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Thermodynamic equilibrium for the dehydration of 1-butanol to di-*n*-butyl ether

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ABSTRACT

The thermodynamic equilibrium of the bimolecular dehydration of 1-butanol to di-*n*-butyl ether (DNBE) and water in the liquid phase was studied. Equilibrium experiments were performed at 4 MPa and in the temperature range of 413–463 K over the ion exchange resin Amberlyst-70. The thermodynamic equilibrium for the side reactions (dehydration to 1-butene, olefins isomerization, olefins hydration and branched ether formation) was also studied. The equilibrium constant for the dehydration reaction of 1-butanol to di-*n*-butyl ether and water was found to be independent of the operating temperature, within the limits of the experimental error ($\pm 5.2\%$). The experimental equilibrium constants at 413–463 K allows to estimate the standard enthalpy change of reaction ($\Delta_r H^0_{(l)} = -0.3 \pm 2.9\,\mathrm{kJ\,mol^{-1}}$) and the standard entropy change of reaction ($\Delta_r S^0_{(l)} = 26.8 \pm 6.7\,\mathrm{J\,mol^{-1}\,K^{-1}}$). From these values the standard formation enthalpy ($\Delta_f H^0_{\mathrm{DNBE,(l)}}$) and the molar entropy of DNBE ($S^0_{\mathrm{DNBE,(l)}}$) at 298.15 K were computed to be $-370.5 \pm 10.9\,\mathrm{kJ\,mol^{-1}}$ and $408.3 \pm 6.8\,\mathrm{J\,mol^{-1}\,K^{-1}}$, respectively.

1. Introduction

During the last twenty years European Regulation has become increasingly stringent in terms of emissions standards (Regulation EC 715/2007), quality of fuels (Directive 2009/30/EC) and the mandatory use of biofuels, setting a 10% minimum target for the share of biofuels in transport petrol and diesel consumption by 2020 (Directive 2009/28/EC).

A valuable option to meet these requirements without modification of existing diesel engines is the reformulation of diesel to include oxygenates. A number of different oxygenates (various alcohols, ethers and esters) have been considered as diesel fuel components. Among them, linear monoethers show the best properties to be added to diesel given their high cetane number, cold flow properties and mixture stability (Pecci et al., 1991). Linear ethers have also proved to reduce diesel exhaust such as CO, particulate matter and unburned hydrocarbons and to substantially improve the trade-off between particulate and NO$_x$ due to the presence

of oxygen in the ether molecules (Marchionna et al., 1996). Di-*n*-butyl ether (DNBE) is considered a highly promising oxygenate as it keeps a good balance between cetane number and cold flow properties and, in addition, it can be obtained from biobutanol what means that it can be considered a new bioether.

In a previous work (Pérez et al., 2014) we showed that di-*n*-butyl ether can be successfully synthesized through the bimolecular dehydration of 1-butanol over acidic ion-exchange resins. Among the tested resins, Amberlyst-70 proved to be the most suitable catalyst for industrial use due to its high selectivity to DNBE and its thermal stability, up to 473 K.

However, to develop a potential industrial process a reliable knowledge of the reaction kinetics and the chemical equilibrium is required and, to the best of our knowledge, equilibrium data for the liquid-phase DNBE synthesis have not been reported yet. To overcome this lack of thermodynamic data, in this work we present experimental values of

Nomenclature

a_j	activity of compound j
DNBE	di-n-butyl ether
DVB	di-vinyl benzene
$\Delta_c S^0_j$	effect of vapor compression from the saturation pressure P^s_j to the standard pressure P^0 for compound j (J mol^{-1} K^{-1})
$\Delta_f H^0_{j,(l)}$	liquid-phase standard molar enthalpy change of formation of compound j (kJ mol^{-1})
$\Delta_{ig} S^0_j$	deviation of ideality of the vapor at 298.15 K and 1.013 bar for compound j (J mol^{-1} K^{-1})
$\Delta_r G^0_{i,(l)}$	liquid-phase standard free energy change of reaction i (kJ mol^{-1})
$\Delta_r H^0_{i,(l)}$	liquid-phase standard molar enthalpy change of reaction i (kJ mol^{-1})
$\Delta_r S^0_{i,(l)}$	liquid-phase standard molar entropy change of reaction i (J mol^{-1} K^{-1})
$\Delta_{vap} H^0_j$	standard vaporization enthalpy of compound j (J mol^{-1})
$\Delta_v S^0_j$	entropy change due to phase change for compound j (J mol^{-1} K^{-1})
$K_{eq,i}$	thermodynamic equilibrium constant of reaction i
$K_{\gamma,i}$	equilibrium constant of reaction i in terms of activity coefficients
K_Γ	Poynting correction factor
$K_{x,i}$	equilibrium constant of reaction i in terms of molar fractions
P	pressure (Pa)
P^0	standard pressure (Pa)
$P_{c,j}$	critical pressure of compound j
P^s_j	vapor pressure at standard temperature for compound j (Pa)
R	gas constant (J mol^{-1} K^{-1})
V_j	molar volume of compound j (m^3 mol^{-1})
$S^0_{j,(g)}$	gas-phase molar entropy of compound j (J mol^{-1} K^{-1})
$S^0_{j,(l)}$	liquid-phase molar entropy of compound j (J mol^{-1} K^{-1})
T	temperature (K)
TCD	thermal conductivity detector
$T_{c,j}$	critical temperature of compound j
x_j	molar fraction of compound j

