Reaction from Dimethyl Carbonate to Diphenyl Carbonate. 1. Experimental Determination of the Chemical Equilibria

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New experimental equilibrium data of the reaction of dimethyl carbonate (DMC) and phenol to methyl phenyl carbonate (MPC) and the subsequent disproportion and transesterification reaction of MPC to diphenyl carbonate (DPC) are presented and interpreted in terms of the reaction equilibrium coefficients. Experiments have been carried out in the temperature range between 160 and 200 °C and for initial reactant ratios of DMC/phenol from 0.25 to 3. By employing activities instead of "only" mole fractions in the calculation of the reaction equilibrium coefficients, the influence on the reactant ratio DMC/phenol on the derived equilibrium values for the reaction of DMC to MPC could be reduced, especially for temperatures of 160 °C. The activity based equilibrium coefficient for the transesterification reaction from MPC with phenol to DPC and methanol is constant within experimental uncertainty and, therefore, largely independent of the initial reactant ratio DMC/phenol at temperatures of 160 and 180 °C. The temperature dependence of the equilibrium coefficients $K_{a,1}$ and $K_{a,2}$ has been fitted by applying the well-known Van't Hoff equation, resulting in the expressions $\ln K_{a,1} = -2702/T[\mathrm{K}] + 0.175$ and $\ln K_{a,2} = -2331/T[\mathrm{K}] - 2.59$. It has been demonstrated that these equations have fair, in the case of $\ln K_{a,1}$, and excellent, in the case of $\ln K_{a,2}$, predictive capabilities, even for experimental conditions that deviate significantly from those used in this study. Hence, it is expected that the derived temperature dependent correlations for $K_{a,1}$ and $K_{a,2}$ based on activities can be used in reactive distillation models to assess different process configurations in the manufacture of DPC starting from DMC and phenol.

1. Introduction

Diphenyl carbonate is a precursor in the production of polycarbonate (PC). Polycarbonate is widely employed as an engineering plastic important to the modern lifestyle; it is used in, for example, the manufacture of electronic appliances, office equipment, and automobiles. About 3.4 million tons of PC was produced worldwide in 2006. Production is expected to increase by around 6% per year until 2010 with the fastest regional growth expected in East Asia, averaging 8.7% per year through 2009.[1]

Traditionally, PC is produced using phosgene as an intermediate. The phosgene process entails a number of drawbacks. First, 4 tons of phosgene are needed to produce 10 tons of PC. Phosgene is very toxic, and when it is used in the production of PC, the formation of undesired hazardous salts as byproduct cannot be avoided. Furthermore, the phosgene-based process uses 10 times as much solvent (on a weight basis) as PC is produced. The solvent, methylene chloride, is a suspected carcinogen and is soluble in water. This means that a large quantity of wastewater has to be treated prior to discharge.[2]

Many attempts have been made to overcome the disadvantages of the phosgene based process.[3] The main point of focus has been a route through dimethyl carbonate (DMC) to diphenyl carbonate (DPC), which then reacts further with bisphenol-A to produce PC. The most critical step in this route is the synthesis of DPC from DMC via transesterification to methyl phenyl carbonate (MPC), usually followed by a disproportionation and/or transesterification step to DPC. The equilibrium conversions

of the reactions to MPC and DPC are highly unfavorable: in a batch reactor with an equimolar feed, an equilibrium conversion to DMC of only 3% can be expected. Therefore, good process engineering is required in the design of a process to successfully carry out the reaction of DMC to DPC on a commercial scale. The reaction appears to be a candidate for being carried out in a reactive distillation column to help realize high conversions.[4] Reactive distillation appears to be a viable production technology as methanol, an intermediate product, can be separated from the other components by simple distillation and hence the conversion of DMC and phenol in the transesterification step can be increased. Regardless of the type of reactor chosen, it is important to know the chemical equilibria and kinetics involved in this system. In this paper, chemical equilibrium data determined from batch reactor experiments are presented.

2. Reactions

The synthesis of diphenyl carbonate (DPC) from dimethyl carbonate (DMC) and phenol takes place through the formation of methyl phenyl carbonate (MPC) and can be catalyzed either by homogeneous or heterogeneous catalysts. The reaction of DMC to DPC is a two-step reaction. The first step is the transesterification of DMC with phenol to the intermediate MPC and methanol.[2,5]

For the second step, two possible routes exist: the transesterification of MPC with phenol or the disproportionation of two molecules of MPC yielding DPC and DMC (reaction 3).

Ono[2] suggests that DMC and phenol may also react to produce anisole (see Scheme 4).
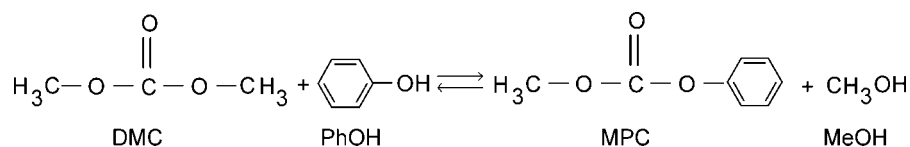
3. Thermodynamics

The reaction of DMC to DPC can either proceed through the transesterification−disproportionation step (see Schemes 1

