

Importance of Debye and Keesom Interactions in Separating *m*-Xylene and *p*-Xylene in GC–MS Analysis Utilizing PEG Stationary Phase

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Abstract

In electron impact gas chromatography (GC)–mass spectrometry analysis of a complex mixture, such as gasoline, two coeluting solutes can be distinguished if each has a unique major ion. The boiling-point difference between *m*-xylene and *p*-xylene, which also has identical major ions (mz^{-1} : 91 and 106 Da), is 0.77°C. These cannot be separated even on a crossed-linked polydimethylsiloxane capillary column, which has a minimum of 5000 plates/m. They are separated on a crossed-linked polar polyethylene glycol (PEG) capillary column. GC separation on a stationary phase depends on the relative strengths of solute–solute, stationary phase–stationary phase, and solute–stationary phase interactions. Although the calculated molar electronic polarization and refractivity factor of Lorenz–Lorentz equation for *m*-xylene and *p*-xylene are nearly equal because of its greater dipole moment difference (0.30 and 0.02), the calculated orientation polarization of *m*-xylene is 80 times greater than *p*-xylene. This implies the dipole reinforcement through inductive polarization by the hydroxyl of PEG stationary phase molecules is greater on *m*-xylene than *p*-xylene. In addition, as the permanent dipole moment of *m*-xylene is 15 times greater than *p*-xylene, *m*-xylene has a stronger Keesom interaction with PEG. In order for *m*-xylene and *p*-xylene to solvate in PEG, analytes must overcome the PEG–PEG Keesom/hydrogen bonding interaction forces. Physical and chemical parameters indicate that compared with *p*-xylene, *m*-xylene has a greater Debye–Keesom interaction tendency with PEG molecules. This is supported by the 0.12-min. retention-time difference between them.

Introduction

A gasoline is a complex mixture of several hundred compounds. Depending on the refining process, the proportions of paraffins, olefins, naphthenes, and aromatics (PONA) of different gasolines

vary. A crossed-linked polydimethylsiloxane (PDMS) capillary column that has a minimum of 5000 plates/m is available to analyze most components of gasoline by gas chromatography (GC)–mass spectrometry (MS). Reformulated gasoline also contains oxygenates that can be analyzed by GC–MS (1).

In electron impact (EI) GC–MS analysis of gasoline, a minor component masked by an adjacent major component, or two

Table I. The GC Retention Data of Analytes Determined on PDMS and PEG Columns

Analyte	Boiling point* (°C)	Dipole moment†		t_R (min)‡		C§ (%)
		(°C)	(D)	PDMS	PEG	
Toluene- d_8	110			1.74	1.35	–22
Toluene	110.6	20	0.31	1.82	1.42	–22
<i>m</i> -Xylene	139.12	20	0.30	3.45	2.84	–18
<i>o</i> -Xylene	144.42	20	0.45	3.85	3.44	–11
<i>p</i> -Xylene	138.35	20	0.02	3.48	2.72	–22
Ethylbenzene- d_{10}	134.60			3.25	2.55	–21
Ethylbenzene	136.19	20	0.37	3.32	2.65	–20
1,3,5-Trimethylbenzene	164.70			4.97	4.19	–16
1,2,4-Trimethylbenzene	168.89			5.41	4.73	–12
2-Isopropyltoluene	178.0			6.04	4.84	–20
1,2-Dichlorobenzene	180.48	20	2.14	6.09	7.31	20
1,3-Dichlorobenzene	173.0	25	1.54	5.64	6.37	13
1,4-Dichlorobenzene	174.12	0	0.24	5.68	6.68	18
<i>m</i> -Chlorotoluene	161.25	25	1.82	4.81	5.12	6
<i>o</i> -Chlorotoluene	158.97	20	1.43	4.78	5.02	5
<i>p</i> -Chlorotoluene	161.99	25	1.88	4.85	5.15	6
<i>p</i> -Pentanol	137.3	25	1.70	1.55	3.79	144

* Refer to references (2,3).

† Refer to references (2,3).

‡ Retention time (t_R) was adjusted to benzene for determinations on HP-PONA (PDMS) and HP-INNOWAX (PEG) columns; values are the average of five determinations and its uncertainty is ± 0.02 min.

§ Percent difference between t_R of analytes determined on PDMS and PEG columns.

