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Correlation between the Turbidity Temperature of *p*-Anisaldehyde in Mineral Oil and the Aniline Point

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Supporting Information

ABSTRACT: Due to the toxicity of aniline, it is desirable to find a replacement for aniline in the aniline point method. Here correlations between the aniline point and the turbidity temperature for 1,2-dimethoxybenzene, *o*-anisaldehyde, and *p*-anisaldehyde are presented. 1,2-Dimethoxybenzene correlates well to the aniline point but with a significantly lower turbidity point compared to the aniline point. *p*-Anisaldehyde also correlates well to the aniline point, and both the aniline point and the turbidity temperature are very similar in magnitude, making it a very strong candidate for replacement of aniline in the aniline point analysis.

INTRODUCTION

In many industrial applications, it is often desirable to know the "solvent power" of a solvent, that is, how readily a particular substance can be dissolved in the liquid. When the solvent in question is a hydrocarbon, the solvent power is often referred to as its capability to dissolve polar substances. This is, in particular, important in the printing ink industry, where polar dyes, resins, and other additives need to be dissolved in a hydrocarbon liquid.[1] A similar situation exists in the lubrication industry, where additives such as antioxidants and friction modifiers are often dissolved in the base oil.[2] The base oil should then have sufficient solubility power to dissolve the substances and allow them to stay in solution. An opposite problem can occur where the solubility power of a liquid is sufficiently high to readily migrate into rubber seals to such a degree that both the dimension stability and elasticity of the rubber changes sufficiently to destroy its function.[3]

From this perspective, it is desirable to characterize the solubility properties of petroleum products so that accurate predictions of the liquid's solubility and compatibility with other materials can be made. One such analysis method is the aniline point at which equal volumes of the hydrocarbon liquid and aniline are heated until they become miscible. The temperature at which the solution becomes turbid is called the aniline point. A low aniline point is indicative of a high solubility power and vice versa. The aniline point analysis was originally designed as a quick and easy way to determine the aromatic content in petroleum fuel.[4] Since then the aniline point method has become formalized into several standards, such as the ASTM D611,[5] IP 2,[6] and ISO 2977,[7] and it is now a common way to, for example, estimate aromatic content in lubricant base oils,[2] gauge the rubber compatibility[3] of petroleum products, and aid in the formulation of printing inks.[1] The method is attractive due to its simplicity, repeatability, and the availability of aniline.

However, a number of health and safety concerns have been raised over the use of aniline. It is suspected to cause cancer and genetic defects, and it is very toxic to aquatic life.[8] This raises the question if it is possible to find a replacement for aniline in the aniline point analysis[5] with fewer health and safety concerns.

It is possible to characterize solubility using other methods, such as the Hansen solubility parameters.[9] The Hansen solubility parameters are based on the Hildebrand solubility parameter, which is a function of the cohesive energy density of a material.[10] Different materials with similar Hildebrand parameters tend to be soluble in each other. This works well for nonpolar materials but less well for polar ones. Hansen tried to compensate for this by separating the solubility parameter into three components, each corresponding to either the dispersive, polar, or hydrogen bonding interactions. Again, two compounds with similar Hansen solubility parameters tend to be soluble in each other. However, to determine the Hansen solubility parameters for such a complex liquid as a typical base oil is a very labor intensive process, not suitable for routine analysis and batch control in the industry. But it may be possible to find a compound with sufficiently similar Hansen solubility parameters to those of aniline with less health and safety concerns to complement or replace aniline in the aniline point test.

Many such candidates were found; however, most of those candidates suffered from similar health and safety concerns as those of aniline. A few compounds were promising, and 1,2-dimethoxybenzene, *o*-anisaldehyde, and *p*-anisaldehyde were selected to see if their turbidity temperatures correlated well with the aniline point. 1,2-Dimethoxybenzene is registered with the European Chemicals Agency (ECHA)[11] as a nonclassified chemical. *o*-Anisaldehyde and *p*-anisaldehyde are currently not registered with ECHA but are unlikely to be registered as classified chemicals.[11]

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Table 1. Selected Safety Information for the Different Substances[12]

	aniline	1,2-dimethoxybenzene	*o*-anisaldehyde	*p*-anisaldehyde
symbol	GHS05, GHS06, GHS08, GHS09	GHS07	GHS07	none
signal word	danger	warning	warning	none
hazard statements	H301, H311, H317, H318, H331, H341, H351, H372, H400	H302	H315, H319, H335	none
precautionary statements	P261, P273, P280, P301 + P310, P305 + P351 + P338, P311	none	P261, P305 + P351 + P338	none