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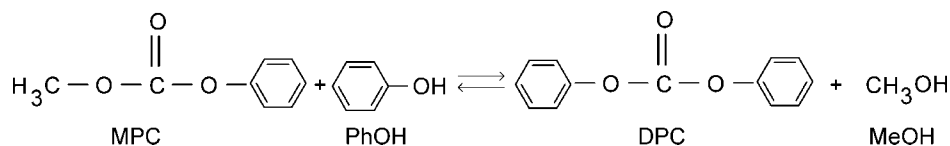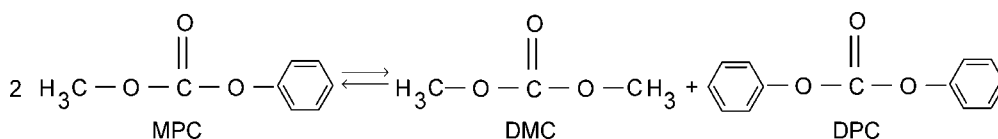† University of Twente.
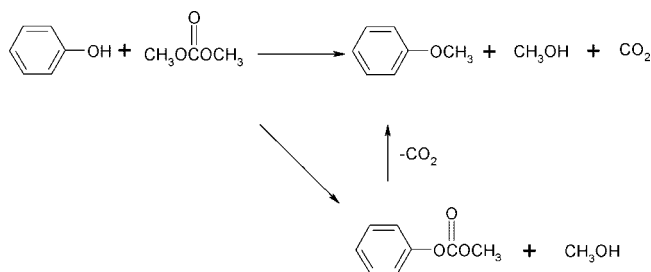‡ Clarkson University.

Scheme 1. Transesterification 1

Scheme 2. Transesterification 2

Scheme 3. Disproportionation

Scheme 4. Side Reaction Forming Anisole, Methanol, and Carbon Dioxide

and 2) or the transesterification—transesterification step (see Schemes 1 and 3). From a thermodynamic point of view, the second step from MPC to DPC—via either the transesterification reaction 2 or the disproportionation reaction 3—is interchangeable, and one of the reaction equilibria involved can be left out of the thermodynamic description.

First, the special case of the equilibrium coefficients with all activity coefficients set to one will be considered to compare the equilibrium values derived from the experiments in this study to those in the literature. At the end of this section, the general formulation of the equilibrium coefficients incorporating activity coefficients will be presented. The mathematical formulation of the different simplified equilibrium coefficients is given in eqs 1—4, with the overall equilibrium coefficient as defined by eq 4.

$$K_{x,1} = x_{MPC} x_{MeOH} x_{DMC}^{-1} x_{PhOH}^{-1} \tag{1}$$

$$K_{x,2} = x_{DPC} x_{MeOH} x_{MPC}^{-1} x_{PhOH}^{-1} \tag{2}$$

$$K_{x,3} = x_{DPC} x_{DMC} x_{MPC}^{-2} = \frac{K_{x,2}}{K_{x,1}} \tag{3}$$

$$K_{x,ov} = x_{DPC} x_{MeOH}^{2} x_{DMC} x_{PhOH}^{2} = K_{x,1} K_{x,2} = (K_{x,1})^2 K_{x,3} \tag{4}$$

The reaction equilibrium coefficients for reactions 1—3 have been determined by several authors as summarized in Table 1 (note: in this table, the equilibrium coefficients have been calculated on a mole fraction basis). The equilibrium coefficients for both transesterification reactions are quite low,[4,6] and it must be concluded that these values do not allow for high conversions if the reaction is carried out in a batch reactor. In Table 1,

equilibrium data taken from the literature are reported at 298 and at 491 K for the equilibrium coefficients of all three reactions. Unfortunately, only one value for one reaction is provided in the relevant temperature window between 433 and 473 K. Therefore a systematic experimental study has been carried out to determine the equilibrium values of the three different reactions at varying experimental conditions as e.g. different initial reactant ratios and temperatures.

The values of the equilibrium coefficients given in Table 1 taken from different sources should be interpreted with some care. It is unclear if the values of the equilibrium coefficient reported by Rivetti[4] were determined experimentally or were calculated from standard Gibbs enthalpies at 298 K. Furthermore, the equilibrium coefficient given by Tundo et al.[7] must be interpreted carefully as only the reaction temperature of 453 K is given in the source; no information is provided concerning reactant ratio and reaction time. Harrison et al.[6] give all of the liquid phase concentrations needed to calculate the $K_{x,i}$ values and also most of the experimental conditions. From the experimental data given in the patent,[6] equilibrium coefficients of reactions 1 and 3 can be estimated. For the calculation of the equilibrium values the concentrations of the involved species, given in example 1 and 3 of the patent, were used and averaged.

The thermodynamically sounder formulation of the chemical equilibrium would involve the additional use of activity coefficients of the species and the following equations for the reaction equilibrium coefficients:[8]

$$K_{a,i} = K_{x,i} \cdot K_{\gamma,i} \tag{5}$$

$$K_{a,i} = \underbrace{\frac{\prod_{j=1}^{n} x_{Products}^{j}}{\prod_{k=1}^{n} x_{Reactants}^{k}}}_{K_{x,i}} \cdot \underbrace{\frac{\prod_{j=1}^{n} \gamma_{Products}^{j}}{\prod_{k=1}^{n} \gamma_{Reactants}^{k}}}_{K_{\gamma,i}} \tag{6}$$

The activity coefficients needed for the evaluation of the activity based chemical equilibrium coefficients can, in principle, be calculated with any applicable activity coefficient model, e.g. NRTL, Wilson, UNIQUAC, or UNIFAC.[9] In this study, it has been decided to use the UNIFAC model as this then provides a predictive character not shared by any of the other activity coefficient models mentioned above.

In order to apply the UNIFAC method in this study, a new UNIFAC group had to be introduced, namely the carbonate

Table 1. Literature Values of the Equilibrium Coefficients for the DPC Synthesis

equilibrium constant	$K_{T=298K}$	$K_{T=453K}$	$K_{T=491K}$	ΔG_{298K} (kJ mol^{-1})
	4	7	6	4
$K_{x,1}$	6.3×10^{-5}	3.0×10^{-4}	2.72×10^{-3}	+ 23.9
$K_{x,2}$	1.2×10^{-5}		5.73×10^{-4}	+ 28.1
$K_{x,3}$	1.9×10^{-1}		2.11×10^{-1}	+ 4.2
$K_{x,ov}$ reaction 1 + 2	7.6×10^{-10}		1.56×10^{-6}	+ 50.7
$K_{x,ov}$ reaction 1 + 3	1.2×10^{-5}		5.74×10^{-4}	+ 28.1

group O−CO−O, which was until now not present in the published UNIFAC database. For the exact determination of the interaction parameters between the OCOO group and the other functional groups involved in the present system, the reader is referred to the thesis of Haubrock.[10] The UNIFAC interaction parameters which are employed in this study to calculate the relevant activity coefficients can be found in Table 3 in the Supporting Information.

