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Hydrocarbon absorption in tetrachloroaluminate catalysts effects of catalyst cation, hydrocarbon polarity and charge transfers via molecular modeling

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Abstract

Absorption levels were obtained for five hydrocarbons of increasing polarity in three tetrachloroaluminate catalysts of increasing cation size. Obtained absorption levels were found to correlate with cation size and hydrocarbon polarity. Molecular modeling was used to calculate charge transfers from absorbed hydrocarbons to the catalysts. Obtained charge transfers were also found to correlate with hydrocarbon absorption levels. Lastly, polarities calculated for absorbed free-radicals suggest a mechanism for previous findings. In the previous effort, resid conversion was found to go through a maximum with increasing hydrogen tetrachloroaluminate contents in a sodium tetrachloroaluminate catalyst. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

In previous work [1], tetrachloroaluminates were investigated as catalysts for molecular weight reduction of petroleum and shale oil resids. The reason for using these catalysts was to provide a highly polar surface to trap free radicals and/or ions produced during molecular weight reduction. The absorbed/stabilized free radicals or ions would then react with each other to form low molecular weight aromatic products. The products would have about the same hydrogen/carbon ratio as the resid feed thereby minimizing the large hydrogen consumptions normal with commercial technology.

Our primary catalyst to perform molecular weight reductions and subsequent free-radical/ion reactions was molten sodium tetrachloroaluminate (NaTA). We also used molten hydrogen tetrachloroaluminate (HTA) as a hydrogen transfer catalyst to remove sulfur and other heteroatoms.

We noted that resid conversion to liquid product first increased and subsequently decreased as the level of HTA was increased (Fig. 1). The method of liquid product removal was via a continuous hydrogen purge through the reaction vessel. Other investigators [2] have also noted yield maximums due to variations in tetrachloroaluminate compositions.

We reasoned that the liquid product increase was due to a stronger catalyst attraction for free radicals with increasing HTA content. The opposing force causing the conversion decrease was due to increasing

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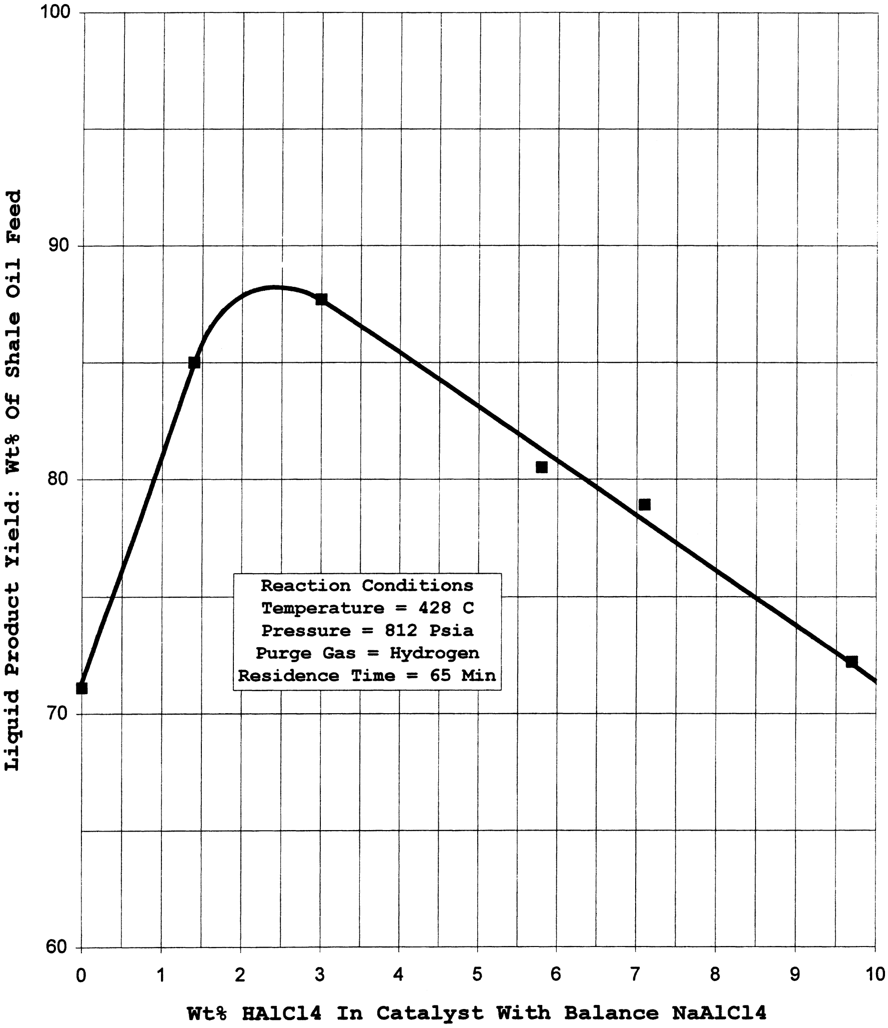

Fig. 1. Liquid product yield versus catalyst $HAlCl_4$ content.

liquid product absorption levels on the catalyst as HTA content increased. The results of this work suggest that these two opposing mechanisms are correct.