EXPERIMENTAL SECTION

Materials. Aniline was of analytical grade (99.5%) and purchased from VWR. *o*-Anisaldehyde (2-methoxybenzaldehyde, ≥97%), *p*-anisaldehyde (4-methoxybenzaldehyde, 98%) and 1,2-dimethoxybenzene (99%) were purchased from Sigma-Aldrich. All chemicals were used without further purification, and relevant safety information for the chemicals can be found in Table 1. The petroleum products were selected to include a wide range of aniline points. Specifically, naphthenic and paraffinic base oils were used, as were two different poly-α-olefins (PAO). These base oils also represented a wide range of crude origins, viscosities, degrees of refining, and boiling point intervals to ensure that the tested mineral oils were as diverse as possible. Heptane is also included, as it is a reference material specified in the ASTM D611[5] method with a known aniline point of 69.3 °C. The Hansen solubility parameters[9] for the substances are shown in Table 2, and the molecular structures are shown in Figure 1.

Table 2. Hansen Solubility Parameters for the Different Substances[a]

	dispersion	polarity	hydrogen bonding
aniline	19.4	5.1	10.2
1,2-dimethoxybenzene	19.2	4.4	9.4
o-anisaldehyde	19.4	11.9	8.3
p-anisaldehyde[b]	N/A	N/A	N/A

[a]From ref 9. [b]To the authors knowledge, no Hansen solubility parameters for *p*-anisaldehyde have been published.

Methods. The aniline point measurements were performed using an automatic aniline point tester (NAE 440, Normalab, France) using a modified ASTM D611 method. The method specifies that the average of at least three consecutive temperature recordings of the temperature at which the oil–aniline mixture becomes turbid is to be used as the aniline point. The modification of the method consisted only of using the average of two consecutive temperature recordings of the turbidity temperature instead of the specified three, provided that the temperatures did not differ more than 0.1 °C. The automatic aniline point tester was also used in determining the turbidity point for *p*-anisaldehyde and 1,2-dimethoxybenzene in oil using the same modified ASTM D611 method. As *o*-anisaldehyde is a solid at room temperature (mp = 34–40 °C), the mass corresponding to 20 mL was added to a beaker together with 20 mL of oil. The mixture was then heated and stirred until the mixture became miscible. The solution was then allowed to cool under continuous stirring, and the temperature at which the solution turned turbid was recorded. The average of at least three such recordings was reported as the turbidity temperature. The viscosity and density were determined using an Anton Paar SVM 3000 Stabinger viscometer, and the refractive index was measured using a Schmidt + Haensch automatic refractometer.

RESULTS AND DISCUSSION

The aniline point and the turbidity temperature for mineral oil and 1,2-dimethoxybenzene can be seen in Figure 2. A very

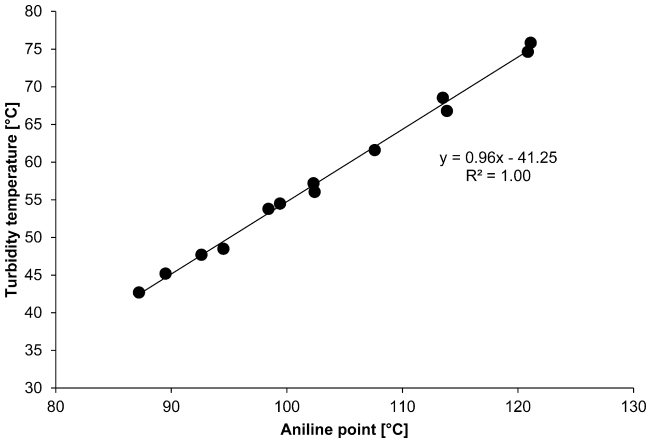
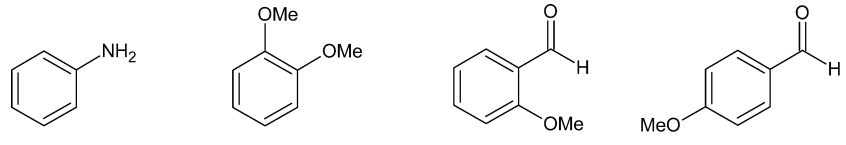