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coeluting peaks of nearly equal concentration can be differentiated if each has a major distinguishing ion. Because ethylbenzene and three xylenes all have identical major ions whose mz^{-1} are 91 and 106 Da, even in EI-GC-MS analysis these compounds must be first separated chromatographically.

m-Xylene and *p*-xylene have a boiling temperature difference of 0.77°C (Table I) but are not separated on a PDMS column (see Figure 1) and are separated on a polar stationary phase such as aromatic amines and crossed-linked polyethylene glycol (PEG) columns. These are also separated on a liquid crystalline phase column (4).

Aside from the operating conditions of the instrument and physical properties of the column, the GC solute retention time (t_R) is determined by its vapor pressure (boiling point), interaction forces of the solute-solute, stationary phase-stationary phase, and solute-stationary phase molecules. These forces include dispersion (induced dipole-induced dipole), Keesom (dipole-dipole), Debye (dipole-induced dipole), and hydrogen bonding interaction forces (5,6). Lacking a heteroatom, xylenes are generally considered to be nonpolar. However, because of their aromatic structure and direct effects of methyl substituents, these have polarizable electrons and even have small dipole moments.

A major function of a state laboratory includes providing a reliable data to different programs and sometimes defending them in court even under intense cross-examination by defense attorneys. With this prospect in mind, the intent of this study has been to find out the GC retention characteristics of these early-eluting alkylbenzenes found in most gasolines by correlating their t_R determined on PDMS-PEG columns with their chemical and physical properties. These include boiling point, refractive index, molar electronic polarizability calculated by Lorenz-Lorentz equation (7), orientation polarizability of vapor phase molecules with permanent dipole according to Debye-Langevin equation (8), ionization potential, dipole moment, and molecular structure. This was compared with similar data obtained from the analyses of chlorotoluene and dichlorobenzene analogs of xylenes. The results were then rationalized through molecular

interaction forces. Quantitative application of molecular interaction equations (9,10) are hindered by a number of ideal assumptions made in their derivations. However, conceptual application of these equations are useful in understanding the mechanism of GC retention.

Experimental

A Hewlett-Packard (HP, Palo Alto, CA), Model 5980 GC was interfaced to an HP Model 5970 mass selective detector (MSD) equipped with EI and a quadrupole mass analyzer. The ionizing voltage was set at 70 eV at the factory, and the source temperature was set at 250°C. HP Models 300 and 7946 formed the data station. An HP PONA fused column (50 m × 0.2 mm, coated with 0.5 μm crossed-linked 100% PDMS) and an HP INNOWAX fused column (50 m × 0.2 mm, coated with 0.4 μm crossed-linked PEG) were used. The injector and MSD transfer line temperatures were set at 225°C and 260°C, respectively. The GC oven was programmed from an initial temperature of 35°C for 1.0 min and ramped at the rate of 15°C/min to a final temperature of 200°C, which was maintained for 15 min. For gasoline analysis on the HP-PONA column, the injector and MSD transfer line temperatures were set at 250°C and 270°C, respectively. The oven temperature was programmed from the initial temperature of 35°C, which was maintained for 5.0 min, ramped at the rate of 15°C to the final temperature of 250°C, and maintained for 10 min. The helium cylinder and head pressures were set at 30 and 15 psi, respectively. The helium flow rate was set at 1.5 mL/min. A vacuum of 1.8×10^{-6} Torr was attained when the GC oven temperature was at 100°C. The MS was calibrated with PFTBA.

A 1.0-μL amount of appropriate standards (listed in Table I) and benzene (0.1–1.0 μg/L prepared in isooctane) were injected into the GC and scanned from 35 to 160 Da at 1.65 scans/s. The retention time of analyte ion chromatographic peak was adjusted to benzene peak. For gasoline sample analysis, 1.0 mL of a 87 octane gasoline spiked with benzene- d_6 was injected into the GC and scanned from 35 to 300 Da. The PDMS-PEG t_R data are the average of five determinations. Standards were purchased from Aldrich Chemical Company (Milwaukee, WI).

