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

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1 Supporting Information Available

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

Table 4: UNIFAC interaction parameters used to calculate relevant activity coefficients taken from Haubrock.¹⁰

Interaction Group _m -Group _n	$A_{m,n}$	$A_{n,m}$
CH ₃ OH-OCOO	180	300
OH-OCOO	80	250
CH ₂ -OCOO	450	500
ACH-OCOO	-220	250
ACOH-OCOO	189	187

Table 5: Raw data equilibrium measurements and activity coefficients at 160° C, 180° C and 200° C. Mole fractions at equilibrium have been experimentally determined, the activity coefficients at equilibrium have been determined using UNIFAC (see¹⁰).

Ratio											
T [° C]	$\frac{n_{DMC}}{n_{PhOH}}$	x_{MeOH}	x_{DMC}	x_{MPC}	x_{PhOH}	x_{DPC}	γ_{MeOH}	γ_{DMC}	γ_{MPC}	γ_{PhOH}	γ_{DPC}
160° C	1.06	$1.884 \cdot 10^{-2}$	$4.872 \cdot 10^{-1}$	$1.417 \cdot 10^{-1}$	$4.797 \cdot 10^{-2}$	$9.324 \text{E-}05$	1.267	0.788	1.060	0.820	0.918
	1.04	$1.909 \cdot 10^{-2}$	$4.763 \cdot 10^{-1}$	$1.472 \cdot 10^{-1}$	$4.898 \cdot 10^{-2}$	$1.121 \cdot 10^{-4}$	1.245	0.781	1.064	0.827	0.933
	1.02	$2.018 \cdot 10^{-2}$	$4.760 \cdot 10^{-1}$	$1.428 \cdot 10^{-1}$	$4.894 \cdot 10^{-2}$	$8.684 \text{E-}05$	1.245	0.782	1.065	0.826	0.934
	2.11	$1.705 \cdot 10^{-2}$	$6.783 \cdot 10^{-1}$	$1.071 \cdot 10^{-1}$	$2.939 \cdot 10^{-2}$	$4.163 \text{E-}05$	1.727	0.900	0.932	0.660	0.619
	2.07	$1.501 \cdot 10^{-2}$	$6.816 \cdot 10^{-1}$	$1.189 \cdot 10^{-1}$	$2.914 \cdot 10^{-2}$	$5.129 \text{E-}05$	1.740	0.900	0.928	0.659	0.613
	3.14	$1.453 \cdot 10^{-2}$	$7.621 \cdot 10^{-1}$	$1.004 \cdot 10^{-1}$	$2.133 \cdot 10^{-2}$	$3.314 \text{E-}05$	1.958	0.942	0.840	0.580	0.482
	2.91	$1.350 \cdot 10^{-2}$	$7.342 \cdot 10^{-1}$	$1.160 \cdot 10^{-1}$	$2.406 \cdot 10^{-2}$	$3.659 \text{E-}05$	1.884	0.928	0.872	0.609	0.527
	0.53	$2.031 \cdot 10^{-2}$	$3.437 \cdot 10^{-1}$	$1.451 \cdot 10^{-1}$	$6.214 \cdot 10^{-2}$	$1.662 \cdot 10^{-4}$	0.983	0.698	1.086	0.906	1.087
	0.51	$1.866 \cdot 10^{-2}$	$3.103 \cdot 10^{-1}$	$1.610 \cdot 10^{-1}$	$6.548 \cdot 10^{-2}$	$1.736 \cdot 10^{-4}$	0.925	0.676	1.081	0.923	1.113
	0.51	$2.000 \cdot 10^{-2}$	$3.081 \cdot 10^{-1}$	$1.402 \cdot 10^{-1}$	$6.577 \cdot 10^{-2}$	$1.268 \cdot 10^{-4}$	0.919	0.675	1.083	0.924	1.119
	0.38	$1.981 \cdot 10^{-2}$	$2.754 \cdot 10^{-1}$	$1.426 \cdot 10^{-1}$	$6.904 \cdot 10^{-2}$	$2.115 \cdot 10^{-4}$	0.865	0.655	1.078	0.938	1.142
	0.35	$2.072 \cdot 10^{-2}$	$2.290 \cdot 10^{-1}$	$1.310 \cdot 10^{-1}$	$7.370 \cdot 10^{-2}$	$1.601 \cdot 10^{-4}$	0.791	0.627	1.070	0.955	1.174

