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Excess Gibbs Energies and Excess Volumes of Methyl *tert*-Butyl Ether (MTBE) + Dichloromethane, + Chloroform, or + Tetrachloromethane

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Isothermal *P–x–y* and excess volume data for methyl *tert*-butyl ether (MTBE) + dichloromethane, MTBE + chloroform, and MTBE + tetrachloromethane are measured. The vapor–liquid equilibrium data were reduced according to the maximum-likelihood principle. The system MTBE + tetrachloromethane shows an almost ideal behavior, while MTBE + chloroform shows strong negative deviations from ideality and exhibits a maximum-boiling azeotrope. The system MTBE + dichloromethane presents an intermediate behavior, with moderate negative deviations.

Introduction

Methyl *tert*-butyl ether (MTBE) is an oxygenated petrochemical with increasing popularity as an octane booster for lead-free or low-leaded gasolines. The regulation regarding lead reduction is going to speed construction of MTBE production plants, specially in Europe. If all planned projects are built, the world output of this ether will reach about six million metric tons/year by the early 1990s. Likewise, MTBE is also increasingly valued as a solvent and a chemical reactive. However, there is a paucity of vapor–liquid equilibrium data for mixtures containing MTBE.

This paper reports the results of the measurements on vapor–liquid equilibria for the binary systems MTBE + dichloromethane at 308.15 K, MTBE + chloroform at 313.15 K, and MTBE + tetrachloromethane at 313.15 K. The experimental excess volumes at 298.15 K for the three systems are also reported.

Experimental Section

Materials. Dichloromethane and tetrachloromethane were obtained from Panreac, with a guaranteed minimum purity of 99.0%. Chloroform was a pharmaceutical-quality product from AcoFarma with a stated minimum purity of 99.0%. It contained 0.5% ethanol as stabilizing agent.

MTBE was received from the PETRONOR (Somorrostro, Spain) producing plant, with an initial observed purity of 98.5%.

All the starting chemicals were purified by several fractional distillations at atmospheric pressure, using a column (20-mm i.d. and 900-mm length) packed with 2 × 2 mm Dixon rings, until gas chromatographic analysis failed to show any significant impurities. The measured densities and vapor pressures of the purified compounds are listed in Table I, along with the literature values.

Table I. Densities ρ and Vapor Pressures P of Pure Compounds

	ρ(298.15 K)/(g cm^{-3})		$P(T)$/kPa		
compound	this work	lit.	this work	lit.	T/K
MTBE	0.735 66	0.735 3[a]	49.624	49.755[d]	308.15
			59.847	59.942[d]	313.15
CH_2Cl_2	1.316 20	1.316 3[a]	85.266	85.265[e]	308.15
		1.316 30[b]		85.609[a]	
$CHCl_3$	1.479 65	1.479 38[a]	48.463	48.347[e]	313.15
CCl_4	1.584 62	1.584 3[a]	28.443	28.444[e]	313.15
		1.584 52[c]		28.444[a]	313.15

[a] Reference 8. [b] Reference 9. [c] Reference 10. [d] Reference 11. [e] Reference 12.

Table II. Experimental Molar Excess Volumes $V^{E\circ}$ at 298.15 K as a Function of the Mole Fraction x_1°