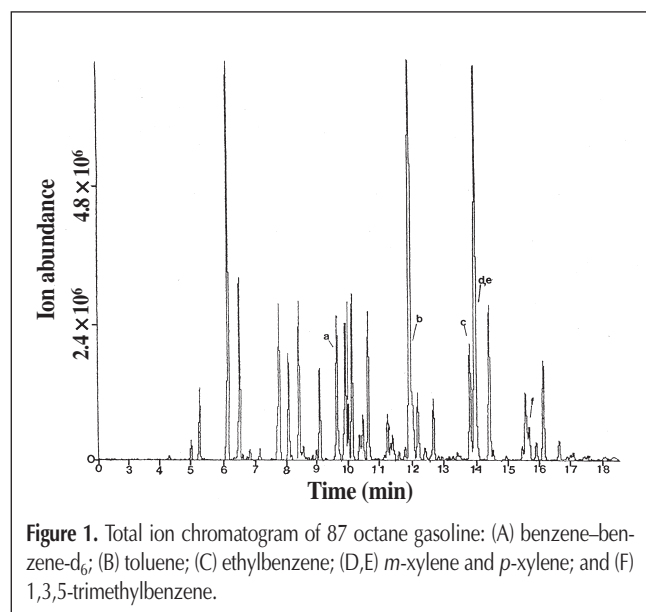


Figure 1. Total ion chromatogram of 87 octane gasoline: (A) benzene-benzene- d_6 ; (B) toluene; (C) ethylbenzene; (D,E) *m*-xylene and *p*-xylene; and (F) 1,3,5-trimethylbenzene.

Table II. Basicity Constants in HF and Ionization Potentials of Some Alkylbenzenes

Analyte	Basicity constant (K _b)*	Ionization potential (e.v.)†
Benzene	1.05×10^{-8}	$8.82 \pm .01$
Toluene	2.0×10^{-7}	$8.56 \pm .01$
<i>o</i> -Xylene	5.8×10^{-7}	$8.56 \pm .01$
<i>m</i> -Xylene	8.7×10^{-6}	$8.44 \pm .01$
<i>p</i> -Xylene	5.7×10^{-7}	
1,2,4-Trimethylbenzene	2.7×10^{-5}	
1,3,5-Trimethylbenzene	3.2×10^{-3}	$8.39 \pm .01$
<i>p</i> -Chlorotoluene		$8.69 \pm .01$

* Refer to reference (11).

† Refer to reference (23).

Results and Discussion.

Properties of analytes and stationary phases

Because of their aromatic electrons, alkylbenzenes behave as a very weak base in certain chemical environments. Both IR and NMR studies have confirmed the proton addition complexes of toluene, xylenes, and mesitylenes in strong acids. The decisive factor in the addition of a proton onto aromatic hydrocarbons is the transition of a trigonally sp^2 -hybridized carbon atom to a tetragonally sp^3 -hybridized one. Because of this fact, any proton addition complex can be detected by proton NMR. Analysis of IR spectra shows that the new bands can be assigned to previously IR inactive benzene vibrations that are symmetry-forbidden transitions. This means the addition of the proton is associated with lowering of symmetry. Thus, the D_{6h} of benzene is lowered to C_{2v} in the complex, and particularly marked changes occur on complex formation in the region between 670 and 900 cm^{-1} , where the number and position of the bands in this region depend on the number of adjacent hydrogen atoms (11,12).

Valence bond structures of alkylbenzenes show their suitability for polarization. It is known that ortho and para positions relative to an electron releasing methyl group are preferred for proton addition. For example, 1,3,5-trimethylbenzene has three points available for addition, and they are activated in the same manner because, in each case, two methyl groups in ortho positions and one methyl in the para position are re-enforced. The basicity con-

stants in Table II indicate that, in strong acids, even alkylbenzenes have very weak basic properties, and 1,3,5-trimethylbenzene is 10^5 times more basic than benzene.

Also, because of electron delocalization, the inductive effect of the C-Cl group is decreased in chlorotoluenes and dichlorobenzenes as compared with saturated molecules such as chlorocyclohexane. Alkylbenzene should be more basic than its chlorotoluene and dichlorobenzene analogs. Three dichlorobenzenes have different dipole moments but have similar solubilities in benzene, which indicates that the dipole moment of bond or group are of greater significance than the dipole moment of the whole molecule (13).

