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A MOLECULAR PROPERTY APPROACH FOR THE RESPONSE PREDICTION OF THE THERMAL CONDUCTIVITY DETECTOR

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SUMMARY

The response of the gas chromatographic thermal conductivity detector has been correlated with the physical properties of the solute. In this investigation we have determined that detector response represented as relative molar response factors can be accurately predicted from the critical constants, thermal conductivity coefficient and molecular weight of both the chromatographic fraction and the carrier gas. The "molecular diameter" approach has been employed in conjunction with appropriate thermal conductivity and molecular weight terms which appear in our relative molar response equation. This expression is applicable to polar and non-polar compounds when helium, hydrogen, and nitrogen are carrier gases.

INTRODUCTION

The quantitative interpretation of thermal conductivity cell response has received considerable attention. Initially, ROSIE AND GROB¹ and others^{2,3} chose benzene as an internal standard to successfully obtain accurate quantitative data with helium as carrier gas. KAISER⁴ and HARA *et al.*⁵ experimentally measured relative molar response (*RMR*) factors for selected compounds with hydrogen as carrier gas while JAMESON⁶⁻⁹ compiled extensive tabulations of *RMR* data for many classes of compounds with nitrogen as a carrier.

There have been several attempts to calculate *RMR* factors theoretically from either convective heat effects¹⁰ or the kinetic theory of gases^{3,11-14}. In our recent paper¹⁴ we adopted LITTLEWOOD'S¹² extension of the rigorous Chapman-Enskog theory governing the thermal conductivity of a binary gas mixture (eluted solute and carrier gas). When helium and hydrogen are employed as carrier gases it was determined that response behavior for compounds of vastly different functionalities can be accurately predicted by the following equation:

$$RMR_i = \left[\frac{\sigma_i + \sigma_1}{\sigma_1} \right]^2 \left[\frac{M_i - M_1}{M_\phi - M_1} \right]^{1/4} \times 100 \quad (1)$$

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where σ indicates molecular diameter and M represents molecular weight. The subscripts i , c , and b refer to the solute under consideration, the carrier gas and benzene (the internal standard), respectively. The first bracketed term is the resultant of the expression proposed by LITTLEWOOD¹² whereas the second term was incorporated by us to explain the increase in RMR with a corresponding increase in molecular weight.

The significance and implications of the molecular diameter term in eqn. 1 have previously been discussed¹². In short, they depict how the presence of the solute vapor alters the thermal conductivity of the carrier gas. The carrier gas is responsible for the heat dissipation in the sensing filament and the solute vapor interferes with the process in proportion to their cross-sectional areas

$$[(\sigma_c + \sigma_i)/2]^2$$

Response factors were calculated by eqn. 1 for 68 compounds of various classes with helium as carrier gas in addition to 20 substances using hydrogen as carrier gas. It was found that the predicted RMR values with these carrier gases were indeed a linear function of molecular weight for compounds belonging to a homologous series and could illustrate the decrease in response associated with increased molecular symmetry for isomeric compounds.

With nitrogen as a carrier gas our equation failed to reproduce the experimental RMR data. Although this carrier gas has been a nemesis to response predictors because of its low thermal conductivity and relatively high molecular weight, the calculation of RMR factors with nitrogen as carrier gas is the subject of the present investigation.

EXPERIMENTAL

The experimental apparatus and procedures were conventional and have been described previously¹⁴. Hydrogen was not used as a carrier gas. The Gow-Mac Model 9677 thermal conductivity detector equipped with thermistors was operated at 6 mA and at a controlled flow rate in the range 21–37 ml/min. These conditions minimized the formation of W-shaped peaks.

CONCEPT AND DETERMINATION OF MOLECULAR DIAMETERS

The thermal conductivity of a vapor is dependent upon its molecular weight and distance of closest approach among other molecular properties. We have defined the distance of closest approach by the σ term in the Lennard-Jones (12-6) intermolecular potential function

$$v(r) = 4e_0 \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (2)$$

in which e_0 is the maximum energy of attraction of two colliding molecules, $v(r)$ is the potential energy of interaction and r is the internuclear distance. The rigid Chapman-Enskog theory¹⁵ has related the parameters σ and e_0 to the viscosity and thermal conductivity of a gas near atmospheric pressure. These constants may be determined from the experimental measurements by choosing the set of σ and e_0 which reproduces the data most accurately.

