Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Vapor-liquid equilibrium data for the 2-methoxy-2-methylpropane (MTBE)-ethanol, MTBE-ethanol-calcium chloride, and MTBE-ethanol-copper chloride

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To cite this Article Al-Rub, Fahmi A. Abu , Abdel-Jabbar, Nabil , Darwish, Naif A. and Ghanem, Hanadi(2002) 'Vapor-liquid equilibrium data for the 2-methoxy-2-methylpropane (MTBE)-ethanol, MTBE-ethanol-calcium chloride, and MTBE-ethanol-copper chloride', Separation Science and Technology, 37: 8, 1911 — 1926

To link to this Article: DOI: 10.1081/SS-120003051

URL: http://dx.doi.org/10.1081/SS-120003051

SEPARATION SCIENCE AND TECHNOLOGY, 37(8), 1911–1926 (2002)

VAPOR–LIQUID EQUILIBRIUM DATA FOR THE 2-METHOXY-2-METHYLPROPANE (MTBE)–ETHANOL, MTBE–ETHANOL–CALCIUM CHLORIDE, AND MTBE–ETHANOL–COPPER CHLORIDE

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ABSTRACT

Isobaric vapor–liquid equilibrium data were measured for the methyl *tert*-butyl ether (MTBE)–ethanol, MTBE–ethanol–calcium chloride, and MTBE–ethanol–copper chloride at an atmospheric pressure of 702 mmHg using a modified Malanowski equilibrium still. The experimental data of the salt-free system were compared with those predicted by the ASOG, original UNIFAC, and UNIFAC–Dortmund methods of prediction, which predicted the bubble-point temperatures with root-mean-square deviations (RMSD) of: 1.30, 0.16, and 0.38K, respectively. The

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RMSD values of the vapor-phase compositions given by these models were: 0.0197, 0.0049, and 0.007, respectively. The experimental data of the salt-free system were also correlated by the Wilson, NRTL, and UNIQUAC models. The calculated data using both the Wilson and NRTL models were in good agreement with the experimental results.

The salts used in this study, calcium chloride and copper chloride, resulted in salting-out the MTBE and shifting the azeotropic point from 94.0 to 96.0 mol% MTBE. The experimental data of the salt-saturated systems were compared with those predicted by the Tan–Wilson equation and the results were in good agreement with the experimental data.

Key Words: Methyl *tert*-butyl ether; Ethanol; Vapor–liquid eqilibrium; Data; Salt

INTRODUCTION

Methyl *tert*-butyl ether (MTBE), a relatively new petroleum-derived product produced by the reaction of methanol with isobutylene in the liquid phase over a strongly acidic ion-exchange resin catalyst (1), has been recommended to be used as a blending agent in the motor gasoline, for enhancing the octane number in substitution of the currently used leaded compounds. Ether based oxygenates enhance octane number and help complete combustion of blended fuels, and are thus used to reduce the carbon monoxide in the exhaust gas of cars. They have been preferred by refiners over the alcohol oxygenates (e.g., ethanol) due to the lower polarity and hence better blending characteristics with gasoline. Methyl *tert*-butyl ether emerged as a technological fix to transform methanol into a more acceptable oxygenate and now is one of the largest chemical compounds produced in the United States. The MTBE blends result in substantial reduction of carbon monoxide and unburned hydrocarbons in tail-pipe emissions due to lower vapor pressure and dilution of hydrocarbons in gasoline, which results in reducing the formation of ozone (2). Thus, a blend of gasoline and 7–15% MTBE has been used for high-performance premium gasoline. Methyl *tert*-butyl ether has advantages over other ethers in that it minimizes handling and storage problems associated with peroxide formation and exhibits excellent oxidative stability, preventing peroxide formation without the need to add inhibitors (3). Moreover, gasoline containing MTBE is considered “fungible,” i.e., it can be shipped and transported through all normal pipeline transportation channels (2). In addition to be used as a blending agent, mixtures of ether–alcohols (e.g., MTBE–alcohols) have been also considered as octane enhancers. Thus, phase-equilibrium data for these mixtures are essential for predicting vapor-compositions of these mixtures. In the literature, only recently some studies have been reported on the measurement of the vapor–liquid eqilibrium (VLE) of MTBE–alcohols (4–11).

