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Equilibrium Constants for Methyl *tert*-Butyl Ether Liquid-Phase Synthesis

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Equilibrium constants for the liquid-phase synthesis of methyl *tert*-butyl ether (MTBE) were determined experimentally in the temperature range 40–80 °C. Equilibrium was established in the methanol addition to isobutylene for obtaining MTBE over the sulfonic acid resin Lewatit SPC 118 as the catalyst in a batch reactor maintained at 1.6 MPa. The experimental equilibrium constant is given as a function of temperature, and enthalpy, free energy, and entropy changes have been determined as well. At 298 K, $\Delta H° = -38.0 \pm 0.8$ kJ mol^{-1}, $\Delta G° = -13.6 \pm 0.8$ kJ mol^{-1}, and $\Delta S° = -81.7 \pm 0.5$ J mol^{-1} K^{-1}. The UNIFAC estimates of activity coefficients have been used to describe the liquid-phase nonideality. A comparison of experimental, thermodynamic, and literature data has been carried out.

Introduction

There is currently great interest in methyl *tert*-butyl ether (MTBE) because of its excellent antiknock and poisoning emission reduction properties. The MTBE production is expected to be doubled in a few years.

MTBE is obtained by the addition reaction of methanol to isobutene. The reaction is reversible, moderately exothermic, and usually catalyzed by macroporous sulfonic ion resins (mainly Amberlyst 15 and Lewatit SPC 118). The selectivity is extremely high, but some byproducts such as dimethyl ether and diisobutylene can appear if the temperature is high enough and the molar methanol/isobutylene ratio is far from the stoichiometric one (*1*). The presence of *tert*-butyl alcohol is also possible if the reactor feed contains water.

Despite the fact that more than 1000 papers about MTBE can be found in the literature, only a very few of them bring out the reaction thermodynamics (*1–4*). Besides, as it will be presented in the Results and Discussion, the dispersion of data is significant in such a way that it would be a big problem to choose the better one.

The aim of the present work is to determine experimental values of the equilibrium constant by direct measurement of the mixture composition at equilibrium and to compare them with those calculated from thermodynamic data and those found in the open literature. The temperature range covers 40–50 °C, for which we did not find experimental equilibrium constants.

Experimental Section

Materials. Methanol HPLC (ROMIL Chemicals), with a minimum purity of 99.8% containing less than 0.2% water, and MTBE (MERCK, Schuchard) with a minimum purity of 99% containing less than 0.1 wt % water were used. Isobutylene of 99% purity was supplied by SEO, Barcelona, the main impurities being isobutane and linear butenes which do not react under our reaction conditions, and used without further purification. Nitrogen supplied by SEO, Barcelona, with a minimum purity of 99.998% was used to achieve the suitable pressure to maintain the reacting mixture in the liquid phase.

The ion-exchange resin Lewatit SPC 118 BG (now K-2631) (Bayer), used as the catalyst, is a macroporous sulfonated copolymer of styrene–divinylbenzene (DVB) containing a matrix cross-linked with approximately 18% DVB with a surface area (BET method) of 36 ± 1 m^2·g^{-1} and an exchange capacity determined by titration of 4.83 mequiv of HSO_3·g^{-1} of dry resin. The bead size distribution ranges from 0.25 to 1.6 mm, and the effective bead size is 0.63 mm (±0.05 mm).

Apparatus. The experiments were performed in a stainless steel jacketed reactor (200 cm^3) in a batchwise operation. Figure 1 shows the experimental setup. The temperature was measured with a thermocouple submerged in the liquid phase and was controlled within ±0.2 °C by thermostated water (thermostatic bath, LAUDA s15/12) containing propylene glycol that flows through the jacket. The reactor was connected directly to the liquid sampling valve (VALCO 4-CL4WE) which injects a small pressurized liquid volume (0.2 μL) to the gas chromatograph (HP 5890A). This technique has been shown to be suitable to analyze liquids and liquified gases with an excellent reproducibility (*5*).

