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Equilibrium Constant for Ethyl *tert*-Butyl Ether Vapor-Phase Synthesis

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Equilibrium constants for the vapor-phase synthesis of ethyl *tert*-butyl ether (ETBE) were determined experimentally at temperatures from 319 to 373 K. Equilibrium was established in the addition of ethanol to isobutene for obtaining ETBE over Amberlyst-15 in a flow reactor maintained at atmospheric pressure. The equilibrium constants obtained in the present work were compared with estimates from thermochemical data. The values of $\Delta\hat{H}^\circ$, $\Delta\hat{G}^\circ$, and $\Delta\hat{S}^\circ$ at 298 K were obtained from the variation of equilibrium constant with temperature: $\Delta\hat{H}^\circ = -14.87 \pm 0.5$ cal·mol^{-1}, $\Delta\hat{G}^\circ = -2.8 \pm 0.8$ kcal·mol^{-1}, and $\Delta\hat{S}^\circ = -40.5 \pm 1.3$ cal·mol^{-1}·K^{-1}. By use of published thermochemical data together with the experimental data, the enthalpy of formation, $\Delta\hat{H}_f{}^\circ_{298}$, free energy of formation, $\Delta\hat{G}_f{}^\circ_{298}$, and absolute entropy, $\hat{S}^\circ_{298}$, of ETBE were calculated to be -75.03 ± 0.5 kcal·mol^{-1}, -29.14 ± 0.5 kcal·mol^{-1}, and 97.1 ± 1 cal·mol^{-1}·K^{-1}, respectively.

Introduction

ETBE, a good octane booster (*1*), can be obtained by the reaction of addition of ethanol to isobutene catalyzed by sulfonic ion-exchange resins with a high selectivity, both in liquid (*2-9*) and also in gaseous phase (*10*), according to

$$(CH_3)_2C{=}CH_2 + CH_3CH_2OH \rightleftharpoons (CH_3)_3COCH_2CH_3 \quad (1)$$

The reaction is reversible and exothermic and yields are therefore subject to thermodynamic limitation. ETBE synthesis, just like methyl *tert*-butyl ether (MTBE) synthesis, could be used as a means for separation of isobutene from 1-butene of C_4 cuts following a similar reaction scheme. The ether is obtained in liquid phase on an ion-exchange resin and then decomposed in gaseous phase over modified γ-alumina (*11*). Nevertheless, the decomposition step can be performed on ion-exchange resins at atmospheric pressure and temperatures lower than 100 °C (*12*). If ethanol is readily available, pure isobutene could be obtained from C_4 cuts by making use of ETBE synthesis.

This paper reports an experimental investigation of the thermodynamic equilibrium for the ethanol-isobutene-ETBE system in vapor phase at temperatures lower than 100 °C. Equilibrium constants and thermodynamic properties calculated from those data are presented.

Experimental Section

***Materials*.** Ethanol (Romil Chemicals Ltd, Shepshed), with a minimum purity of 99.5% containing less than 0.2% water, and isobutene (Abelló, Barcelona) with a minimum purity of 99% were used without further purification. ETBE was synthesized in the laboratory and later purified until the ETBE-ethanol azeotrope (79 wt % ETBE, bp 66.6 °C (*13*, *14*)) was obtained, because of the lack of availability of this ether on the market. Vapor-phase addition of ethanol to isobutene to give ETBE was performed in a fixed-bed (downflow) reactor over the ion-exchange resin Amberlyst-15 at atmospheric pressure and 85 °C. A molar ratio of isobutene/ethanol in the feed of 1.7 and an spatial velocity of 0.4 mol·h^{-1}·g^{-1} were used. The mixture of reactants and products was condensed in an ice trap, and afterward the ETBE-ethanol azeotrope was obtained by batch distillation of the condensed mixture.

In the equilibrium runs, ethanol, isobutene, and ETBE were fed into the reactor diluted in nitrogen to obtain the highest possible variation of their partial pressures and also to facilitate evaporation and transport of the ethanol and the ETBE. Nitrogen (SEO, Barcelona) with a minimum purity of 99.998% was used.