MTBE (1)–CH_2Cl_2 (2)		MTBE (1)–$CHCl_3$ (2)		MTBE (1)–CCl_4 (2)	
x_1°	$V^{E\circ}$/(cm^3 mol^{-1})	x_1°	$V^{E\circ}$/(cm^3 mol^{-1})	x_1°	$V^{E\circ}$/(cm^3 mol^{-1})
0.0369	−0.082	0.0703	−0.416	0.0261	−0.044
0.0411	−0.103	0.1525	−0.718	0.1116	−0.191
0.0481	−0.117	0.2167	−0.774	0.1414	−0.245
0.0606	−0.177	0.2927	−0.958	0.1941	−0.281
0.1114	−0.218	0.3770	−1.004	0.2227	−0.362
0.1519	−0.318	0.4760	−1.051	0.2450	−0.342
0.2864	−0.418	0.5782	−1.006	0.2522	−0.354
0.3621	−0.456	0.6053	−0.986	0.3133	−0.401
0.3746	−0.448	0.6576	−0.954	0.4101	−0.471
0.3856	−0.455	0.7776	−0.734	0.4274	−0.485
0.4291	−0.449	0.7895	−0.735	0.5776	−0.489
0.4367	−0.488	0.8209	−0.585	0.6531	−0.490
0.4829	−0.473	0.8637	−0.477	0.6799	−0.486
0.5057	−0.505	0.8681	−0.427	0.6946	−0.468
0.5741	−0.503	0.9439	−0.230	0.7284	−0.448
0.6042	−0.494			0.8161	−0.402
0.6433	−0.477			0.9035	−0.282
0.6581	−0.493			0.9171	−0.277
0.7316	−0.455			0.9226	−0.262
0.8092	−0.345			0.9732	−0.188
0.8904	−0.234				
0.9096	−0.199				
0.9358	−0.187				

Apparatus and Procedure. The isothermal vapor–liquid equilibrium data were obtained by using the recirculation still and the technique described by Berro et al. (*1*). The temperature inside the equilibrium cell was measured by means of a Lauda R 42 digital thermometer, with a platinum resistance, calibrated for the measurement range with a high-precision mercury thermometer. The temperature uncertainty is 0.01 K. The temperature was kept constant by using the method previously described by Berro et al. (*2*). Pressures were measured to within ±0.01 kPa by means of a Digiquartz Series 700 Paroscientific precision gauge, calibrated against a mercury manometer.

Liquid and vapor compositions were determined by densimetric analysis, using an Anton Paar DMA 60 densimeter and two DMA 601 M cells. The measuring cells were thermoregulated better than 0.01 K. The uncertainty on the density measurement was ±0.000 01 g cm^{-3}. In order to perform the continuous measurement of both phase compositions, sampling of condensate vapor and liquid phases from the ebulliometer was carried out, withdrawing very small streams by means of two peristaltic micropumps and returning them back into the still

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Table III. Excess Volumes, Parameters A_j, Equation 1, Standard Deviations $\sigma(A_j)$, $\sigma(\rho)$, and $\sigma(V^E)$ in A_j, ρ, and V^E, Respectively

	at 298.15 K		
	MTBE (1)–CH_2Cl_2 (2)	MTBE (1)–$CHCl_3$ (2)	MTBE (1)–CCl_4 (2)
$A_j \pm \sigma(A_j)$/($cm^3\ mol^{-1}$)	−1.943 ± 0.026	−4.122 ± 0.079	−1.955 ± 0.045
	−0.170 ± 0.076	0.667 ± 0.144	−0.572 ± 0.079
	−1.01 ± 0.13	−1.42 ± 0.32	−0.89 ± 0.19
$\sigma(\rho)$/(g cm^{-3})	0.0002	0.0004	0.0002
$\sigma(V^E)$/($cm^3\ mol^{-1}$)	0.018	0.038	0.031

after having been passed through the densimetric cells, as described elsewhere (*1*).

Results and Data Treatment

Excess Volume. Table II shows the molar excess volumes V^E calculated from the measured densities ρ. The mixtures were prepared by weighing into syringes equipped with three-way valves. Careful attention was given to reduce the vapor volume and to dry the internal parts of the valve, in order to prevent the partial evaporation of samples. Excess volume data were fitted to the polynomial

$$V^E/x_1x_2 = \sum_{j=1}^{m} A_j(x_1 - x_2)^{j-1} \tag{1}$$

The parameters A_j of eq 1 are given in Table III, together with the standard deviations $\sigma(Q)$ calculated as

$$\sigma(Q) = \left(\frac{\sum^{N}(Q - Q_{cal})^2}{N - m}\right)^{1/2} \tag{2}$$

where $Q = V^E$ or ρ, N is the number of experimental values Q, and m is the number of parameters A_j.