Analysis. Helium (SEO, Barcelona) with a minimum purity of 99.998% was used to help the liquid sample to vaporize and, at the same time, to carry it to the conductivity sensor at a flow rate of 30 cm^3 min^{-1}. A 3 m × 3.2 mm o.d. stainless steel GLC column packed with Chromosorb 101 (80/100 mesh) was used to separate the mixture of MTBE, methanol, isobutylene, and nitrogen. The column was temperature programmed with a 5-min initial hold at 110 °C followed by a 10 °C/min ramp up to 220 °C, and held for 5 min.

Procedure. The methodology was as follows.

(1) A calculated amount of methanol and about 10 g of dry resin were charged into the open reactor. The resin was dried at 105 °C for 24 h, and the residual water amount, titrated by the Karl-Fisher method, was less than 3 wt %.

(2) After the reactor was closed, it was pressurized with N_2 at about 21 bar so as to check its sealing. This step was also used to remove the air.

(3) Then the reactor pressure was reduced to 3 bar, and an isobutylene quantity, given by the planned methanol/isobutylene ratio, was measured at 8 bar in a calibrated buret and charged into the reactor by shifting with nitrogen.

(4) At this time, the magnetic-drive stirrer was switched on at 500 rpm. The reactor pressure was at once set at 16 bar (absolute pressure), and a liquid amount of about 15 cm^3 was allowed to fill the auxiliary circuit (see Figure 1) for analysis using the liquid injection valve mentioned above. After waiting for thermal equilibrium between the 0.2 μL of liquid and the valve (about 30 s), the sample was injected to the chromatograph which allowed us to determine the initial concentration accurately.

(5) The remaining liquid in the auxiliary circuit was returned to the reactor by closing the sample valve (V_2 in Figure 1) and by opening the valve V_1 which allows nitrogen at 17 bar to shift the liquid. The reactor pressure was restored at 15 bar by a relief valve, V_8. The total pressure was maintained at 15 bar to ensure the liquid phase at every temperature.

(6) At the desired temperature, the reaction took place for enough time to reach the equilibrium, which was checked by taking samples at successive times until a stationary composition was obtained, within the limits of experimental error. Depending on temperature, it took several hours to get the equilibrium. Obviously, the waiting time was longer when the

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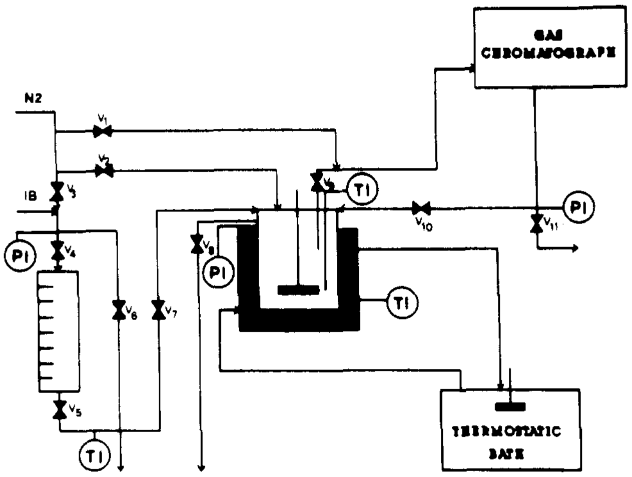

Figure 1. Experimental setup.

temperature was lower. The number of samples was as small as possible in order to reduce and avoid compound losses, particularly the isobutylene, every time that the reactor pressure was restored.

(7) If the amount of byproducts was negligible, the same charge was used to study the equilibrium at other temperatures. On the contrary, a fresh mixture was replaced.

(8) At lower temperatures (40 and 50 °C) a MTBE amount was initially charged into the reactor to lower the waiting time to reach the equilibrium. Even under that strategy the waiting time lasted sometimes 8 or more h.

(9) Experimental equilibrium constant K_x values were computed from the composition by using the following expression:

$$K_x = x_{\mathrm{MTBE}}/x_{\mathrm{MeOH}}x_{i\text{-}\mathrm{C_4H_8}} \tag{1}$$

It must be recognized that only the reacting species have to be considered for the K_x calculation, but all the species present in solution, both reacting and inert, have to be taken into account to calculate K_γ.