Figure 2. Correlation between the aniline point and the turbidity temperature for 1,2-dimetoxybenzene.

strong correlation between the aniline point and turbidity temperature was observed. The correlation displays a linear behavior with little scatter, and the data can be fitted well using simple linear regression. The resulting relationship between the turbidity temperature (TT) and the aniline point (AP) can be described as $TT = 0.96*AP - 41.25$ °C, with a coefficient of determination (R^2) very close to unity. While the correlation is strong and the slope of the regression line is close to one, the turbidity temperature is significantly lower than the corresponding aniline point. This would make it difficult to use 1,2-dimethoxybenzene as a replacement for aniline for products



Aniline | 1,2-Dimethoxy-benzene | *o*-Anisaldehyde | *p*-Anisaldehyde

Figure 1. Molecular structure of the substances used in the experiments.

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with an aniline point below 70 °C, as the resulting turbidity temperature would be close to or below ambient temperature. The equipment used to determine the turbidity temperature would then have to be able to handle subambient temperatures, which is not always the case. However, from this it also follows that it might be easier to determine the turbidity temperature for 1,2-dimethoxybenzene for heavy products with a high aniline point, as the heating requirements would be correspondingly lower.

The aniline point and the turbidity temperature for both *o*-anisaldehyde and *p*-anisaldehyde are shown in Figure 3. The

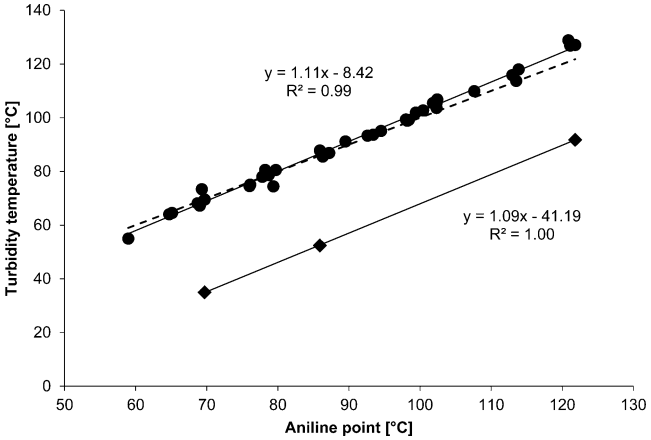

Figure 3. Correlation between the aniline point and the turbidity temperature for *p*-anisaldehyde (●) and *o*-anisaldehyde (◆). As a reference, a dashed line with a slope of unity and an intercept of zero is included.

turbidity temperature for *o*-anisaldehyde was found to correlate well to the aniline point. Only a few oils were tested, as the substance is solid at ambient temperature, which makes it impractical as a replacement for aniline. While *o*-anisaldehyde might be unsuitable as a replacement, *p*-anisaldehyde would probably be a better candidate, as it is liquid at room temperature. To the best of our knowledge, the Hansen solubility parameters of *p*-anisaldehyde have not been determined nor calculated. However, it is reasonable to assume that the solubility parameters of *p*-anisaldehyde should be similar to that of aniline. As can be seen in Figure 3, the aniline point correlates very well to the turbidity temperature of *p*-anisaldehyde. The relationship between the turbidity temperature and the aniline point can be described as $TT = 1.11*AP - 8.42$ °C, again with a R^2 very close to unity. Further, both the aniline point and the turbidity temperature are very similar in magnitude for all products tested here. This is illustrated in Figure 3, where a dashed line with slope of unity and an intercept of zero is included for comparison. This shows that within experimental errors aniline could simply be replaced with *p*-anisaldehyde in the aniline point method.