Difficulties are encountered in this procedure as there frequently exist multiple sets of σ , e_0 values which reproduce the same viscosity data. Moreover, trends in various homologous series are not smooth, that is, the addition of a methylene group does not contribute a constant amount to either the collision diameter or the energy of interaction. These affects have been described earlier¹⁰.

To eliminate the irregularities of σ values, diameters have been calculated by the empirical expressions reported in the literature. The diameter expressions employed in this study and the appropriate designation by which they will be subsequently referred to are presented in Table I. By utilizing diameters calculated in the above fashion a consistent set of collision cross-sections can be generated because of the regular, periodic variation of these properties within a series of similar compounds. P_c , V_c and T_c represent critical pressure, volume and temperature, respectively. The acentric factor, W , is indicative of the reduced vapor pressure $P(v.p.)_r$ of a substance near its normal boiling point and may be defined as

$$W = -\log P(v.p.)_r - 1.00|T_r = 0.7 \quad (3)$$

The acentric factor¹⁰ provides a convenient measure between a given molecule and an inert gas. The critical constants and acentric factors of many organic compounds have been tabulated²⁰.

TABLE I
MOLECULAR DIAMETER EXPRESSIONS

Designation	Expression	Source
1	$\sigma = 2.36 (T_c/P_c)^{1/3}$	17
2	$\sigma = (2.35 + 0.297 W) (T_c/P_c)^{1/3}$	17
3	$\sigma = (0.812 + 0.168 W) V_c^{1/3}$	17
4	$\sigma = 0.785 V_c^{1/3}$	18

FORMULATION OF AN RMR EXPRESSION

For the case where helium, hydrogen and nitrogen are carrier gases the response behavior of assorted compounds can be predicted accurately by an equation of the form:

$$RMR_i = \left[\frac{\sigma_i + \sigma_1}{\sigma_\phi + \sigma_1} \right]^2 \left[\frac{K_1 - K_i}{K_1 - K_\phi} \right] \left[\frac{M_i - M_1}{M_\phi - M_1} \right]^\alpha \times 100 \quad (4)$$

The subscripts i , 1 , and ϕ have been previously defined. K and M refer to thermal conductivity and molecular weight, respectively. Since the thermal conductivity of nitrogen has the same order of magnitude as benzene and other organic molecules, it is reasonable that an appropriate term should appear in an empirical response equation. However, due to the very high thermal conductivity of helium and hydrogen, the magnitude of the thermal conductivity term is approximately unity. In fact, if the exponent α equals $1/4$, eqn. 4 reduces to our original response equation described earlier.

The factor of 100 represents the response of benzene arbitrarily assigned a

value of 100 response units per mole. In the calculation of the *RMR* factor the collision diameters of the substance indicated in eqn. 4 were computed from the same diameter expression. Thermal conductivity coefficients at 100° for the compounds studied are listed in Table II.

TABLE II

THERMAL CONDUCTIVITIES^a AT 100°C FOR VARIOUS COMPOUNDS

Compound	Thermal conductivity $\times 10^5$ (cal/cm·sec·°K)	Molecular weight
<i>n</i> -Pentane	5.20	72.15
<i>n</i> -Hexane	4.90	86.17
<i>n</i> -Heptane	4.80	100.20
<i>n</i> -Octane	4.50	114.22
<i>n</i> -Nonane	4.50	128.25
Benzene	4.10	78.11
Toluene	4.60	92.13
Cyclohexane	4.20	84.16
Diethyl ether	5.20	74.12
Acetone	4.20	58.08
Ethyl acetate	4.17	88.10
Acetonitrile	3.27	41.05
Methylene chloride	2.50	89.94
Chloroform	2.30	119.39
Carbon tetrachloride	2.10	153.84
Carbon disulfide	2.80	76.13
Methanol	5.20	32.04
Ethanol	5.00	46.07
<i>n</i> -Propanol	4.92	60.09
<i>n</i> -Butanol	4.84	74.12
Isobutanol	4.77	74.12
Pentanol	4.54	88.15
Helium	40.11	4.003
Hydrogen	49.48	2.016
Nitrogen	7.21	28.016

^a Selected from refs. 21-24.