Computation of the Equilibrium Constant from Thermochemical Data

The thermodynamic equilibrium constant for a liquid-phase reaction of a nonideal system is given by

$$K = \prod_{i=1}^{S}(a_i)_e^{\nu_i} = \prod_{i=1}^{S}(\gamma_i)_e^{\nu_i}(x_i)_e^{\nu_i} = \prod_{i=1}^{S}(\gamma_i)_e^{\nu_i}\prod(x_i)_e^{\nu_i} = K_\gamma K_x \tag{2}$$

and can be related to the thermodynamic properties of the system through the equation

$$K = \exp(-\Delta G^\circ_{(l)}/RT) \tag{3}$$

The standard free energy change for the liquid-phase reaction can be computed from the standard enthalpy and entropy changes:

$$\Delta G^\circ_{(l)} = \Delta H^\circ_{(l)} - T\Delta S^\circ_{(l)} \tag{4}$$

The standard entropy change for the liquid-phase reaction can be deduced from the vaporization heats through the expression

$$\Delta S^\circ_{(l)}(T) = \Delta S^\circ_{(g)} - (1/T)\sum_{i=1}^{S}\nu_i\Delta H^\circ_{vi}(T) \tag{5}$$

where each ΔH°_{vi} is obtained by the Watson relation (eq 6):

$$\Delta H^\circ_{v}(T) = \Delta H^\circ_{v}(T_0)((1 - T/T_C)/(1 - T_0/T_C))^{0.38} \tag{6}$$

Similarly, the reaction enthalpy change is given by

$$\Delta H^\circ_{(l)} = \Delta H^\circ_{(g)} - \sum_{i=1}^{S}\nu_i\Delta H^\circ_{vi}(T) \tag{7}$$

Table I. Thermochemical Data of Methanol, Isobutene, and MTBE (Standard State, Liquid at 1 atm and 298 K) and Constants for the Equation $C_p/(\mathrm{J\ mol^{-1}\ K^{-1}}) = a + b(T/\mathrm{K}) + c(T/\mathrm{K})^2 + d(T/\mathrm{K})^3$

	methanol	isobutene	MTBE
$\Delta H^\circ_{vi}/(\mathrm{J\ mol^{-1}})$	37 940	20 660	30 380
a_i	1391.6^a	596.9^a	53.18^b
b_i	−12.36^a	−4.638^a	0.7173^b
$c_i \times 10^2$	3.781^a	1.440^a	−0.1533^b
$d_i \times 10^3$	−3.719^a	−1.372^a	−0.2024^b
T_c/K	512.6	417.9	496.4

^{a} Calculated from the Gallant fitting of a third-order equation (*16*). ^{b} Estimated by the Rowlinson equation (*17*).

By introducing eqs 5 and 7 in eqs 3 and 4, we can finally get the dependence of $\Delta G^\circ_{(l)}$ and K on temperature.

The dependence of $\Delta H^\circ_{(l)}$ on temperature can also be computed by integration of the Kirchoff equation (eq 7):

$$\mathrm{d}\Delta H^\circ_{(l)}/\mathrm{d}T = \sum_{i=1}^{S}\nu_i C_{p(l)i} \tag{8}$$

where $C_{p(l)}$ are the molar heat capacities in the liquid phase of the species that take part in the reaction and are usually expressed in the polynomial form

$$C_{p(l)i} = a_i + b_iT + c_iT^2 + d_iT^3 \tag{9}$$

By integrating eq 8 and taking into account eq 9, we obtain

$$\Delta H^\circ_{(l)} = I_K + aT + (b/2)T^2 + (c/3)T^3 + (d/4)T^4 \tag{10}$$

where

$$a = \sum_{i=1}^{S}\nu_i a_i \qquad b = \sum_{i=1}^{S}\nu_i b_i \qquad c = \sum_{i=1}^{S}\nu_i c_i \qquad d = \sum_{i=1}^{S}\nu_i d_i \tag{11}$$

The integration of the van't Hoff equation (eq 7)

$$\mathrm{d}\ln K/\mathrm{d}T = \Delta H^\circ/RT^2 \tag{12}$$

considering eq 10 gives

$$\ln K = I_H - I_K/RT + (a/R)\ln T + (b/2)RT + (c/6)RT^2 + (d/12)RT^3 \tag{13}$$

The constants I_K and I_H can be calculated from the temperature dependence relationship for the enthalpy change of reaction and for the equilibrium constant, respectively.

