Electronic supplementary information

Appendix 1: Kirchoff's laws applied to the glycerol-ethylene carbonate system

The equilibrium constant can be related to the Gibbs enthalpy of reaction with the following relationship:

$$\ln K = -\frac{\Delta G_r^0}{R \cdot T} \qquad (1)$$

in which R is the ideal gas constant, T is the temperature, and ΔG^0_r is the standard Gibbs free energy, which can further be defined by Equation 2:

$$\Delta G_r^0 = \Delta H_r^0 - T \cdot \Delta S_r^0 \qquad (2)$$

where ΔH^0_r and ΔS^0_r are the enthalpy and entropy of reaction, respectively. Both can be defined taking into account the stoichiometric coefficients vi of the reaction (positive for reaction products and negative for reactants), the enthalpies of formation ($\Delta H^0_{f,i}$) and entropies (S^0_i) along with the contribution to the enthalpy and entropy from the standard temperature (298 K) to the temperature considered in each case, for which the specific heat capacity as a function of temperature, $C_p(T)$, must be considered:

$$\Delta H_r^0 = \sum_i \upsilon_i \cdot \Delta H_{f,i}^0 + \sum_i \nu_i \cdot \int_{298}^{T} C_{p,i}(T)\,dT \qquad (3)$$

$$\Delta S_r^0 = \sum_i \upsilon_i \cdot S_i^0 + \sum_i \nu_i \cdot \int_{298}^{T} \frac{C_{p,i}(T)}{T}\,dT \qquad (4)$$

Tables A1.1, A1.2 and A1.3 summarize the calculations and bibliographic information related to the thermodynamic study presented in equations 1 through 4. Specifically, Table 3 compiles the equilibrium constants calculated at the temperatures at which the reactions were performed, and their values were high enough to consider that the reaction is shifted towards the products (with observed experimental equilibrium conversions virtually reaching completion in all cases).

Table A1.1 Enthalpies of formation and entropies of the components taking part in the transesterification of EtCarb and Gly.

Component	ΔH_0^f (kJ·mol^{-1})	Reference	Observations	S_0 (J·mol^{-1}·K^{-1})	Reference	Observations
Gly	-668.52	43		206.30	43	
EtCarb	-573.50[a]	44 and 45	$\Delta H^0_{f,g}$=-510.7 kJ·mol^{-1} λ_v=62.8 kJ·mol^{-1}	107.60[b]	46	S^0_g=132.54 J·mol^{-1}·K^{-1} T_{eb}= 533.8 K
GlyCarb	-784.90[a]	44 and 45	$\Delta H^0_{f,g}$=-699 kJ·mol^{-1} λ_v=85.9 kJ·mol^{-1}	230.11[b]	47	S^0_g=386.20 J·mol^{-1}·K^{-1} T_{eb}= 550.3 K
MEG	-455.30	43		163.20	43	

[a] The standard enthalpy of formation in liquid state was calculated as the difference between the standard molar enthalpy of formation in gas phase and the standard latent heat of vaporization: $\Delta H^0_{f,l} = \Delta H^0_{f,g} - \lambda^0_v$.

[b] The standard entropy in liquid state was calculated as the difference between the standard molar entropy in gas phase and the ratio between the latent heat and temperature: $S^0_l = S^0_g - \lambda^0_v/T$.

Table A1.2 Specific heat capacity correlations and parameters as a function of temperature found in literature for the components involved in the transesterification of EtCarb and Gly

Component	Equation and parameters				Reference
	$C_p\left(J\cdot mol^{-1}\cdot K^{-1}\right) = R\cdot\left[A + B\frac{T}{100} + C\left(\frac{T}{100}\right)^2\right]$				
	A	B	C		
Gly	5.1401	1.4964	0.1523		47
EtCarb	-34.3637	0.1359	0		48
	$C_p(J\cdot mol^{-1}\cdot K^{-1}) = a + b\cdot T + c\cdot T^2 + d\cdot T^3$				
	a	b	c·10^3		
GlyCarb	-108.9200	-1.7968	4.4743		49
MEG	75.8780	0.6418	-1.6493	1.6940	49

Table A1.3 Enthalpy, entropy standard Gibbs free energy of reaction and chemical equilibrium constant of the transesterification of EtCarb and Gly at the temperatures tested in this work

Temperature (ºC)	ΔH^0_r (kJ·mol^{-1})	ΔS^0_r (J·mol^{-1}·K^{-1})	ΔG^0_r (kJ·mol^{-1})	K
100	108.26	2186.66	-707.37	14.42
110	106.53	2487.25	-846.08	20.78
120	104.91	2790.85	-991.89	30.04
130	103.41	3097.22	-1144.77	43.55
140	102.04	3406.11	-1304.69	63.29

Appendix 2: Activity coefficients calculated by means of COSMO-RS

COSMO-RS (COnductor like Screening Model for Real Solvents) is a quantum-chemical computer-based method developed by Klamt and co-workers to predict the thermodynamic equilibrium properties of fluids and liquid mixtures [A2.1]. This methodology processes the screening charge densities on the surface of molecules from quantum chemical calculations, and subsequently introduces a statistical thermodynamic procedure for the molecular surface interactions to estimate the chemical potentials of the species in solution, which are the basis for the calculation of the thermodynamic equilibrium properties [A2.2]. A feature of this prediction method is that only structural information of the compounds is required to perform the thermodynamic estimations. Thus far, different publications have supported the general suitability of COSMO-RS to estimate the thermodynamic properties of a broad variety of systems, including the activity coefficients of fluid mixtures [A2.3]

The activity coefficients were computed at 100, 110, 120, 130 and 140 ºC and different composition of the mixtures within the range of variation of the composition interval given the initial molar ratios of ethylene carbonate to glycerol,. Table A2.1 compiles the average values obtained from computing these activity coefficients.

Table A2.1 Average activity coefficients for each component at the temperatures experimentally tested obtained from calculations by COSMO-RS

Temperature	Molar ratio of EtCarb to Gly =2				Molar ratio of EtCarb to Gly =3			
(ºC)	γ_{Gly}	γ_{EC}	γ_{GC}	γ_{MEG}	γ_{Gly}	γ_{EC}	γ_{GC}	γ_{MEG}
100	1.464	1.201	0.887	1.317	1.767	1.122	0.865	1.488
110	1.425	1.179	0.898	1.286	1.692	1.108	0.878	1.437
120	1.388	1.160	0.908	1.257	1.624	1.096	0.890	1.391
130	1.354	1.142	0.917	1.231	1.561	1.085	0.900	1.350
140	1.322	1.126	0.924	1.207	1.504	1.075	0.908	1.312

References

A2.1 A. Klamt, in *COSMO-RS: From quantum chemistry to fluid phase thermodynamics and drug design*, Elsevier Science Ltd., Amsterdam, 2005.

A2.2 A. Klamt, F. Eckert, A. Wolfgang. *Annual Review of Chemical and Biomolecular Engineering.* 2010, **1**, 101-122

A2.3 M. Gonzalez-Miquel, J. Palomar, F. Rodriguez. *The Journal of Physical Chemistry B.* 2013, **117**, 296-306