Table 5 – Continued

Ratio											
T [° C]	$\frac{n_{DMC}}{n_{PhOH}}$	x_{MeOH}	x_{DMC}	x_{MPC}	x_{PhOH}	x_{DPC}	γ_{MeOH}	γ_{DMC}	γ_{MPC}	γ_{PhOH}	γ_{DPC}
0.36	2.134·10 ⁻²	2.467·10 ⁻¹	1.330·10 ⁻¹	1.330·10 ⁻²	7.185·10 ⁻¹	1.630·10 ⁻⁴	0.819	0.638	1.076	0.948	1.166
180° C	1.04	1.961·10 ⁻²	4.926·10 ⁻¹	1.862·10 ⁻¹	4.690·10 ⁻¹	1.392·10 ⁻⁴	1.280	0.844	1.042	0.868	0.912
	1.12	1.941·10 ⁻²	4.729·10 ⁻¹	1.806·10 ⁻¹	4.895·10 ⁻¹	1.253·10 ⁻⁴	1.237	0.835	1.049	0.879	0.934
	1.01	1.808·10 ⁻²	4.700·10 ⁻¹	2.046·10 ⁻¹	4.913·10 ⁻¹	1.793·10 ⁻⁴	1.235	0.832	1.048	0.881	0.935
	1.99	2.149·10 ⁻²	6.160·10 ⁻¹	1.426·10 ⁻¹	3.482·10 ⁻¹	5.797E-05	1.549	0.900	0.984	0.787	0.761
	2.03	2.156·10 ⁻²	6.592·10 ⁻¹	1.278·10 ⁻¹	3.064·10 ⁻¹	5.592E-05	1.649	0.919	0.954	0.755	0.701
	1.97	1.880·10 ⁻²	6.512·10 ⁻¹	1.541·10 ⁻¹	3.145·10 ⁻¹	7.887E-05	1.634	0.914	0.958	0.765	0.712
	3.10	1.790·10 ⁻²	7.330·10 ⁻¹	1.279·10 ⁻¹	2.363·10 ⁻¹	4.391E-05	1.834	0.947	0.890	0.698	0.593
	2.92	1.656·10 ⁻²	7.393·10 ⁻¹	1.275·10 ⁻¹	2.313·10 ⁻¹	4.632E-05	1.852	0.948	0.884	0.694	0.584
	2.99	1.656·10 ⁻²	7.172·10 ⁻¹	1.460·10 ⁻¹	2.515·10 ⁻¹	5.124E-05	1.801	0.939	0.904	0.713	0.616
	0.56	1.890·10 ⁻²	3.007·10 ⁻¹	1.917·10 ⁻¹	6.610·10 ⁻¹	2.304·10 ⁻⁴	0.922	0.755	1.072	0.950	1.079
	0.51	2.091·10 ⁻²	3.007·10 ⁻¹	1.888·10 ⁻¹	6.592·10 ⁻¹	2.526·10 ⁻⁴	0.926	0.758	1.074	0.948	1.081
	0.50	2.138·10 ⁻²	2.989·10 ⁻¹	1.793·10 ⁻¹	6.616·10 ⁻¹	2.314·10 ⁻⁴	0.922	0.757	1.075	0.949	1.083
	0.36	1.766·10 ⁻²	2.084·10 ⁻¹	1.753·10 ⁻¹	7.562·10 ⁻¹	2.750·10 ⁻⁴	0.778	0.713	1.064	0.974	1.126