The thermochemical data required for evaluation of equilibrium constants are the heats of evaporation of methanol, isobutylene, and MTBE, at the standard state, as well as their molar heat capacities in the form of power functions. Table I shows all these thermochemical data. The required standard enthalpy and entropy changes of the reaction in the gas phase have been taken from our previous work (*6*): $\Delta H^\circ_{(g)} = -65.4$ kJ mol^{-1} and $\Delta S^\circ_{(g)} = -174$ J mol^{-1} K^{-1}. Thermochemical data yield the following values at 298 K by using eqs 4–7: $\Delta H^\circ = -37.1$ kJ mol^{-1}, $\Delta G^\circ = -13.5$ kJ mol^{-1}, and $\Delta S^\circ = -79.3$ J mol^{-1} K^{-1}. From the first two, an equation for the theoretical temperature dependence of the equilibrium constant, using eqs 10 and 13, is obtained:

$$\ln K = 1145 - 14740T^{-1} - 233\ln T + 1.066T - 1.077 \times 10^{-3}T^2 + 5.306 \times 10^{-7}T^3 \tag{14}$$

The values of the theoretical equilibrium constant predicted by eq 14 are shown in Figure 3 (dashed line).

Table II. Experimental Conditions and Obtained Equilibrium Constants

run	T/K	$r_{M/I}$	x_M	x_I	x_E	K_x	γ_M	γ_I	γ_E	K_γ	K
1	313.7	1.06	0.076	0.028	0.896	426.3	2.773	1.265	1.006	0.287	122.3
2	313.7	1.23[a]	0.072	0.032	0.895	382.3	2.813	1.258	1.005	0.284	108.6
3	313.7	1.45[a]	0.095	0.023	0.882	397.9	2.642	1.292	1.010	0.296	117.7
4	313.7	1.50	0.295	0.007	0.697	319.8	1.746	1.680	1.112	0.379	121.2
5	323.5	1.00	0.058	0.063	0.879	242.7	2.938	1.221	1.001	0.279	67.8
6	323.5	1.06	0.093	0.037	0.870	250.4	2.634	1.275	1.008	0.300	75.2
7	323.5	1.23[a]	0.090	0.043	0.868	227.5	2.667	1.269	1.007	0.298	67.7
8	323.5	1.45[a]	0.113	0.033	0.854	226.9	2.510	1.304	1.013	0.309	70.2
9	333.3	1.00	0.081	0.071	0.847	146.3	2.733	1.240	1.003	0.296	43.3
10	333.3	1.06	0.112	0.049	0.839	153.7	2.504	1.288	1.011	0.313	48.2
11	333.3	1.27	0.254	0.022	0.724	128.4	1.865	1.542	1.074	0.373	48.0
12	333.3	1.48	0.342	0.015	0.643	126.8	1.616	1.749	1.139	0.403	51.1
13	333.3	1.50	0.356	0.014	0.630	125.8	1.584	1.785	1.151	0.407	51.2
14	343.2	1.00	0.106	0.083	0.811	92.8	2.560	1.261	1.006	0.312	28.9
15	343.2	1.06	0.134	0.061	0.805	98.0	2.374	1.305	1.014	0.327	32.1
16	343.2	1.27	0.275	0.031	0.694	81.9	1.795	1.565	1.082	0.385	31.5
17	343.2	1.48	0.367	0.021	0.612	79.7	1.560	1.787	1.153	0.414	33.0
18	343.2	1.50	0.383	0.020	0.597	79.7	1.524	1.834	1.169	0.419	33.4
19	353.2	1.06	0.160	0.076	0.764	62.7	2.246	1.328	1.019	0.341	21.4
20	353.2	1.27	0.296	0.042	0.662	53.6	1.738	1.586	1.089	0.395	21.2
21	353.2	1.48	0.389	0.029	0.582	51.5	1.515	1.818	1.165	0.423	21.8

[a] MTBE is used at the beginning.