4. Chemicals

All chemicals were used as received from the supplier. Dimethyl carbonate (purity: 99+%) was purchased from Aldrich; Phenol (99+%) and the catalyst tetra-(*n*-butyl orthotitanate) (98+%) were acquired from Merck. The catalyst was stored over molecular sieves (type 4a) to prevent degradation due to moisture from air. For more information on the catalyst choice, the reader is referred to the work of Haubrock et al.[11]

5. Experimental Setup and Procedure

The setup used for the experiments is shown schematically in Figure 1 and consisted of a stainless steel reactor of 200 mL and a storage vessel of 300 mL. The reactor could be heated with an oil-bath, and the storage vessel, with an electrical heater. The pipes of the apparatus were traced to maintain the desired reaction temperature and to prevent cold spots and possible condensation of phenol. Valve 8 separates the two vessels (see Figure 1) and was opened to start the reaction; this is also the moment when the recording of data was started. The two reactants were heated separately to prevent reaction prior to their introduction into the reactor. The catalyst was located in the reactor with the reactant phenol. Both vessels were connected to a nitrogen source, which allowed the reaction to proceed under a complete nitrogen atmosphere to suppress possible oxidation reactions. The temperature of both vessels was monitored. The reactor itself was also provided with a pressure transducer for recording the pressure during the experiment. During the reaction, samples of 1 mL could be taken from the liquid phase in the reactor by means of a syringe sampling system.

After the sampling procedure, the filled vials were cooled down in an ice-bath to stop the reaction. The time from the start of the experiment ($t = 0$) to the moment the vials were put in the ice-bath was taken as the reaction time. All vials were analyzed with a GC within 24 h after the experiment concluded. The gas chromatograph used in this study was a Varian 3900 equipped with a flame ionization detector (FID). The column in the GC was a 50-m long fused silica column (Varian CP 7685). The gas chromatograph applied a temperature ramp for the analysis: the column temperature was kept at 50 °C for 2 min, then the temperature was raised 20 °C per minute until a temperature of 300 °C was reached. This temperature

was maintained for three minutes before the column oven was cooled down to 50 °C for the next analysis run.

For the quantification of the components present in the samples, two internal standards were used in the GC analysis, namely toluene and *n*-tetradecane. These internal standards were chosen because their retention times are close to those of the components to be measured and, moreover, the peaks of the two internal standards do not overlap with other peaks. Roughly 4 wt % of each internal standard was added to each sample. Toluene was used as internal standard for methanol and DMC, whereas *n*-tetradecane was used as the internal standard for phenol, MPC, and DPC. The relative error in the GC analysis was typically <5% for species such as DMC and phenol, <10% MPC, <15% methanol, and up to 20% for DPC as this species was only present in very small amounts. The GC error for DPC was generally smaller (<10%) for experiments where an initial excess of DPC was added to the reactants.

To verify that the reaction was effectively stopped after the sample has been taken from the reactor, a sample from the reactor was divided in several identical subsamples. The time between sampling and analysis of these subsamples was varied between 0 and 48 h. The sample analysis showed no sign of change with increasing time, demonstrating that no reaction (including degradation/side reactions) occurred during the first 48 h between the sampling and the analysis.

6. General Remarks on the Experimental Results

The equilibrium conversion of the reactants phenol and DMC at 180 °C was typically around 4%. The time to achieve chemical equilibrium depended on two factors, namely the amount of catalyst and the ratio of DMC/phenol, but was typically in the range of 15 min to 1 h. As expected, a larger amount of catalyst results in a higher reaction rate and chemical equilibrium is achieved faster. Experiments have been performed with around 130 g overall reactant mixture and with different catalyst mole fractions ($\sim 1.0 \times 10^{-4}$ and 2.5×10^{-4}) while maintaining otherwise the same experimental conditions. No indication has been found that the amount of catalyst changes the numerical value of the inferred reaction equilibrium coefficient.

A material balance calculation for the experiments showed a mismatch in the amounts of the reaction products: methanol on one side and (MPC + 2 DPC) on the other side. Looking at reaction 1, it can be expected that both methanol and MPC would be produced in equal amounts. However, as MPC can react further to DPC according to reactions 2 or 3, again under the formation of methanol, the mole fraction of MPC would be expected to be lower than the mole fraction of methanol. However, the sum of the mole fractions of MPC and 2 DPC should be equal or higher (in which case a good deal of methanol would be present in the gas phase) than the mole fraction of methanol and this typically was not seen. On the basis of vapor−liquid equilibrium (VLE) calculations, it has been estimated that the amount of methanol in the liquid phase is more than 95% of the overall amount of methanol. The molar amount of methanol in the liquid phase should, therefore, be around 5% less than the cumulated molar amount of MPC+ 2 DPC.

