

Solubility of gasoline components in different lubricants for combustion engines determined by gas–liquid partition chromatography

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ABSTRACT

The solubility of typical gasoline fuel components in different lubricants for gasoline engines was determined at temperatures between 90 and 150°C. Solubility is an important parameter in combustion engine research, as the fuel during intake and compression dissolves in the lubricant film on the cylinder wall, thus escaping from the combustion processes. During the expansion and exhaust stroke the fuel is desorbed again and in this way contributes to the formation of unburned hydrocarbons in the exhaust gas. The solubility is characterized by Henry's constant. A gas–liquid partition chromatographic technique was used for the determination of Henry's constants, and gave values in good agreement with the known values for selected reference components.

INTRODUCTION

Hydrocarbon emissions from passenger cars constitute a serious environmental problem. The presence of unburned hydrocarbons in the exhaust gas from gasoline vehicles is partly due to the fact that the fuel dissolves in the lubricant film on the cylinder wall during intake and compression. Later, during the expansion and exhaust strokes, the fuel is desorbed at a time where the cylinder temperature is too low for total oxidation of the desorbed fuel, and part of the fuel is thus exhausted unburned to the environment.

There is therefore a need for more insight into the absorption/desorption phenomena, including information about the solubility of fuel components in the lubricant. Henry's constant describes the relationship between the fuel concentration in the gas phase and the concentration in the lubricant film and is therefore a measure of the solubility. From an automotive engineer's point of view, it would be advantageous to be able to select lubricants and fuels with favourable solubility characteristics in order to reduce emissions. For this study a broad range of fuel components and lubricants were selected in order to measure Henry's constant. Gas–liquid partition chromatography (GLC) was chosen as the experimental method, as this is a rapid and well documented method for this purpose [1,2].

EXPERIMENTAL

The lubricant in question was coated on Celite 545 (80–100 mesh). The coating was carried out by dissolving the support material and the lubricant in an ether. The ether was then removed by heating until only the coated material was left. The material was packed in a 1 m × 1/8 in I.D. glass column and conditioned for 24 h at 150°C. A level of 10% (w/w) of coating material was used, as 10–15% was recommended by Sugiyama *et al.* [1].

The gas chromatograph used was a Shimadzu GC 9A equipped with a thermal conductivity detector. Helium was used as the carrier gas at a flow-rate of *ca.* 25 ml/min. According to Sugiyama *et al.* [1], the influence of carrier gas flow-rate on the specific retention volume is very small. The column temperature was held constant in each experiment. The amount of fuel injected was as small as possible to ensure that Henry's law holds.

THEORY

Henry's law can be written in the following way:

$$p_2 = HX_2 \quad (1)$$

where p_2 is the partial pressure of the fuel in the gas phase, H is Henry's constant and X_2 is the molar concentration of the fuel in the liquid phase.

Henry's constant for the fuel dissolved in the lubricant can be derived from the specific retention volume according to the following equation (see, *e.g.*, Sugiyama *et al.* [1], Schramm [3] and Schramm and Sorenson [4]):

$$H = \frac{RT}{V_R M_1} \quad (2)$$

where R is the gas constant, T the column temperature, V_R the specific retention volume and M_1 the molar weight of the lubricant. As the molar weight of the lubricant can only be approximated and in some practical situations is unknown, it is more convenient to express the solubility as another constant, H^* , which is proportional to H according to

$$H^* = \frac{M_1}{M_2} \cdot H \quad (3)$$

where M_2 is the molar weight of the fuel component. The meaning of H^* can be seen by rewriting eqn. 1 in the following way:

$$\begin{aligned} p_2 = HX_2 &= H \cdot \frac{n_2}{n_1 + n_2} \approx H \cdot \frac{n_2}{n_1} \\ &= H \cdot \frac{m_2/M_2}{m_1/M_1} \end{aligned}$$

$$\begin{aligned}
 &= H^* \cdot \frac{m_2}{m_1} \\
 &= H^* Y_2
 \end{aligned} \tag{4}$$

where n_1 is the number of moles of lubricant in the liquid phase, n_2 the number of moles of fuel component in the liquid phase, m_1 the mass of lubricant in the liquid phase, m_2 the mass of fuel component in the liquid phase and Y_2 the mass concentration of fuel component in the liquid phase.

By introducing H^* instead of H , eqn. 2 can be rewritten as

$$H^* = \frac{RT}{V_R' M_2} \tag{5}$$

where M_2 is known exactly for pure hydrocarbons.