Results and Discussion

The experiments were carried out at the temperature range 313–353 K, under a pressure of 16 bar and with an initial methanol/isobutene ratio from 1 to 1.5. That molar ratio range was chosen seeing that, for methanol/isobutylene ratios less than 1, the byproduct diisobutene was significantly produced, even at low temperatures, and when the ratio was greater than 1.5 the undesirable dimethyl ether was also formed.

The mass balance was checked by comparing the molar variations of isobutene, methanol, and MTBE. The average discrepancy was about 5%, which could be explained by considering the small losses (by evaporation) of species on restoring the pressure after the chemical analysis, and the small amount of isobutylene changed into diisobutylene that probably was in the detection boundary of the chromatograph. We assumed that the nitrogen amount dissolved in the reactant mixture (about 0.6%) was negligible and did not affect the chemical equilibrium at all.

Table II shows the experimental conditions and results as well as the nonideal behavior of the system calculated by the UNIFAC method. It is computed that the experimental error of molar fractions is ±0.002, which allows the expression of the molar fractions to three decimal places. The amounts of diisobutene and dimethyl ether detected at the highest temperatures, only in the runs in which isobutene or methanol were used in great excess, were in the boundary of the chromatograph mass detection. Those quantities yielded molar fractions less than or equal to the experimental one mentioned above, particularly diisobutene whose molecular weight is high. Moreover, their effect on the activity coefficients of methanol, isobutene, and MTBE was negligible. Hence, the diisobutene and dimethyl ether amounts were not presented in Table II.

As can be seen, MTBE activity coefficients are very close to unity. In contrast, isobutylene and, mainly, methanol activity coefficients are higher than 1. The validity of UNIFAC predictions for that reacting system was already checked (*2*). The parameters needed for the use of UNIFAC have been taken from the tables published by Skjold-Jorgensen et al. (*9*), Gmehling et al. (*10*), Almeida et al. (*11*), and Tiegs et al. (*12*). It is worth nothing that at each temperature the *K* values obtained were not affected by the initial molar ratio, under otherwise uniform conditions. Also, these pseudoexperimental equilibrium constants followed the general trend of lowering when temperature increased, as expected for an exothermic reaction. Therefore, we can conclude that the experimental method followed and UNIFAC predictions are suitable for equilibrium constant determinations, at least, for MTBE synthesis or decomposition. A comparison, however, with theoretical and literature data is necessary to back up that conclusion.

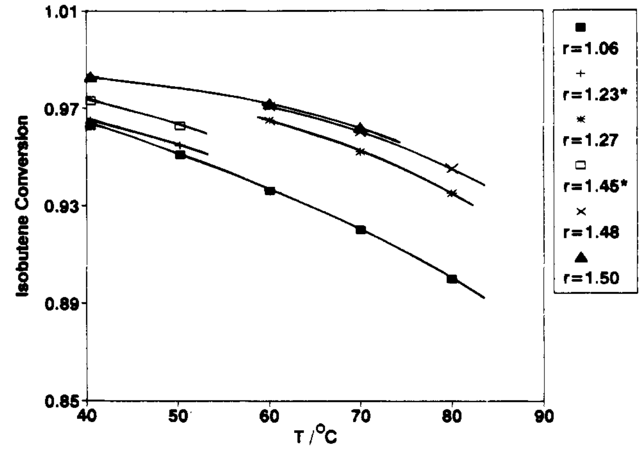

Figure 2. Equilibrium isobutene conversions at different temperatures.