RESULTS AND DISCUSSION

Although the light carrier gases have replaced nitrogen for use with the thermal conductivity detector, the parameters underlying detector response with this carrier remain to be elucidated. Unlike the cases for helium and hydrogen as carriers, *RMR* values with nitrogen fluctuate and may be dependent on experimental conditions²⁵. Nevertheless, we have assumed that the low thermal conductivity and relatively high molecular weight of nitrogen are the primary factors responsible for the peculiar response observed with this carrier gas. The *RMR* factors at a customary 100° calculated from eqn. 4 are presented in Table III. The experimental data are included for comparison. Unfortunately, our analysis was limited by the lack of thermal conductivity coefficients for many compounds. However, the selected compounds exhibit substantial differences in molecular weight and structure.

TABLE III

PREDICTED *RMR* DATA AT 100° WITH NITROGEN AS CARRIER GAS

Compound	Experimental <i>RMR</i> ^a		Predicted <i>RMR</i> ^b							
	A	B	$\alpha = 1/2$				$\alpha = 1/4$			
			1	2	3	4	1	2	3	4
<i>n</i> -Pentane	59	51	61	62	61	61	63	64	63	63
<i>n</i> -Hexane	90	91	88	89	88	86	84	86	85	83
<i>n</i> -Heptane	112	124	109	112	111	107	100	102	101	97
<i>n</i> -Octane	141	153	143	148	146	139	125	129	127	121
<i>n</i> -Nonane	163	182 ^c	163	170	167	157	137	143	140	132
Benzene	100	100	100	100	100	100	100	100	100	100
Toluene	120	116	97	98	98	96	91	92	92	90
Cyclohexane	87	103-106	103	103	102	103	100	100	99	100
Diethyl ether	64	53-82 ^c	61	61	59	59	62	62	61	60
Acetone	65	62-64	68	69	66	65	78	79	75	74
Ethyl acetate	107	119 ^c	108	111	108	104	103	106	103	100
Acetonitrile	49	—	60	61	53	52	85	86	74	73
Dichloromethane	—	144-147	140	140	141	141	133	133	133	134
Chloroform	194	188-195	189	189	194	194	162	162	167	167
Carbon tetrachloride	254	253 ^c	251	251	250	251	200	199	199	199
Methanol	14	13-21	13	14	13	12	26	27	25	24
Ethanol	29	34	35	37	37	33	45	48	47	43
<i>n</i> -Propanol	57	57 ^c	53	56	56	51	59	63	63	58
Isopropanol	40	49	46	50	50	44	52	56	56	50
<i>n</i> -Butanol	73	87	77	82	82	75	78	83	84	77
Isobutanol	67	61	74	78	79	72	75	80	80	73
Pentanol	102	116	99	105	105	97	95	100	100	93

^a A = *RMR* values determined in the present study; B = *RMR* values extracted from ref. 3.

^b The numbers 1-4 refer to the expressions 1-4.

^c Values extracted from refs. 6-9.

Better overall agreement is produced by assigning α a value of $1/2$ although trends in response and orders of magnitude are adequately predicted for both non-polar compounds with our original exponent, $1/4$. This improvement possibly represents the predominant role played by a heavy carrier gas in use with this detector. We may have compensated for the "heat capacity effect" observed by BOHEMEN AND PURNELL²⁶. HOFFMANN'S³ equation, which yielded good data with helium and hydrogen, was also modified to reproduce the experimental *RMR* values with nitrogen as carrier.

Previously we reported that *RMR* data evaluated with helium and hydrogen are dependent only on molecular constants and the molecular weight of the solute and carrier gas. With the heavier nitrogen, the thermal conductivities of the carrier and most organic substances are similar in magnitude. The selected thermal conductivity expression $(K_1 - K_t)/(K_1 - K_\phi)$ varies from 0.67 to 1.64 for the compounds chosen.

The importance of the thermal conductivity and diameter terms can be illustrated by considering the compounds *n*-pentanol, cyclohexane, and dichloromethane — species which differ greatly in *RMR* but have approximately $1/2$ the same molecular weight. On the other hand, incorporation of the diameter expression and molecular weight term yields excellent agreement for substances having identical thermal conductivity coefficients but differing in *RMR* and molecular weight, e.g. methanol and pentane. The same holds true for the set acetone, cyclohexane and ethyl acetate.

Therefore, a net thermal conductivity difference is not the only analytical mechanism prevailing.