The ion-exchange resin Amberlyst-15 (Rohm & Haas), used as the catalyst, is a macroporous sulfonated copolymer of styrene-divinylbenzene containing 20% divinylbenzene with a surface area (BET method) of 43 ± 1 m^2·g^{-1} (*15*) and an exchange capacity determined by titration against standard base of 4.8 mequiv of HSO_3·g^{-1} of dry resin. Catalyst samples with a particle diameter of between 0.063 and 0.08 mm were obtained by crushing and sieving the manufactured resin, dried at 110 °C for 14 h, and stored in a desiccator over sulfuric acid. In order to obtain a good contact model between reactants and catalyst and an isothermal bed, the catalyst was diluted with quartz. Before the equilibrium experiments the bed was preheated in the reactor at 103 °C for 2-3 h in a stream of nitrogen of about 10 cm^3·s^{-1}.

***Apparatus*.** The experiments were carried out in a packed-bed downflow microreactor connected directly to the sampling valve of an HP 5890A gas chromatograph equipped with a heat conductivity sensor (Figure 1). Nitrogen and isobutene were fed independently into the vaporizer from pressure bottles through a microregulation valve and an orifice meter. ETBE-ethanol blends were metered to the vaporizer by means of a syringe pump. The reactor, a jacketed Pyrex tube (length, 45 cm; internal diameter, 1.2 cm) with a porous plate to hold the catalyst bed, was thermostated by pumping water containing propylene glycol (30-50 vol %) from an external thermostatic bath. Temperatures were measured with two platinum resistance thermometers (accuracy ±0.1 °C), the first one inserted axially in the center of the catalyst bed and the second one located in the reactor jacket close to the catalyst bed. In the temperature range explored gradients were not higher than 0.3 °C.

***Analysis*.** The sample valve injected 0.25 cm^3 of product stream into the gas chromatograph. Helium (SEO, Barcelona) with a minimum purity of 99.998% was used as carrier gas 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 ETBE, ethanol, isobutene, and nitrogen. The column was temperature programmed with a 2-min initial hold at 130 °C followed by a 20 °C/min ramp up to 200 °C and held for 4 min. Peak areas were measured with an HP 3392A integrator, and from the areas of the peaks for ETBE, ethanol, isobutene, and nitrogen the composition of the stream was calculated.

***Procedure*.** The methodology consisted of feeding a mixture of ETBE, ethanol, isobutene, and nitrogen whose composition corresponded to that equilibrium and checking that the composition of the mixture did not become altered in the reactor whenever the contact time was long enough. Briefly, the ex-

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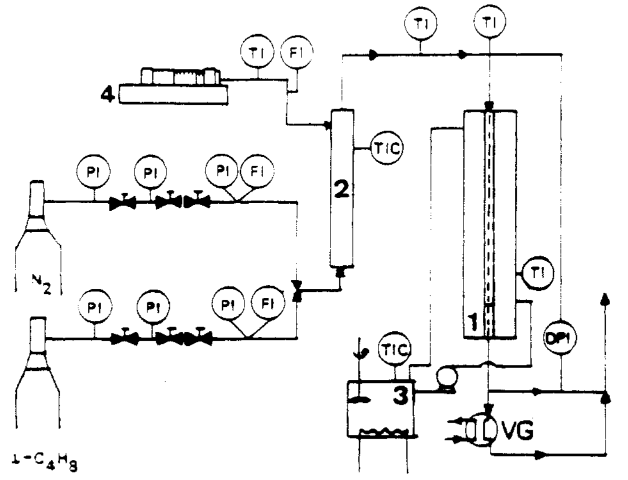

Figure 1. Experimental apparatus: (1) reactor; (2) vaporizer; (3) thermostatic bath; (4) syringe pump; (VG) sampling valve.

perimental procedure consisted of the following (further details of the apparatus and procedures are described elsewhere (*16*, *17*)).

1. A catalyst bed (0.3–0.6 g of resin diluted with 2–3 volumes of quartz; depth, 3–4 cm) was prepared in the abovementioned manner. A quartz bed (depth, 4 cm) was placed over the catalyst bed to assure that the gases would arrive at the catalyst bed at exactly the temperature of the experiment.