2. Objectives

The purpose of the current investigation was to obtain experimental absorption data and correlate it to catalyst type and the polarity of absorbed hydrocarbons. In an absorption test, known weights of hydrocarbon and catalyst were first mixed at room temperature. Then, the mixture was heated to 400°C at 0.8 atm under a nitrogen blanket. Under these conditions, part of the hydrocarbon was vaporized off and collected via cooling to room temperature. The difference between the initial and vaporized hydrocarbon weights was equated to that absorbed. We noted neither cracked hydrocarbon fragments in the vaporized hydrocarbons nor any coke formation on the catalyst. Hence, there were no hydrocarbon reactions that occurred in these absorption tests.

We also wanted to obtain via molecular modeling the charged transfers occurring during absorption, and to correlate these charge transfers with the level of hydrocarbon absorption. To this end, we used the

Table 1
Hydrocarbon and catalyst properties

Hydrocarbon data		Catalyst data	
Hydrocarbon	Polarity debye	Catalyst	Cation radius[a] (Å)
N-Methyl-2-pyrrolidinone	4.09		
Quinoline	2.18	$KAlCl_4$	1.51
Diethylamine	1.11	$NaAlCl_4$	1.13
o-Xylene	0.45	$Zn(AlCl_4)_2$	0.74
Decane	0.00		

[a] Cation radius for coordination number equal to 4.

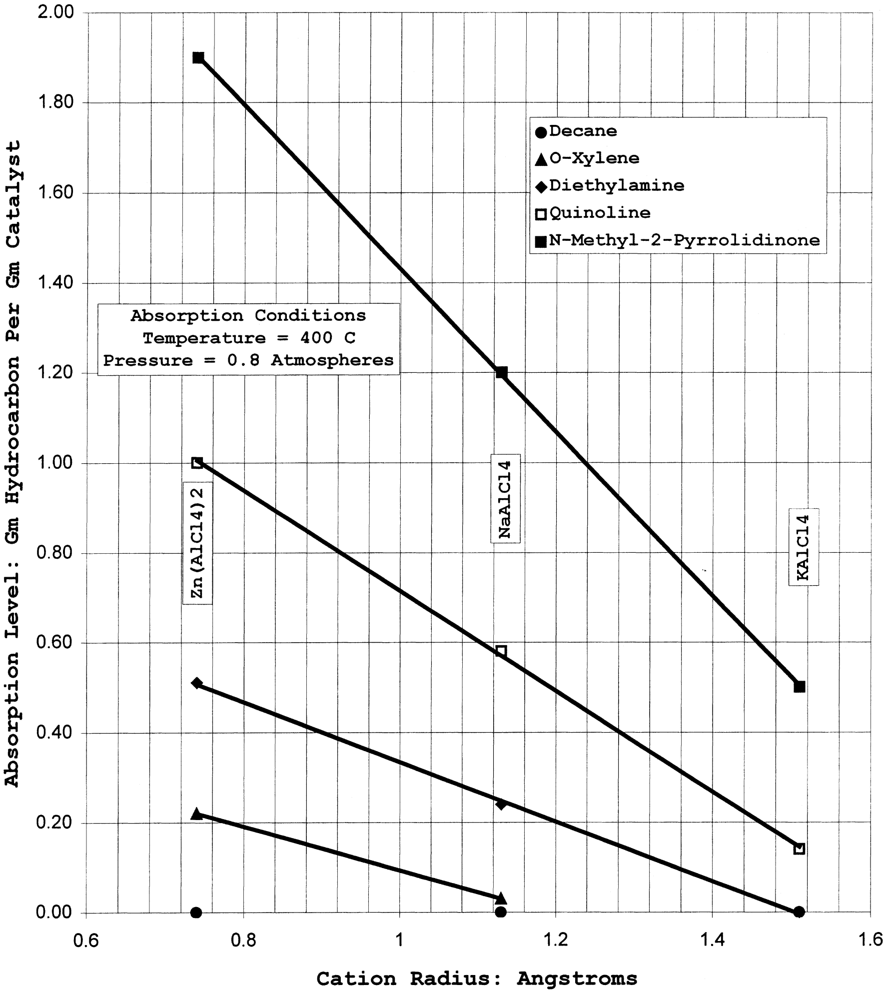

Fig. 2. Absorption of hydrocarbons with various polarities into tetrachloroaluminates with cations of differing ionic sizes.

semi-empirical quantum mechanics model ZINDOS/1 in the HyperChem® program.

The final objective of both these two efforts was to explain the yield maximum obtained in the previous work via increasing HTA in NaTA.

3. Materials evaluated

We tested five hydrocarbons of increasing polarity in Debye units [3] i.e., decane, *o*-xylene, diethylamine (DEA), quinoline and *n*-methyl-2-pyrrolidinone (NMP). Three tetrachloroaluminates were used i.e., zinc ($ZnTA_2$), sodium (NaTA) and potassium (KTA). The properties of the hydrocarbons and catalysts tested are given in Table 1.