Different PEG stationary phases differ primarily by the molecular weight or length of the polymer chain. HP-INNOWAX is a form of Carbowax 20M. Polysiloxanes are distinguished by their alternating silicon and oxygen linear backbone and two functional groups attached to each silicon. In PDMS, two functional groups are 100% methyl substituted. The HP-PONA column is a form of PDMS.

The Hawkes index is one of several empirical methods that has assigned empirical values of molecular interaction forces to a number of stationary phases. The values for PDMS-PEG are dispersion (9.0/8.6), polarity (dipole) (0/8.0), Bronsted basicity (0/4), and Lewis acidity (0/0) (14).

Table III. The Effects of Dipole Moment, Refractive Index, and Temperature Differences of Two Analytes Determined on PDMS and PEG Columns in GC Separation*

Analytes	Temp. (°C)	Difference dipole moment (D)	Refractive index	Separation factor (α) PEG-PDMS (min)
<i>m</i> -xyl- <i>p</i> -xyl	0.77	0.28	0.0016	0.12/0.03
<i>o</i> -xyl- <i>p</i> -xyl	6.12	0.43	0.0101	0.72/0.37
<i>m</i> -xyl- <i>o</i> -xyl	5.10	0.15	0.0085	0.60/0.40
<i>o</i> -xyl-etben	8.23	0.08	0.0099	0.79/0.53
1,3,5-triben-1,2,4-triben	4.19	na [†]	0.0046	0.54/0.44
1,2-diclben-1,3-diclben	7.48	0.60	0.0027	0.94/0.45
1,2-diclben-1,4-diclben	6.36	1.90	0.0275	0.68/0.41
1,3-diclben-1,4-diclben	1.12	1.30	0.0248	0.31/0.04
<i>m</i> -cltolu- <i>o</i> -cltolu	2.78	0.39	0.0024	0.10/0.03
<i>m</i> -cltolu- <i>p</i> -cltolu	0.24	0.06	0.0015	0/0.04
<i>o</i> -cltolu- <i>p</i> -cltolu	3.02	0.45	0.0015	0.13/0.07
tolu- <i>d</i> ₈ -tolu	0.60	na	0.0021	0.07/0.08
etben- <i>d</i> ₁₀ -etben	1.59	na	0.0031	0.10/0.07

* Toluene-*d*₈ (tolu-*d*₈); toluene (tolu); *m*-xylene (*m*-xyl); *o*-xylene (*o*-xyl); *p*-xylene (*p*-xyl); ethylbenzene-*d*₁₀ (etben-*d*₁₀); ethylbenzene (etben); 1,3,5-trimethylbenzene (1,3,5-triben); 1,2,4-trimethylbenzene (1,2,4-triben); 2-isopropyltoluene (2-isopropyltolu); 1,2-dichlorobenzene (1,2-diclben); 1,3-dichlorobenzene (1,3-diclben); 1,4-dichlorobenzene (1,4-diclben); *m*-chlorotoluene (*m*-cltolu); *o*-chlorotoluene (*o*-cltolu); and *p*-chlorotoluene (*p*-cltolu).

[†] Not available.

Table IV. Molar Electronic Polarizabilities Calculated from Lorenz-Lorentz Equation*[†]

Analyte	Refractive index [‡] (n_D^{20-25})	$f = (n^2 - 1)/(n^2 + 2)$	$P_M = (n^2 - 1)/(n^2 + 2)(M/d) = R_M$ (cm ³ /mol)
Toluene- <i>d</i> ₈	1.4940	0.2911	30.91
Toluene	1.4961	0.2922	31.08
<i>m</i> -Xylene	1.4973	0.2927	35.79
<i>o</i> -Xylene	1.5058	0.2970	35.79
<i>p</i> -Xylene	1.4950	0.2919	35.99
Ethylbenzene- <i>d</i> ₁₀	1.4926	0.2904	35.54
Ethylbenzene	1.4959	0.2920	35.80
1,3,5-Trimethylbenzene	1.4998	0.2940	40.91
1,2,4-Trimethylbenzene	1.5044	0.2963	40.65
2-Isopropylbenzene	1.5000	0.2941	44.96
1,2-Dichlorobenzene	1.5485	0.3178	35.81
1,3-Dichlorobenzene	1.5458	0.3165	36.12
1,4-Dichlorobenzene	1.5210 [§]	0.3044	29.20
<i>m</i> -Chlorotoluene	1.5214	0.3045	35.97
<i>o</i> -Chlorotoluene	1.5238	0.3058	35.78
<i>p</i> -Chlorotoluene	1.5199	0.3039	35.96
1-Pentanol	1.4100	0.2477	26.81

* Molar electronic polarizability (P_M) is calculated from Lorenz Lorentz equation. When Maxwell's relation [dielectric constant (ϵ) = (n^2) refractive index] holds, ϵ of Clausius Mossetti equation can be substituted with n^2 , molar refractivity (R_M) = P_M ; M , molecular mass; d , density; and f , refractivity factor. Refer to reference (7).

