.2)	737.9(0.2)	740.1(0.1)
l_{mean}	739.2(3.2)	741.3(0.2)	733.3(3.8)	737.9(0.4)	739.9(0.4)
Δl_{mean}	98.7	100.8	92.8	97.4	99.4
Benzene, 70 °C					
l_{max1}	734.6(1.1)	739.5(0.1)	745.6(0.1)	738.2(0.04)	740.5(0.4)
l_{max2}	731.8(1.6)	740.3(0.1)	745.4(2.3)	738.4(0.1)	740.8(0.1)
l_{max}	732.2(1.4)	739.9(0.1)	745.5(1.6)	738.3(0.08)	740.7(0.3)
Δl_{max}	91.3	99.0	104.6	97.4	99.8
l_{mean1}	731.8(1.6)	739.9(0.05)	758.3(3.4)	738.6(0.1)	743.4(0.6)
l_{mean2}	733.9(0.3)	740.7(0.1)	759.7(3.7)	738.8(0.02)	743.4(0.1)
l_{mean}	732.9(1.1)	740.3(0.08)	759.0(3.6)	738.7(0.07)	743.4(0.4)
Δl_{mean}	86.4	93.8	112.5	92.2	96.9
2-Pentanone, 60 °C					
l_{max1}	780.1(0.8)	788.2(0.5)	787.8(6.1)	785.4(0.1)	783.8(0.1)
l_{max2}	784.2(4.0)	788.8(0.5)	790.2(2.5)	783.6(0.6)	783.1(0.1)
l_{max}	782.2(2.9)	788.5(0.5)	789.0(4.6)	784.5(0.4)	783.5(0.1)
Δl_{max}	150.7	157.0	157.5	153.0	152.0
l_{mean1}	783.5(3.6)	788.9(0.8)	787.8(6.5)	785.5(0.5)	783.5(0.8)
l_{mean2}	782.4(1.0)	789.5(0.8)	793.2(5.0)	784.3(0.8)	783.4(0.2)
l_{mean}	783.0(2.6)	789.2(0.8)	790.5(5.7)	784.9(0.7)	783.5(0.6)
Δl_{mean}	144.1	150.3	151.6	146.0	144.6
2-Pentanone, 70 °C					
l_{max1}	778.3(0.4)	792.7(0.1)	801.2(0.3)	785.7(0.2)	781.0(0.1)
l_{max2}	782.7(0.1)	792.0(0.2)	790.0(2.9)	784.2(0.02)	781.7(0.3)
l_{max}	780.5(0.3)	792.4(0.1)	795.6(2.0)	785.0(0.1)	781.4(0.2)
Δl_{max}	147.4	159.3	162.5	151.9	148.3
l_{mean1}	775.9(0.8)	790.0(0.4)	802.7(0.2)	783.3(0.9)	785.1(0.2)
l_{mean2}	777.7(4.5)	789.4(0.9)	804.1(3.5)	783.3(0.7)	786.1(0.6)
l_{mean}	776.8(3.2)	789.7(0.7)	803.4(2.5)	783.3(0.8)	785.6(0.4)
Δl_{mean}	144.1	157.0	170.7	150.6	152.9

(continued)

TABLE 2 (continued)