Vapor-Liquid Equilibrium. The experimental vapor-liquid equilibrium data are reported in Table IV.

In order to correct the departure from the ideality in the vapor phase, the method of Hayden and O'Connell described by Prausnitz et al. (*3*) was used. The second virial coefficients for each binary system are listed in Table V.

The reduction of measured vapor-liquid equilibrium data was carried out by using the observed deviation method proposed by Péneloux et al. (*4*, *5*) and Neau and Péneloux (*6*).

The molar excess Gibbs energy G^E was correlated by using a Redlich-Kister polynomial

$$\frac{G^E}{RTx_1x_2} = \sum_{j=1}^{m} A_j y_j \tag{3}$$

where

$$y_j = (2j - 1)(x_1 - x_2)^{j-1} \tag{4}$$

The degree of the polynomial, not fixed in advance, is chosen during the reduction as the lowest degree allowing one to avoid systematic deviation due to the model.

The A_j parameters in eq 3, as well as the experimental uncertainties on densities and on temperatures, were estimated according to the maximum-likelihood principle. The experimental uncertainty on pressure was fixed to the value 0.01 kPa, according to the calibration of the manometer.

The thermodynamic consistency of experimental values was checked by fitting the vapor-liquid equilibrium data to eq 3 for the appropriate number of parameters. The reduction was performed by minimizing the objective function S defined in Appendix A of ref 7. The weighting factors of S were calculated with the values of the experimental uncertainties according to the maximum-likelihood principle. The weighted root mean square deviation (WRMSD) was calculated as

Table IV. Experimental Vapor Pressures $P°$, Liquid Mole Fractions $x_1°$, and Vapor Mole Fractions $y_1°$

$x_1°$	$y_1°$	$P°$/kPa	$x_1°$	$y_1°$	$P°$/kPa
MTBE (1)–Dichloromethane (2) at 308.15 K					
0.0112	0.0046	844.98	0.3579	0.2187	665.72
0.0330	0.0141	834.02	0.3880	0.2457	650.96
0.0579	0.0253	822.02	0.4387	0.2965	625.69
0.0924	0.0416	804.81	0.5036	0.3686	596.51
0.1318	0.0615	784.95	0.5749	0.4564	568.33
0.1665	0.0804	767.19	0.6736	0.5882	536.89
0.2034	0.1022	748.00	0.7676	0.7176	516.20
0.2482	0.1314	724.22	0.8476	0.8238	504.55
0.2900	0.1612	702.11	0.9093	0.9002	499.26
0.3322	0.1975	680.05	0.9529	0.9502	497.20
MTBE (1)–Chloroform (2) at 313.15 K					
0.0129	0.0059	480.89	0.3994	0.3934	403.54
0.0343	0.0162	475.52	0.4053	0.4024	403.46
0.0588	0.0291	469.07	0.4175	0.4211	403.10
0.0880	0.0463	461.24	0.4350	0.4508	403.22
0.1246	0.0705	451.58	0.4586	0.4880	404.31
0.1575	0.0961	442.91	0.4909	0.5411	407.97
0.1919	0.1260	434.32	0.5351	0.6108	415.35
0.2361	0.1705	424.30	0.5897	0.6916	429.26
0.2808	0.2224	415.66	0.6465	0.7653	447.09
0.3141	0.2656	410.17	0.7056	0.8293	470.19
0.3337	0.2928	407.64	0.7776	0.8913	501.72
0.3473	0.3122	406.39	0.8341	0.9287	527.58
0.3588	0.3291	405.42	0.9030	0.9642	558.09
0.3715	0.3479	404.67	0.9456	0.9816	578.41
0.3860	0.3679	403.83	0.9969	0.9990	600.88
MTBE (1)–Tetrachloromethane (2) at 313.15 K					
0.0664	0.1261	303.74	0.5082	0.6818	441.32
0.0850	0.1581	309.63	0.5983	0.7560	471.68
0.1126	0.2043	317.78	0.7102	0.8363	507.72
0.1883	0.3205	340.80	0.7580	0.8674	522.38
0.2303	0.3789	353.65	0.8170	0.9032	541.54
0.2837	0.4477	369.56	0.8692	0.9328	557.87
0.3478	0.5229	390.63	0.9155	0.9576	571.82
0.3864	0.5645	402.78	0.9480	0.9742	584.10
0.4577	0.6356	425.42	0.9748	0.9874	592.65