[†] Interaction of the electrons of polarizable molecules with the oscillating electric field of the radiation slows down the velocity of light. Permanent dipoles of the molecules also interfere but the visible radiation used to measure the refractive index carries such a rapidly alternating electric field ($\sim 10^{15}$ Hz) that the molecules are unable to orient themselves rapidly enough to keep up with the field. Only the polarizability interferes with the passage of light, thus $\epsilon = n^2$ applies for nonpolar and polar molecules. Refer to references (7,16).

[‡] Refer to references (2,3).

[§] n_D^{80} .

Polarizability

Molecular interaction forces can be loosely classified into two categories. The first is purely electrostatic in origin, arising from the permanent dipole moment, such as in Keesom and hydrogen-bonding forces. The second is a polarization force that arises from the dipole moments induced in molecules by the electric fields of nearby permanent dipoles, such as in Debye force and also polarization induced by instantaneous dipole moment formed in a neutral molecule as in dispersion (induced dipole–induced dipole) force. This may be conceptually understood as follows: the time average of dipole moment of a nonpolar molecule is zero, yet at any instant there exists a finite dipole moment given by the instantaneous positions of the electrons about the nucleus. This electric field polarizes a nearby nonpolar molecule (7).

Both nonpolar and polar molecules—when placed in an electric field, such as the one that exists between plates of a charged condenser or electric field emanating from nearby molecules—displace a negatively charged electron cloud relative to the positively charged nucleus. Polarizability is the constant of proportionality (α) between the induced dipole moment (μ_{ind}) and the electric field (E). That is [$\mu_{\text{ind}} = \alpha E$]. This is electronic polarization (P_e). Vibrational or atomic polarization (P_v) may also be present owing to the distortion of the molecular skeleton. The P_v is approximately 10% of P_e (15) and will not be considered in this study. In addition to P_e , when molecules possessing permanent dipole are present in the vapor phase, application of an electric field produces a small preferential orientation of dipoles in the

field direction leading to orientation polarization (P_o). For this type of molecules, total polarization (P_t) = $P_e + P_o$ (16). As listed in Table III, P_o of *m*-xylene is more than 80% greater than *p*-xylene at 300 K, and at 500 K, P_o of all the analytes has decreased by 40%.

Refractive index gives a tendency of a molecule to undergo polarization. Among the alkylbenzenes, refractive indices of *o*-xylene, 2-isopropyltoluene, and 1,2,4-trimethylbenzene are greater than the rest, and chlorotoluenes–dichlorobenzenes are even greater. The Lorenz–Lorentz equation (whose unit is cm^3/mole) relates refractive index to molar refractivity and molar electronic polarization. Among alkylbenzenes, increasing the size or the molecular mass also increases the electronic polarizability. However, an increase in molecular volume also increases its radius and the distance of the closest approach of the other interacting molecule, which decreases the interaction force through the $1/r^6$ factor (Table IV). The “f” factor in Table IV gives a tendency of refractivity exclusive of volume factor in the Lorenz–Lorentz equation. Note that refractive indices seems to correlate with structural properties of the analytes.

Dispersion, Debye, and Keesom interactions

Although it is not linear under temperature program condition, it is widely known that a decrease in stationary phase film thickness also decreases the t_R (17). If dispersion was the sole interaction force operating between analytes and PDMS–PEG, the t_R determined on PEG should generally be shorter because its film thickness is 0.1- μm less than PDMS. The t_R of alkylbenzenes is shorter, but chlorotoluenes, dichlorobenzenes, and 1-pentanol have a longer t_R when determined on PEG compared with the PDMS column. This decrease for alkylbenzenes is between 11% and 22%, and increases for chlorotoluenes and dichlorobenzenes are between 5% and 20%.