4. Experimental absorption results

We found that absorption level decreased with increasing cation radius. The published cation radius data used [4] is for a coordination number (CN) of four. The largest levels of absorption were obtained

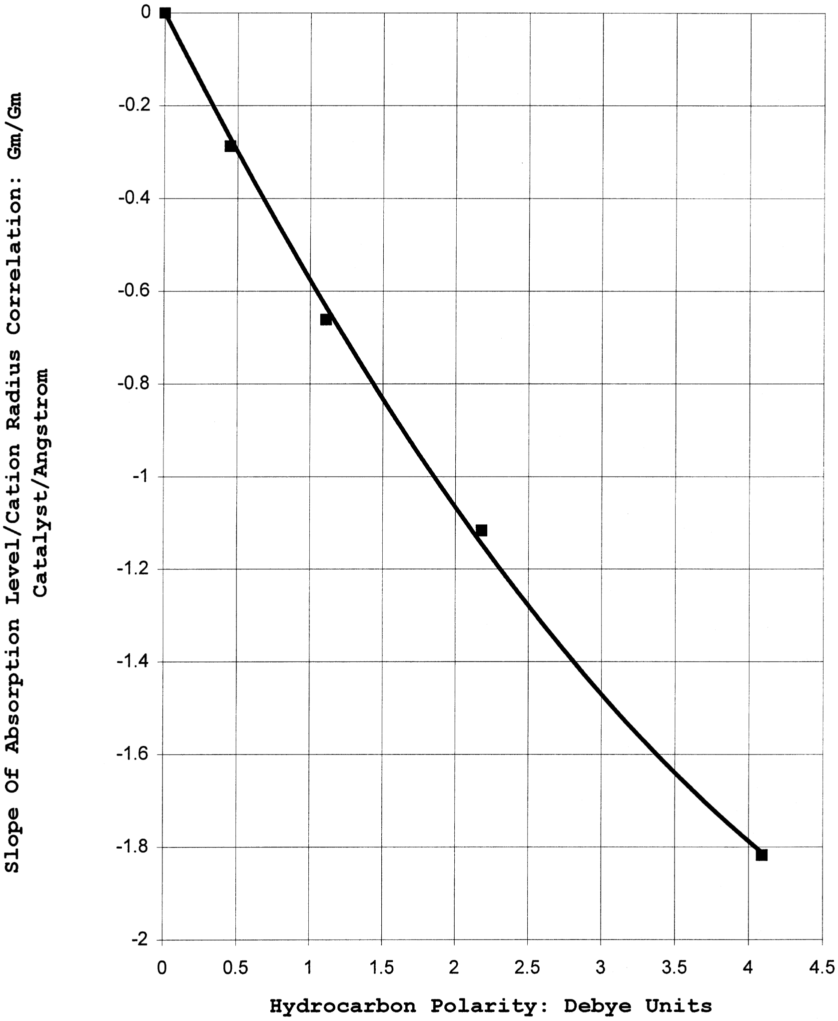

Fig. 3. Slope of absorption level/cation radius correlation versus absorbed hydrocarbon polarity.

with NMP which exhibits the highest polarity (Fig. 2). In contrast, decane with the lowest polarity did not absorb in any of the catalysts. We also noted that the slopes and absorption intercepts of the correlations in Fig. 2 are very accurately related to hydrocarbon polarity (Figs. 3 and 4). Based on these results, one can calculate absorption levels for tetrachloroaluminates by knowing only the hydrocarbon polarity and cation size. However, this correlation may not be universal for other molten salts. Also, it does not explain the resid yield maximum obtained in the previous work.

5. Molecular modeling approach

First, all hydrocarbon and catalyst structures were energy minimized separately. A linear correlation was found between published cation radius data and the separation distance between the aluminum atom and the cation calculated via the ZINDOS/1 model (Fig. 5). This result shows that the ZINDOS/1 model yields consistent results for all the cations studied.

Then energy minimization was again performed after docking, mathematical absorption, of specific