2. In each run, isobutene, nitrogen, and a liquid mixture of ethanol and ETBE (the azeotrope or an ethanol-enriched azeotrope) were fed to the reactor at such flow rates that the composition of the mixture arriving at the reactor chamber corresponded roughly to that of equilibrium composition. In order to do this, prior estimation of the equilibrium constant at the run temperature was required. Then, the flow rates of isobutene, of the ethanol–ETBE mixture, and of nitrogen were slightly modified in order to get the catalytic bed to reach the initial temperature again.

3. To ensure that the mixture was in chemical equilibrium, we proceeded to slightly vary the flow rate of the gases or the liquid feed, making use of the fact that reaction 1 is fairly exothermic. Thus, a decrease in the flow rate of isobutene gave rise to a decrease of reactor temperature, an increase in the flow rate of isobutene gave rise to an increase of reactor temperature, etc. Once we confirmed that the final mixture of step 2 was roughly in chemical equilibrium, we proceeded to restore the flow rate and to check that the composition of the gas agreed with that deduced from the flow rate and composition of the feed, within the limits of experimental error.

4. The equilibrium constant at the working temperature was computed from composition and total pressure of the system by using the following expression, in which ideal behavior is considered:

$$K_f \simeq K_p = \prod_{i=1}^{n}(p_i)_e = \left(\prod_{i=1}^{n}(y_i)_e\right)P^{\sum_i^n \nu_i} = K_y P^{\sum_i^n \nu_i} \qquad (2)$$

Computation of the Equilibrium Constant from Thermochemical Data

The temperature dependence of the equilibrium constant is given by

$$\ln K_p = I_K - I_H/RT + (a/R)\ln T + (b/2R)T + (c/6R)T^2 + (d/12R)T^3 \qquad (3)$$

where I_H and I_K are the constants of integration of the Kirchoff and van't Hoff equations, respectively. Parameters *a*, *b*, *c*, and *d* can be deduced from the molar heat capacities of the compounds that take part in the reaction in the form $\hat{C}_{p,i} = a_i + b_iT + c_iT^2 + d_iT^3$, and I_H can be calculated from the temperature dependence relationship for the enthalpy change of reaction.

Table I. Thermochemical Data of Ethanol, Isobutene, and ETBE (Standard State: Ideal Gas at 1 atm and 298 K)[a]

	ethanol	isobutene	ETBE
$\Delta\hat{H}_f°$, kcal·mol^{-1}	–56.12	–4.04	–74.53[b]
$\Delta\hat{G}_f°$, kcal·mol^{-1}	–40.22	13.88	–29.78[c]
$\hat{S}°$, cal·mol^{-1}·K^{-1}	67.4[d]	70.17[d]	100.88[b]
$\hat{C}_p = a + bT + cT^2 + dT^3$, cal·mol^{-1}·K^{-1}			
a	2.153	3.834	–0.155[e]
$b \times 10^2$	5.113	6.698	15.15[e]
$c \times 10^5$	–2.004	–2.607	–8.359[e]
$d \times 10^9$	0.328	2.173	57.90[e]

[a] Data source: "Property Data Bank" (*18*). [b] Estimated by the Anderson–Beyer–Watson method (*18*, *19*). [c] Estimated by means of the expression $\Delta\hat{G}_f°_{g,E} = \Delta\hat{G}° + \Delta\hat{G}_f°_{g,Et} + \Delta\hat{G}_f°_{g,I}$, where $\Delta\hat{G}°$, the change of free energy of the reaction, was computed to be –3.44 kcal·mol^{-1}. [d] Reference *19*. [e] Estimated by the Rihani–Doraiswamy method (*18*).

