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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%.

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.

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.

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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Table II. Experimental Excess Volume Data at 298.15 K as a Function of the Mole Fraction $x°_1$

MTBE (1) + *trans*-1,2-$C_2H_2Cl_2$ (2)		MTBE (1) + CH_3CN (2)	
$x°_1$	$V^E/(cm^3\ mol^{-1})$	$x°_1$	$V^E/(cm^3\ mol^{-1})$
0.0053	−0.0319	0.0085	−0.0265
0.0181	−0.0447	0.0143	−0.0396
0.0279	−0.1165	0.0565	−0.1369
0.0356	−0.1076	0.1168	−0.2594
0.0734	−0.2453	0.1199	−0.2721
0.1239	−0.3323	0.1251	−0.2756
0.1274	−0.3847	0.1731	−0.3599
0.2069	−0.5072	0.2699	−0.4766
0.2858	−0.6677	0.3923	−0.5674
0.3214	−0.7418	0.4437	−0.5681
0.3803	−0.9759	0.4912	−0.5976
0.3838	−0.8778	0.5270	−0.5960
0.4853	−1.0393	0.6514	−0.5497
0.7529	−1.0753	0.6687	−0.5409
0.9512	−0.2326	0.7088	−0.5107
0.9526	−0.2664	0.7482	−0.4745
		0.8067	−0.4025
		0.8579	−0.3318
		0.9013	−0.2518
		0.9378	−0.1740

Table III. Excess Volumes at 298.15 K: Parameters A_j, Equation 1, and Standard Deviations $\sigma(V^E)$ in $V^\neq$ (D = 35)

MTBE (1) + *trans*-1,2-$C_2H_2Cl_2$ (2)	MTBE (1) + CH_3CN (2)
$A_j/(cm^3\ mol^{-1})$	
-3.1659	-2.4849
-0.9927	0.7204
-3.2135	-1.1079
$\sigma(V^E)/(cm^3\ mol^{-1})$	
0.0422	0.0067

measurement of both phase compositions, sampling of condensate vapor and liquid phases from the ebulliometer was carried out by withdrawing very small streams by means of two peristaltic pumps and returning them back into the still after being passed through the densimetric cells (*5*).

The excess volumes at 298.15 K were calculated from density data, obtained by using the aforementioned Anton Paar DMA 60 densimeter and DMA 601 cells. For density measurements, solutions of known composition were prepared by weighing into syringes equipped with three-way valves. Careful attention was given to dry the internal parts of the valves and to reduce the vapor space in order to prevent the partial evaporation of samples.

Results and Data Treatments

***Excess Volume*.** The experimental data are given in Table II. The excess volume data were fitted using the polynomial expansions in the form

$$V^E/X_1X_2 = \sum_{j=1}^{m} A_j y_j \qquad (1)$$

where

$$y_j = \left[X_1 - \frac{1}{(1 + Dx_1)}\right]^{j-1} \qquad (2)$$

The calculations were performed with the value D = 35. The parameters A_j of eq 1 are given in Table III, together with values of the standard deviations of the excess volumes:

$$\sigma(V^E) = \left(\sum^{N} \frac{(V^E - V^E_{cal})^2}{N - m}\right)^{1/2} \qquad (3)$$