	D_4	MD_4M	D_5	MD_5M	MD_7M
n-Propanol, 60 °C					
$l_{\text{max}1}$	675.6(4.1)	675.7(0.6)	699.7(3.5)	671.1(0.6)	667.1(0.1)
$l_{\text{max}2}$	671.0(2.5)	674.6(0.6)	731.6(2.3)	670.5(0.6)	669.1(0.2)
l_{max}	673.3(3.4)	675.2(0.6)	715.7(2.9)	670.8(0.6)	668.1(0.1)
Δl_{max}	183.0	184.9	225.4	180.5	177.8
$l_{\text{mean}1}$	685.5(3.7)	675.5(0.8)	711.6(7.9)	670.8(3.9)	679.1(3.1)
$l_{\text{mean}2}$	680.4(1.0)	674.5(0.8)	735.0(0.4)	670.4(0.8)	669.3(3.5)
l_{mean}	683.0(2.7)	675.0(0.8)	723.4(5.5)	670.6(2.8)	675.2(3.3)
Δl_{mean}	194.9	186.9	235.3	187.1	187.1
n-Propanol, 70 °C					
$l_{\text{max}1}$	664.2(2.0)	674.8(0.1)	713.9(6.0)	670.6(0.3)	670.2(0.1)
$l_{\text{max}2}$	665.8(1.3)	673.1(0.3)	718.2(2.0)	671.7(0.1)	666.1(0.5)
l_{max}	665.0(1.7)	674.0(0.2)	716.1(4.4)	671.2(0.2)	668.2(0.4)
Δl_{max}	175.5	184.5	226.6	181.7	178.7
$l_{\text{mean}1}$	663.2(4.8)	670.2(0.9)	709.2(2.0)	666.0(2.6)	670.0(9.4)
$l_{\text{mean}2}$	674.1(0.4)	668.5(2.6)	707.6(7.0)	667.2(2.3)	665.8(1.4)
l_{mean}	668.7(3.4)	669.4(1.9)	708.4(5.1)	666.6(2.5)	667.9(6.7)
Δl_{mean}	177.1	177.8	216.8	175.0	176.3
Nitropropane, 60 °C					
$l_{\text{max}1}$	876.3(1.8)	884.2(0.1)	874.4(0.9)	882.1(0.5)	880.5(0.2)
$l_{\text{max}2}$	874.9(0.2)	884.1(0.2)	878.3(3.0)	880.4(0.1)	882.4(0.4)
l_{max}	875.6(1.3)	884.2(0.2)	876.4(2.2)	881.3(0.4)	881.5(0.3)
Δl_{max}	215.9	224.5	216.7	221.6	221.8
$l_{\text{mean}1}$	878.2(1.9)	885.7(0.7)	886.1(1.0)	882.4(0.4)	885.2(0.8)
$l_{\text{mean}2}$	874.0(0.2)	885.6(0.6)	886.0(0.9)	882.0(0.7)	883.3(0.6)
l_{mean}	876.1(1.3)	885.7(0.7)	886.1(1.0)	882.2(0.6)	884.3(0.7)
Δl_{mean}	217.0	226.6	227.0	223.1	225.2
Nitropropane, 70 °C					
$l_{\text{max}1}$	871.3(0.4)	884.6(4.0)	878.0(3.7)	880.5(3.9)	883.9(0.2)
$l_{\text{max}2}$	873.0(2.2)	884.7(3.8)	877.2(1.0)	879.6(3.6)	882.9(1.0)
l_{max}	872.2(1.6)	884.7(3.9)	877.6(2.7)	880.1(3.8)	883.4(0.7)
Δl_{max}	207.6	220.1	213.0	215.5	218.8
$l_{\text{mean}1}$	875.8(0.2)	885.4(2.0)	874.0(0.2)	881.4(2.0)	882.8(0.3)
$l_{\text{mean}2}$	877.3(2.7)	885.5(2.0)	881.2(3.4)	888.4(1.8)	879.8(0.8)
l_{mean}	876.6(1.9)	885.5(2.0)	877.6(2.4)	884.9(1.9)	881.3(0.6)
Δl_{mean}	213.8	222.7	214.8	222.1	218.5

TABLE 3
Ranges and Orders of Kovats Indices for Solutes Using Different Oligomers

Solute	I_{max} Range	I_{max} Order	I_{mean} Range	I_{mean} Order
		60 °C		
Ethyl acetate	20.5	$D_5 > MD_4M > MD_5M \sim MD_7M > D_4$	30.9	$D_5 > MD_7M \sim MD_4M > MD_5M > D_4$
Dioxane	13.9	$D_5 > MD_4M > MD_7M \sim MD_5M > D_4$	17.1	$D_5 > MD_4M > MD_7M \sim MD_5M > D_4$
Benzene	6.2	$MD_4M \sim MD_7M > MD_5M > D_4 \sim D_5$	8.0	$MD_4M > MD_7M \sim D_4 \sim MD_5M > D_5$
2-Pentanone	6.3	$MD_4M > MD_5M \sim D_5 \sim MD_7M > D_4$	7.5	$D_5 \sim MD_4M > MD_5M \sim MD_7M \sim D_4$
n-Propanol	47.6	$D_5 > MD_4M > D_4 > MD_5M > MD_7M$	52.8	$D_5 > D_4 > MD_7M \sim MD_4M > MD_5M$
Nitropropane	8.6	$MD_4M > MD_7M \sim MD_5M > D_5 > D_4$	12.1	$D_5 \sim MD_4M \gtrsim MD_7M \gtrsim MD_5M > D_4$
		70 °C		
Ethyl acetate	28.9	$D_5 > MD_4M > MD_5M \sim MD_7M > D_4$	28.8	$D_5 > D_4 > MD_4M > MD_7M \sim MD_5M$
Dioxane	19.1	$D_5 > MD_4M > MD_5M \sim MD_7M > D_4$	33.9	$D_5 > MD_4M > MD_5M \sim MD_7M > D_4$
Benzene	13.3	$D_5 > MD_7M \sim MD_4M \gtrsim MD_5M > D_4$	26.1	$D_5 > MD_7M > MD_4M > MD_5M > D_4$
2-Pentanone	15.1	$D_5 > MD_4M > MD_5M > MD_7M \sim D_4$	26.6	$D_5 > MD_4M > MD_7M > MD_5M > D_4$
n-Propanol	51.1	$D_5 > MD_4M > MD_5M > MD_7M > D_4$	41.8	$D_5 > MD_4M \sim D_4 \sim MD_7M \sim MD_5M$
Nitropropane	12.5	$MD_4M \gtrsim MD_7M > MD_5M > D_5 > D_4$	8.9	$MD_4M \sim MD_5M > MD_7M > D_5 \sim D_4$

