Salt Effect on Vapor–Liquid Equilibrium of Methyl *tert*-Butyl Ether + Methanol at 298.15 K

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Isothermal vapor–liquid equilibrium data were determined at 298.15 K for the systems methyl *tert*-butyl ether (MTBE) + methanol with $Ca(NO_3)_2$, LiCl, and LiBr, by using a saturation method. The vapor pressures of methanol saturated with these salts have been measured by a vapor pressure osmometry method. The experimental data have been satisfactorily fitted by using four activity coefficient models usually employed for systems without salt. The thermodynamic consistency was checked by the Redlich–Kister consistency test.

Introduction

Methyl *tert*-butyl ether (MTBE) is an oxygenated petrochemical with excellent antiknock properties, and the use of MTBE pure (*1*) or mixed with C_4 alcohols has been recommended (*2*) as a high octane blending agent for motor gasoline. For that reason, MTBE is rapidly emerging as one of the most successful octane boosters for lead-free or low-leaded gasolines. On the other hand, high-purity MTBE is also increasingly valued as a solvent and chemical reactive.

MTBE is produced on a commercial scale by heterogeneous catalytic reaction, starting from isobutylene and methanol as raw materials. The catalysts are acidic ion exchange resins and typically consist of sulfonated polystyrene cross-linked with divinylbenzene. The reactor output is distilled to recover MTBE product. However, due to the existence of a minimum-boiling azeotrope, the mixture MTBE + methanol cannot be separated into the pure components by ordinary distillation.

In order to obtain pure MTBE, several procedures using azeotropic distillation with *n*-pentane (*3*) and extractive distillation with ethylene glycol, propylene glycol, and glycerol (*4*), as well as many other solvents, are under patent. A literature search revealed indeed that salt-effect distillation has not been used for this purpose.

Whereas salt solubility in MTBE is insignificant, most of the salts are relatively soluble in methanol. This effect reduces the activity of methanol and, consequently, the relative volatility of MTBE increases, providing a useful method for separation of the mixture components by distillation.

As part of a continuing effort to study the salt effect on vapor–liquid equilibrium (VLE), in this paper we report the results obtained for the mixtures MTBE + methanol + LiCl, + LiBr, + $CaCl_2$, + $Ca(NO_3)_2$, and + NaI. In order to reduce the complexity of the experimental data treatment, the measurements were carried out at 298.15 K and with a salt-saturated liquid phase.

Experimental Section

Materials. All the chemicals used, LiCl (Baker), LiBr (Aldrich), $Ca(NO_3)_2{\cdot}4H_2O$ (Panreac), NaI (Aldrich), and $CaCl_2{\cdot}2H_2O$ (MERCK, were analytical reagent grade. Anhydrous salts were desiccated in the oven at 120 °C until constant weight was obtained. Anhydrous calcium chloride and calcium nitrate were obtained by desiccating the hydrated compounds in a microwave oven. Commercial MTBE was treated with a molecular sieve prior to rectification at 1 atm of pressure in a packed column with an efficiency equivalent to 25 theoretical plates. The intermediate fraction distilling at constant temperature was collected. AR grade methanol (Panreac) was dried over magnesium and then distilled in the packed column under the same conditions as described for MTBE. Gas chromatographic analysis failed to show any significant impurities for both MTBE and methanol.

Apparatus and Procedure. Vapor–liquid equilibrium data were obtained by a saturation method. This method is based on the isothermal saturation of a flow of dry nitrogen passing through the liquid phase embedded in a packed column. The vapor phase is condensed in a liquid air trap, and the condensate is dissolved in an adequate solvent (*p*-dioxane in this work) for gas chromatography analysis. A more detailed description of the experimental equipment and operating procedure can be found in a previous paper (*5*).

The equilibrium temperature, T, was measured accurately to 0.05 K with a PROTON mercury thermometer previously calibrated with a Hewlett-Packard, Model 2804A, certified quartz thermometer.

The liquid mixture was prepared from weighed amounts of MTBE and methanol, and a salt was added in excess. The vaporized fraction of the liquid phase being very small ($<0.5\%$), it was not necessary to make corrections for the liquid composition calculated directly from the weighed amounts charged to the column. The mole fraction of the liquid phase, x, is accurate to within 0.0002. The composition of the vapor phase, y, was determined with a Hewlett-Packard, Model 5890, gas chromatograph equipped with a flame ionization detector and a Hewlett-Packard, Model 3390, electronic integrator. The capillary column, 50 m long, was packed with Carbowax 20M and was operated isothermally at 60 °C. The chromatograph was calibrated with synthetic mixtures of MTBE and methanol. The mole fraction of the vapor phase, y, accurate to within 0.001 was calculated from the peak area ratio of the samples. The validity of the method has been tested on several other salt systems (*6*).