The objectives of this study are to measure the VLE of MTBE(1)–ethanol (2) mixtures at atmospheric pressure of 702 mmHg and to investigate the effect of salt addition, either copper chloride or calcium chloride on the VLE of these mixtures. The salt-free experimental data will be compared with those predicted using three activity coefficient methods: the ASOG, original UNIFAC, and UNIFAC–Dortmund prediction methods. In addition, the experimental data will be correlated to the Wilson, the UNIQUAC, and the NRTL models. The experimental data of the salt-saturated mixtures will be analyzed using the Tan and coworkers approach.

EXPERIMENTAL

Chemicals

Methyl *tert*-butyl ether (purity: 99.8%, supplier: Acros) and ethanol (purity 99.8 + , supplier: GCC) were used in this study without further purification. Purity of these chemicals was checked out by reproducing their boiling points at the operating pressure. The salts used were calcium chloride (purity: +99%, supplier: Analar) and copper chloride (purity: +99%, supplier: Panreac).

Procedure

Isobaric VLE data at 702 mmHg for the MTBE–ethanol, MTBE–ethanol–copper chloride, and MTBE–ethanol–calcium chloride mixtures were measured using a modified Malanowski equilibrium still, which circulates both the vapor and liquid phases through a Cottrell pump. A detailed description of this still can be found elsewhere (12). The pressure in the still was measured using a mercury column barometer with an accuracy of ± 1 mmHg. Steady state was reached after 30 min, when the temperature was measured using a calibrated mercury-in-glass Beckman thermometer with a resolution of ± 0.05K. Samples of liquid and condensed vapor were withdrawn and analyzed with a precision better than 0.0002 mol fraction, using a gas chromatograph (Verian 3400) with a flame ionization detector (FID) and a column with the following specifications: type: 10% didecyl phthalate chromosorb W/Hp 80/100, length: 4.0 m and diameter: 0.3175 cm. The column temperature was 413.15K. Nitrogen with a flow rate of 20 mL/min was used as the carrier gas. For the salt experiments, mixtures were prepared using ethanol saturated with the salt.

RESULTS AND DISCUSSION

The experimental VLE data ($T-x-y$) for the MTBE–ethanol mixtures at 702 mmHg are tabulated in Table 1 and shown in Fig. 1. These results show that

Table 1. Isobaric Vapor–Liquid Eqilibrium Data for MTBE(1)–Ethanol(2) System at 702 mmHg. Antoine Constants (10): $A_1 = 6.07034$, $B_1 = -1158.19$, $C_1 = -43.200$, $A_2 = 7.16879$, $B_2 = -1552.601$, and $C_1 = -50.731$

Temperature (K)	x_1	y_1
349.50	0.0000	0.0000
348.72	0.0060	0.0350
348.10	0.0124	0.0620
346.42	0.0301	0.1380
345.15	0.0450	0.1930
343.12	0.0705	0.2780
341.15	0.0998	0.3560
339.35	0.1250	0.4188
337.72	0.1501	0.4650
336.45	0.1800	0.5090
335.76	0.1987	0.5311
333.80	0.2500	0.5900
332.95	0.2800	0.6150
332.34	0.3001	0.6259
331.62	0.3300	0.6500
331.16	0.3511	0.6620
330.85	0.3750	0.6725
330.20	0.4120	0.6800
329.55	0.4500	0.7125
328.80	0.5000	0.7280
328.40	0.5400	0.7550
327.60	0.6150	0.7800
327.35	0.6498	0.7912
327.10	0.7000	0.8130
326.47	0.7380	0.8200
326.20	0.8100	0.8560
326.00	0.8600	0.8800
325.94	0.8899	0.9026
325.76	0.9250	0.9314
325.65	0.9400	0.9400
325.52	0.9590	0.9520
325.95	1.0000	1.0000

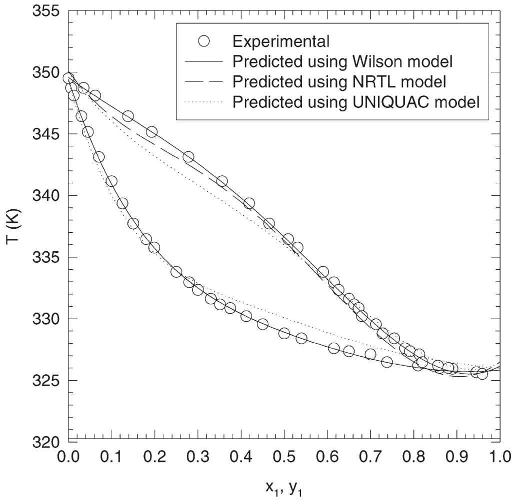

Figure 1. Isobaric T–x–y data of the MTBE–ethanol mixtures at 702 mmHg.