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) + *trans*-1,2-Dichloroethylene (2) at 313.15 K					
0.0000	0.0000	76.964	0.5961	0.5494	59.760
0.0066	0.0037	76.732	0.6010	0.5558	59.692
0.0131	0.0073	76.483	0.6160	0.5747	59.495
0.0209	0.0117	76.187	0.6289	0.5911	59.363
0.0383	0.0208	75.582	0.6491	0.6168	59.148
0.0676	0.0392	74.451	0.6788	0.6564	58.920
0.0967	0.0567	73.385	0.7020	0.6832	58.784
0.1352	0.0825	72.049	0.7319	0.7202	58.635
0.1788	0.1139	70.485	0.7617	0.7565	58.561
0.2402	0.1622	68.406	0.7783	0.7763	58.538
0.3356	0.2493	65.437	0.7966	0.7975	58.522
0.3913	0.3064	63.891	0.8150	0.8184	58.537
0.4260	0.3442	63.028	0.8328	0.8383	58.567
0.4542	0.3765	62.338	0.8602	0.8679	58.665
0.4878	0.4155	61.615	0.9037	0.9127	58.910
0.5243	0.4591	60.895	0.9257	0.9341	59.068
0.5508	0.4923	60.395	0.9635	0.9688	59.403
0.5733	0.5206	60.050	0.9776	0.9811	59.518
0.5800	0.5290	59.967	0.9901	0.9918	59.648
0.5848	0.5349	59.919	1.0000	1.0000	59.766
0.5864	0.5417	59.848			
MTBE (1) + Acetonitrile (2) at 313.15 K					
0.0000	0.0000	22.706	0.4070	0.6877	54.292
0.0122	0.1237	25.649	0.4561	0.7055	55.501
0.0189	0.1642	26.851	0.6203	0.7614	58.511
0.0263	0.2039	28.254	0.6891	0.7870	59.548
0.0339	0.2484	29.580	0.7381	0.8067	60.134
0.0485	0.2975	31.691	0.7792	0.8252	60.532
0.0669	0.3725	34.065	0.8278	0.8504	60.864
0.1036	0.4549	38.213	0.8539	0.8651	60.971
0.1406	0.5089	41.593	0.8810	0.8831	61.023
0.1652	0.5431	43.786	0.9119	0.9064	60.918
0.2110	0.5847	46.582	0.9360	0.9268	60.747
0.2372	0.6035	48.003	0.9540	0.9443	60.544
0.2490	0.6120	48.659	0.9673	0.9588	60.343
0.2773	0.6291	49.940	0.9781	0.9716	60.138
0.3060	0.6439	51.084	0.9846	0.9801	60.000
0.3262	0.6536	51.814	0.9902	0.9868	59.882
0.3501	0.6646	52.644	1.0000	1.0000	59.766
0.3742	0.6747	53.389			

where N is the number of experimental values V^E and m is the number of parameters A_j.

***Vapor–Liquid Equilibrium*.** Experimental vapor–liquid equilibrium data are given in Table IV.

The experimental data were regressed to determine binary parameters for the van Laar, Wilson, NRTL, and UNIQUAC models for the excess Gibbs energy. The corresponding expressions for the Wilson and UNIQUAC models are given in Appendix B of ref 7. For the NRTL model the following equation was used

$$G^E/RT = -\frac{X_1X_2}{\alpha}\left[\frac{G_{21}\ln G_{21}}{X_1 + G_{21}X_2} + \frac{G_{12}\ln G_{12}}{X_2 + G_{12}X_1}\right] \qquad (4)$$

and, according to the rules recommended by Renon and Prausnitz (*8*), the value α = 0.30 was used for both systems studied in this work.

A regression procedure, based on an algorithm developed by Marquardt (*9*), was established to minimize the following equation for the standard deviation, which was used as the objective function:

$$\text{std dev} = \left(\frac{\sum^{N}\left[\left(\frac{\gamma°_1 - \gamma_{1,cal}}{\gamma°_1}\right)^2 + \left(\frac{\gamma°_2 - \gamma_{2,cal}}{\gamma°_2}\right)^2\right]}{2N - 1}\right)^{1/2} \qquad (5)$$

Vapor-phase nonidealities are small and were calculated from the Peng and Robinson (*10*) equation of state with the

Table V. Results of VLE Data Correlation with the van Laar, Wilson, NRTL, and UNIQUAC Models

MTBE (1) + *trans*-1,2-Dichloroethylene (2) at 313.15 K

van Laar

$A_{12} = -0.3769$, $A_{21} = -0.4630$
$100[\sigma(P)/P] = 0.16$
$100[\sigma(y_1)] = 0.13$
azeotrope: $x_1 = y_1 = 0.7979$, $P = 58.455$ kPa

Wilson

$\Lambda_{12} = 1.4754$, $\Lambda_{21} = 0.9885$
$100[\delta(P)/P] = 0.16$
$100[\delta(y_1)] = 0.14$
azeotrope: $x_1 = y_1 = 0.7986$, $P = 58.457$ kPa

NRTL

$G_{12} = 0.9496$, $G_{21} = 1.1759$, $\alpha = 0.30$
$100[\delta(P)/P] = 0.15$
$100[\delta(y_1)] = 0.13$
azeotrope: $x_1 = y_1 = 0.7975$, $P = 58.453$ kPa