Molecular diameters defined by the Lennard-Jones potential are functions of molecular properties; thus, the computed diameters provide a relative measure of the diameter of the solute to that of the carrier gas and reference substance ((benzene)). However, these calculated diameters should not be confused with the concept of a "true" molecular diameter. They are either directly proportional to $V_c^{1/3}$ or indirectly through $(T_c/P_c)^{1/3}$ and have a unique implication. If the organic vapor is assumed to be a sphere with a volume equal to $4/3\pi(\sigma/2)^3$, a direct path to a simulated geometrical dimension is obtained. In addition, the critical constants and acentric parameter of a substance are representative of the intramolecular forces affecting its size and shape. The molecular constants, in fact, may be used to evaluate second virial coefficients.

STIEL AND THODOS¹⁸ devised diameter expression 4 for polar species. Inspection of Table III shows that the computed RMR data of non-polar compounds accurately reproduces the experimental data while the remaining expression formulated for non-polar species yields excellent agreement for polar molecules. We interpret these results as a consequence of the environment of the eluted solute. As the mole

TABLE IV

PREDICTED RMR DATA WITH HELIUM AND HYDROGEN AS CARRIER GASES USING MOLECULAR DIAMETER EXPRESSIONS 3 AND 4

Compound	Helium				Hydrogen			
	Experimental RMR		Computed RMR		Experimental RMR		Computed RMR	
	Ref. 14	Ref. 2	Eqn. 3	Eqn. 4	Ref. 5	Ref. 3	Eqn. 3	Eqn. 4
<i>n</i> -Pentane	106	105	102	101	104	102	103	102
<i>n</i> -Hexane	122	123	118	115	118	123	118	115
<i>n</i> -Heptane	136	143	133	128	133	132	133	128
<i>n</i> -Octane	151	160	150	142	150	152	149	141
<i>n</i> -Nonane	164	177	164	154	—	185	163	153
Benzene	100	100	100	100	100	100	100	100
Toluene	114	116	113	111	112	116	113	111
Cyclohexane	110	114	107	108	106	105	107	108
Diethyl ether	107	109 ^a	97	97	112	101	98	97
Acetone	83	86	86	84	86	89	86	84
Ethyl acetate	108	111	110	106	—	—	110	106
Acetonitrile	70	—	74	72	—	—	75	73
Methylene chloride	—	94 ^b	95	95	—	87	94	94
Chloroform	104	108 ^b	112	112	—	99	111	111
Carbon tetrachloride	116	120 ^b	126	127	—	112	126	126
Carbon disulfide	—	86 ^a	84	86	—	84	83	85
Methanol	55	55	59	55	62	59	60	56
Ethanol	72	72	77	70	75	69	78	71
<i>n</i> -Propanol	86	83	92	84	—	—	93	85
Isopropanol	85	85	95	83	—	—	96	84
<i>n</i> -Butanol	99	95	108	98	—	—	108	99
Isobutanol	98	—	108	98	—	—	108	98
Pentanol	115	—	121	112	—	—	121	112

^a Ref. 3.

^b Ref. 27.

fraction of the solute is usually $\ll 1$, solute-carrier gas interactions predominate. The appropriate molecular constants therefore, are a relative indication for the size and geometry of the solute-carrier-benzene system.

For the case where helium and hydrogen serve as carrier gases, *RMR* factors at 100° have been computed from eqn. 2 with $\alpha = 1/4$. Insertion of the thermal conductivity term slightly improves the agreement between the previously calculated¹⁴ (eqn. 1) and experimental *RMR* data. The magnitude of this term lies in the range of 0.97 to 1.04 for the compounds considered. Utilizing diameter expressions 3 and 4 typical examples are presented in Table IV. Close examination of the tabulated *RMR* values indicates that both sets of data are nearly identical for a given substance with these carriers.

CONCLUSIONS

The present study illustrates that the relative response of the thermal conductivity detector can be correlated with fundamental molecular properties of the chromatographic solute and carrier gas. More significantly it has been found that thermal conductivity is not the only analytical property under consideration. We suggest that absolute signal strength may now be divided into three components: a cell factor, an electrical factor and a "molecular property" term.

Anomalous peak behavior has been commonly observed in the analysis of organic substances with nitrogen as carrier and in the determination of hydrogen in helium. W-shaped peaks have been attributed to the temperature gradient between the detector block and sensing filament, the molar flow rate, heat capacity and sample size. In addition to these parameters, we propose that a similarity in magnitude of the various molecular properties considered here is also partially responsible for peak distortion. Additional investigations, particularly with "heavy" carrier gases should elucidate the response of this versatile and inexpensive detector.

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