$$\Delta\hat{H}° = I_H + aT + (b/2)T^2 + (c/3)T^3 + (d/4)T^4 \qquad (4)$$

The thermochemical data required for evaluation of equilibrium constants are the heats and free energies of formation, at the standard state, of ethanol, isobutene, and ETBE as well as their molar heat capacities in the form of power functions. Given that thermochemical data for ETBE were not found in the literature, these were estimated by the Anderson, Beyer and Watson method (*18*, *19*). This estimation procedure was selected because the estimated of $\Delta\hat{H}_f°$ for MTBE (–67.53 kcal·mol^{-1}) is very close to the experimental value (–67.67 kcal·mol^{-1} (*20*)). As computed and experimental values for MTBE practically coincide, we assumed the estimated of $\Delta\hat{H}_f°$ for ETBE would be very close to the experimental one. From the thermochemical data reported in Table I, the enthalpy and free energy changes of reaction at 298 K were computed to be $\Delta\hat{H}° = -14.4$ kcal·mol^{-1} and $\Delta\hat{G}° = -3.44$ kcal·mol^{-1}. From these, equations for the temperature dependence of the equilibrium constant and enthalpy change of reaction were obtained:

$$\ln K_p = -2.18 + 6970T^{-1} - 3.102 \ln T + (8.432 \times 10^{-3})T - (3.155 \times 10^{-6})T^2 + (2.332 \times 10^{-9})T^3 \qquad (5)$$

$$\Delta\hat{H}° = -13800 - 6.142T + (1.670 \times 10^{-2})T^2 - (1.250 \times 10^{-5})T^3 + (1.485 \times 10^{-8})T^4 \qquad (\text{cal·mol}^{-1})$$

The values of the equilibrium constant predicted by eq 5 are shown as a semilogarithmic function of reciprocal absolute temperature in Figure 2.

Results and Discussion

The experiments were carried out at approximately atmospheric pressure in the temperature range 46–100 °C. It was not possible to work at temperatures lower than 46 °C because of the lack of availability of pure ether. At these temperatures the reaction rate of ETBE synthesis is very low and, in addition, the ETBE content of the azeotrope ETBE–ethanol is not high enough to give measurable changes in composition (and as a consequence of temperature). Table II shows the equilibrium composition and the values obtained for K_p at each temperature.

The K_p values obtained were not affected either by the space velocity or by the composition of the feed in the reactor. Runs 3, 5, and 6 at 90 °C were performed at different space ve-

Table II. Experimental Conditions and Obtained Equilibrium Constants

run	P, atm	T_r, K	V, mol·h^{-1}·g^{-1}	y_E	y_{Et}	y_I	y_N	K_y	K_p, atm^{-1}
1	1.055	373.4	6.37	0.007	0.063	0.150	0.780	0.723	0.695
2	1.046	363.4	5.08	0.009	0.071	0.100	0.820	1.314	1.256
3	1.055	363.5	6.17	0.008	0.060	0.087	0.845	1.450	1.375
4	1.063	363.5	6.19	0.010	0.062	0.124	0.805	1.265	1.190
5	1.083	363.5	2.67	0.009	0.077	0.085	0.828	1.399	1.293
6	1.138	363.5	1.43	0.007	0.065	0.075	0.853	1.486	1.306
7	1.045	353.4	2.95	0.012	0.049	0.101	0.839	2.31	2.21
8	1.057	343.9	6.49	0.019	0.052	0.087	0.843	4.23	4.00
9	1.071	343.9	7.05	0.016	0.052	0.066	0.866	4.70	4.39
10	1.037	343.9	6.52	0.023	0.052	0.111	0.814	3.97	3.83
11	1.060	333.9	6.71	0.025	0.038	0.082	0.855	8.25	7.78
12	1.065	338.9	6.83	0.026	0.048	0.094	0.833	5.79	5.44
13	1.057	328.9	6.73	0.026	0.030	0.070	0.874	12.05	11.4
14	1.056	323.7	6.30	0.037	0.025	0.093	0.845	15.6	14.8
15	1.056	323.8	6.34	0.036	0.025	0.086	0.854	16.8	15.9
16	1.064	319.8	7.10	0.032	0.021	0.072	0.876	21.7	20.4