Table V. Second Molar Virial Coefficients B_{ij}

	at 308.15 K	at 313.15 K	
	MTBE (1)–CH_2Cl_2 (2)	MTBE (1)–$CHCl_3$ (2)	MTBE (1)–CCl_4 (2)
B_{11}/($cm^3\ mol^{-1}$)	−2059	−1937	−1937
B_{22}/($cm^3\ mol^{-1}$)	−856	−804	−1006
B_{12}/($cm^3\ mol^{-1}$)	−792	−834	−926

$$\mathrm{WRMSD} = \left(\frac{S}{2N - m}\right)^{1/2} \tag{5}$$

where N is the total number of measurements and m is the number of parameters A_j. The value of WRSMD found in this way should be equal to 1 for perfectly consistent data; a value close to 2 would indicate the existence of systematic errors of the same magnitude as the random errors in the measurements.

Results of vapor-liquid equilibrium data reduction are given in Table VI. Vapor-liquid equilibrium data were also fitted to the Wilson, NRTL, and UNIQUAC models; the corresponding expressions for the Wilson and UNIQUAC models are given in Appendix B of ref 7, while the expression used for the NRTL model is as follows

$$G^E/RT = -\frac{x_1x_2}{\alpha}\left[\frac{G_{21}\ln G_{21}}{x_1 + G_{21}x_2} + \frac{G_{12}\ln G_{12}}{x_2 + G_{12}x_1}\right] \tag{6}$$

Table VI. Results of Vapor–Liquid Equilibrium Data Reduction: Coefficients A_j, Equation 3, and Standard Deviations $\sigma(A_j)$, Estimated Experimental Uncertainties $\sigma_e(x_1)$, $\sigma_e(T)$, and $\sigma_e(P)$, and Weighted Root Mean Square Deviations (WRMSD), Equation 5

	at 308.15 K	at 313.15 K	
	MTBE (1)–CH_2Cl_2 (2)	MTBE (1)–$CHCl_3$ (2)	MTBE (1)–CCl_4 (2)
$A_j \pm \sigma(A_j)$	-0.46262 ± 0.00076	-1.07642 ± 0.00044	0.00689 ± 0.00097
	-0.02483 ± 0.00040	0.00807 ± 0.00035	0.00583 ± 0.00063
	-0.01114 ± 0.00047	0.02954 ± 0.00042	0.00062 ± 0.00071
$\sigma_e(x_1)$	$0.00001 < \sigma_e(x_1) < 0.0007$		
$\sigma_e(T)$/K	0.01	0.01	0.01
$\sigma_e(P)$/kPa	0.01	0.01	0.01
WRMSD	1.71	1.59	1.86

Table VII. Results of the Vapor–Liquid Equilibrium Data Correlation with the NRTL, Wilson, and UNIQUAC Models

MTBE (1)–Dichloromethane (2) at 308.15 K

NRTL

$G_{12} = 1.2989$, $G_{21} = 0.7263$, $\alpha = 0.05635$
$100[\delta(P)/P] = 0.21$
$100[\delta(y_1)] = 0.11$

Wilson

$\Lambda_{12} = 1.7624$, $\Lambda_{21} = 0.8182$
$100[\delta(P)/P] = 0.36$
$100[\delta(y_1)] = 0.20$

UNIQUAC

$A_{12} = 136.12$, $A_{21} = -136.30$
$100[\delta(P)/P] = 1.20$
$100[\delta(y_1)] = 0.69$