Analyte solubility in a stationary phase is determined by the extent of analyte–analyte, stationary phase–stationary phase, and analyte–stationary phase interactions. According to the Hawkes

Table V. The Orientation Polarization Values of Molecules in Vapor Phase Calculated at Different Temperatures*

Analyte	Dipole moment (D)	Orientation polarizability, $P_o = \times 10^{-40}(\text{C}^2\text{m}^2/\text{J})$			
		P_o (300 K)	P_o (350 K)	P_o (400 K)	P_o (500 K)
Toluene	0.31	0.86	0.73	0.64	0.51
<i>m</i> -Xylene	0.30	0.81	0.69	0.60	0.48
<i>o</i> -Xylene	0.45	1.81	1.55	1.34	1.08
<i>p</i> -Xylene	0.02	< 0.01	< 0.01	< 0.01	< 0.01
Ethylbenzene	0.37	1.22	1.05	0.91	0.73
1,2-Dichlorobenzene	2.14	41.09	35.76	30.88	24.68
1,3-Dichlorobenzene	1.54	21.21	18.18	15.91	12.79
1,4-Dichlorobenzene	0.24	0.51	0.44	0.39	0.31
<i>m</i> -Chlorotoluene	1.82	29.71	25.42	22.24	17.79
<i>o</i> -Chlorotoluene	1.43	18.32	15.24	13.78	10.99
<i>p</i> -Chlorotoluene	1.88	31.65	27.13	23.23	18.99

* (k) Refer to references (7,8). If a molecule has dipole moment (μ), there is tendency for it to become oriented parallel to the field direction, but this tendency is opposed by the thermal motion, which tends to make the orientation random. The component of the dipole moment in the field direction is $\mu \cos \omega$, where ω is the angle between the dipole orientation and the field direction. The potential energy (V) of the dipole in a local field of intensity F is $-\mu \cos \omega F$, which is small in comparison to kT (Boltzmann constant, temperature, K) under ordinary experimental conditions. By use of the Boltzmann distribution and Langevin functions, the orientation polarization of molecule with dipole moment in vapor phase was formulated by Debye. Debye–Langevin equation: $P_o = \mu^2/3kT$, where P_o = orientation polarizability ($\text{C}^2\text{m}^2/\text{J}$); C = Coulomb; u = dipole moment (D) = 3.336×10^{-30} C m; m = meter; k = Boltzmann constant = 1.38×10^{-23} J/K; J = joule; K = temperature in degrees Kelvin; and P_e = electronic polarizability. Debye–Langevin equation: total polarizability of polar molecule (P) = $P_e + P_o$.

Table VI. Intermolecular Interaction Equations*

London dispersion (induced dipole–induced dipole) energy:

$$E_l = -3/2 \frac{(A_1 A_2 - I_1 I_2)}{R_d^6 (I_1 I_2)}$$

A_1 and A_2 : polarizabilities of molecules 1 and 2.
 I_1 and I_2 : ionization potentials of molecules 1 and 2.
 R_d : distance between 1 and 2.
 E_l : dispersion interaction energy.

Debye (dipole–induced dipole) energy:

$$E_d = (1/R_d)(A_1 U_1 + A_2 U_2)$$

$U_1 U_2$: dipole moments of molecules 1 and 2.
 $A_1 A_2$: polarizabilities of molecules 1 and 2.
 R_d : distance between 1 and 2.
 E_d : Debye interaction energy.

Keesom (dipole–dipole) energy:

$$E_k = -2/3 \frac{(U_1^2)(U_2^2)}{R_d^6 kT}$$

$U_1 U_2$: permanent dipoles molecules 1 and 2.
 R_d : distance between two dipoles.
 T : temperature ($^\circ\text{K}$).
 k : Boltzmann constant.
 E_k : Keesom interaction energy.