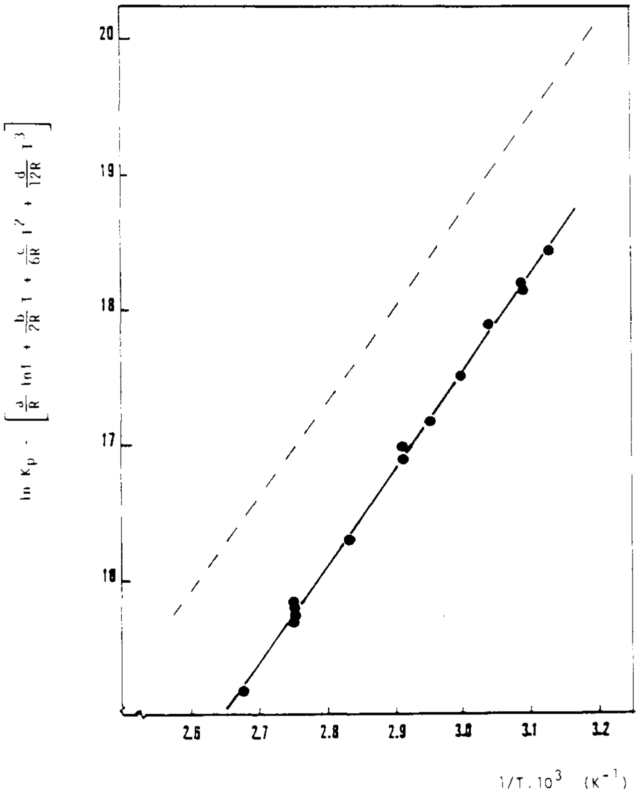

Figure 2. Plot of ln K_p + $f(T)$ against 1/T. Comparison between the values obtained experimentally (solid line) and those predicted from thermodynamic data (dashed line).

locities, but a constant composition of the feed was maintained to check that the K_p values obtained were not affected by the space velocity. Moreover, runs 8, 9, and 10 at 70 °C as well as experiments 3 and 4 at 90 °C were carried out at approximately the same space velocity, but mixtures of different compositions were fed into the experimental device. In all these experiments the values obtained for the equilibrium constant present no trends, and the dispersion between them is within the limits of experimental error.

If the heat of reaction is assumed to be constant over the temperature range, the temperature dependence of the equilibrium constant can be found by using the integrated form of the van't Hoff equation:

$$\ln K_p = \Delta\hat{H}^\circ/RT + C \tag{6}$$

When the K_p values in Table II were fitted to this model by ordinary least squares, the equation obtained was

$$\ln K_p = -20.2 + 7441T^{-1} \tag{7}$$

Table III. Fit of a Linear Model to ln K_p and 1/T Data: Analysis of Variance

	equation	
	ln K_p = b_0 + b_1/T	ln K_p + $f(T)$ = b'_0 + b'_1/T
intercept	-2.024 × 10^1	-4.103
slope	7.441 × 10^3	7.223 × 10^3
regression coeff	9.991 × 10^{-1}	9.989 × 10^{-1}
residuals variance	2.359 × 10^{-3}	2.569 × 10^{-3}
error variance	3.423 × 10^{-3}	3.423 × 10^{-3}
tabulated F(14,7) for α = 0.05	3.617	3.617
exptl F	0.69	0.75
intercept variance	6.55 × 10^3	2.69 × 10^2
slope variance	17.6	16.59
exptl F for intercept	1.91 × 10^6	7.87 × 10^4
exptl F for slope	5.14 × 10^3	4.85 × 10^3
tabulated F(1,7) for α = 0.05	5.591	5.591
confidence interval for intercept	b_0 ± 0.644	b'_0 ± 0.644
confidence interval for slope	b_1 ± 222.4	b'_1 ± 222.4

If, however, the variation of the heat of reaction with temperature is taken into account, a more general temperature dependence of K_p is given by eq 3. Equation 3 can be rearranged as

$$\ln K_p - [(a/R)\ln T + (b/2R)T + (c/6R)T^2 + (d/12R)T^3] = I_K - I_H/RT$$

The heat capacity data for ETBE, ethanol, and isobutene from Table I were substituted into the rearranged form of eq 3, and the K_p values in Table II were fitted to this equation (Figure 2) to yield the more correct expression for the temperature dependence of K_p:

$$\ln K_p = -4.10 + 7223T^{-1} - 3.102\ln T + (8.432 \times 10^{-3})T - (3.155 \times 10^{-6})T^2 + (2.332 \times 10^{-9})T^3 \tag{8}$$

Table III shows the results of both fits. In both cases the analysis of variance was done by taking the dispersion of the K_p obtained at various temperatures as a measure of the experimental error. The F-test shows that for a 95% probability level eq 7 and 8 as well as their parameters were significant.