RESULTS

Henry's constants were measured at 90, 110, 130 and 150°C, as this covers the normal range for the oil-film temperature in gasoline engines. The lubricants chosen for investigation were two crude oil-based lubricants, two partly synthetic lubricants and two fully synthetic lubricants. Data for the lubricants are given in Table I. The following fuel components were tested:

paraffins: *n*-hexane, *n*-heptane, isooctane (2,2,4-trimethylpentane), cyclohexane;

olefins: 2-methyl-2-butene, trimethylpentene;

aromatics: benzene, toluene, *o*-, *m*- and *p*-xylene, ethylbenzene, *n*-propylbenzene, isopropylbenzene, trimethylbenzene;

ethers: methyl *tert.*-butyl ether (MTB).

TABLE I
PROPERTIES OF LUBRICANTS

Property	Lubricant					
	A	B	C	D	E	F
Molecular weight	425	550	550	500	—	—
Density (kg/m ³) at 15°C	870	864	961	881	874	884
Viscosity (cSt) at 40°C	82.8	107	81.5	95.5	91.4	121.7
Viscosity (cSt) at 100°C	12.0	18.1	13.7	14.3	13.9	17.0
SAE classification	10W-30	5W-50	10W-40	10W-40	10W-40	15W-50
<i>Base oil composition</i>						
Synthetic-based (%)	40 ^a	100 ^a	100 ^b	0	30 ^a	0
Crude oil-based (%)	60	0	0	100	70	100

^a Based on poly(α -olefin).

^b Based on polyol ester.

TABLE II

Lubricant	Temperature (°C)	Fuel component					
		Methyl- tert.-butyl- ether	2-Methyl- 2-butene	Trimethyl- pentene	Cyclo- hexane	<i>n</i> -Hexane	<i>n</i> -Heptane
A	90	796	1401	188	343	597	248
	110	1114	1642	304	551	772	385
	130	1302	—	478	745	—	554
	150	1521	2655	604	926	1366	724
B	90	730	1119	177	334	514	233
	110	1060	1333	299	484	723	355
	130	1138	—	388	645	900	468
	150	1527	2065	529	823	1206	745
C	90	1011	1817	257	487	893	365
	110	1112	2006	434	715	1065	554
	130	—	3340	658	1146	—	1009
	150	1987	5433	1053	1484	1512	1506
D	90	1161	1506	191	355	610	244
	110	1237	1968	325	578	—	414
	130	1400	2135	447	737	1060	575
	150	2584	2982	635	1083	1496	781
E	90	767	—	—	—	—	—
	110	982	—	—	—	—	—
	130	1498	—	—	—	—	—
	150	1502	—	—	—	—	—
F	90	672	—	—	—	—	—
	110	1121	—	—	—	—	—
	130	1465	—	—	—	—	—
	150	2188	—	—	—	—	—

MTB was chosen because it is commonly added to unleaded gasoline to increase the octane number.

Henry's constants, H^* , calculated from eqn. 5 are given in Table II. H^* is shown as a curve for isooctane and *m*-xylene in Figs. 1 and 2 to give a clearer impression of the temperature dependence.

It can be seen that H^* generally increases with increasing temperature. The increase in most instances is almost proportional to the temperature although some curves have a tendency to approach a potential function:

$$H^* = aT^b + c \quad (6)$$

where b is slightly larger than 1. This tendency is most pronounced for lubricant C.

Some general features of the lubricants' influence on solubility can be seen. The differences in H^* values are generally small from one lubricant to another, except for lubricant C. The differences seem to increase with increasing temperature. Lubricant

Iso-octane	Benzene	Toluene	<i>o</i> -Xylene	<i>m</i> -Xylene	<i>p</i> -Xylene	Ethylbenzene	<i>n</i> -Propylbenzene	Isopropylbenzene	Trimethylbenzene
222	411	160	52	61	62	68	31	39	24
343	596	264	95	108	111	124	58	72	47
498	957	381	156	179	187	197	102	125	82
700	1124	537	235	271	270	287	160	186	135
211	388	148	50	59	61	67	30	38	24
315	549	239	88	105	105	118	56	70	45
446	—	341	141	163	157	193	94	108	76
551	971	482	205	238	241	252	143	162	119
335	385	153	51	61	62	68	30	40	—
476	567	250	92	110	111	123	60	74	49
769	1124	452	181	212	229	238	127	148	103
1034	1524	638	300	321	320	342	207	234	161
299	429	160	51	60	61	69	31	39	24
363	677	270	92	108	111	121	57	72	46
507	807	388	150	175	179	192	101	117	80
853	1227	572	250	274	277	294	166	193	135
220	400	154	—	—	—	—	—	—	—
323	599	250	—	—	—	—	—	—	—
464	815	386	—	—	—	—	—	—	—
609	1070	525	—	—	—	—	—	—	—
211	371	145	—	—	—	—	—	—	—
321	587	258	—	—	—	—	—	—	—
477	920	384	—	—	—	—	—	—	—
659	1082	563	—	—	—	—	—	—	—

C shows the highest H^* value in almost every instance, the only exceptions being with MTB, benzene and toluene. For all the paraffins and olefins tested the performance of lubricant C is considerably different. This is obviously due to the special structure of lubricant C, which is a fully synthetic lubricant with a polyol ester structure. As an ester is a much more polar compound than paraffins and olefins it will not dissolve these components as easily as the other lubricants that mainly consist of paraffins and olefins.