MTBE (1)–Chloroform (2) at 313.15 K

NRTL

$G_{12} = 1.0674$, $G_{21} = 1.0372$, $\alpha = 0.09705$
$100[\delta(P)/P] = 0.43$
$100[\delta(y_1)] = 0.49$
azeotrope: $x_1 = y_1 = 0.4034$, $P = 40.744$ kPa

Wilson

$\Lambda_{12} = 1.5799$, $\Lambda_{21} = 1.6493$
$100[\delta(P)/P] = 0.51$
$100[\delta(y_1)] = 0.56$
azeotrope: $x_1 = y_1 = 0.4018$, $P = 40.798$ kPa

UNIQUAC

$A_{12} = 85.52$, $A_{21} = -166.39$
$100[\delta(P)/P] = 0.44$
$100[\delta(y_1)] = 0.49$
azeotrope: $x_1 = y_1 = 0.4043$, $P = 40.467$ kPa

MTBE (1)–Tetrachloromethane (2) at 313.15 K

NRTL

$G_{12} = 0.7399$, $G_{21} = 1.2638$, $\alpha = 0.3544$
$100[\delta(P)/P] = 0.09$
$100[\delta(y_1)] = 0.15$

Wilson

$\Lambda_{12} = 0.6897$, $\Lambda_{21} = 1.3848$
$100[\delta(P)/P] = 0.24$
$100[\delta(y_1)] = 0.11$

UNIQUAC

$A_{12} = -0.753$, $A_{21} = -0.009$
$100[\delta(P)/P] = 0.23$
$100[\delta(y_1)] = 0.12$

The values of mean deviations on pressure and vapor composition are reported in Table VII, calculated as

$$100[\delta(P)/P] = \frac{100}{N}\sum^{N}\left[\frac{(|P^\circ - P_{\mathrm{cal}}|)}{P^\circ}\right] \qquad (7)$$

and

$$100[\delta(y_1)] = \frac{100}{N}\sum^{N}(|y_1^\circ - y_{1,\mathrm{cal}}|) \qquad (8)$$

The composition and pressure of the maximum-boiling azeotrope for the MTBE + chloroform system were calculated from the corresponding fitted parameters for each model, as shown in Table VII.

Conclusion

The system MTBE + tetrachloromethane shows very small deviations from the ideal behavior, while the MTBE + dichloromethane and MTBE + chloroform systems show negative deviations. The negative deviations from ideality are particularly strong for MTBE + chloroform, which exhibits a maximum-boiling azeotrope. This behavior is characteristic of chloroform–ether systems and is due to hydrogen bonding.

Glossary

A_j	parameters of polynomial model, eq 1 or 3
A_{ij}	parameters of UNIQUAC model, K
B_{ij}	second molar virial coefficients, $cm^3\ mol^{-1}$
G_{ij}	parameters of NRTL model, dimensionless
m	number of parameters A_j
N	total number of measurements
P	total vapor pressure, kPa
Q	any property
R	molar gas constant, 8.3145 J K^{-1} mol^{-1}
S	objective function
T	temperature, K
V	molar volume of pure liquid or liquid mixture, cm^3 mol^{-1}
WRMSD	weighted root mean square deviation of S, eq 5
x_i	liquid molar fraction of component i
y_i	vapor molar fraction of component i

Greek Letters

α	parameter of NRTL model, dimensionless
δ	mean deviation, eq 7 or 8
Λ_{ij}	parameters of Wilson model, dimensionless
ρ	density of pure liquid or liquid mixture, g cm^{-3}
σ	standard deviation, eq 2
σ_e	experimental uncertainty

Superscripts

E	excess property
°	experimental value

Subscripts

1,2	molecular species
cal	calculated property

Registry No. MTBE, 1634-04-4; CH_2Cl_2, 75-09-2; $CHCl_3$, 67-66-3; CCl_4, 56-23-5.

