Some Study on Esterification of Maleic Acid with 2-Ethyl hexyl Alcohol

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Summary: Di-2-ethylhexyl maleate, as one of the synthetic aliphatic esters is considered as an example of the aliphatic plasticizers. It is prepared via the esterification of maleic acid with 2-ethyl hexyl alcohol at 170°C using tetrabutyl titanate, and/or triisopropyl aluminate as catalyst. At the same temperature the esterification was conducted without catalyst and with other catalysts such as $TiCl_4$, $SnCl_4$ and their prepared quaternary ammonium metallic salts for the purpose of comparison.

The reaction was followed up by measuring the amounts of produced water, also by measuring the amount of unreacted acid in the reaction mixture. Imperical equation of reaction rate has indicated that esterification of this type is of apparent second order with respect to the acid.

Introduction

Nowadays, plasticizers are used in large quantities for the plasitification of many polymers, particularly polyvinyl chloride. Most of the usual plasticizers are esters of phthalic acid, adipic, sebacic and trimellitic acids.

The chemical industry has become adept at structuring other plasticizers to do specific jobs such as aliphatic esters which show good flexibility at low temperature. The catalysts used were initially acids, such as sulphuric acid or p-toluene sulphonic acid. The use of titanium and zirconium compounds as esterification catalysts has been known for a fairly long time and has undergone considerable expansion in recent years [1-4].

Hindered carboxylate esters [5] and carboxylate esters with good hue and good oxidation resistance [6] were prepared over catalysts selected from chlorides of tin, titanium and zinc. The most wide spread studies concern the search for new esterification catalysts. Polymer supported catalyst was prepared and used for esterification with high conversion and selectivity [7].

Solid acid catalysts (p-containing ZrO_2) can be used in the manufacture of α,β unsaturated carboyxlic acid esters with reduced formation of polymerized substances [8,9] or with increased catalyst life [10]. The dual component catalyst comprises sand carrier, stannous oxalate and sodium aluminate is particularly useful in making phthalates, adipates, sebacates and azelates [11]. The present work concerns some studies on the esterification of maleic acid and 2-ethylhexyl alcohol in the presence of some catalysts such as tetrabutyl titanate, triisopropyl aluminate, tin and titanium tetrachlorides. A comparison has been conducted between the above mentioned catalysts and the prepared quaternary ammonium metallic salts.

Results and Discussion

There is provided a new series of compounds by condensing an amine with a halide of tetravalent element of group IV of the periodic system, to produce a quaternary ammonium compound [12].

These compounds have been evaluated as esterification catalysts at a temperature of 170°C, compared to other catalysts such as tetrabutyl titanate, triisopropyl aluminate, tin and titanium tetrachlorides.

The technique followed in the present work for the preparation of di-2-ethylhexyl maleate by removal of water formed in the reaction at 170°C in a Dean-Stark apparatus, ensures the irreversibility of the reaction and capability for obtaining higher conversions.

The integral method (empirical orders) was applied for the exploitation of the experimental results in order to obtain kinetic parameters for the

Table-1: The chemical formula and elemental analysis of the prepared metallic tetraamine complexes.

Metallic tetraamine complexes	Chemical formula		Elemental Analysis %			
			C	H	N	Cl
Tetradodecyl ammonium tin tetrachloride	$[(C_{12}H_{25}.NH_2)_4Sn]^{+4}.4Cl^-$	Calculated	57.5417	10.8643	5.5920	14.1539
		Found	56.9321	9.9522	5.6700	13.9534
Tetradodecyl ammonium titanium tetrachloride	$[(C_{12}H_{25}.NH_2)_4Ti]^{+4}.4Cl^-$	Calculated	61.9189	11.6908	6.0174	15.2306
		Found	60.8200	10.5610	5.9023	14.9041