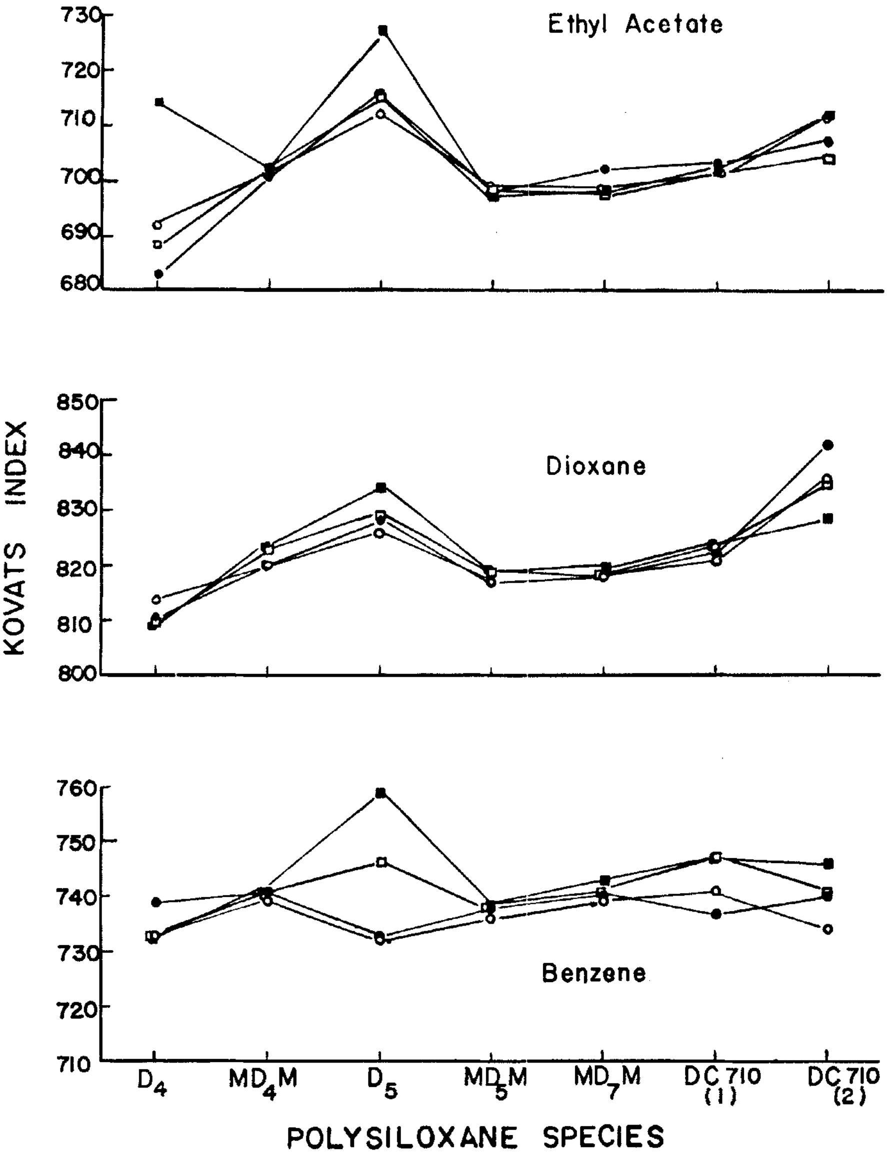

FIG. 2A. Kovats indices for ethyl acetate, dioxane, and benzene.