* Refer to reference (6).

index, dispersion force of PDMS is slightly greater than PEG, which is also capable of strong Debye–Keesom and hydrogen-bonding interactions with analytes possessing similar properties. Alkylbenzenes are highly polarizable, yet their permanent dipole moments are not as strong as the hydroxyl group of PEG to form strong Debye–Keesom interactions with these molecules. This factor and decrease of film thickness by 0.1 μm in the PEG stationary phase may account for their short column residence time compared with PDMS. This is supported by the following data: (i) Among the alkylbenzenes, *o*-xylene—which has the largest dipole moment (0.45 D), orientation polarizability ($1.81 \times 10^{-40} \text{ C}^2 \text{ m}^2/\text{J}$ at 300°K), and refractivity factor (0.2970)—has the smallest decrease in t_R (11%) when determined on PEG, compared with PDMS. (b) The chlorotoluene and dichlorobenzene analogs that have greater polarizabilities and permanent dipole moments should have even stronger Debye–Keesom interactions with PEG, and this is reflected in their t_R . (c) There are dispersion, Debye and strong Keesom–hydrogen bonding interactions between 1-pentanol–PEG, which may explain the 144% increase in t_R when analyzed on PEG, compared with PDMS (see Tables I and V).

Effect of temperature on interaction forces

As discussed previously, induced dipoles in dispersion and Debye forces result from two different polarization mechanisms. Also, all molecules have electronic polarization, and only a molecule with a permanent dipole moment has additional polarization because of orientation. Therefore, according to dispersion equation listed in Table VI for nonpolar molecules, there is no temperature effect on dispersion within the usual GC operating conditions. In some cases there is a temperature effect on Debye force. This is attributable to the P_0 contribution to the total polarization of molecules with permanent dipole moment. But in very high electric field or sufficiently low temperature, P_0 vanishes, in which case this interaction is independent of temperature. According to the Keesom equation, with increasing temperature this orientation force decreases and the stationary phase becomes nonselective. This temperature effect should also apply to hydrogen bonding interaction as it is a type of Keesom force.

Separation of *m*-xylene and *p*-xylene

Although the calculated P_e and f parameters for *m*-xylene and *p*-xylene are nearly equal, because of its greater permanent dipole moment difference (0.30/0.02 D), the calculated P_0 of *m*-xylene is 80 times greater than *p*-xylene (see Tables V and VI). This implies the dipole moment re-enforcement through inductive polarization by the hydroxyl group of PEG stationary molecules is greater on *m*-xylene than *p*-xylene. Furthermore, as the permanent dipole moment of *m*-xylene is 15 times greater than *p*-xylene, its Keesom interaction with PEG is stronger. These analytes must overcome the Keesom–hydrogen bonding interaction forces operating among PEG molecules to solvate in this stationary phase. Physical and chemical parameters indicate that, compared with *p*-xylene, *m*-xylene has greater Keesom–hydrogen interaction tendency with PEG molecules, and this fact is supported by the 0.12-min t_R difference between the two analytes.

The effect of these Debye–Keesom interactions on separation in PEG is magnified in the separation of 1,3-dichlorobenzene and 1,4-dichlorobenzene. Their boiling point and dipole moment dif-

ferences are 1.12°C and 1.30 D, respectively, and they produced a 0.31-min separation on this column, compared with 0.04 min on PDMS. If the dipole moment difference is small, as in *m*-chlorotoluene and *p*-chlorotoluene, there is no improvement in separation on PEG. The Debye–Keesom effect is less when the temperature difference is large, such as 1,2-dichlorobenzene and 1,4-dichlorobenzene (6.36°C) and *o*-xylene and *p*-xylene (6.12°C) (see Table III). Although the strength of the Debye interaction force is generally considered to be less than Keesom, its utility in separating aromatic compounds in either chromatography or solvent extraction (18) is significant. The t_R difference of *m*-xylene and *p*-xylene of this study agrees with similar studies determined on nonbonded Carbowax 20M stationary phase (19).

Dipole moments of symmetrical *p*-xylene and 1,4-dichlorobenzene

p-Xylene (0.02 D) and 1,4-dichlorobenzene (0.24 D) belong to C_{2v} symmetry, and because of the cancellation of the C–CH₃ and C–Cl groups, the bond dipole moment vectors should cancel to zero in the absence of ring distortion. The electron diffraction studies on para disubstituted benzenes show that the electropositive substituent elongates and electronegative substituent compresses the aromatic ring by changing the ipso angle (20–22). The ipso angles for benzene, *p*-xylene, 1,4-dichlorobenzene, and 1,4-difluorobenzene are 120°, 117.1° ± 0.3°, 121.6° ± 0.2°, and 123.5° ± 0.1°, respectively. This compression and elongation explain the nonzero dipole moments of *p*-xylene and 1,4-dichlorobenzene.