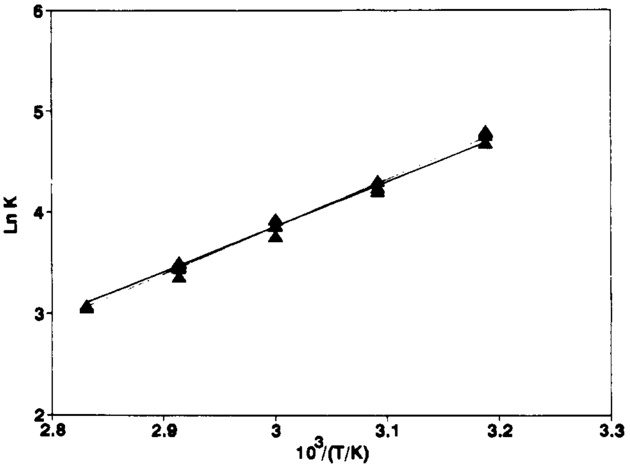

Figure 3. ln *K* against 1/*T*. Comparison between the values obtained experimentally (solid line) and those predicted from thermal data (dashed line).

Figure 2 is a plot of the isobutene equilibrium conversion as a function of 1/*T*. A maximum conversion is obtained at 40.5 °C for a methanol/isobutene ratio of 1.5.

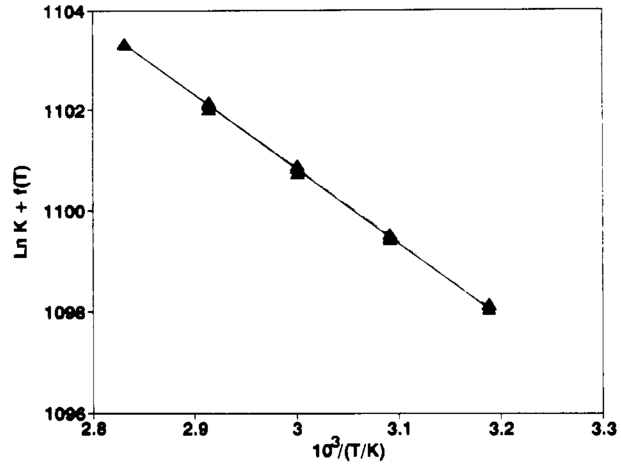

Figure 4. ln $K + f(T)$ against $1/T$. Comparison between the values obtained experimentally (solid line) and those predicted from thermal data (dashed line).

If the enthalpy change of reaction is assumed to be constant over the temperature range, the temperature dependence of the pseudoequilibrium constant can be found by using the equation

$$\ln K = \Delta S^\circ/R - (\Delta H^\circ/R)(1/T) \qquad (15)$$

which is deduced from eqs 3 and 4. Thus, when the K values in Table II are fitted to this equation, we can calculate ΔH° from the slope and ΔS° from the intercept. Obtained values are

$$\Delta H^\circ = -39100 \pm 800 \text{ J mol}^{-1}$$

$$\Delta S^\circ = -85.3 \pm 0.5 \text{ J mol}^{-1}\text{ K}^{-1}$$

The solid line in Figure 3 is the line fitted to pseudoexperimental data, and the dashed line denotes the ln K values predicted theoretically by eq 15 with $\Delta H^\circ = -37.1$ kJ mol^{-1} and $\Delta S^\circ = -79.3$ J mol^{-1} K^{-1}. A very slight difference may be seen between the two lines which implies that the experimental slope is slightly greater than the theoretical one.

If, however, the variation of the enthalpy change of reaction is significant, eq 14 must be used to fit the data (Figure 4). In this case, we obtain I_K from the slope and I_H from the intercept, and therefore, a more correct expression for the temperature dependence of K is

$$\ln K = 1144 - 14634T^{-1} - 233 \ln T + 1.066T - 1.077 \times 10^{-3}T^2 + 5.306 \times 10^{-7}T^3 \qquad (16)$$

In Figure 4, it can be seen that the difference between the solid line (experimental values) and the dashed line (theoretical values) is smaller than in Figure 2. This fact indicates that ΔH° variation with temperature is enough to take into account on working out equilibrium constants. Rehfinger and Hoffman (*1*) found theoretically that ΔH° is in the range −37.7 to −43.6 kJ mol^{-1} for 298 and 363 K, respectively. At the same temperature range we found for ΔH° −37.1 to −43.1 kJ mol^{-1}.