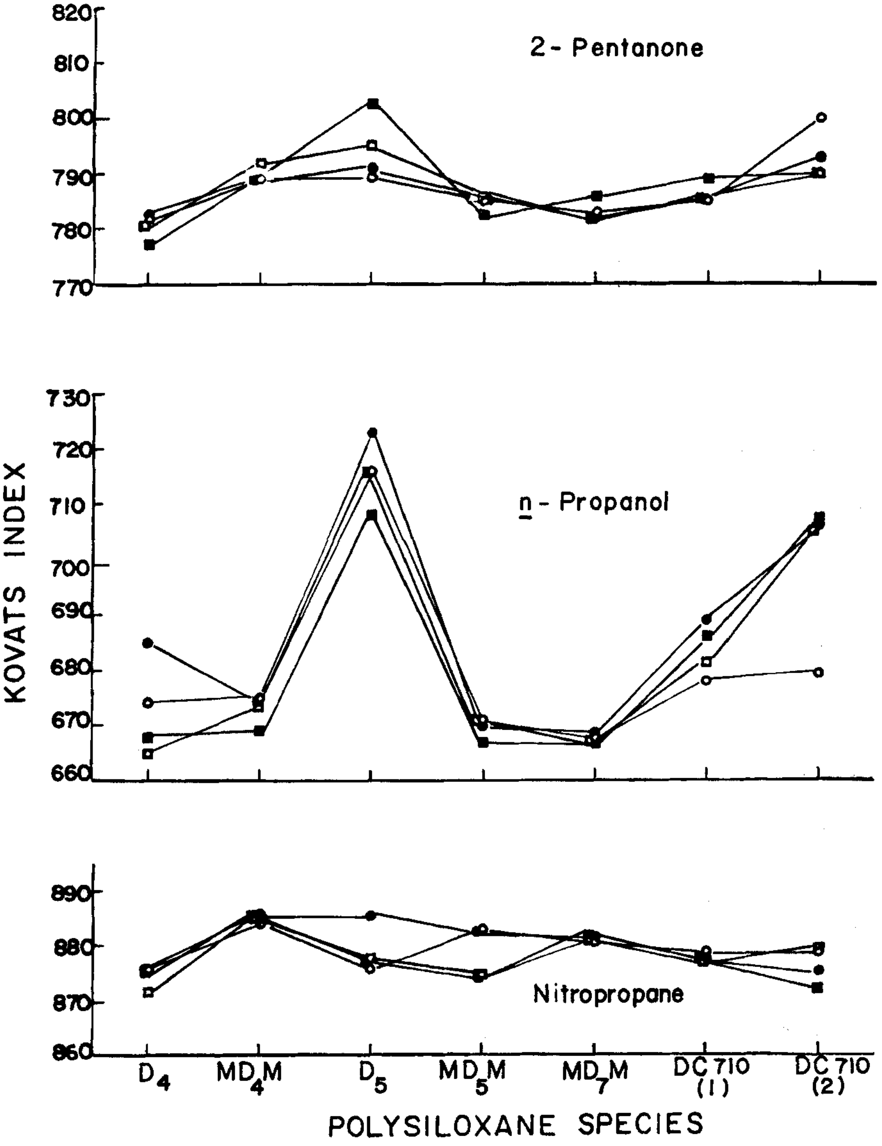

FIG. 2B. Kovats indices for 2-pentanone, *n*-propanol, and nitropropane.

TABLE 4
Kovats Indices for Different Solutes on Squalane at 60 and 70 °C

Solute	60 °C		70 °C	
	I_{max} (std. dev.)	I_{mean} (std. dev.)	I_{max} (std. dev)	I_{mean} (std. dev.)
Ethyl acetate	572.0(0.2)	578.2(1.1)	575.6(0.1)	581.6(0.6)
Dioxane	649.1(1.1)	671.1(3.3)	653.6(0.3)	653.3(6.1)
Benzene	637.8(0.5)	640.5(1.0)	640.9(0.2)	646.5(0.3)
2-Pentanone	631.5(0.5)	638.9(1.0)	633.1(0.7)	632.7(2.1)
n-Propanol	490.3(0.2)	488.1(6.0)	489.5(1.0)	491.6(1.1)
Nitropropane	659.7(0.1)	659.1(0.8)	664.6(0.4)	662.8(1.7)

There were other general trends that should be noted. First, at 60 °C the cyclic pentamer (D_5) usually exhibited a larger index than D_4. For the solutes, the largest index was for ethyl acetate followed by dioxane, *n*-propanol, and 2-pentanone; the smallest index was obtained for benzene and for nitropropane. Second, the cyclic tetramer (D_4) usually exhibited the smallest index for ethyl acetate, dioxane, 2-pentanone, and nitropropane and one of the smallest indices for benzene; only for *n*-propanol was the index fairly high compared to the other oligomers. (Only for nitropropane did the order of the compounds disagree, depending on whether one used I_{max} or I_{mean}.) The linear species fell between the two cyclic species. Of the linear species (MD_4M, MD_5M, MD_7M), the linear tetramer generally exhibited the largest index value, while the pentamer and heptamer had about the same value, with MD_5M being only slightly larger than MD_7M. The cyclic oligomers species (D_4 and D_5) showed little interaction with nitropropane and benzene (at 60 °C).