References

1. H. Kanai, V. Inouye, R. Goo, L. Yazawa, and J. Maka. GC-MS analysis of oxygenates in gasoline. *Anal. Chem.* **66**: 924–27 (1994).
2. P.H. Howard. *Handbook of Physical Properties of Organic Compound*, Lewis Publishers, New York, NY, 1997, pp. 1–78.
3. *Aldrich Handbook of Fine Chemicals*. Aldrich Chemical Co., Milwaukee, WI, 1998. pp.133,653,1359.
4. Z. Witkiewicz. Liquid crystalline stationary phase for gas chromatography. *J. Chromatogr. Chromatogr. Rev.* **251**: 311–37 (1982).
5. C.F. Poole and S.K. Poole. Characterization of solvent properties of gas chromatographic liquid phases. *Chem. Rev.* **89**: 377–94 (1989).
6. H. Rotzsche. *Stationary Phases in Gas Chromatography*. Elsevier, New York, NY, 1991, pp. 80–83.
7. J.N. Israelachvili. *Intermolecular and Surface Forces*. Academic Press, New York, NY, 1992, pp.67–107.
8. G.M. Barrow. *Physical Chemistry*, 5th ed. McGraw-Hill Book Co. New York, NY, 1988, pp. 662–72.
9. R.J.W. Le Fevre. Molecular refractivity and polarizability. *Adv. Phys. Org. Chem.* **3**: 1–71 (1965).
10. H. Ratajczak and W.J. Orville-Thomas. *Molecular Interactions*, Vol. 3. John-Wiley & Sons, New York, NY, 1982, pp. 201–16.
11. H.H. Perkampus and E. Baugarten. Proton addition complexes of aromatic hydrocarbons. *Angew. Chem. Int. Ed.* **3**: 776–83 (1964).
12. H. Perkampus. The basicity of unsaturated organic compounds. *Adv. Phys. Org. Chem.* **4**: 195–304 (1966).
13. J.K. Ridick, W.B. Bunger, and T. Sakai. *Techniques of Chemistry: Organic Solvents, Physical Properties and Methods of Separation*, 4th ed. John Wiley & Sons, New York, NY, 1986, pp. 63–83.
14. H.W. Burns and S. Hawkes. Choice of stationary phase in gas chromatography. *J. Chromatogr. Sci.* **15**: 185–90 (1977).
15. W.J. Moore. *Physical Chemistry*, 3rd ed. Prentice Hall, Englewood Cliff, NJ, 1964, pp. 554–62.

16. D.P. Shoemaker and C.W. Garland. *Experiments in Physical Chemistry*. McGraw-Hill Book Co., New York, NY, 1962, pp. 275–79.
17. D. Rood. *A Practical Guide to the Care, Maintenance and Troubleshooting of Capillary Gas Chromatographic Systems*, 3rd ed. Wiley-VCH, New York, NY, 1999, pp. 75–77.
18. J.H. Rytting, D.R. McHan, T. Higuchi, and D.J.W. Grant. Importance of Debye interaction in organic solutions: Henry's law constant in polar liquids in nonpolar solvents and vice versa. *J. Solution Chem.* **15**: 694–703 (1988).
19. J. Bermejo, J.S. Canga, O.M. Gayol, and M.D. Guillen. Utilization of physico-chemical properties and structural parameters for calculating retention indices of alkylbenzenes. *J. Chromatogr. Sci.* **22**: 252–55 (1984).
20. G. Schultz and I. Hargittai. Molecular structure and ring distortions of p-dichlorobenzene as determined by electron diffraction. *J. Mol. Struct.* **68**: 281–92 (1980).
21. A. Domenicano, G. Schultz, M. Kolonis, and I. Hargittai. Molecular structure and ring distortions of p-xylene as determined by electron diffraction. *J. Mol. Struct.* **53**: 197–209 (1979).
22. A. Domenicano. Molecular structure and ring distortion of p-fluorobenzene as determined by electron diffraction. *J. Mol. Struct.* **78**: 97–111 (1982).
23. K. Watanabe. Ionization potentials. *J. Chem. Physics.* **26**: 542–47 (1956).

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