Vapor pressure measurements of salt solutions in methanol were carried out by using a Knauer vapor pressure osmometer (Herbert Knauer & Co., GmbH). It makes use of the vapor pressure osmometry technique to find the concentration of a salt solution of known vapor pressure that is isopiestic to that under measurement. A more detailed description of the experimental technique can be found in another paper (*7*).

Results and Discussion

The experimental data have been interpreted, considering the solution of the salt in the mixtures of the two volatile components as a pseudobinary system constituted by each one of the volatile components being salt-saturated. Using this approach, Sada (*8*) found that the integrated form of the Gibbs–Duhem equation is applicable to salt solutions, whenever the composition of the liquid phase without salt and the vapor pressures of the salt-saturated volatile compounds are used.

The thermodynamic consistency of the experimental data was analyzed by using the Redlich–Kister area test (*9*). The systems MTBE + methanol, MTBE + methanol + LiBr, MTBE + methanol + LiCl, and MTBE + methanol + $Ca(NO_3)_2$ were found to be thermodynamically consistent. The MTBE +

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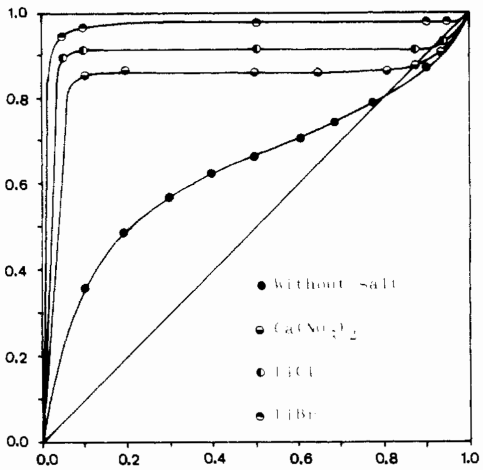

Figure 1. Equilibrium diagrams for MTBE (1) + methanol (2) and MTBE (1) + methanol (2) + salt systems: ●, ◒, ◐, ◓, experimental values; —, fit of the LEMF equation.

methanol + NaI system, however, was found to be nonconsistent (data not shown). From a careful analysis of the data, it was evident that there were important deviations from expected results when the solution was particularly enriched in methanol and, therefore, when there was more dissolved salt. The solution, starting colorless, acquired during the experiment a yellowish color. A tiny crystal of sodium thiosulfate was enough to restore the solution colorless again. Therefore, it was interpreted that, somehow, the ion I^- was progressively oxidized to I_2, with unknown effects on the liquid-phase composition.

The MTBE + methanol + $CaCl_2$ system was found to be slightly nonconsistent. This was attributed to the excess of added salt needed to attain a completely saturated solution. Further analysis showed that, in effect, the excess solid salt retained methanol and, therefore, the liquid-phase composition was dependent on the amount of excess salt added. The trials to determine the liquid-phase composition after saturation gave poor results, because the imprecision associated with the analysis was higher than the one implicit in the supposition that the amount of methanol retained by the $CaCl_2$ excess is negligible. For this reason, the measurements were made with use of a very slight $CaCl_2$ excess. However, the thermodynamic consistency was poor, and the results are not shown.

Table I and Figure 1 present the experimental x-y-T VLE data for the systems MTBE + methanol, MTBE + methanol + LiCl, MTBE + methanol + LiBr, and MTBE + methanol + $Ca(NO_3)_2$ at 298.15 K. Also, Table I shows the calculated values of the total vapor pressures, P, liquid-phase activity coefficients, γ_i, and vapor-phase fugacity coefficients, ϕ_i. As the measurement technique does not provide experimental data for the total vapor pressures, P, an alternative procedure is necessary. Therefore, these values of P, as well as the activity coefficients, γ_i, and the fugacity coefficients, ϕ_i, were derived from the x, y, and T experimental values and the vapor pressure of the components by means of an iterative procedure. For this purpose, the dimensionless excess Gibbs energy, G^E/RT, has been fitted by using the four-parameter Margules equation. Details of this computation procedure can be found elsewhere (*6*).