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Vapor–Liquid Equilibria and Excess Volumes for Binary Systems of Methyl *tert*-Butyl Ether (MTBE) with *trans*-1,2-Dichloroethylene and Acetonitrile

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Isothermal vapor–liquid equilibria (VLE) at 313.15 K and excess volumes at 298.15 K were measured for the binary mixtures of methyl *tert*-butyl ether (MTBE) with *trans*-1,2-dichloroethylene and acetonitrile. The liquid-phase activity coefficients were fitted by using the van Laar, Wilson, NRTL, and UNIQUAC equations. A minimum-pressure azeotrope was observed for MTBE + *trans*-1,2-dichloroethylene, while MTBE + acetonitrile exhibits a maximum-pressure one.

Introduction

Methyl *tert*-butyl ether (MTBE), produced by catalytic reaction of isobutylene and methanol, is one of the most successful products of the oxygenated compounds group used as octane enhancers for lead-free or low-leaded gasolines (*1*, *2*). Likewise, MTBE is also increasingly valued as a solvent and chemical reactive (*3*). Problems of availability and feedstock costs have been overcome for the most part, and at the present time MTBE is a commodity chemical, as readily available as is, for instance, toluene. To design efficient separation operations, a primary concern is to understand vapor–liquid equilibria (VLE) of involved mixtures. However, there is a paucity of vapor–liquid equilibrium data for mixtures containing MTBE.

As a continuation of a project for studying the thermodynamic behavior of MTBE mixtures (*4*), in this paper we present isothermal VLE at 313.15 K and excess volumes at 298.15 K for the binary systems MTBE + *trans*-1,2-dichloroethylene and MTBE + acetonitrile.

Experimental Section

Materials. MTBE was received from the PETRONOR (Somorrostro, Spain) production plant, with an initial purity, determined by gas–liquid chromatography, of 98.5%. Acetonitrile was the RS product of HPLC grade from Carlo Erba, with an indicated purity of at least 99.8%. *trans*-1,2-Dichloroethylene was an Aldrich product with a stated purity of 98%.

All the starting chemicals were purified by rectification at atmospheric pressure in a column (20-mm i.d. and 900-mm length) packed with 2 × 2 mm stainless steel Dixon rings. The first and last portions of the distillate were discarded, and the middle (ca. 60%) fraction was used for the experiments. The final purity of all the substances, estimated by gas–liquid chromatography, was at least 99.85%. Prior to final rectification, MTBE was repeatedly washed with water and then dried over molecular sieve type 3A. The measured densities and vapor pressures of the purified compounds are listed in Table I, along with the literature values.

Table I. Densities ρ and Vapor Pressures P of Pure Compounds

	p(298.15)/(g cm^{-3})		P(313.15 K)/kPa	
compound	this work	lit.	this work	lit.
MTBE	0.735 66	0.735 3[a]	59.766	59.942[b]
trans-1,2-$C_2H_2Cl_2$	1.227 68	1.246 30[f]	76.964	77.618[c] 77.706[c]
CH_3CN	0.776 82	0.776 49[d]	22.706	22.745[e]

[a] Reference 11. [b] Reference 12. [c] Reference 13. [d] Reference 14. [e] Reference 15. [f] Extrapolated from ref 14.

Apparatus and Procedure. The isothermal vapor–liquid equilibrium data were obtained by using the recirculation still and the technique described by Berro et al. (*5*). The temperature inside the equilibrium still was measured by means of a Lauda R 42 digital thermometer calibrated for the measurement range with a high-precision mercury thermometer. The temperature uncertainty is 0.01 K. The temperature was maintained constant by using the method described elsewhere (*6*). Pressures were measured to within ±0.01 kPa by means of a Digiquartz Series 700 Paroscientific precision gauge, calibrated against a mercury manometer.

Liquid and vapor compositions were determined by densimetric analysis, using an Anton Paar DMA 60 densimeter and two DMA 601 M cells. The measuring cells were thermoregulated better than 0.01 K so that the uncertainty in density was ±0.000 01 g cm^{-3}. In order to perform the continuous

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