UNIQUAC

$A_{12} = 147.8$, $A_{21} = -148.1$
$100[\delta(P)/P] = 0.38$
$100[\delta(y_1)] = 0.49$
azeotrope: $x_1 = y_1 = 0.7987$, $P = 58.867$ kPa

MTBE (1) + Acetonitrile (2) at 313.15 K

van Laar

$A_{12} = 1.3757$, $A_{21} = 1.2197$
$100[\delta(P)/P] = 0.91$
$100[\delta(y_1)] = 0.57$
azeotrope: $x_1 = y_1 = 0.8787$, $P = 60.755$ kPa

Wilson

$\Lambda_{12} = 0.3897$, $\Lambda_{21} = 0.5248$
$100[\delta(P)/P] = 0.46$
$100[\delta(y_1)] = 0.36$
azeotrope: $x_1 = y_1 = 0.8819$, $P = 60.838$ kPa

NRTL

$G_{12} = 0.8552$, $G_{21} = 0.7546$, $\alpha = 0.30$
$100[\delta(P)/P] = 0.80$
$100[\delta(y_1)] = 0.52$
azeotrope: $x_1 = y_1 = 0.8793$, $P = 60.782$ kPa

UNIQUAC

$A_{12} = 313.3$, $A_{21} = -45.0$
$100[\delta(P)/P] = 0.83$
$100[\delta(y_1)] = 0.53$
azeotrope: $x_1 = y_1 = 0.8812$, $P = 60.736$ kPa

value of the interaction coefficient set equal to zero.

The fitted binary parameters for the van Laar, Wilson, NRTL, and UNIQUAC equations are given in Table V, together with the mean deviations of the pressure and vapor-phase mole fraction, calculated by using the following expressions:

$$100[\delta(P)/P] = \frac{100}{N}\sum^{N}\left[\frac{(|P^{\circ} - P_{\mathrm{cal}}|)}{P^{\circ}}\right] \qquad (6)$$

$$100[\delta(y_1)] = \frac{100}{N}\sum^{N}(|y^{\circ}_1 - y_{1,\mathrm{cal}}|) \qquad (7)$$

Furthermore, Table V contains the coordinates (composition and total pressure) of the azeotropic point for both binary systems, calculated from the fitted parameters for each excess Gibbs energy model.

As can be seen from Table V, both binary systems MTBE + *trans*-1,2-dichloroethylene and MTBE + acetonitrile show very good agreement between correlated and experimental data. For the system MTBE + *trans*-1,2-dichloroethylene, the van Laar, Wilson, and NRTL equations lead to better results than that obtainable with the UNIQUAC equation. In the case of the system MTBE + acetonitrile, the Wilson equation correlates the data better than the van Laar, NRTL, and UNIQUAC equations.

Conclusions

The system MTBE + *trans*-1,2-dichloroethylene shows moderate negative deviations from ideality and exhibits a minimum-pressure azeotrope. These negative deviations are due to the hydrogen bonds between the positive hydrogen atom in the *trans*-1,2-dichloroethylene and the oxygen atom in the MTBE ether group. On the contrary, the system MTBE + acetonitrile shows positive deviations from ideality and presents a maximum-pressure azeotrope.

Glossary

A_j	parameters of the polynomial model, eq 1
A_{ij}	parameters of the van Laar model, dimensionless, or UNIQUAC model, K
G_{ij}	parameters of the NRTL model, dimensionless
m	number of polynomial parameters A_j
N	total number of measurements
P	total vapor pressure, kPa
R	molar gas constant, 8.3145 J K^{-1} mol^{-1}
T	temperature, K
V	molar volume of pure liquid or liquid mixture, cm^3 mol^{-1}
x_i	liquid mole fraction of component *i*
y_i	vapor mole fraction of component *i*

Greek Letters

α	parameter of the NRTL model, dimensionless
δ	mean deviation, eq 6 or 7
Λ_{ij}	parameters of the Wilson model, dimensionless
ρ	density of pure liquid, g cm^{-3}
σ	standard deviation, eq 3
γ	liquid-phase activity coefficient, eq 5

Superscripts

E	excess property
°	experimental measured value

Subscripts

1,2	molecular species
cal	calculated property

Registry No. MTBE, 1634-04-4; CH_3CN, 75-05-8; *trans*-1,2-CH_2Cl_2, 156-60-5.

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