At 70 °C the cyclic pentamer (D_5) again had the highest index value of all solutes, except for nitropropane where it had one of the smallest. The cyclic tetramer (D_4) had the smallest index for all solutes with the exception of ethyl acetate. Likewise, ethyl acetate was the only solute for which I_{max} and I_{mean} gave a different order.

Changes of Indices with Temperature

Depending on the solute, the retention index increased or decreased with temperature relative to the *n*-alkanes. Since the indices were determined at only 60 and 70 °C, it was difficult to calculate accurately the temperature coefficient of the change in index values for the solutes. The trends over the 60 to 70 °C range indicated that dioxane, 2-pentanone and,

TABLE 5
Enthalpies of Solution for Solutes on Different Siloxane Stationary Phases (kcal/mole)

	Ethyl acetate		Dioxane		Benzene		2-Pentanone		*n*-Propanol		Nitropropane	
Stationary phase	max	mean	max	mean	max	mean	max	mean	max	mean	max	mean
D_4	6.5	6.2	9.4	8.1	8.0	7.2	8.5	7.7	7.3	7.2	9.8	9.9
MD_4M	9.0	7.9	9.5	9.3	9.2	8.8	9.5	9.3	8.8	9.3	10.6	10.6
D_5	6.7	4.9	7.9	5.8	4.8	4.4	6.2	5.6	8.8	9.5	7.5	8.5
MD_5M	6.1	5.0	6.9	6.4	6.1	5.7	7.0	8.1	5.2	6.0	8.1	7.4
MD_7M	8.8	8.9	9.6	7.6	8.1	8.6	9.8	7.3	8.2	8.5	10.2	10.6
DC-710(1)	9.3	7.8	10.9	8.4	6.2	6.2	7.7	6.9	7.3	7.9	6.9	7.0
DC-710(2)	6.5	7.6	8.4	7.7	6.7	5.7	8.7	6.6	6.5	8.1	9.3	9.0