Figure 2 shows that the values of K_p obtained experimentally are 200% smaller in the range of temperatures explored than the values for K_p deduced theoretically. This discrepancy can be attributed to the following causes: (1) the nonideality of the system; (2) the presence of side reactions; (3) the lack of accuracy of the thermochemical data used for the estimation of the equilibrium constants.

Table IV shows the fugacity coefficients of the components of the mixtures in equilibrium computed by using the virial equation as a function of the pressure (*18*, *21*). As can be seen, the fugacity coefficients, like K_φ, are very close to unity.

Table IV. Coefficients of Fugacity of the Components of the Mixtures in Equilibrium

run	φ_{Et}	φ_I	φ_E	φ_N	K_φ
1	0.989	0.991	0.984	1.000	1.004
2	0.989	0.991	0.984	1.000	1.004
3	0.990	0.992	0.985	1.000	1.004
4	0.988	0.990	0.983	1.000	1.005
5	0.989	0.991	0.984	1.000	1.004
6	0.989	0.991	0.984	1.000	1.004
7	0.989	0.990	0.983	1.000	1.004
8	0.987	0.989	0.981	0.999	1.005
9	0.988	0.990	0.982	1.000	1.005
10	0.986	0.988	0.980	0.999	1.006
11	0.986	0.988	0.980	0.999	1.006
12	0.985	0.988	0.979	0.999	1.006
13	0.986	0.989	0.980	0.999	1.006
14	0.983	0.987	0.977	0.999	1.007
15	0.984	0.987	0.977	0.999	1.007
16	0.984	0.987	0.978	0.999	1.007

Table V. Comparison of Free Energy, Enthalpy, and Entropy Changes of the Reaction for Obtaining ETBE in Vapor Phase with Computed Values

	$\Delta\hat{G}°_{298}$, kcal·mol^{-1}	$\Delta\hat{H}°_{298}$, kcal·mol^{-1}	$\Delta\hat{S}°_{298}$, cal·mol^{-1}·K^{-1}
this work	−2.8 ± 0.8	−14.87 ± 0.5	−40.5 ± 1.3
computed from bibliographical data	−3.44	−14.37	−36.7

Therefore, the ETBE–ethanol–isobutene system behaves ideally. On the other hand, no byproducts were detected in the analysis of the mixture in equilibrium. Thus, the presence of side reactions can be also rejected. Therefore, the lack of accuracy of the thermochemical data can be considered the most probable cause of the discrepancy between computed and experimental values of K_p.

At any given temperature, it is shown that

$$\ln K_p = -\Delta\hat{G}°/RT = \Delta\hat{S}°/R - \Delta\hat{H}°/RT \qquad (9)$$

Thus, from eq 8, 4, and 9, equations for the temperature dependence of $\Delta\hat{H}°$, $\Delta\hat{S}°$, and $\Delta\hat{G}°$ can be obtained:

$$\Delta\hat{H}° = -14300 - 6.142T + (1.671 \times 10^{-2})T^2 - (1.250 \times 10^{-5})T^3 + (1.385 \times 10^{-8})T^4 \quad (\text{cal·mol}^{-1}) \qquad (10)$$

$$\Delta\hat{S}° = -14.27 - 6.142 \ln T + (3.343 \times 10^{-2})T - (1.874 \times 10^{-5})T^2 + (1.847 \times 10^{-8})T^3 \quad (\text{cal·mol}^{-1}\text{·K}^{-1}) \qquad (11)$$

$$\Delta\hat{G}° = -14300 + 8.124T + 6.142T \ln T - (1.671 \times 10^{-2})T^2 + (6.247 \times 10^{-6})T^3 - (4.617 \times 10^{-9})T^4 \quad (\text{cal·mol}^{-1}) \qquad (12)$$