The vapor-phase nonidealities were calculated from the Peng–Robinson (*10*) equation of state. The values used for the critical constants and the accentric factor were taken from literature (*11*). The binary interaction constant, δ_{12}, was set as zero for all the systems.

Table I shows the experimental vapor pressure of methanol saturated with every one of the salts used in the persent work. All the analyses carried out failed to show any one of these salts to be soluble in MTBE and, therefore, the MTBE vapor pressure was taken from literature (*12*,*13*).

Table I. Experimental x-y Data and Calculated Values of P, γ_i, and ϕ_i at 298.15 K

x_1	y_1	P	γ_1	γ_2	ϕ_1	ϕ_2
System MTBE (1) + Methanol (2)						
0	0	16.937		1		0.9959
0.104	0.347	24.240	2.426	1.040	0.9890	0.9939
0.191	0.472	27.607	2.043	1.060	0.9873	0.9932
0.296	0.564	30.477	1.736	1.110	0.9859	0.9926
0.396	0.614	32.444	1.503	1.219	0.9849	0.9922
0.494	0.657	33.768	1.341	1.346	0.9843	0.9920
0.605	0.702	34.695	1.201	1.539	0.9838	0.9918
0.682	0.734	35.084	1.126	1.725	0.9836	0.9918
0.775	0.780	35.302	1.060	2.029	0.9834	0.9919
0.899	0.865	34.861	1.000	2.740	0.9836	0.9921
1	1	33.505	1		0.9838	
System MTBE (1) + Methanol (2) + LiCl						
0	0	3.266		1		0.9959
0.051	0.895	30.157	15.820	1.019	0.9858	0.9933
0.099	0.913	35.933	9.883	1.058	0.9831	0.9920
0.500	0.913	35.220	1.919	1.876	0.9835	0.9922
0.874	0.913	34.506	1.075	7.262	0.9838	0.9923
0.939	0.929	34.545	1.019	12.260	0.9837	0.9924
1	1	33.505	1		0.9838	
System MTBE (1) + Methanol (2) + LiBr						
0	0	0.933		1		0.9959
0.048	0.937	15.686	9.220	1.113	0.9926	0.9965
0.100	0.975	27.223	7.949	0.809	0.9872	0.9941
0.500	0.972	32.388	1.886	1.730	0.9848	0.9929
0.900	0.975	33.189	1.073	8.864	0.9844	0.9928
0.945	0.975	33.269	1.025	16.150	0.9843	0.9928
1	1	33.505	1		0.9838	
System MTBE (1) + Methanol (2) + $Ca(NO_3)_2$						
0	0	5.332		1		0.9959
0.101	0.860	35.843	9.103	1.042	0.9832	0.9919
0.197	0.858	35.976	4.673	1.188	0.9831	0.9919
0.499	0.860	35.231	1.818	1.839	0.9834	0.9920
0.642	0.860	35.707	1.426	2.608	0.9832	0.9919
0.805	0.863	35.803	1.144	4.698	0.9832	0.9919
0.817	0.861	35.812	1.125	5.081	0.9832	0.9919
0.877	0.878	35.847	1.070	6.641	0.9831	0.9919
0.940	0.900	35.532	1.014	11.060	0.9833	0.9921
1	1	33.505	1		0.9838	

The MTBE + methanol, MTBE + methanol + LiCl, MTBE + methanol + LiBr, and MTBE + methanol + $Ca(NO_3)_2$ data were used to obtain the adjustable parameters in the van Laar (*14*), Mato (*15*), NRTL (*16*) and LEMF (*17*) equations by a nonlinear regression method. The following objective function, OF, was minimized

$$\mathrm{OF} = \sum_{i=1}^{N}\left[\left(\frac{\gamma_{1,\mathrm{exptl}} - \gamma_{1,\mathrm{calcd}}}{\gamma_{1,\mathrm{exptl}}}\right)^2 + \left(\frac{\gamma_{2,\mathrm{exptl}} - \gamma_{2,\mathrm{calcd}}}{\gamma_{2,\mathrm{exptl}}}\right)^2\right] \quad (1)$$

where N is the number of experimental points. The model parameters are shown in Table II along with the average absolute deviations in vapor mole fraction

$$\Delta(y_i) = \sum |y_{i,\mathrm{calcd}} - y_{i,\mathrm{exptl}}|/N \quad (2)$$

The MTBE + methanol data were fitted with the Wilson (*18*) equation. This equation is not suitable for mixtures of partially miscible liquids, and therefore, it has not been used in the analysis of the salt systems.