MTBE–ethanol mixtures exhibit a minimum azeotropic boiling temperature point at 94.00 mol% MTBE and 325.65K. A comparison between the experimental data of this study and other studies in terms of azeotropic point is shown in Table 2.

The activity coefficients of each component, γ_i, were calculated using the equation

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^0} + \frac{(B_{ii} - v_i^{\mathrm{L}})(P - P_i^0)}{RT} + \frac{(1 - y_i)^2 P \delta_{ij}}{RT} \tag{1}$$

$$\delta_{ij} \equiv 2B_{ij} - B_{ii} - B_{jj}$$

and the molar virial coefficients, B_{ij}, were estimated by the method of Hayden and O'Connell (13). The vapor pressures, P_i^0, were calculated using the Antoine

Table 2. Azeotropic Points for MTBE–Ethanol System

x_1	T (K)	P (kPa)	References
0.9550	327.94	101.3	(6)
0.9370	328.06	101.3	(10)
0.9400	325.65	93.57	This work

equation

$$\log(P_i^0/\mathrm{kPa}) = A + \frac{B}{C + T/\mathrm{K}} \tag{2}$$

using the Antoine constants given in Table 1.

The molar excess Gibbs energy, G^{E}, which gives an indication of the deviation of the mixture from ideal solution behavior can be calculated using the equation

$$G^{\mathrm{E}}/RT = x_1\ln(\gamma_1) + x_2\ln(\gamma_2) \tag{3}$$

The molar excess Gibbs energy of MTBE–ethanol mixtures is calculated using Eq. (3) and the results are plotted against the mole fraction of MTBE in the liquid phase, as shown in Fig. 2. This figure shows that this system exhibits a positive deviation from ideal solution behavior ($G^{\mathrm{E}}/RT > 0$). Shown also in Fig. 2, the molar Gibbs energy of mixing for the MTBE–ethanol mixtures at 702 mmHg, which is calculated using the equation

$$\frac{G^{\mathrm{m}}}{RT} = \frac{G^{\mathrm{E}}}{RT} + x_1\ln(x_1) + x_2\ln(x_2) \tag{4}$$

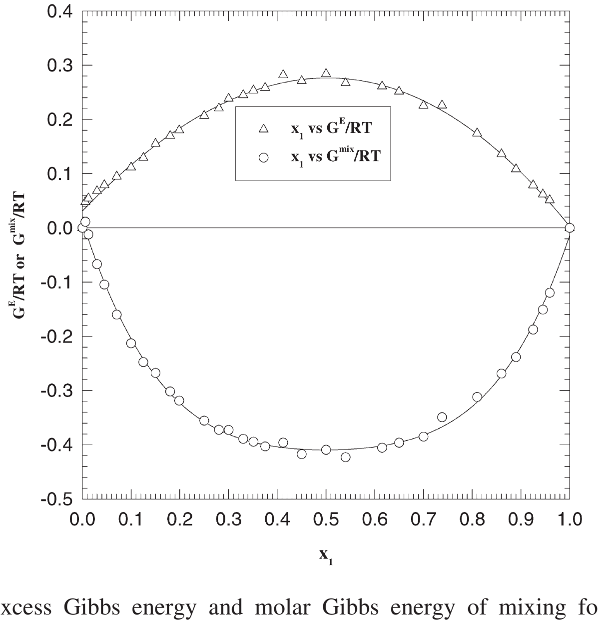

Figure 2. Excess Gibbs energy and molar Gibbs energy of mixing for the system MTBE–ethanol at 702 mmHg.

The curve of the molar Gibbs energy of mixing, as noticed, is above its tangent over the whole composition range (other than 0.0 and 1.0 mol fractions) indicating that MTBE–ethanol mixtures are miscible over the whole composition range under the experimental conditions.