Subscript
BuOBu' 1-(1-methylpropoxy) butane

Greek letters
γ_j	activity coefficients of compound j
ν_j	stoichiometric coefficient of compound j

the equilibrium constant of 1-butanol to di-n-butyl ether and water determined by direct measurement of the composition of the liquid mixture at equilibrium. The equilibrium constants of potential side reactions (intramolecular dehydration of 1-butanol to 1-butene, isomerization of 1-butene to *cis*-2-butene and *trans*-2-butene, olefins hydration to 2-butanol and 1-(1methylpropoxy) butane formation from the reaction between 1-butanol and the olefins) were also determined. From these values, thermodynamic properties such as the standard enthalpy change $\Delta_r H^0_{(l)}$, the standard entropy

change $\Delta_r S^0_{(l)}$ and the standard Gibbs energy $\Delta_r G^0_{(l)}$ of reactions were computed and compared with estimated and experimental values found in data banks. Whenever possible, recommended values for these thermochemical properties, as well as for the standard enthalpy of formation ($\Delta_f H^0_{(l)}$) and for the standard molar entropy ($S^0_{(l)}$) for the compounds present in the system are provided.

2. Materials and methods

2.1. Chemicals and catalyst

1-butanol ($\geq$99.4% pure; $\leq$0.1% butyl ether; $\leq$0.1% water) and DNBE ($\geq$99.0% pure; $\leq$0.05% water) supplied by Acros Organics, 1-butene ($\geq$99.0% pure) and 1,4-dioxane ($\geq$99.8% pure) supplied by Sigma Aldrich and *cis*-2-butene ($\geq$98.0% pure) supplied by TCI were used without further purification. Deionised water (resistivity 18.2 mΩ cm) was obtained in our laboratory.

The macroreticular thermostable resin Amberlyst-70 supplied by Rohm and Haas was used as catalyst. Amberlyst-70 is a low cross-linked (8%DVB) chlorinated and sulfonated copolymer of styrene-divinybenzene. Its maximum operating temperature is 473 K. The acid capacity, determined by titration against standard base following the procedure described by Fisher and Kunnin (1955), was found to be 2.65 meq. H$^+$/g. The catalyst was used in its commercial form (mean bead diameter = 0.59 mm).

2.2. Experimental setup

Experiments were carried out in a 100-mL-cylindrical high pressure autoclave (Autoclave Engineers, M010SS) made of 316 stainless steel (temperature limit: 232 °C, pressure range: 0–15 MPa). The system was equipped with a magnetic drive stirrer and with a 400 W electrical furnace for heating. Temperature was measured by a thermocouple located inside the reactor and stirring speed was measured by a tachometer. Both operation variables were controlled to ±1 °C and ±1 rpm, respectively, by an electronic control unit. The pressure was set to 4 MPa by means of N$_2$ to ensure that the medium is in liquid phase over the whole temperature range. One of the outlets of the reactor was connected directly to a liquid sampling valve, which injected 0.2 μL of pressurized liquid into a gas–liquid chromatograph (Agilent Technologies, 7820A).

2.3. Analysis

The composition of the liquid mixture was analyzed in-line using a dimethylpolysiloxane HP-Pona (50 m × 0.200 mm × 0.50 μm) capillary column. Chromatograph parameters were as follows: helium ($\geq$99.4% pure supplied by Abello Linde) at 70 mL min^{-1} constant flow was used as the carrier gas; volume injection 0.2 μL; split ratio 100:1; inlet temperature 423 K. The oven was programed with a 5.5 min initial hold at 423 K, followed by a 50 K min^{-1} ramp up to 453 K and held isotherm for 10 min.

The chromatograph was equipped with a TCD detector and the used parameters were as follows: detector temperature 523 K; reference flow 20 mL min^{-1}; makeup flow 4.9 mL min^{-1}.

2.4. Procedure

Preliminary experiments carried out at 423 K and 4 MPa showed that, when starting from pure 1-butanol, equilibrium