From Figs. 1 and 2 it can also be seen that lubricant B in every instance gives the lowest H^* value although the deviations from the other lubricants are smaller than with lubricant C.

The measurements have thus show that the fully synthetic lubricants B and C lie in the outer sections of the observed H^* range. This indicates that the use of more specialized (synthetic) lubricants results in solubility behaviour that is substantially different from that of typical crude oil-based lubricants. This could be important in efforts to reduce hydrocarbon emissions from gasoline engines, as the use of synthetic

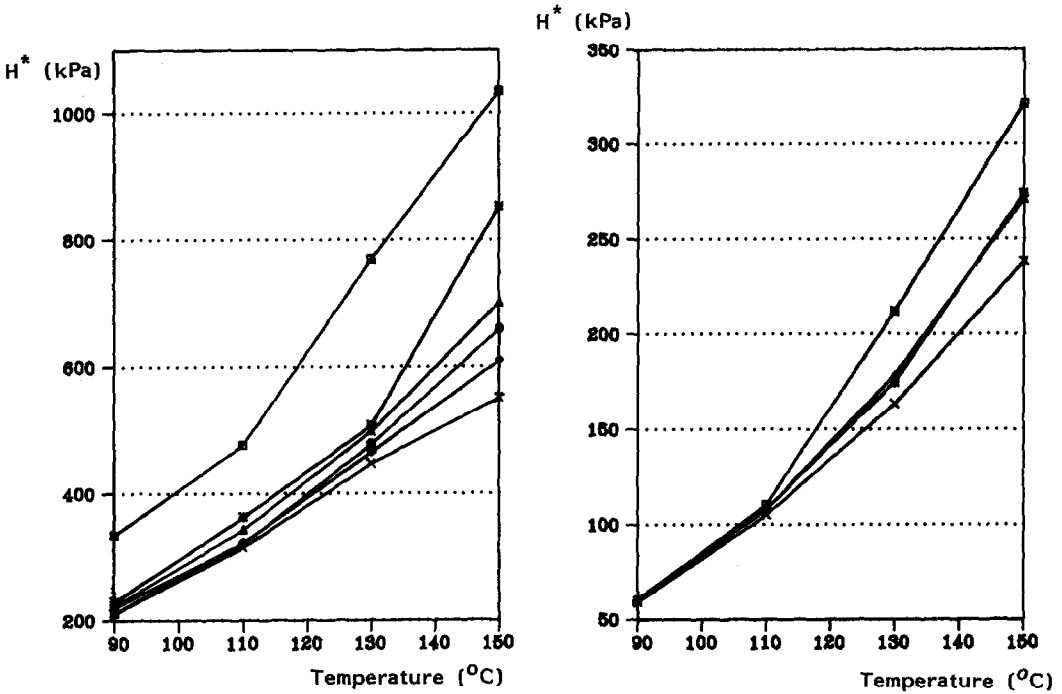


Fig. 1. H^* as a function of temperature for isooctane in equilibrium with six different oils: Δ = oil A; \times = oil B; \square = oil C; $*$ = oil D; \diamond = oil E; \circ = oil F.

Fig. 2. H^* as a function of temperature for *m*-xylene in equilibrium with four different oils: Δ = Oil A; \times = oil B; \square = oil C; $*$ = oil D.

lubricants with very high H^* values would reduce the amount of fuel dissolved in the lubricant film, and therefore the amount of unburned hydrocarbons found in the exhaust gas.

In Table III the observed H^* values for *n*-hexane and *n*-heptane are compared with results of other workers. Sugiyama *et al.* [1] measured the solubility of *n*-hexane and *n*-heptane in C_{28} – C_{36} *n*-alkane solvents, while Dent and Lakshminarayanan [5] suggested an extrapolation method for calculating the Henry's constant of *n*-alkanes in squalane ($\text{C}_{30}\text{H}_{62}$), based on measurements of Henry's constants for methane, ethane, propane and *n*-butane in squalane from Chappelow and Prausnitz [6]. The values of H^* , calculated by this method, are given in Table III. As the number of carbon atoms found in lubricant molecules is of the same magnitude as that for squalane, this is an acceptable comparison.