The experimentally determined mole fractions of MPC + 2 DPC and methanol were deviating by around 20 to 35% whereupon the latter one was always larger. This deviation cannot be attributed to an analysis fault caused by the gas chromatograph (GC) as the GC error is estimated to be no more than 5%.
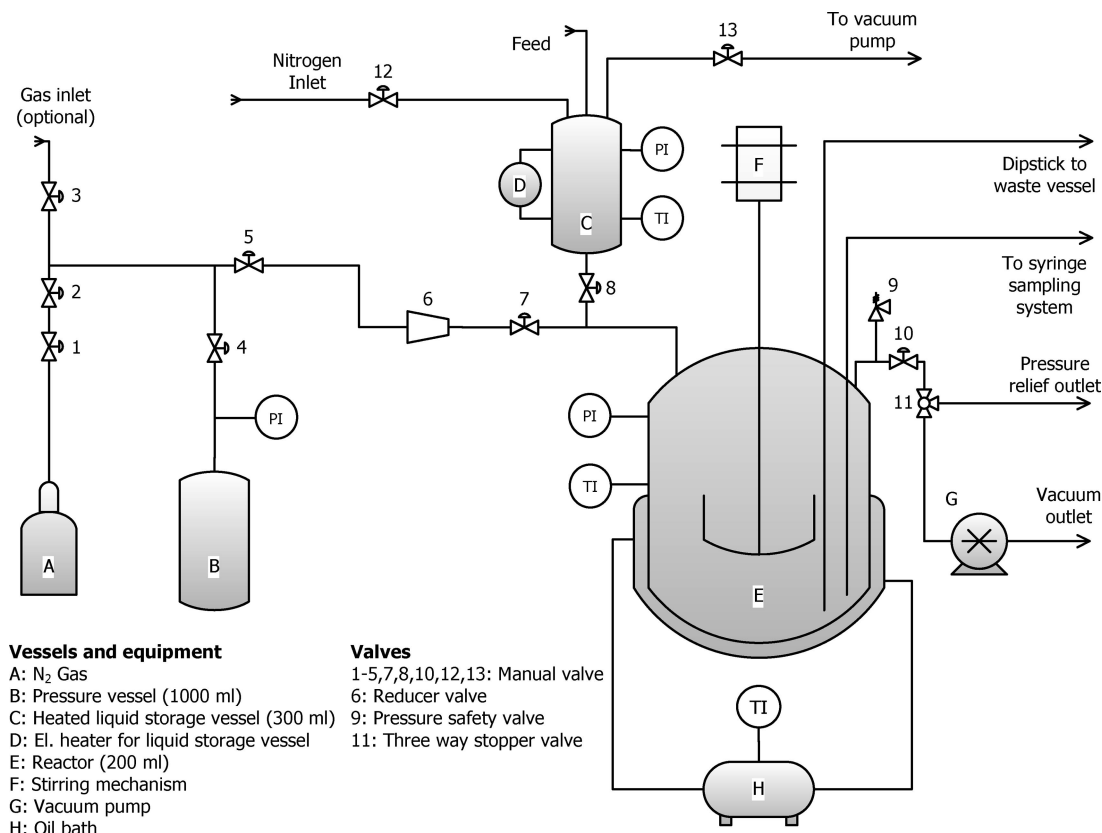
Figure 1. Experimental Setup: closed batch reactor with supply vessel containing DMC.

A GC analysis of the starting reactants phenol and DMC showed that there was an initial amount of methanol present in DMC, typically around 0.5 wt % of the amount of DMC. This also explains why the methanol mole fraction was never zero at the start of an experiment. The amount of methanol in the reactant DMC was always less than 0.50 wt %, but considering the low conversion of the reactants and hence low yields of the products, this initial amount can easily explain the previously mentioned mismatch in the mass balance. As the initial mole fraction of methanol in the reactor depends on the ratio of phenol/DMC (with phenol having no methanol in it), the mismatch in the mass balance also increased with decreasing ratio of phenol to DMC.

Anisole was not detected by GC analysis in any of the experiments within the detection limit of the GC (mole fraction anisole <0.001%). It can be concluded that the side reaction to make anisole either does not occur or if it occurs it is to a very small extent. In addition, no peaks, other than those expected, appeared in the GC plots, suggesting that no other byproducts were formed.

An extra series of measurements at 180 °C was carried out in which a small amount of DPC was added to the reaction mixture at the start of the experiment. The initial concentration of DPC of around 1 mol % is between 10 and 50 times larger than the actual equilibrium concentration of DPC. It was hoped that these experiments would demonstrate that the same equilibrium state is approached even if the initial DPC concentration was not zero.

Experiments show that chemical equilibrium is achieved in a relatively short time (<60 min) and that the catalyst amount does not influence the results in terms of the equilibrium coefficients (up to a catalyst mole fraction of at least 2.5×10^{-4}). Our own reference experiments with no additional catalyst show that even after 24 h the composition was still far
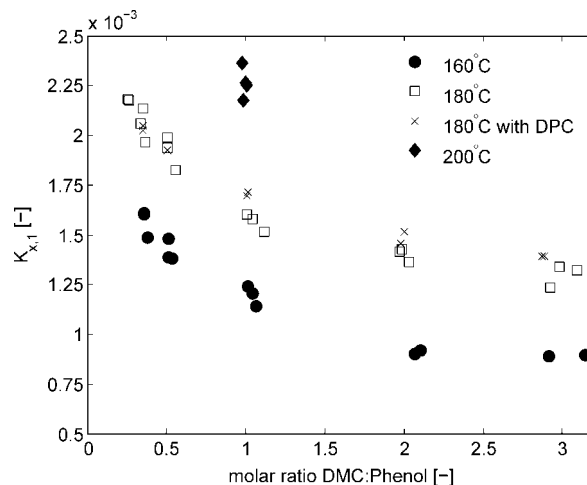

Figure 2. $K_{x,1}$ over the initial reactant ratio at three different temperatures.

from chemical equilibrium (<5% of the equilibrium concentration of MPC was detected after 24 h). It can be concluded that even if a partial deactivation/decomposition of the catalyst takes place, the influence on the chemical equilibrium measurements is negligible.