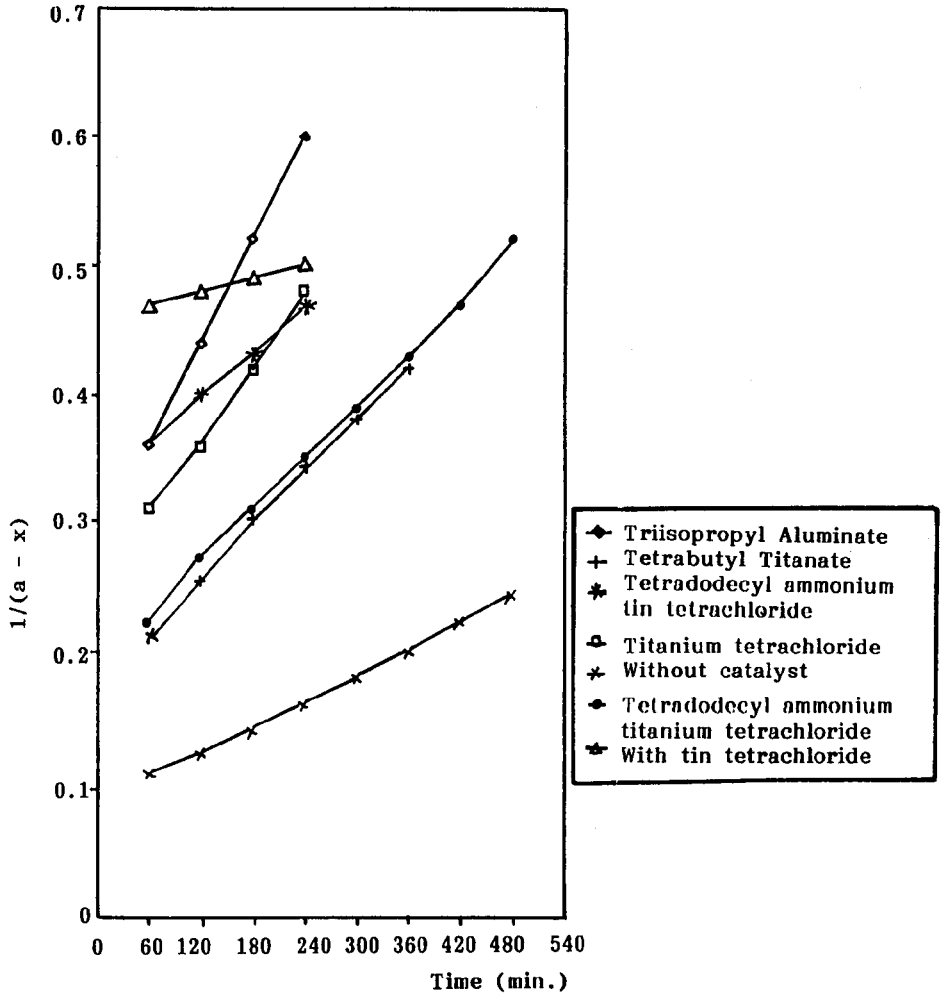

Fig. 1: Esterification of maleic acid by 2-ethyl hexyl alcohol with and without catalyst, at 170°C.

reaction. The best adapted empirical equation for experimental data was conducted, the integrated form of the rate equation was used as follows:

$$\left(\frac{1}{a-x}\right)^{u-1} = \left(\frac{1}{a}\right)^{u-1} = (u-1)kt$$

where : a : initial concentration of acid (mol L^{-1})

a - x : concentration of acid at timt t (mol L^{-1}).

k : apparent rate constant of the total reaction.

u: order with respect to acid.

It is clear from Fig. 1 that the esterification is of apparent 2nd order with respect to maleic acid. The calculated rate constants [k} are given in Table-2.

Table-2: The apparent rate constants k of the total reaction

Catalyst	k x 10^4, L g mol^{-1} sec^{-1}
No catalyst	3.11
Tin tetrachloride	1.66
Tetradodecyl ammonium tin tetrachloride	5.83
Triisopropyl aluminate	6.66
Tetrabutyl titanate	7.22
Titanium tetrachloride	9.16
Tetradodecyl ammonium titanium tetrachloride	13.30

The k values given in Table-2 show that, using tin tetrachloride as a catalyst has inhibited the reaction rate to the half. The k value for the reaction using tin tetrachloride is 0.00166 min^{-1} whereas it is 0.0031 min^{-1} for the reaction carried out without any catalyst.