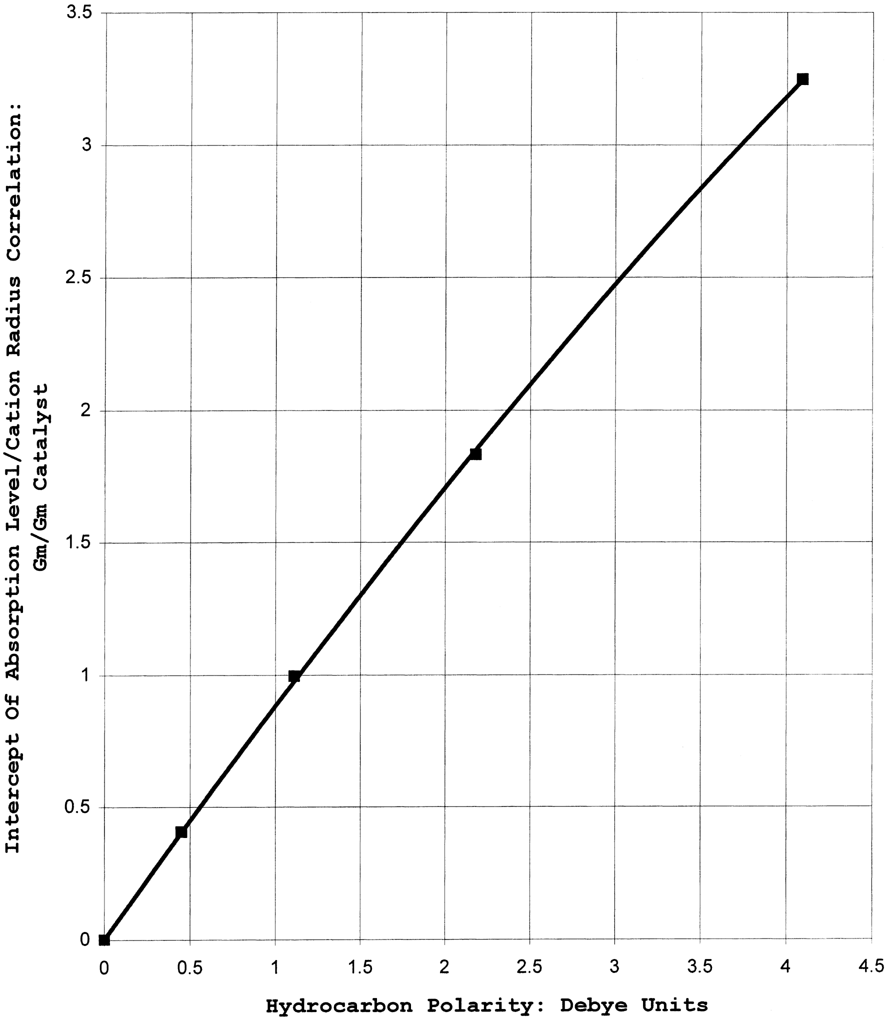

Fig. 4. Intercept of absorption level/cation radius correlation versus absorbed hydrocarbon polarity.

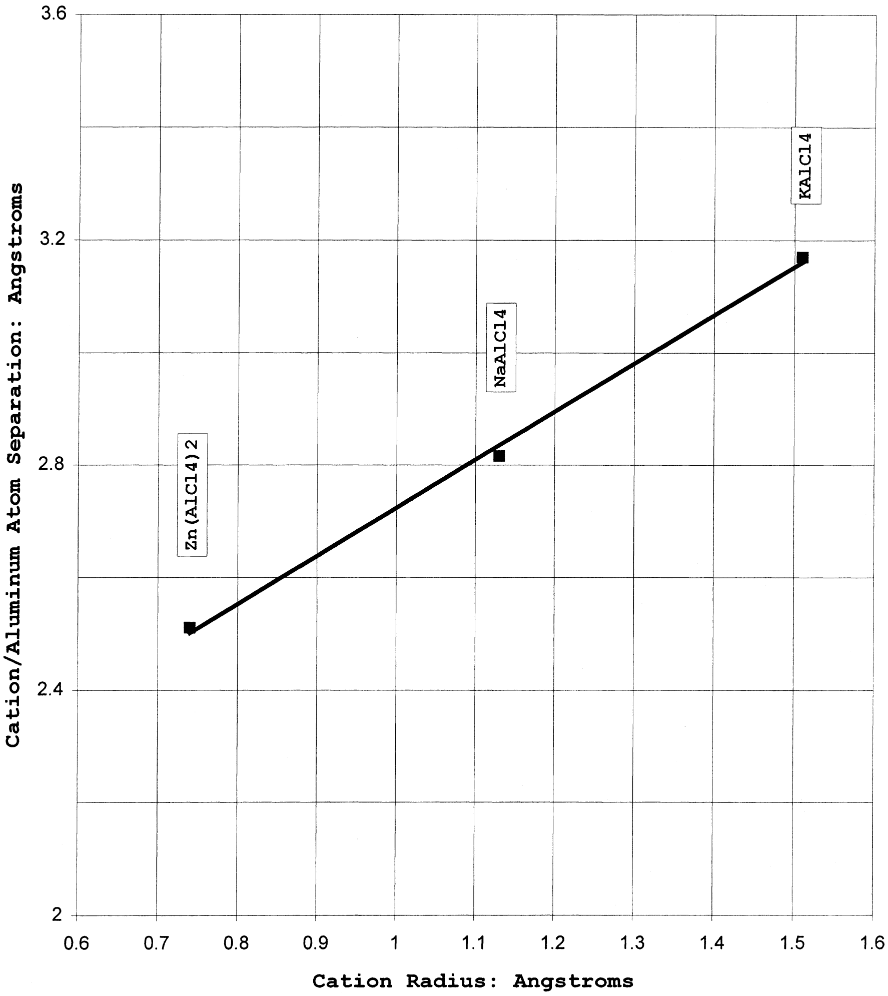

Fig. 5. Separation distance between aluminum atom in the tetrachloroaluminate ion and the cation versus cation radius.

hydrocarbons and catalysts. Several initial docking positions were tried for each hydrocarbon/catalyst combination to find the lowest final absorbed energy levels. Generally, the lowest energy levels were obtained with an initial position of the most negative atom of the hydrocarbon near the Al atom in the $AlCl_4$ anion. The exception was the NMP/NaTA combination where the initial NMP position was between the Al atom and the Na cation. This is probably due to NMP having two well separated negatively charged atoms, i.e., nitrogen and oxygen. In most energy minimized absorbed structures, the chlorine atoms form an umbrella around the cation. The absorbed hydrocarbon is near the aluminum atom at the top of the umbrella, e.g., Fig. 6.