7. Equilibrium Coefficients $K_{x,1}$ and $K_{x,2}$

The raw data of the experiments carried out for this study are given in Table 4 of the Supporting Information. On the basis of the experimentally determined mole fractions (Table 4), the equilibrium coefficient $K_{x,1}$ (eq 1) of the reaction from DMC and phenol to MPC and methanol has been calculated. In Figure 2, the reaction equilibrium coefficient $K_{x,1}$ has been plotted over the initial reactant ratio DMC/phenol for temperatures of 160, 180, and 200 °C. At 200 °C, only experiments at a DMC/phenol
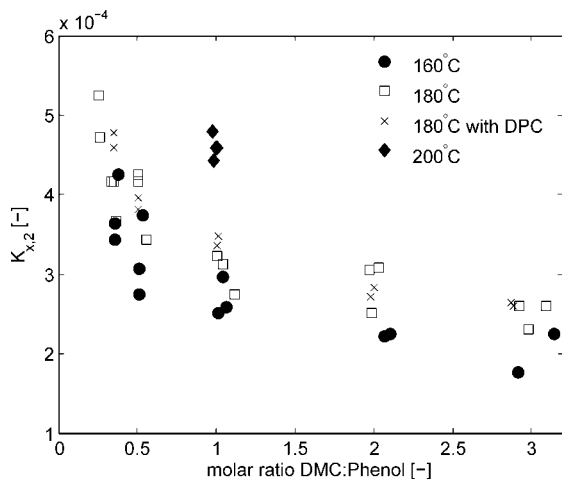
Figure 3. $K_{x,2}$ over the initial reactant ratio at three different temperatures.

Figure 4. Van't Hoff plot for $K_{x,i}$ with our own experimental results and literature values taken from Table 1.

ratio of 1 have been carried out and therefore only the $K_{x,1}$ values at this ratio are shown in Figure 2. From thermodynamic considerations (see also Table 1), it was expected that the equilibrium coefficient will increase slightly with increasing temperature, as the transesterification reaction of DMC to MPC is endothermic. This behavior is confirmed by experimental results as shown in Figure 2.

As can be seen from Figure 2, the mole-fraction-based reaction equilibrium coefficients show the same trend regardless of the temperature. For initial DMC/phenol ratios lower than 1, the equilibrium coefficient is increasing more strongly with decreasing DMC/phenol ratio than for ratios above 1. For the lowest measured DMC/phenol ratio of 0.25, the equilibrium coefficient at 180 °C is around 35% larger than the equilibrium coefficient at a DMC/phenol ratio of 1. A similar trend, although less pronounced, can be observed for the equilibrium coefficient at 160 °C.

The experiments at 180 °C where an initial amount of DPC far beyond the expected equilibrium mole fraction (~10−50 times more than expected) is added show that nearly the same values of the equilibrium coefficient $K_{x,1}$ are attained as in the experiments with no DPC present initially. Moreover, the trend of $K_{x,1}$ over the initial ratio of DMC/phenol is the same for the experiments with and without the initial presence of DPC at 180 °C. The experimental results show that the GC error is probably lower for the experiments with initial DPC present as the reproducibility is generally better (the deviation is <5%) than that of the DPC "free" experiments (where the deviation generally is <10%).

As already indicated, the reaction from the intermediate MPC to the desired product DPC can proceed via two different pathways. Since the equilibrium value $K_{x,3}$ can be computed from the values of $K_{x,2}$ and $K_{x,1}$ (see eq 3), only the results of $K_{x,2}$ will be shown.

In Figure 3, the reaction equilibrium coefficient $K_{x,2}$ has been plotted over the initial reactant ratio DMC/phenol for temperatures of 160, 180, and 200 °C. At 200 °C, only experiments at a DMC/phenol ratio of 1 have been carried out and therefore only the $K_{x,2}$ values at this ratio are shown in Figure 3.

From the data in Table 1, it was expected that the value of the equilibrium coefficient $K_{x,2}$ will increase slightly with temperature, something that also is observed in the present study (see Figure 3).

As can be seen from Figure 3, the equilibrium coefficient shows the same trend irrespective of temperature. The equilib-
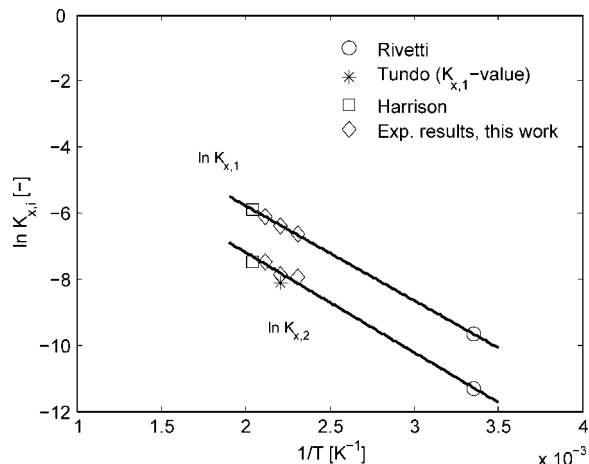
rium coefficient is increasing with decreasing DMC/phenol ratio, especially for ratios below 1. For the lowest measured DMC/phenol ratio of 0.25, the equilibrium coefficient at 180 °C is around 50% larger than the equilibrium coefficient at a DMC/phenol ratio of 1.

Moreover, it can be concluded that the initial presence of DPC seems to reduce the scatter of the inferred equilibrium coefficient at 180 °C. This is mainly due to a larger relative error made in the GC analysis for experiments with no DPC initially present. Comparison of Figures 2 and Figure 3 shows that the scatter of the $K_{x,2}$ coefficients in the DPC "free" experiments is indeed larger compared to the corresponding $K_{x,1}$ coefficients.