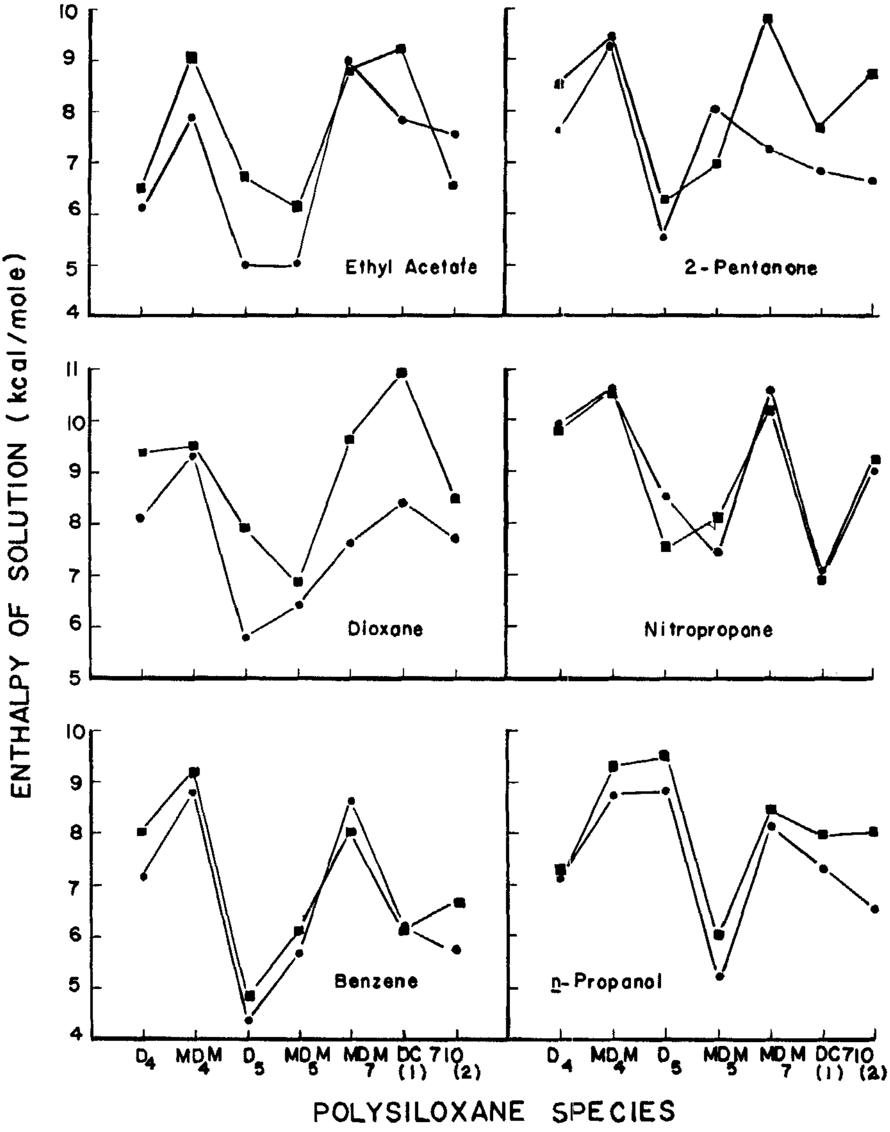

FIG. 3. Enthalpy of solution for polysiloxane species.

possibly, benzene had a positive temperature coefficient whereas nitropropane and, possibly, ethyl acetate and *n*-propanol had negative temperature coefficients. Note that larger changes in index with temperature were exhibited for mean-based indices than for maxima-based indices.

Enthalpies of solution (ΔH_{soln}) for each solute on the stationary phases tested are shown in Table 5. In order to calculate precise and accurate thermodynamic data, the capacity ratios at a number of different temperatures should be determined; however, on the basis of only two temperatures, one should get reliable indications of the trends. The average deviation in the ΔH_{soln} was about ± 0.3 kcal/mole for the maxima-based calculations and ± 0.6 kcal/mole for the moment-based calculations. Figure 3 shows that there were differences between batches of DC-710 and between mean- and maxima-based results for each oligomer. The results for benzene and nitropropane on DC-710 were of the same magnitude as those on OV-17 (also a 50% phenyl, methyl polysiloxane) obtained by Reinbold and Risby (*36*). In general, the largest values of ΔH_{soln} were exhibited by the linear tetramer (MD_4M) while the smallest were by D_5 (except for *n*-propanol). The decreasing order of ΔH values were $MD_4M > MD_7M > D_4 > MD_5M \sim D_5$.

Comparisons of McReynolds Constants for Stationary Phases

The McReynolds constants for the test solutes on each stationary phase are shown in Tables 1 and 2 and Figs. 4A and 4B. The trends were the same as for the Kovats indices but the McReynolds constants were useful for relative comparisons of polarities of stationary phases. The results indicated that, in general, the cyclic pentamer was the most polar oligomer, whereas the cyclic tetramer was the least polar oligomer. The differences between oligomers and between two batches of DC-710 were definitely greater than experimental error. The McReynolds constants for DC-710 were comparable to those found in the literature (*35*).

DISCUSSION

In this work we have tried to minimize the sources of error for the determination of retention indices that have been pointed out by various authors: impure stationary phase, poor temperature control, column aging, adsorption or tailing, sample size effects, and inaccuracies in the time base for data acquisition. Keeping the columns sealed before use and silanizing the glass capillary columns minimized aging and adsorption,