Table 5 – Continued

Ratio											
T [° C]	$\frac{n_{DMC}}{n_{PhOH}}$	x_{MeOH}	x_{DMC}	x_{MPC}	x_{PhOH}	x_{DPC}	γ_{MeOH}	γ_{DMC}	γ_{MPC}	γ_{PhOH}	γ_{DPC}
0.34	1.863·10 ⁻²	2.134·10 ⁻¹	1.769·10 ⁻¹	1.769·10 ⁻²	7.500·10 ⁻¹	2.966·10 ⁻⁴	0.785	0.715	1.067	0.973	1.127
	0.35	2.137·10 ⁻²	2.154·10 ⁻¹	1.608·10 ⁻¹	7.470·10 ⁻¹	2.343·10 ⁻⁴	0.785	0.717	1.074	0.971	1.135
	0.27	2.017·10 ⁻²	1.557·10 ⁻¹	1.362·10 ⁻¹	8.102·10 ⁻¹	2.581·10 ⁻⁴	0.701	0.692	1.062	0.983	1.155
180° C	1.01	1.211·10 ⁻²	4.555·10 ⁻¹	3.191·10 ⁻¹	5.000·10 ⁻¹	4.434·10 ⁻⁴	1.239	0.774	1.052	0.849	0.940
with	1.02	1.274·10 ⁻²	4.659·10 ⁻¹	3.076·10 ⁻¹	4.902·10 ⁻¹	4.108·10 ⁻⁴	1.259	0.782	1.050	0.842	0.929
4 DPC	2.00	1.045·10 ⁻²	6.291·10 ⁻¹	3.011·10 ⁻¹	3.300·10 ⁻¹	2.699·10 ⁻⁴	1.577	0.862	0.981	0.742	0.735
	1.98	1.011·10 ⁻²	6.236·10 ⁻¹	3.013·10 ⁻¹	3.359·10 ⁻¹	2.722·10 ⁻⁴	1.552	0.857	0.987	0.752	0.750
	2.87	8.962·10 ⁻³	7.058·10 ⁻¹	2.819·10 ⁻¹	2.569·10 ⁻¹	2.138·10 ⁻⁴	1.684	0.881	0.951	0.712	0.674
0.51	2.88	8.571·10 ⁻³	6.997·10 ⁻¹	2.978·10 ⁻¹	2.617·10 ⁻¹	2.370·10 ⁻⁴	1.674	0.879	0.954	0.717	0.682
	0.50	1.200·10 ⁻²	2.908·10 ⁻¹	3.100·10 ⁻¹	6.655·10 ⁻¹	6.815·10 ⁻⁴	0.932	0.674	1.056	0.935	1.091
	0.50	1.201·10 ⁻²	2.840·10 ⁻¹	3.056·10 ⁻¹	6.728·10 ⁻¹	6.523·10 ⁻⁴	0.919	0.669	1.055	0.938	1.097
0.35	1.082·10 ⁻²	2.135·10 ⁻¹	2.972·10 ⁻¹	2.972·10 ⁻²	7.449·10 ⁻¹	9.770·10 ⁻⁴	0.805	0.625	1.036	0.963	1.132
	0.35	1.138·10 ⁻²	2.188·10 ⁻¹	2.909·10 ⁻¹	7.399·10 ⁻¹	8.668·10 ⁻⁴	0.813	0.629	1.038	0.962	1.131

Table 5 – Continued

T [° C]	Ratio		x_{MeOH}	x_{DMC}	x_{MPC}	x_{PhOH}	x_{DPC}	γ_{MeOH}	γ_{DMC}	γ_{MPC}	γ_{PhOH}	γ_{DPC}
	$\frac{n_{DMC}}{n_{PhOH}}$	$\frac{n_{DPC}}{n_{PhOH}}$										
200° C	0.98		$2.459 \cdot 10^{-2}$	$4.585 \cdot 10^{-1}$	$2.181 \cdot 10^{-1}$	$4.949 \cdot 10^{-2}$	$2.103 \cdot 10^{-1}$	1.142	0.757	1.054	0.881	0.990
	0.99		$2.266 \cdot 10^{-2}$	$4.702 \cdot 10^{-1}$	$2.192 \cdot 10^{-1}$	$4.850 \cdot 10^{-2}$	$2.076 \cdot 10^{-1}$	1.174	0.767	1.053	0.870	0.972
	1.00		$2.392 \cdot 10^{-2}$	$4.722 \cdot 10^{-1}$	$2.155 \cdot 10^{-1}$	$4.821 \cdot 10^{-2}$	$1.996 \cdot 10^{-1}$	1.141	0.756	1.052	0.882	0.988