As the experiments reported in the literature as summarized in Table 1 have been carried out at different temperatures, the current experiments cannot easily be compared with them. However, a relative comparison is possible by using the van't Hoff equation:

$$\ln K_{x,1} = \frac{-\Delta H_r}{RT} + \frac{\Delta S}{R} \qquad (7)$$

In Figure 4, a van't Hoff plot with some of the present experimental results and the literature data (see Table 1) is shown. The experimental $K_{x,1}$—and $K_{x,2}$—values along with those taken from the literature have been fitted to the van't Hoff equation (eq 7) to determine the reaction enthalpies and entropies for reactions 1 and 2. The following averaged values of the equilibrium coefficients (at a 1:1 DMC/phenol ratio) derived from the present experiments have been used in Figure 4: at 160 °C, $K_{x,1} = 1.30 \times 10^{-3}$ and $K_{x,2} = 3.56 \times 10^{-4}$; at 180 °C, $K_{x,1} = 1.70 \times 10^{-3}$ and $K_{x,2} = 3.84 \times 10^{-4}$; at 200 °C, $K_{x,1} = 2.25 \times 10^{-3}$ and $K_{x,2} = 5.65 \times 10^{-4}$.

As can be seen in Figure 4, the data points are very well in line, with the exception of the single data point of Tundo et al.[7] If the value taken from Tundo et al.[7] is omitted, the reaction enthalpies ΔH_i and the reaction entropies ΔS_i of reaction 1 and 2 can be determined from the fitted straight lines given in Figure 4 by applying the van't Hoff equation (eq 7). The unit of temperature in the van't Hoff equation is kelvin [K]:

$$\ln K_{x,1} = \frac{-23.8 \text{ kJ mol}^{-1}}{RT} - \frac{0.346 \text{ J mol}^{-1} \text{ K}^{-1}}{R} \qquad (8)$$

$$\ln K_{x,2} = \frac{-25.2 \text{ kJ mol}^{-1}}{RT} - \frac{9.48 \text{ J mol}^{-1} \text{ K}^{-1}}{R} \qquad (9)$$

The two reaction enthalpies $\Delta H_1 = 23.8$ kJ mol^{-1} and $\Delta H_2 = 25.2$ kJ mol^{-1} (see eqs 8 and 9) are within 1% and 10% of

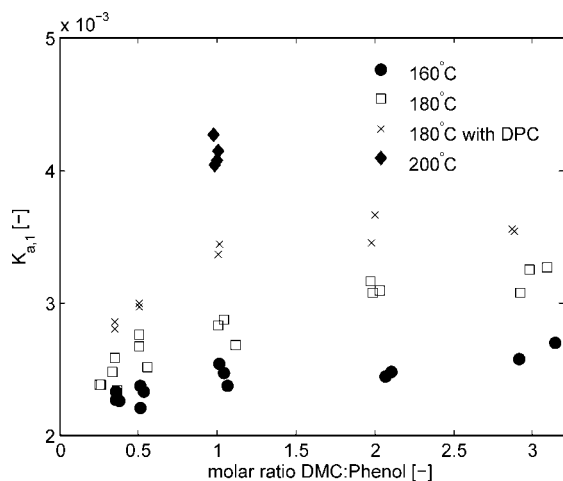**Figure 5.** $K_{a,1}$ over the initial reactant ratio at three different temperatures.

Figure 6. $K_{a,2}$ over the initial reactant ratio at three different temperatures.

the corresponding Gibbs free energy values given by Rivetti,[4] respectively. As the two reactions are only slightly endothermic—in this case the reaction entropy ΔS is small—the inferred values of the reaction enthalpy appear to be reliable.

The values of the two reaction entropies $\Delta S_1 = -0.346$ J mol^{-1} K^{-1} and $\Delta S_2 = -9.48$ J mol^{-1} K^{-1}—a given in eqs 8 and 9—should be interpreted with care as the experimental error has the same order of magnitude as the estimated ΔS values. Thus, the ΔS cannot be considered reliable.

8. Equilibrium Coefficients $K_{a,1}$ and $K_{a,2}$

The equilibrium coefficient $K_{a,1}$ based on activities at temperatures of 160, 180, and 200 °C is plotted versus the initial reactant ratio DMC/phenol in Figure 5. It can be clearly seen that the equilibrium coefficient $K_{x,1}$ depicted in Figure 2 shows a completely different trend than the activity based equilibrium coefficient $K_{a,1}$ as shown in Figure 5.

Of course, this difference is due to the activity coefficients introduced in the equilibrium coefficient $K_{a,1}$. The activity coefficients are supposed to account for the nonidealities in the system and to cause normalization. Hence, it was expected that the equilibrium coefficient $K_{a,1}$ would be nearly independent of the initial concentration of DMC/phenol and would only be a function of temperature.