Fig. 1-7 illustrate the conversion based on measurement of the amount of water collected (or the measurement of the amount of unreacted acid) as a function of time for the esterification of maleic acid with 2-ethylhexanol catalyzed by the above mentioned catalysts. It is clear that the two methods of following up the reaction approach each other in the first 30 min. of the reaction, then the two curves start to diverge from each gradually. For all catalysts the conversion based on measuring of unreacted acid is higher than that based on measuring of water collected. This difference in conversion between the two methods (water and acid measurements) near the end of the reaction may be attributed to the proposal that as the reaction goes towards the end, the phase equilibrium between ester, alcohol, acid and water is always changing and the ester quantity becomes more and more with respect to the acid and alcohol. Also the solubility of water in the ester may be more than that in the acid which makes the amount of water collected near the end of the reaction less than real one. In other words the real conversion based on measuring of unreacted acid is little smaller than the measured one and that based on measuring the water collected is a little higher than the measuring one [9].

Fig. 2-7 also indicate that the prepared metallic tetraamine complexes give high conversion

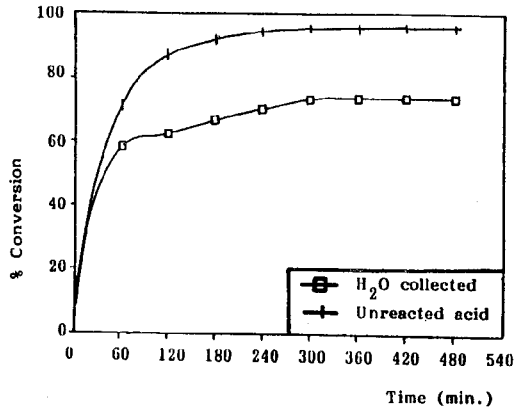

Fig. 2: Conversion vs time for the esterification of maleic acid with 2-ethyl hexyl alcohol using tetrabutyl titanate as catalyst.

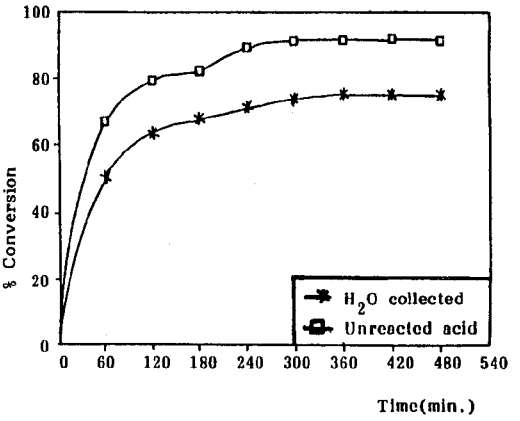

Fig. 3: Conversion vs time for the esterification of maleic acid with 2-ethyl hexyl alcohol using triisopropyl aluminate as catalyst.

percentages. The activity of these complex compounds depends upon the presence of long aliphatic group (lipophilic fatty moiety) which increase hydrophobicity by lowering hydrophile-lipophile balance (HLB). This phenomena lead to lower surface tension and give surface active catalyst [9]

Experimental

Preparation of metallic tetraamine complexes

Anhydrous stannic chloride (0.01 mol) or titanium tetrachloride (1.09 ml) dissolved in acetone was added dropwise at room temperature to dodecylamine (0.04 mol) dissolved in acetone with

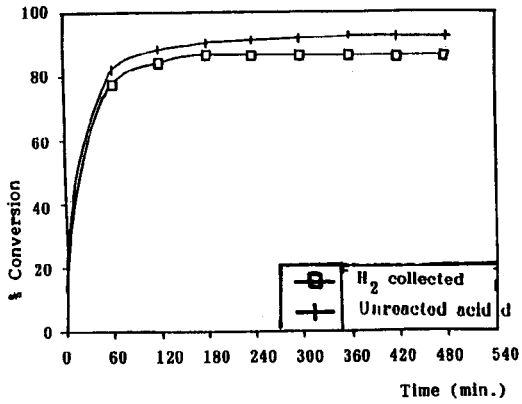

Fig. 4: Conversion vs time for the esterification of maleic acid with 2-ethyl hexyl alcohol using tetradodecyl ammonium tintetrachloride as catalyst.