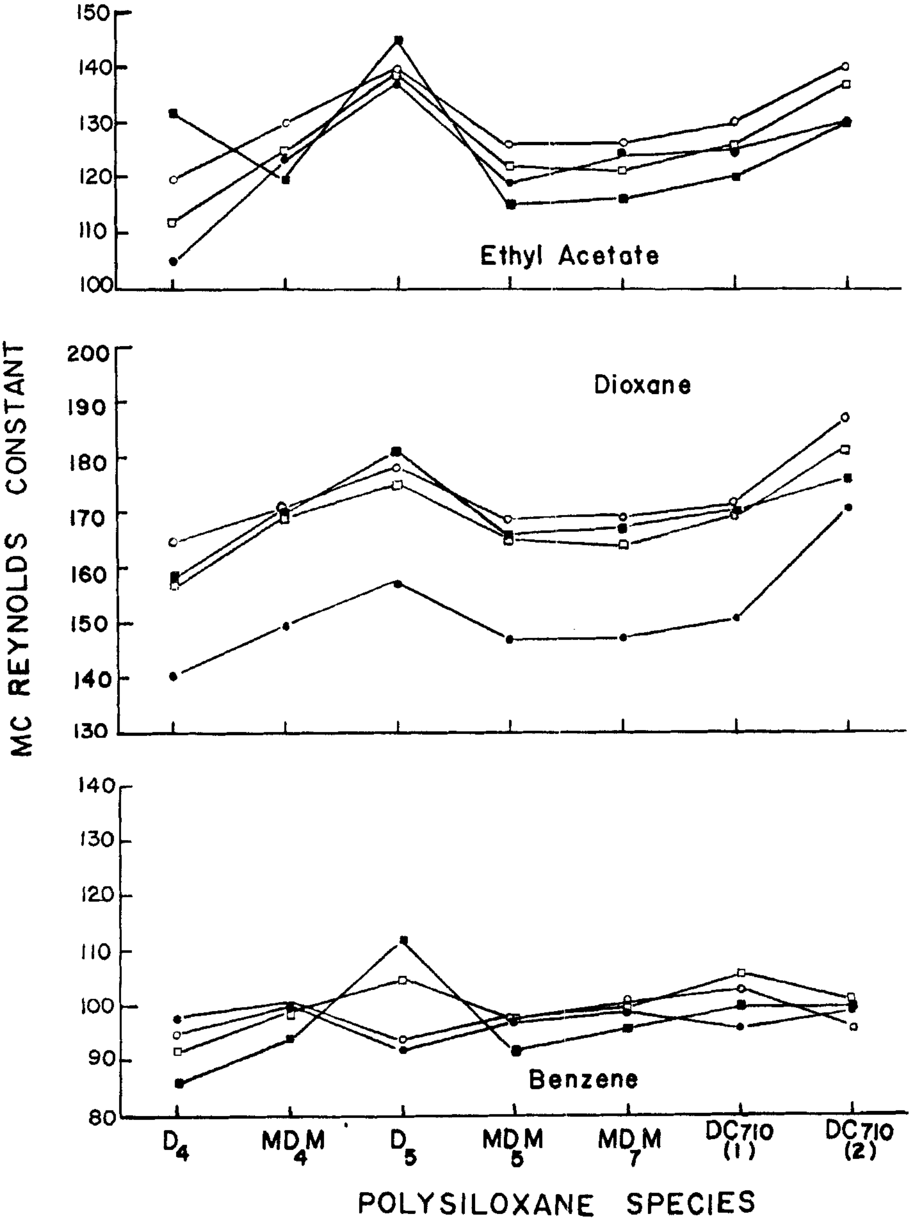

FIG. 4A. McReynolds constants for ethyl acetate, dioxane, and benzene.