In ZINDOS/1 docking, negative charge is transferred between hydrocarbon and catalyst and all atom to atom distances varied to minimize overall absorption energy. After docking, ZINDOS/1 calculates the charges on the hydrocarbon and catalyst molecules in electrostatic units (ESU). We used absolute charges and charge difference between the hydrocarbon and the catalyst to correlate measured absorption levels. Also, ZINDOS/1 calculates hydrocarbon polarity induced by its charge. The induced polarity was always found to be different from that for the hydro-

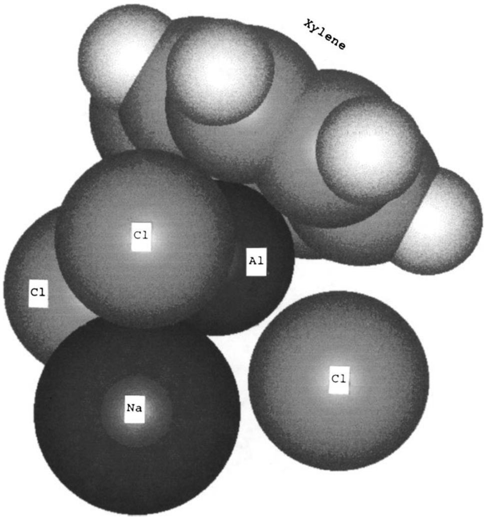

Fig. 6. Xylene absorbed on sodium tetrachloroaluminate.

carbon by itself. We investigated individual hydrocarbon polarity and induced hydrocarbon polarity to correlate absorption results.

6. Molecular modeling results for experimental hydrocarbons

Next, we performed energy minimizations using one to four absorbed hydrocarbon molecules in a monolayer around one $ZnTA_2$ molecule. Our purpose was to determine the number of absorbed molecules that yield significant charge transfers which correlate with hydrocarbon absorption. We found that absorption level correlates very well with total anion charge for one to three molecules in the monolayer (Fig. 7). This is fortuitous in that computational time can be minimized with only one molecule absorption. We

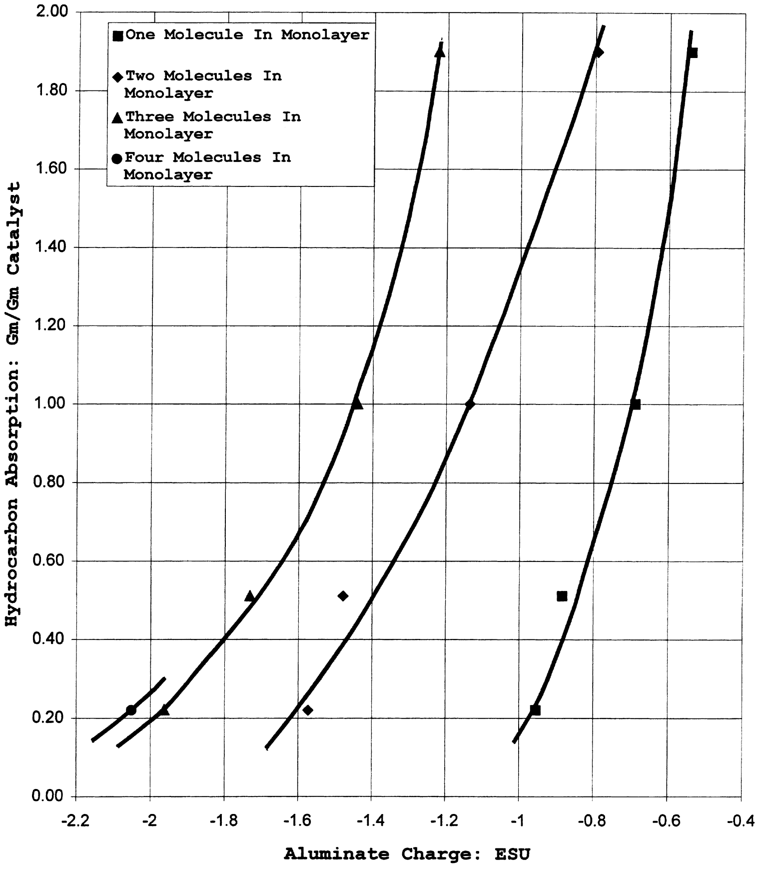

Fig. 7. Hydrocarbon absorption versus aluminate charge and number of molecules in the monolayer around zinc tetrachloroaluminate.