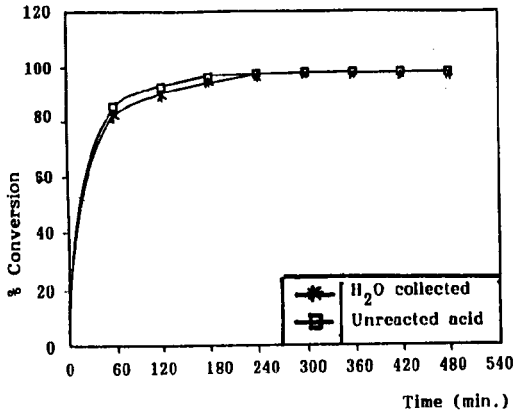

Fig. 5: Conversion vs time for the esterification of maleic acid with 2-ethyl hexyl alcohol using tetradodecyl ammonium titanium tetrachloride as catalyst.

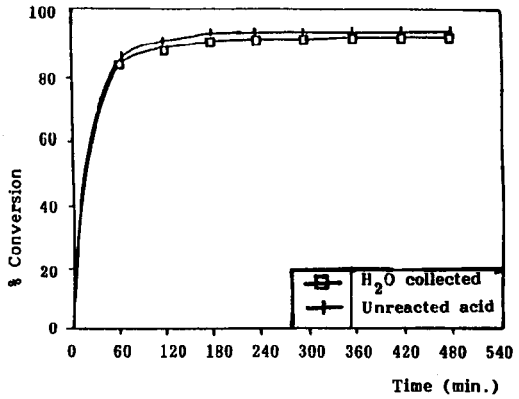

Fig. 6: Conversion vs time for the esterification of maleic acid with 2-ethyl hexyl alcohol using tin tetrachloride as catalyst.

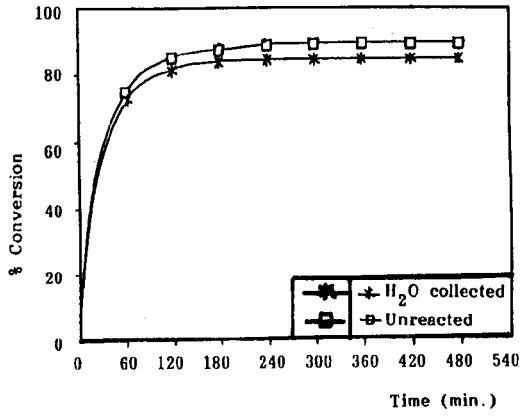

Fig. 7: Conversion vs time for the esterification of maleic acid with 2-ethyl hexyl alcohol using titanium tetrachloride as catalyst.

shaking in a period of 5-10 min. This experiment was carried out according to the method described in Ref. [13]. The proposed chemical formulas of the prepared metallic tetraamine complex were confirmed according to their chemical composition as given below in Table-1:

Esterification of maleic acid with 2-ethyl hexyl alcohol

2-ethyl hexyl alcohol (1 mol) was added at 170°C to maleic acid (0.5 mol) and the above mentioned catalysts (2% by weight of the acid) dissolved in xylene as azeotropic solvent under good stirring conditions. The apparatus and the method were described according to Ref. [13].

The reaction was followed up by two means:

a) by measuring periodically the quantity of water separated in the trap.

b) Determination of unreacted acid: by periodical withdrawal of samples from the reaction mixture, weigh each sample and dissolve it in 25 ml ethyl alcohol then titrate against 0.1 NKOH using phenolphthaline as indicator.

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