From eqs 3, 4, 10, and 13, equations for the temperature dependence of ΔH°, ΔS°, and ΔG° can be obtained:

$$\Delta H^\circ(T) = 121670 - 1935T + 8.8598T^2 - 1.792 \times 10^{-2}T^3 + 1.3230 \times 10^{-5}T^{-4} \quad \text{J mol}^{-1} \qquad (17)$$

$$\Delta S^\circ(T) = 7583 - 1935 \ln T + 17.72T - 2.687 \times 10^{-2}T^2 + 1.765 \times 10^{-5}T^3 \quad \text{J mol}^{-1}\text{ K}^{-1} \qquad (18)$$

$$\Delta G^\circ(T) = 121670 - 9518T + 1935T \ln T - 8.8598T^2 + 8.958 \times 10^{-3}T^3 - 4.4113 \times 10^{-6}T^4 \quad \text{J mol}^{-1} \qquad (19)$$

Table III. Standard Free Energy, Enthalpy, and Entropy Changes of MTBE Synthesis in the Liquid Phase at 298 K

	ΔH°(298 K)/ (kJ mol^{-1})	ΔS°(298 K)/ (J mol^{-1} K^{-1})	ΔG°(298 K)/ (kJ mol^{-1})
ΔH° constant	−39.1 ± 0.8	−85.3 ± 0.5	−13.7 ± 0.8
ΔH° function of T	−38.0 ± 0.8	−81.7 ± 0.5	−13.6 ± 0.8
theory (this work)	−37.1	−79.3	−13.5
theory			
Rehfinger (*1*)	−37.7		−14.0
Arntz (*13*)	−39.2 ± 0.4		
Gicquel (*3*)	−39.8 ± 2		
Obenaus (*14*)	−37.0		
Gupta (*15*)	−36.8		

Table IV. Obtained Equilibrium Constants and Those Published by Other Researchers

T/°C	present work	Rehfinger (*1*)	Colombo (*2*)	Al-Jarallah (*4*)
40	118 ± 9	136	151	
50	70 ± 5	85	100	
60	48 ± 4	54	68	
70	32 ± 2	35	47	38
80	21 ± 1	23	33	16
90		16	24	13
100		11	18	7

Table III shows the values of ΔG°, ΔH°, and ΔS° at 298 K determined for ΔH° assumed to be constant and for ΔH° variable with the temperature, along with those theoretical and experimental values deduced in other works (*1*, *3*, *13*–*15*) using different methodologies and resins. As can be seen, all the values of ΔH° are quite similar at 298 K, within the limits of experimental error, which accounts, again, for the validity of the methodology used in this work. Nevertheless, if values of K are calculated at different temperatures (Table III), we can see discrepancies that cannot be explained unless a ΔH° variation with temperature is assumed (*1*). It may be seen in Table III that the values of Colombo et al. (*2*) are greater due to the fact that they used an almost constant ΔH° of −34.7 kJ mol^{-1}. The theoretical equilibrium constants calculated by Rehfinger and Hoffman are slightly different from those determined by us experimentally, but these discrepancies come out on changing the temperature due to, likely, small different values of ΔH°. Finally, the K values determined by Al-Jarallah et al. (*4*) are also quite similar to ours, and the discrepancies can be explained if we take into account that they covered a high temperature range where we found problems in getting a true equilibrium owing to the presence of side reactions at such temperatures.

Conclusions

The agreement of ΔH° obtained experimentally in this work at 298 K with those determined in other works using different methods in some cases proves that the methodology used is correct. The trends of the K variations with temperature confirm this fact.

From the temperature dependence relationship for the equilibrium constant, equations for the temperature dependence of enthalpy, entropy, and free energy changes of the MTBE synthesis have been determined. These values show that the variation of reaction standard enthalpy with the temperature is important in equilibrium calculations.

The experimental equilibrium constants at lower temperature (40 and 50 °C) determined in this work cover a small gap existing in the open literature for MTBE synthesis in the liquid phase.