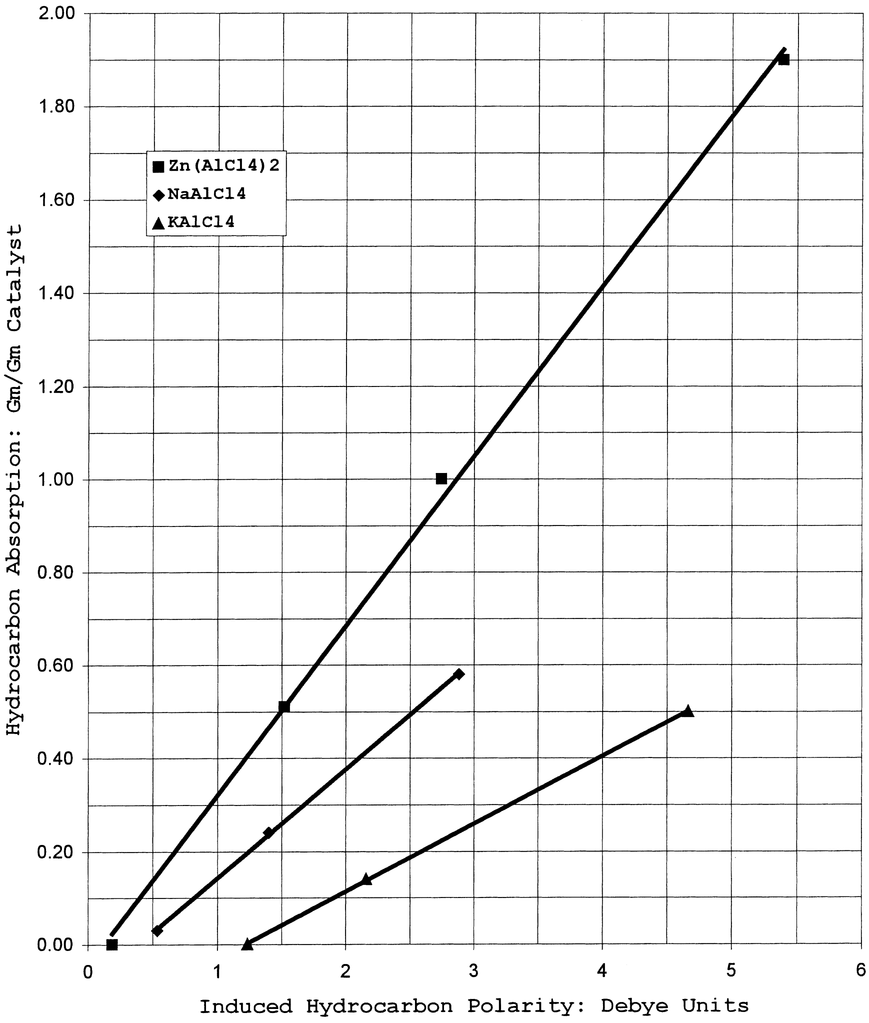

Fig. 8. Hydrocarbon absorption versus hydrocarbon polarity induced by tetarachloroaluminate catalysts.

then calculated the polarity of the hydrocarbons induced by being absorbed on the catalysts. We found that hydrocarbon absorption level correlates linearly with induced hydrocarbon polarity (Fig. 8). Separate correlations were found for each cation of the study. However, we were searching for a more universal single correlation.

Next, we determined that negative charge is transferred from the hydrocarbon to the anion during absorption, e.g., Fig. 9. The more polar hydrocarbons have a greater ability to share their electrons and thus stabilize the partial positive charge on the Al atom. The Al atom is also stabilized by removal of charge from the less polar hydrocarbons, thereby creating carbocations. The overall effect is a decrease in the charge transferred from the hydrocarbon to the anion with increasing hydrocarbon polarity.

The calculated total charge differences between the absorbed hydrocarbons and the tetrachloroaluminate catalysts were found to correlate with hydrocarbon absorption (Fig. 10). This correlation is more universal since it is valid for all three tetrachloroaluminates studied. Again, this correlation shows that the amount of charge