Table V shows the values of $\Delta\hat{H}°$, $\Delta\hat{G}°$, and $\Delta\hat{S}°$ at 298 K for the reaction of synthesis of ETBE. As can be seen, the values obtained experimentally agree fairly well with those estimated from thermochemical data. Nevertheless, the discrepancy between experimental and computed values of $\Delta\hat{G}°$ (by approximately 24%) causes the difference between theoretical and experimental values of K_p observed. A 3% difference in $\Delta\hat{G}°$ for MTBE synthesis causes a 20% discrepancy in the estimated equilibrium constants (*16*). The effect of these small differences on computing the equilibrium constant has been largely discussed elsewhere (*16*, *22*, *23*).

Finally, starting with $\Delta\hat{H}°$, $\Delta\hat{G}°$, and $\Delta\hat{S}°$ at 298 K, the enthalpy and free energy of formation and absolute entropy of ETBE were calculated. From the values of enthalpy and free energy of formation and absolute entropy of ethanol and isobutene (see Table I), the following values are obtained for ETBE at 298 K: $\Delta\hat{H}_f° = -75.03 \pm 0.5$ kcal·mol^{-1}, $\Delta\hat{G}_f° = -29.14 \pm 0.8$ kcal·mol^{-1}, and $\hat{S}° = 97.1 \pm 1.3$ cal·mol^{-1}·K^{-1}. As can be seen in Table VI, these values agree fairly well with those estimated from bibliographical data and the Anderson, Beyer, and Watson method.

Table VI. Comparison of Thermochemical Data of ETBE with Computed Values

	$\Delta\hat{G}_f°_{298}$, kcal·mol^{-1}	$\Delta\hat{H}_f°_{298}$, kcal·mol^{-1}	$\hat{S}°_{298}$, cal·mol^{-1}·K^{-1}
this work	−29.14 ± 0.8	−75.03 ± 0.05	97.1 ± 1
computed from bibliographical data	−29.78	−74.53	100.9

Conclusions

The dispersion of the K_p values obtained in the series of experiments performed by varying the composition of the feed or the space velocity is lower than 10%. This result proves that the experimental method followed is suitable for determinations for the equilibrium constants of sufficiently exothermic reaction systems in the vapor phase, such as ETBE synthesis.

From the temperature dependence relationship for the equilibrium constant, the enthalpy, free energy, and entropy changes for the reaction at 298 K have been determined. These values agree roughly with those deduced from thermochemical data. Nevertheless, the difference between computed and experimental values for the free energy change of the reaction causes computed equilibrium constants to be 3 times higher than the experimental ones. Finally, the thermochemical values determined for ETBE agree fairly well with those computed from bibliographical data and the Anderson, Beyer, and Watson method.

Glossary

a, b, c, d	changes of molar heat capacity coefficients with chemical reaction
a_i, b_i, c_i, d_i	coefficients in equation for molar heat capacity of component i, $\hat{C}_{p,i} = a_i + b_iT + c_iT^2 + d_iT^3$
b_0, b_1	intercept and slope in equation for temperature dependence of K_p assuming that $\Delta\hat{H}°$ is constant with temperature
b'_0, b'_1	intercept and slope in equation for temperature dependence of K_p assuming that $\Delta\hat{H}°$ is a function of temperature
C	constant in eq 6
$\hat{C}_{p,i}$	molar heat capacity of component i, cal·mol^{-1}·K^{-1}
F	variance ratio distribution
I_H	integration constant in Kirchoff's equation, cal·mol^{-1}
I_K	integration constant in van't Hoff's equation
K_f	thermodynamic equilibrium constant
K_p	equilibrium constant based on partial pressures, atm^{-1}
K_y	equilibrium constant based on molar fractions
k_φ	ratio of fugacity coefficients
P	total pressure, atm
p_i	partial pressure of component i, atm
R	gas constant, cal·mol^{-1}·K^{-1}
$\hat{S}°$	standard entropy, cal·mol^{-1}·K^{-1}
T	absolute temperature, K
T_r	reactor temperature, K
V	space velocity, mol·h^{-1}·g^{-1}
y_i	molar fraction of component i