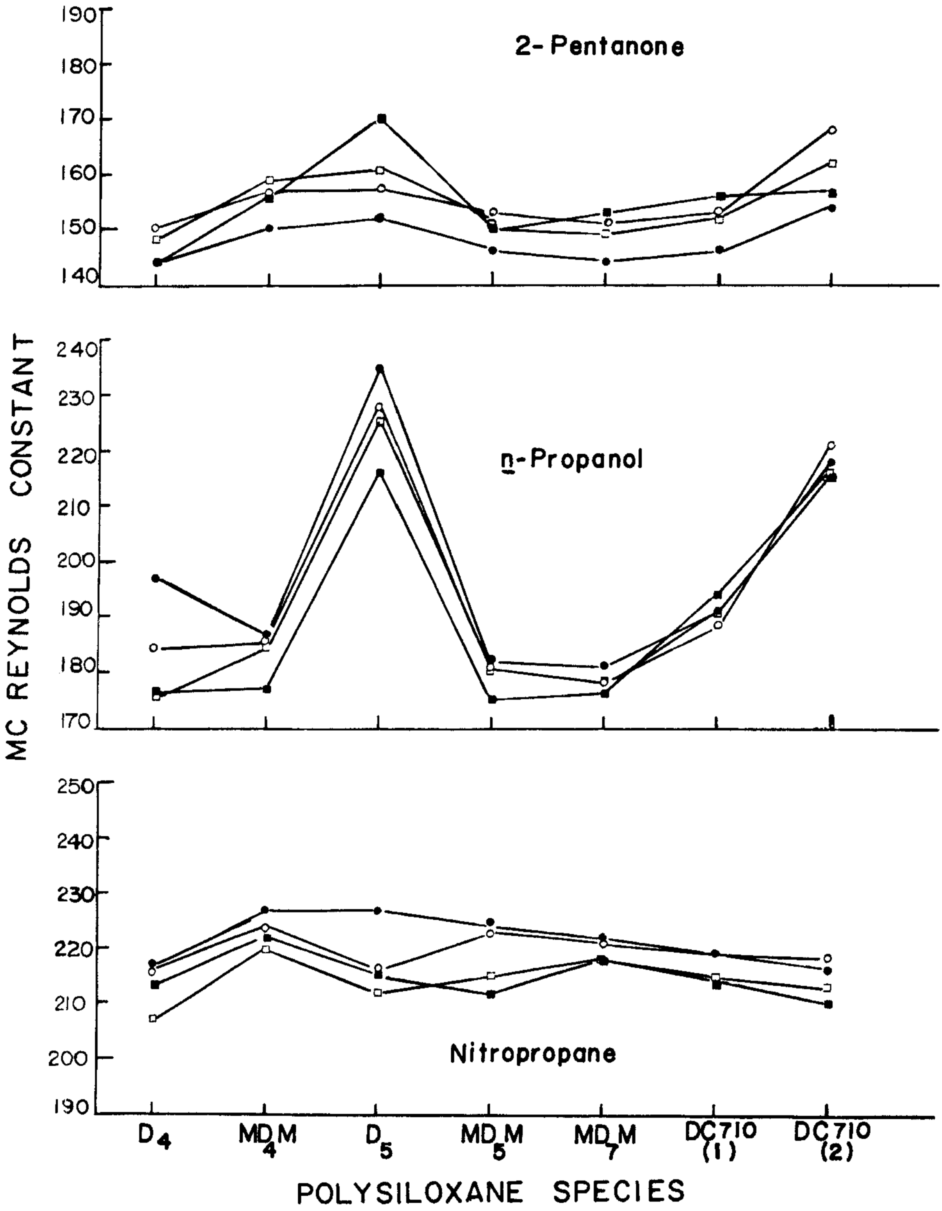

FIG. 4B. McReynolds constants for 2-pentanone, *n*-propanol, and nitropropane.

respectively. Ettre (*37*) has pointed out that the long-term reproducibility of the relative retention data on some open tubular columns is excellent (RSD $\leq$ 1.0% for WCOT columns over a 1-year period). In this work, over the short term (1 month), the reproducibility of retention data in terms of relative standard deviation was <0.6%.

Our standard deviations are larger than those reported by others (*38*). However, it should be noted that we ran each compound alone in an individual experiment rather than taking advantage of the internal-standard approach. This was done for two reasons. First, our apparatus was not easily adapted to the use of several mixtures of standards in addition to the solutes. Second, we wanted to see if the differences between batches of DC-710 and of individual oligomers were large enough to be detected when using more conventional absolute measurements.

The effect of molecular weight of commercially obtained polyethylene glycols on retention data has been demonstrated by several authors (*20*, *21*). In particular, the heats of solution and activity coefficients used in calculating specific retention volumes were shown to be a function of the molecular weight of the stationary phase and thereby revealed changes in solute–solvent interactions. We have shown that there are differences between batches of nominally the same stationary phase. The differences between batches was usually 2 to 5 times the differences obtained for indices on preparations of the same oligomer from different batches.

It can be seen that a solute whose index was high on the cyclic D_5 oligomer had a high value on the bulk DC-710 polymeric stationary phase. For nitropropane and for the maxima-based index for benzene, where the index value for the D_5 species was not high, the index value on DC-710 was not high. These correlations held more closely when considering maxima-based indices rather than moment-based indices. These correlations suggest that the D_5 oligomer may be the dominant species in producing differences from one batch of DC-710 to the next. Therefore, isolation from commercial polymeric stationary phases of one or more individual oligomers for use as stationary phases should increase the precision and accuracy of interlaboratory comparisons of retention data.

The large differences in indices found for the cyclic pentamer (D_5) relative to those for the cyclic D_4 and the linear MD_5M species suggest that its structure results in unusual interactions. Large differences in ΔI correspond to large differences in $\Delta(\Delta G)$ for a given solute because the ΔI value is calculated as a difference in retention for a solute on the squalane reference phase and on a given polysiloxane stationary phase. However, the ΔH values for D_5 were usually among the smallest. This combination of a large $\Delta(\Delta G)$ and a small ΔH suggests that the entropy term for D_5 was much larger than any of the entropy terms for the other oligomeric species. Spectroscopic studies of various types (e.g., NMR) as well as measurements of physical properties (e.g., viscosity) of the pure species and of its binary solutions with these same volatile solutes should reveal the source of those differences.

Finally, McReynolds constants were used for estimating the polarity of potential stationary phases with regard to the nonpolar reference, squalane. The fact that different oligomers exhibited widely different enthalpy values for the solutes emphasizes the importance of specifying the temperature at which a study is made (*39*), as well as the necessity of using a pure stationary phase.

Acknowledgments

This work was supported in part by the U.S. Energy Research and Development Administration under contract E(38-1)-854. In addition, we wish to thank Dr. A. T. Shepard for his help in implementing the stepper-motor interface to the temperature controller.

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Received by editor June 1, 1976