The H^* values for the lubricants (except lubricant C) are very close to the values obtained by other workers at 90 $^{\circ}\text{C}$. At 150 $^{\circ}\text{C}$ the values of Dent and Lakshminarayanan [5] are slightly different from those found in this investigation, but this is probably caused by the uncertainty connected with the calculation method that they proposed.

Table IV gives the H^* values for the different categories of fuel components arranged according to increasing number of carbon atoms. The results showed, as

TABLE III

 H^* VALUES (kPa) FOR *n*-HEXANE AND *n*-HEPTANE DISSOLVED IN DIFFERENT SOLVENTS

Alkane	Temperature (°C)	This study: lubricant				Sugiyama <i>et al.</i> [1]			Dent and Laksh- minarayanan [5]: C ₃₀ H ₆₂
		A	B	C	D	C ₂₈ H ₅₈	C ₃₂ H ₆₆	C ₃₆ H ₇₄	
<i>n</i> -Heptane	78	—	—	—	—	146	157	168	—
	84	—	—	—	—	178	192	206	—
	90	250	230	365	240	216	232	250	244
	96	—	—	—	—	260	281	301	—
	102	—	—	—	—	313	338	360	—
	110	377	353	553	414	—	—	—	346
	130	553	465	1009	577	—	—	—	462
	150	716	744	1507	781	—	—	—	599
<i>n</i> -Hexane	78	—	—	—	—	369	429	454	—
	84	—	—	—	—	468	507	540	—
	90	596	515	900	615	553	598	638	696
	96	—	—	—	—	652	705	752	—
	102	—	—	—	—	768	829	883	—
	110	774	726	1074	841	—	—	—	895
	130	1222	907	1300	1070	—	—	—	1243
	150	1374	1215	1526	1507	—	—	—	1740

expected, that the solubility increases with increasing number of carbon atoms. It can also be seen that aromatic compounds are more soluble than the corresponding paraffins and olefins with the same carbon number. An exception is cyclohexane, which is more soluble than both *n*-hexane and benzene.

n-Heptane is almost as soluble as isooctane, which indicates that a more branched structure results in a lower solubility.

CONCLUSIONS

These experiments have shown that GLC is suitable for determining Henry's constants for fuel components dissolved in lubricants for gasoline engines. This was verified by comparing the results with those given by other workers.

Most of the lubricants investigated gave Henry's constants that did not differ very much at lower temperatures (90°C). At higher temperatures (150°C), the differences were slightly larger. It was remarkable that of the two synthetic lubricants tested, one gave the highest and the other the lowest solubilities of all the oils tested. Henry's constant generally increased in proportion to the temperature.

The results showed, as expected, that the solubility increased with increasing carbon number of the fuel component. Aromatic components were more soluble in the

TABLE IV

*H** VALUES (kPa) ACCORDING TO MOLECULAR STRUCTURE OF THE FUEL COMPONENTS AND ARRANGED IN ORDER OF INCREASING CARBON NUMBER

Compound	Lubricant							
	90°C				150°C			
	A	B	C	D	A	B	C	D
<i>Ether</i>								
MTB	796	730	1011	1161	1521	1527	1987	2584
<i>Olefins</i>								
2-Methyl-2-butene	1401	1119	1817	1506	2655	2065	5433	2982
Trimethylpentene	188	177	257	191	604	529	1053	635
<i>Paraffins</i>								
Cyclohexane	343	334	487	355	926	823	1484	1083
<i>n</i> -Hexane	597	514	893	610	1366	1206	1512	1496
<i>n</i> -Heptane	248	233	365	244	724	745	1506	781
Isooctane	222	211	335	229	700	551	1034	853
<i>Aromatics</i>								
Benzene	411	388	385	429	1124	971	1524	1227
Toluene	160	148	153	160	537	482	638	572
<i>o</i> -Xylene	52	50	51	51	235	205	300	250
<i>m</i> -Xylene	61	59	61	60	271	238	321	274
<i>p</i> -Xylene	62	61	62	61	270	241	320	277
Ethylbenzene	68	67	68	69	287	252	342	294
<i>n</i> -Propylbenzene	31	30	30	31	160	143	207	166
Isopropylbenzene	39	38	40	39	186	162	234	193
Trimethylbenzene	24	24	24	24	135	119	161	135

lubricants than the corresponding paraffins and olefins with the same carbon number. Cyclic paraffins such as cyclohexane are an exception, as cyclohexane was more soluble than benzene.

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