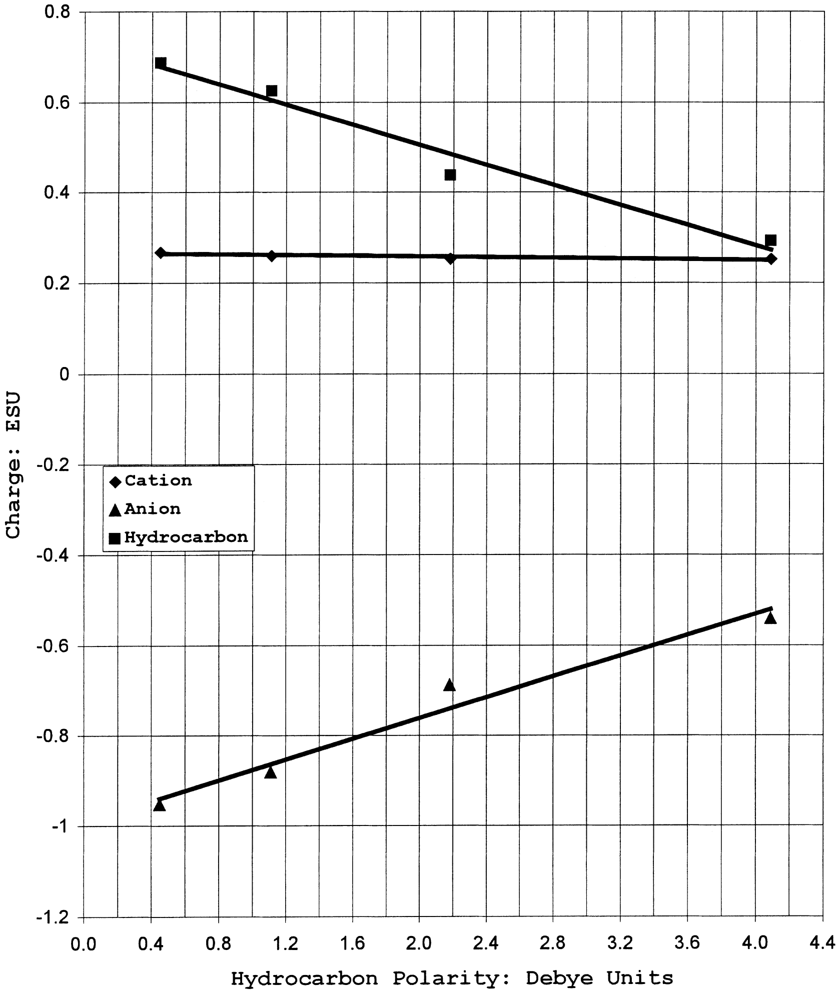

Fig. 9. Absorbed hydrocarbon and zinc tetrachloroaluminate charges versus hydrocarbon polarity.

transfer decreased with the increased absorption levels for the more polar hydrocarbons. An even more universal correlation could include the effect of induced hydrocarbon polarity along with charge transfer.

7. Molecular modeling results for free-radical chemistry

The above charge transfer and induced hydrocarbon polarity results suggest that tetrachloroaluminates do perform, during resid molecular weight reduction, the desired function of stabilizing free radicals for subsequent reactions. To support this point, energy minimizations were made for benzyl and *i*-propyl free-radical reactants and isopropyl benzene (IPB) product absorbed in NaTA, HTA and in a 15.0/85.0 (wt/wt) HTA/NaTA mixture. This mixture was energy minimized starting with a cubic structure in which one face contained a HTA molecule and the remaining five faces contained NaTA molecules.

The energy minimized structure for the catalyst mixture with an absorbed benzyl free radical is shown in Fig. 11. The five Na ions, which are essentially neutral, are at the center of the catalyst and the H ion is

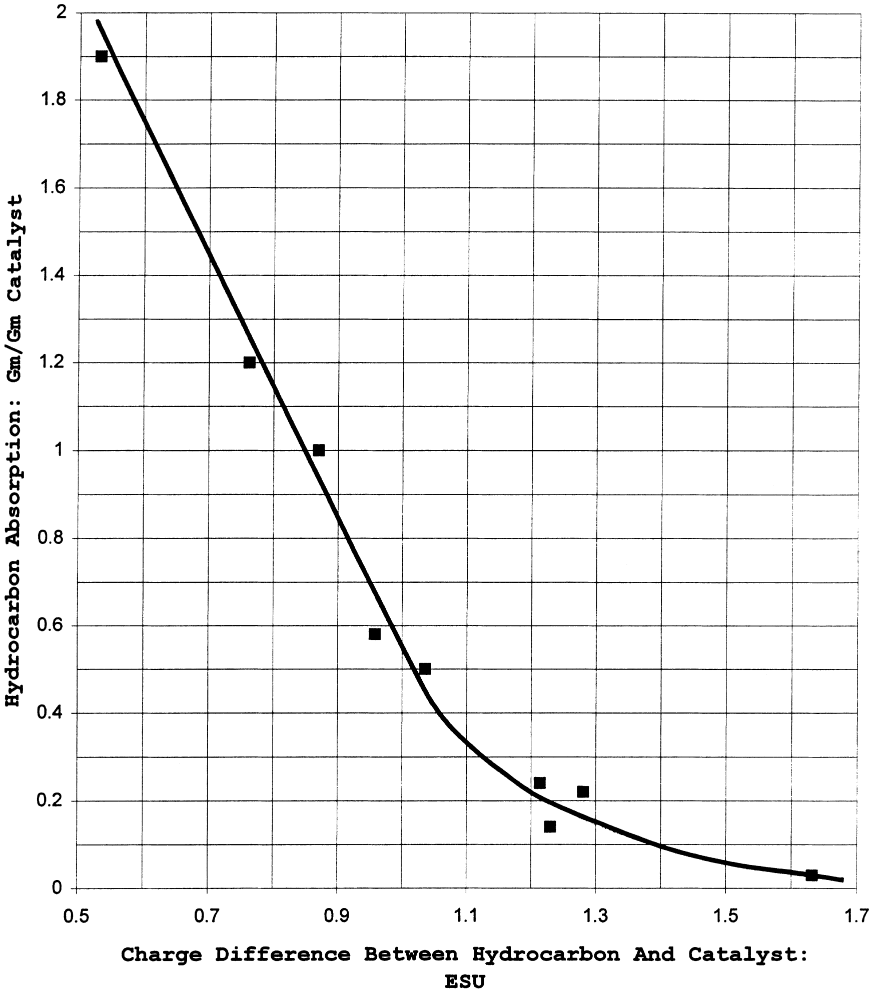

Fig. 10. Hydrocarbon absroption versus charge difference between hydrocarbon and catalyst for zinc, sodium and potassium tetrachloroaluminates.

on the catalyst surface. The Na ions are first surrounded by Al ions and secondly surrounded by Cl ions. The reason for this structure is under current investigation. The absorbed benzyl radical is in a pocket on the surface of the catalyst.