Notation

a,b,c,d = changes of molar heat capacity coefficients with chemical reaction

a_i,b_i,c_i,d_i = coefficients in the equation for molar heat capacity of component i; $C_p = a_i + b_iT + c_iT^2 + d_iT^3$
c_{pi} = molar heat capacity of component i, J mol^{-1} K^{-1}
$G°$ = standard free energy, J mol^{-1}
$H°$ = standard enthalpy, J mol^{-1}
I_H = integration constant in van't Hoff's equation, adimensional
I_K = integration constant in Kirchoff's equation, J mol^{-1}
K = thermodynamic equilibrium constant
K_γ = equilibrium constant based on activity coefficients
K_x = equilibrium constant based on molar fractions
MTBE = methyl *tert*-butyl ether
r = molar ratio
R = gas constant, J mol^{-1} K^{-1}
$S°$ = standard entropy, J mol^{-1} K^{-1}
T = temperature, K
x_i = molar fraction of component i

Greek Symbols

γ_i = activity coefficient of component i
$\Delta G°$ = standard free energy change of reaction, J mol^{-1}
$\Delta H°$ = standard enthalpy change of reaction, J mol^{-1}
$\Delta H°_{vi}$ = standard heat of vaporization of component i, J mol^{-1}
$\Delta S°$ = standard entropy change of reaction, J mol^{-1} K^{-1}
ν_i = stoichiometric coefficient of component i

Subscripts

E = MTBE
e = equilibrium
g = vapor phase
I = isobutene
i = component
l = liquid phase
M = methanol
v = vaporization

Registry No. MTBE, 1634-04-4; K-2631, 120669-56-9; MeOH, 67-56-1; isobutene, 115-11-7.

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Hydrates of Hydrocarbon Gases Containing Carbon Dioxide

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This work presents equilibrium measurements for hydrate three-phase (vapor–hydrate–aqueous liquid) behavior for natural gas components with high concentrations of carbon dioxide, at temperatures between the ice point and the quadruple point of each mixture. Binary hydrate phase equilibria were measured for carbon dioxide with each of the following gases: methane, ethane, propane, isobutane, and normal butane. Data for three of those binary systems (carbon dioxide + ethane, 2-methylpropane (isobutane), and butane) do not exist in the literature. Our results for the other two binary systems are shown to complement or supplant partial data sets from other laboratories. In addition, results are presented for synthetic multicomponent mixtures containing fixed ratios of methane, ethane, propane, 2-methylpropane, and butane, with varying amounts of carbon dioxide. A molecular interpretation is given in terms of hydrate structural properties.

Introduction

Carbon dioxide hydrates have several unique applications. In the earth's permafrost and deep oceans, there is a large resource deposited as hydrocarbon and carbon dioxide hydrates. Kvenvolden (*1*) in 1988 estimated that the amount of carbon in hydrocarbon hydrates is on the order of 10 000 Gtons (1 Gton = 1×10^{15} g), greatly surpassing the resource of all other combustible fossil fuels. Since carbon dioxide is normally produced naturally with hydrocarbon, hydrate phase equilibrium data are necessary to determine both the extent and future recovery of this energy resource. Recently carbon dioxide and hydrocarbon outgassing from such in situ hydrates has been hypothesized to contribute to the global warming process (*1*).

In addition to such natural processes, carbon dioxide plays a substantial industrial role in gas production and processing. Carbon dioxide is used in enhanced oil recovery (EOR) processes, and processing the associated gas involves a risk of hydrate formation. Many natural gas wells produce gas with high carbon dioxide concentrations, such as the wells at the LaBarge reservoir in western Wyoming, and the Natuna production field in Indonesia.

Even with these needs, only two binary systems containing carbon dioxide have been reported in the literature, namely, carbon dioxide + methane, measured by Unruh and Katz (*2*) in 1949 and Berecz and Balla-Achs (*3*) in 1983, and carbon dioxide + propane, measured by Robinson and Mehta (*4*) in 1971. Measurement details of binary mixtures of $CO_2 + CH_4$ were shown to confirm and extend the Unruh and Katz data in our previous paper (*5*).

No published data exist for binary mixtures of carbon dioxide with either ethane, 2-methylpropane (isobutane), or butane. The latter two binaries and the $CO_2 + C_3H_8$ binary form both structure I and structure II hydrates at high carbon dioxide

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