To verify that there is no significant difference in the correlation between the aniline point and turbidity temperature for naphthenic and paraffinic base oils, the correlation for naphthenic base oils can be found in Figure 4. The correlation for paraffinic base oils, including poly-α-olefins, is shown in Figure 5. No significant difference in the slope or the intercept for the linear regression analysis of the two subsets of samples could be noted. From this we can conclude that the correlation between aniline point and the turbidity temperature of *p*-

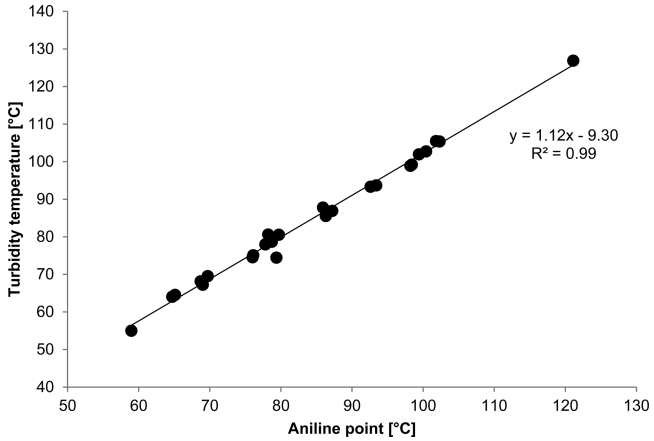

Figure 4. Correlation between the aniline point and the turbidity temperature for *p*-anisaldehyde in naphthenic base oils only.

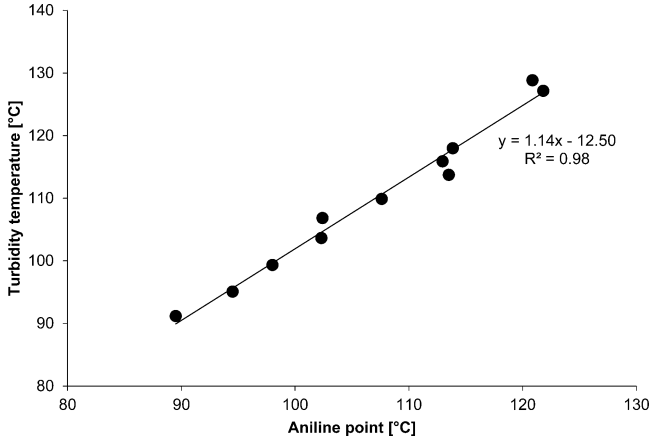

Figure 5. Correlation between the aniline point and the turbidity temperature for *p*-anisaldehyde in paraffinic base oils and poly-α-olefin.

anisaldehyde is equally valid for all products tested here. This makes *p*-anisaldehyde a very suitable candidate to replace or complement aniline in the equivalent aniline point analysis.

As the aniline point method has been used in the industry for a long time, there is a vast empirical knowledge among the users of base oils regarding what aniline point range works for a particular application. It is important to consider how implementations of changes of the current method would affect this particular empirical knowledge. The results presented here could be used to replace aniline with *p*-anisaldehyde locally in the laboratories and the results recalculated and presented as an aniline point. In this way the current standards remain unchanged but the use of *p*-anisaldehyde is unlikely to gain acceptance in the industry. Another possibility is to keep aniline as the standard but allow for the use of *p*-anisaldehyde instead combined with a conversion factor. This would keep the changes to the current standards to a minimum but give the option to replace aniline. Finally, there is the possibility to either replace aniline outright in the current standards or to create a new standard using *p*-anisaldehyde instead. From a practical point of view, to include the option of using *p*-anisaldehyde in the standard is attractive as it would validate the use of the replacement to aniline while still allowing the use of aniline. From an industrial perspective, the base oils included in this study represent such a wide range of crude origins, viscosities, degree of refining, and boiling point intervals that

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any empirical relationship to the aniline point should also hold for the *p*-anisaldehyde turbidity temperature. From a health and safety perspective, it could be worthwhile for the different standardization bodies to investigate phasing out the use of aniline in this application, and *p*-anisaldehyde seems to be a suitable replacement.

CONCLUSIONS

The correlation between the aniline point and the turbidity temperatures for carefully selected compounds has been investigated in an effort to find a possible replacement molecule for the aniline point analysis. The correlation for 1,2-dimethoxybenzene to the aniline point was found to by very linear, with little scatter. However, as the corresponding turbidity temperature for 1,2-dimethoxybenzene was considerable lower than the aniline point, it is less useful as a replacement for petroleum products, with an aniline point below about 70 °C. The correlation for *p*-anisaldehyde to the aniline point was also found to be very linear, with little scatter. Both the aniline point and the turbidity temperature are very similar in magnitude for all products tested here, making it a very strong candidate to replace or complement aniline in the aniline point analysis.

ASSOCIATED CONTENT

Supporting Information

Physical properties for the petroleum products used here. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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