As can be seen from Figure 5 the relative difference between the largest value of $K_{a,1}$ and the smallest value of $K_{a,1}$ at 160 °C is considerably lower than the relative deviation between the largest and the smallest $K_{x,1}$ value (see Figure 2). This is also reflected in the average value of $K_{a,1}$ of 2.41×10^{-3} with a 95% confidence interval of 7.6×10^{-5} compared to an average value of $K_{x,1}$ of 1.24×10^{-3} with a 95% confidence interval of 1.49×10^{-4}. However, at a temperature of 180 °C, the results are less convincing when using the activity based approach. The trend of the equilibrium coefficient $K_{a,1}$ at 180 °C differs from that of the equilibrium coefficient $K_{a,1}$ at 160 °C in the way that it still depends slightly on the reactant ratio of DMC/phenol. Moreover, also the results for the experiments where initially a large excess of DPC was present now deviate by a constant offset of about 15% from the results of the "normal" experiments, where initially no DPC was present (see Figure 5). When no activity coefficients were used in the equilibrium expression, the results using either an initial excess of DPC or no initial DPC matched very well (see Figure 2). When looking further into the results, the dependence of $K_{a,1}$ on the DMC/phenol ratio is strongest at low initial reactant ratios (DMC/phenol = 0.25)
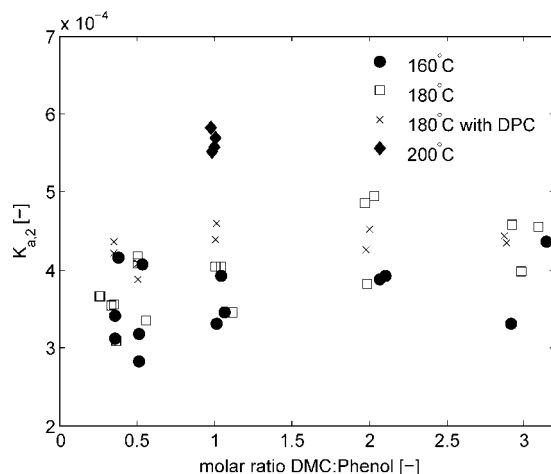
while this influence levels off at ratios around 2. The trend of the equilibrium coefficient $K_{a,1}$ at especially 180 °C (see Figure 5) is almost the same as the trend of $K_{x,1}$ at 180 °C where the value of the equilibrium coefficient is steadily decreasing with increasing DMC/phenol ratio. When comparing the deviation from the average value, it becomes clear that, at 180 °C, the mole fraction based approach ($K_{x,1} = 1.68 \times 10^{-3}$ with a 95% confidence interval of 1.59×10^{-4}) yields a slightly larger deviation than the activity based approach ($K_{a,1} = 2.82 \times 10^{-3}$ with a 95% confidence interval of 1.52×10^{-4}) if the experiments, where DPC is initially present, are neglected. The deviation of the $K_{x,1}$ values of less than 10% found between the two experimental series at 180 °C can mainly be attributed to an error in the GC analysis as the absolute amounts of MPC and DPC are significantly lower in the experiments without DPC present compared to those with DPC present.

The reason for both the remaining dependency on the ratio of DMC/phenol and the offset of the experiments with and without the initial presence of an excess of DPC can probably be attributed to an error in the prediction of one or more activity coefficients. As mentioned previously, UNIFAC typically predicts activity coefficients within an accuracy of 15%, and this is also the following: (1) the margin seen in the offset of the experiments at 180 °C with and without initial DPC and (2) the variation around the average value when changing the ratio of DMC to phenol. A margin of about 15% is not bad at all, considering the inherent (but at this point unavoidable) inaccuracy of UNIFAC.

The equilibrium coefficient $K_{a,2}$ based on activities at temperatures of 160, 180, and 200 °C as a function of the initial reactant ratio DMC/phenol is depicted in Figure 6. It can be seen that, just like $K_{x,1}$, the equilibrium coefficient $K_{a,2}$ (see Figure 6) shows a completely different trend than the concentration based equilibrium coefficient $K_{x,2}$ (Figure 3). Furthermore, it can be observed that the $K_{a,2}$ values at 160, 180, and 200 °C with initial DPC present are (for each series) located within a much smaller bandwidth than the corresponding $K_{x,2}$ values (about a factor of 2), and do not seem to systematically depend on the initial ratio of DMC to phenol. Finally, it can also be seen that there is no systematic offset for the results for $K_{a,2}$ for the two experimental series at 180 °C with and without the initial presence of DPC.

The average $K_{a,2}$ value at 180 °C of 3.98×10^{-4} with a 95% confidence interval of 2.65×10^{-5} (no initial DPC present) is close to the average $K_{a,2}$ (initial DPC present) value at 180 °C of 4.31×10^{-4} with a 95% confidence interval of 1.30×10^{-5}.
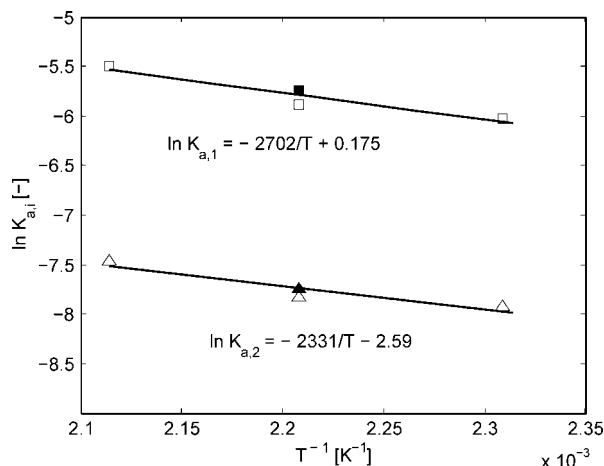
Figure 7. Van't Hoff plot for $K_{a,1}$ and $K_{a,2}$. Open symbols are for experiments without the initial presence of DPC; closed symbols are for the experiments with the initial presence of DPC.

Table 2. Parameter Values for the Equilibrium Coefficients According to the Equation $\ln K_{a,i} = -\Delta H_r/(RT) + \Delta S/R^a$

equilibrium coefficient	ΔH_r [kJ mol^{-1}]	ΔS [kJ mol^{-1} K^{-1}]
$K_{a,1}$	22.5	1.46×10^{-3}
$K_{a,2}$	19.4	21.5×10^{-3}

^{a} See eq 7.

The 95% confidence intervals show quantitatively that the scatter of the $K_{a,2}$ values at 180 °C resulting from DPC "free" experiments is nearly twice as large as that of the $K_{a,2}$ values derived from experiments where initial DPC was present. This is partly caused by the larger error in the determination in the mole fraction of DPC for the experiments where no initial DPC is present but can—with respect to $K_{a,2}$—additionally be influenced by a difference in accuracy of K_γ for both situations.