The LEMF equation yields the lowest deviations in vapor-phase composition, whereas the van Laar and Mato equations give the highest deviations for the salt systems, probably because these systems present strong deviations from ideality.

Different values for the nonrandomness α parameter were used in the NRTL equation with similar results. The value of α = 0.3 was chosen for the MTBE + methanol system and α = 0.2 for the salt systems.

Table II. Parameters A_{12} and A_{21} in the Activity Coefficient Models at 298.15 K for MTBE (1) + Methanol (2) and MTBE (1) + Methanol (2) Salt-Saturated Systems and Average Absolute Deviations in Vapor-Phase Mole Fractions $\Delta(y_1)$

	A_{12}	A_{21}	$\Delta(y_1)$
	Van Laar (*14*)		
without salt	1.108	1.210	0.008
$Ca(NO_3)_2$	2.488	2.535	0.013
LiCl	2.995	2.661	0.009
LiBr	2.300	2.876	0.004
	MATO (*15*)		
without salt	1.108	1.210	0.008
$Ca(NO_3)_2$	2.488	2.535	0.013
LiCl	2.992	2.661	0.009
LiBr	2.300	2.854	0.004
	Wilson[a] (*18*)		
without salt	1.475	1.997	0.008
	NRTL[a] (*16*)		
without salt	0.788	0.863	0.008, $\alpha = 0.3$
$Ca(NO_3)_2$	0.742	0.748	0.012, $\alpha = 0.2$
LiCl	0.760	0.670	0.008, $\alpha = 0.2$
LiBr	0.650	0.827	0.003, $\alpha = 0.2$
	LEMF[a] (*17*)		
without salt	1.066	1.257	0.008
$Ca(NO_3)_2$	2.264	2.099	0.004
LiCl	2.368	2.172	0.002
LiBr	1.896	2.444	0.003

[a] Parameters A_{12} and A_{21} in joules per mole.

Table III. Solubility Limits Predicted from the Correlation Models for the Systems MTBE (1) + Methanol (2) + Salt

salt		NRTL	LEMF	Van Laar	Mato
$Ca(NO_3)_2$	x_1^{I}	0.143	0.124	0.146	0.146
	x_1^{II}	0.860	0.794	0.862	0.862
LiBr	x_1^{I}	0.174	0.261	0.171	0.171
	x_1^{II}	0.912	0.932	0.908	0.910
LiCl	x_1^{I}	0.074	0.077	0.074	0.074
	x_1^{II}	0.892	0.870	0.893	0.892

The $CaCl_2$, $Ca(NO_3)_2$, LiCl, and LiBr salts produce liquid–liquid-phase splitting. Solubility limits were not measured because of the imprecision in measuring the equilibrium points that the presence of the salt produces in this composition range. Table III is a summary of the solubility limits, as predicted by the van Laar, Mato, NRTL, and LEMF models. The predicted values are in good agreement with the experimental results presented in this paper for the consistent salt systems MTBE + methanol + $Ca(NO_3)_2$, + LiCl, and + LiBr. The system MTBE + methanol + LiBr splits in two liquid phases for nearly the overall range of compositions. Consequently, the solubility limits predicted by the previously cited models, though admissible, lead to a poor description of the system.

As can be seen in Figure 1, LiBr > LiCl > $Ca(NO_3)_2$ produce, in this order, the highest favorable effect on the VLE for the MTBE + methanol system. However, taking in consideration other factors such as price, availability, and toxicity, it seems that $Ca(NO_3)_2$ is the salt of choice to be used in the industrial separation of MTBE + methanol mixtures.

Glossary

A	parameter in the Wilson, NRTL, and LEMF equations, J/mol
G	molar Gibbs energy, J/mol
N	number of experimental points
P	total vapor pressure, kPa
T	temperature, K
x	liquid mole fraction, salt free
y	vapor mole fraction

Greek Letters

α	nonrandomness parameter in the NRTL equation
δ	binary interaction coefficient in the Peng–Robinson equation
γ	activity coefficient in the liquid phase
ϕ	fugacity coefficient in the vapor phase

Subscripts

calcd	calculated
exptl	experimental
i	component i (i = 1,2)
1,2	components 1, 2

Superscripts

E	excess property
I,II	liquid phases

Registry No. MTBE, 1634-04-4; $Ca(NO_3)_2$, 10124-37-5; LiCl, 7447-41-8; LiBr, 7550-35-8; methanol, 67-56-1.

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