Greek Symbols

α	significance level
$\Delta\hat{G}°$	standard free energy change of reaction, cal·mol^{-1}
$\Delta\hat{G}_f°_i$	standard free energy of formation of component i, cal·mol^{-1}
$\Delta\hat{H}°$	standard enthalpy change of reaction, cal·mol^{-1}
$\Delta\hat{H}_f°_i$	standard enthalpy of formation of component i, cal·mol^{-1}

$\Delta\hat{S}°$	standard entropy change of reaction, $cal \cdot mol^{-1} \cdot K^{-1}$
υ_i	stoichiometric coefficient of component *i*
φ_i	fugacity coefficient of component *i*

Subscripts

E	ETBE
Et	ethanol
e	equilibrium
f	formation
g	vapor phase
I	isobutene
i	component
N	nitrogen

Registry No. ETBE, 637-92-3; $(CH_3)_2C{=}CH_2$, 115-11-7; CH_3CH_2OH, 64-17-5.

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Volumetric and Viscometric Studies of Binary Liquid Mixtures

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Density and viscosity measurements at 30 °C for the mixtures of *N*-methylaniline + 1,1,2,2-tetrachloroethane and *N*-methylaniline + dimethyl sulfoxide over the entire range of composition were used to calculate excess volume V^E, excess viscosity $\Delta\eta^E$, and excess molar Gibbs free energy of activation of flow $\delta(\Delta G^*)$. Grunberg and Nissan's parameter *d* was also calculated. The excess properties have been attributed to the molecular interaction between the dissimilar molecules of the liquid mixtures.

Introduction

In binary liquid mixtures, the molecular interaction between dissimilar molecules is influenced by structural arrangement along with shape and size of the molecules. The study of Fort and Moore (*1*) has revealed that the positive deviation in viscosity from ideal behavior arises from strong molecular interaction between dissimilar molecules, but if it is found to be negative, the dispersion forces are likely to dominate. The variation of viscosity and molar volume with changing composition of the mixtures has been investigated by various workers (*2-5*). This paper deals with our investigations of thermodynamic and transport properties of binary liquid mixtures and is in continuation of our previous studies (*6-8*). From the experimental results of densities and viscosities for the systems *N*-methylaniline + 1,1,2,2-tetrachloroethane and *N*-methylaniline + dimethyl sulfoxide (DMSO) at 30 °C, excess molar volume V^E, excess viscosity $\Delta\eta^E$, excess molar Gibbs free energy of activation of flow $\delta(\Delta G^*)$, and Grunberg and Nissan's parameter *d* have been computed.

Experimental Section

Materials. *N*-Methylaniline (Kotch-light), dimethyl sulfoxide (Riedel), and 1,1,2,2-tetrachloroethane (Riedel) were used after purification by the standard methods described by Weissberger (*9*). The calculated volumes of liquids were added to get mixtures of different known compositions. The mixtures were kept for 2 h, and then they were used for density and viscosity measurements.

Density Measurements. The densities of pure liquids and mixtures were determined by a double-armed pycnometer having capillaries of narrow bore provided with well-fitting glass stoppers in order to avoid changes in composition due to evaporation. The pycnometer was calibrated with double-distilled water and benzene. The accuracy in density was ±0.01%.

Viscosity Measurements. Viscosities were determined by a viscometer similar to the Cannon-Ubbehlohde viscometer, calibrated with benzene and toluene, and the accuracy in viscosity was ±0.005 cP.

Calculations

Molar volume *V* and viscosity η are calculated from the expressions

$$V = (X_1M_1 + X_2M_2)/\rho \tag{1}$$

$$\eta = \rho(at - b/t) \tag{2}$$

where M_1 and M_2 are molecular weights of the components 1 and 2 and X_1 and X_2 are their mole fractions, respectively. *t* is the time of flow in seconds, *a* and *b* are the constants of the viscometer, and ρ is density.

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