We found that the induced polarities for the above free radicals go through maximums with increasing HTA content (Fig. 12). As noted previously, increasing induced polarity yields increasing absorption. Hence in the range 0–15.0 wt% HTA, the free radicals would be in increasing concentrations on the catalyst surface. This would yield a greater amount of reaction to IPB. Then, with larger amounts of HTA in the catalyst, free radical absorption decreases yielding decreasing reaction to IPB. This result supports our previous finding that resid conversion first increases and then decreases with increasing HTA content (Fig. 1).

We also noted that the induced polarity of IPB product increases with increasing HTA content in the range 0.0–15.0 wt% (Fig. 12). This again supports our previous findings showing a maximum in resid conversion with increasing HTA content. That is, increasing absorption of the low molecular weight

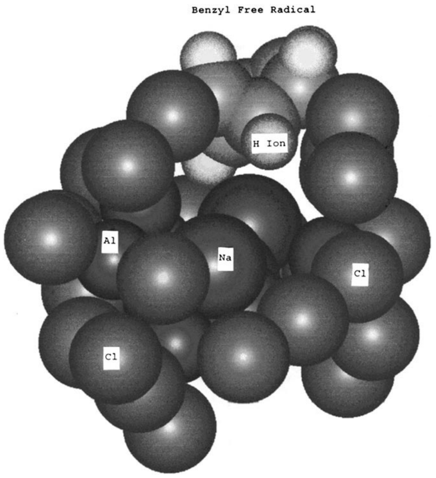

Fig. 11. Benzyl free-radical absorbed on a hydrogen/sodium tetrachloroaluminate cluster of 1/5 mol/mol.

products would probably make their removal more difficult by simple hydrogen stripping from the tetrachloroaluminate catalyst.

8. Conclusions

We have found that the level of hydrocarbon absorption into molten tetrachloroaluminate catalysts correlates to the size of the catalyst cation and to the polarity of the absorbed hydrocarbon. We have also shown, via molecular modeling, that the amounts of charge transfer from the absorbed hydrocarbons to the catalysts correlate to absorption levels. Lastly, free-radical adsorption levels, determined via molecular modeling, suggest a mechanism to explain previous work. In previous work, the level of resid upgrading

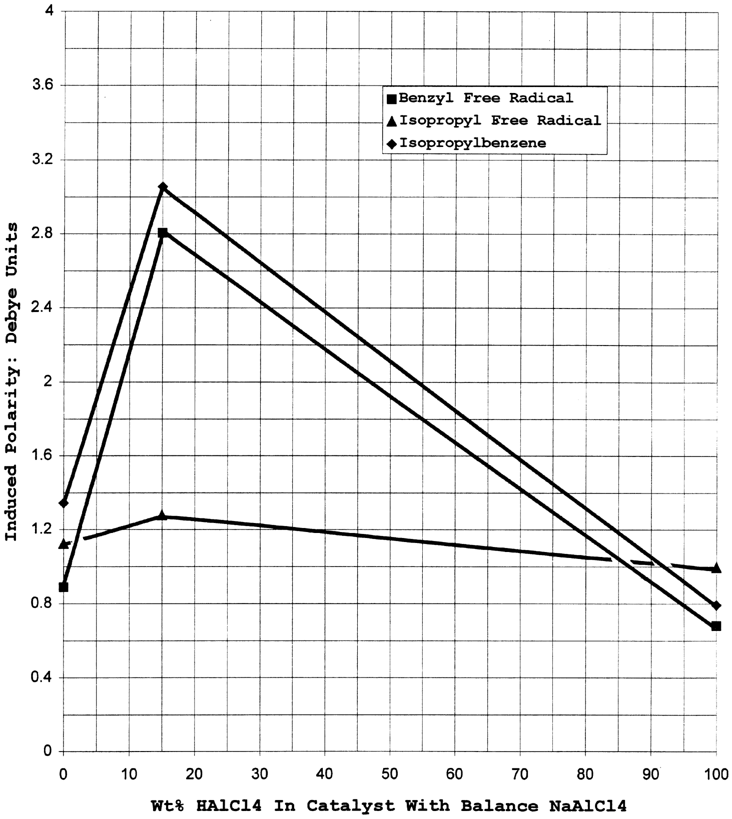

Fig. 12. Hydrocarbon or free-radical induced polarity versus hydrogen and sodium tetrachloroaluminate contents in catalyst.

was found to go though a maximum with increasing HTA concentrations in bulk NaTA catalyst.

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