In all three cases the $K_{a,2}$ value is reasonably constant with a relative deviation of around 10% ($K_{a,2}$ at 180 °C initial DPC) and <15% ($K_{a,2}$ at 160 and 180 °C) in the 95% confidence interval. Hence, it seems that for $K_{a,2}$ the influence of the reactant ratio DMC/phenol on the equilibrium coefficient as observed for $K_{x,2}$ can be reduced by applying activity coefficients.

8.1. Temperature Dependence of the Equilibrium Coefficients $K_{a,1}$ and $K_{a,2}$. The experimental results for all molar DMC/phenol ratios at three different temperatures, namely 160, 180, and 200 °C (see Figures 5 and 6), were used to determine the temperature dependence of the equilibrium coefficient $K_{a,1}$ of reaction 1 and the equilibrium coefficient $K_{a,2}$ of reaction 2. The values for $K_{a,1}$ and $K_{a,2}$ as used in this analysis were the averaged values for these parameters, based on the results presented in Figures 5 and 6. The van't Hoff plots for $K_{a,1}$ and $K_{a,2}$ in the temperature range between 160 and 200 °C are shown in Figure 7.

As the previous sections showed, there is still a dependence of the ratio of DMC/phenol on the respective $K_{a,i}$ values (especially $K_{a,1}$—most probably to a large extent caused by uncertainties in the activity coefficients predicted by UNIFAC), the proposed relation for $K_{a,1}$ and $K_{a,2}$—and the corresponding thermodynamic parameters as reported in Table 2—might change when in future years more reliable data for the activity coefficients become available. To facilitate the reevaluation of the temperature dependence, the originally measured equilibrium data are reported in the Supporting Information and can be used to update the relation for $K_{a,1}$ and $K_{a,2}$.

9. Conclusion

In this study the experimentally determined equilibrium coefficients of the reaction of DMC with phenol yielding the intermediate MPC and the equilibrium coefficient of the consecutive transesterification reaction of MPC with phenol have been presented. The influence of temperature on these equilibrium coefficients in the temperature range between 160 and 200 °C has been measured as well as the influence of the initial reactant ratio of DMC/phenol on the equilibrium coefficient.

It is shown that the chemical equilibrium coefficients in terms of mole fractions display a pronounced dependency on the initial reactant ratio of DMC/phenol. By employing activities instead of only mole fractions in the calculation of the equilibrium coefficient the influence on the reactant ratio DMC/phenol could be reduced. The $K_{a,2}$ value of the transesterification reaction 2 is nearly constant over the whole range of employed initial DMC/phenol ratios, whereas the $K_{a,1}$ value of the first transesterification reaction still shows a dependence, especially at 180 °C. The remaining dependence of the $K_{a,1}$ value on the initial DMC/phenol ratio might on one hand be attributed to experimental (analysis) errors, in particular in the experiments without initial DPC present. Since the experimentally determined mole fractions serve as input for the activity coefficient calculations, any errors in the experimental GC results will be amplified. On the other hand, there is also uncertainty in the UNIFAC parameters derived from the scarce available VLE data in the literature as well as the expected increasing inaccuracy of applying the UNIFAC G^E model to temperatures above 150 °C.

The temperature dependence of the equilibrium coefficients $K_{a,1}$ and $K_{a,2}$ in the temperature range between 160 and 200 °C has been fitted to the well-known Van't Hoff equation. The fitting procedure yielded $\ln K_{a,1} = -22.5$ [kJ mol^{-1}]/$(RT) + 1.46 \times 10^{-3}$ [kJ mol^{-1} K^{-1}]/R and $\ln K_{a,2} = -19.4$ [kJ mol^{-1}]/$(RT) + 21.5 \times 10^{-3}$ [kJ mol^{-1} K^{-1}]/R. The activity based equilibrium coefficients $K_{a,1}$ and $K_{a,2}$ show only a moderate temperature dependence. It might be expected that another G^E model based on experimental VLE data for the components of interest in this study might yield significantly better results with respect to the derived $K_{a,1}$ values, but unfortunately, there is insufficient data in the literature to apply such a model. Nevertheless it is not the goal of this study to eliminate or reduce the remaining uncertainties in the applied G^E model by fitting the interaction parameters to new experimental VLE data as this would require various complete new and extensive VLE studies and is therefore beyond the scope of this work. Despite the inherent uncertainties of the UNIFAC model, the activity based equilibrium coefficients $K_{a,1}$ and $K_{a,2}$ derived from experimental data presented in this work and the activity coefficients calculated with UNIFAC show a fair (in case of $K_{a,1}$) to good (in case of $K_{a,2}$) predictive character.

However, the derived $K_{a,i}$ equations should be used with precautions at completely different experimental conditions as the validity of the $K_{a,i}$ equations at severe other conditions has not been tested exhaustively. Nevertheless, it is expected that the herein presented activity based temperature dependent correlations of $K_{a,1}$ and $K_{a,2}$ can find its application in the modeling of equilibrium based reactive distillation processes for the industrial relevant system presented in this work.

Notation

ΔH_r = reaction enthalpy [kJ mol^{-1}]

ΔS = reaction entropy [kJ mol^{-1} K^{-1}]

γ = activity coefficient [−]

$K_{x,i}$ = mole fraction based equilibrium coefficient [−]

$K_{\gamma,i}$ = product of activity coefficients belonging to $K_{x,i}$ [−]

$K_{a,i}$ = activity based equilibrium coefficient [−]

R = gas constant 8.314×10^{-3} [kJ mol^{-1} K^{-1}]

T = temperature [K]

x_j or x_k = mole fraction of components j and k, respectively [−]

j,k = component j and k, respectively [−]

i = reaction i [−]

Supporting Information Available: Experimental raw data as well as a table with the employed UNIFAC parameters. This information is available free of charge via the Internet at http://pubs.acs.org.

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