Thermodynamic Consistency of the Salt-Free Experimental Data

The thermodynamic consistency of the measured salt-free VLE data of MTBE–ethanol mixtures was examined according to the smoothness test (14), the infinite dilution test of Kojima et al. (15) as modified by Jackson and Wilsak (16), and the integral test as modified by Herington (17). The smoothness test suggests that experimental data can be assumed to be consistent if the plot of the differences between the vapor and liquid phase compositions vs. the liquid composition is smooth. Upon applying this test to our data, the plot was smooth, which suggests that the data can be assumed consistent. The infinte dilution test of Kojima–Jackson–Wilsak, which involves extrapolation of the calculated excess Gibbs energy from the experimental data to the infinite dilution and then comparison between the extrapolated values and the values obtained by extrapolating the ln γ_1 and ln γ_2 curves to infinite dilution. According to this test, the VLE data can be assumed to be consistent if the values agree within 30%. The experimental data of this study, as shown in Table 3, were also found to be thermodynamically consistent according to this test.

The Herington test involves the caculation of two terms; D and J, where

$$D = \frac{100I}{\sum} \tag{5}$$

$$J = \frac{150|\Delta T_{\max}|}{T_{\min}}$$

Table 3. Thermodynamic Consistency Tests for the Experimental Vapor–Liquid Equilibrium Data

	Integral Test		Kojima–Jackson–Wilsak	
System	J	D	Error for Dilute Component 1 (%)	Error for Dilute Component 2 (%)
MTBE–ethanol at 702 mmHg	5.66	10.94	9.9	7.6

where I is the absolute difference between the areas above and below the abscissa of the curve $\ln \gamma_1/\gamma_2$ vs. x_1, $\sum$ is the sum of the absolute values of the areas under the curve $\ln \gamma_1/\gamma_2$ vs. x_1, $\Delta T_{\max}$ is the maximum boiling point range of the system, and $T_{\min}$(K) is the lowest measured boiling point of the system. According to this test, VLE experimental data can be assumed if $|D - J| < 10$. The experimental data of this study, as shown in Table 3, were also found to be thermodynamically consistent according to this test.

Prediction and Correlation of the Vapor–Liquid Eqilibrium of Methyl *tert*-Butyl Ether–Ethanol Mixtures

The experimental results of the salt-free system were predicted using three activity coefficient methods: the ASOG (18), UNIFAC (19), and UNIFAC–Dortmund (20) methods of prediction to calculate the liquid phase activity coefficients. Figure 3 shows a plot of the difference between predicted bubble-point temperatures and experimental ones against the composition of MTBE in the liquid phase and Fig. 4 shows a similar plot, but for the vapor-phase compostions. It can be seen from these figures that the deviations in prediction of both the bubble-point

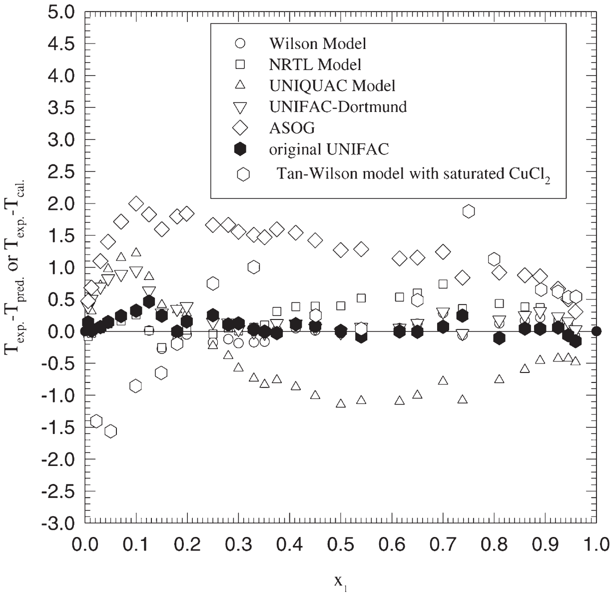

Figure 3. Comparison of bubble-point temperature deviations of the systems MTBE–ethanol and MTBE–ethanol–copper chloride at 702 mmHg.

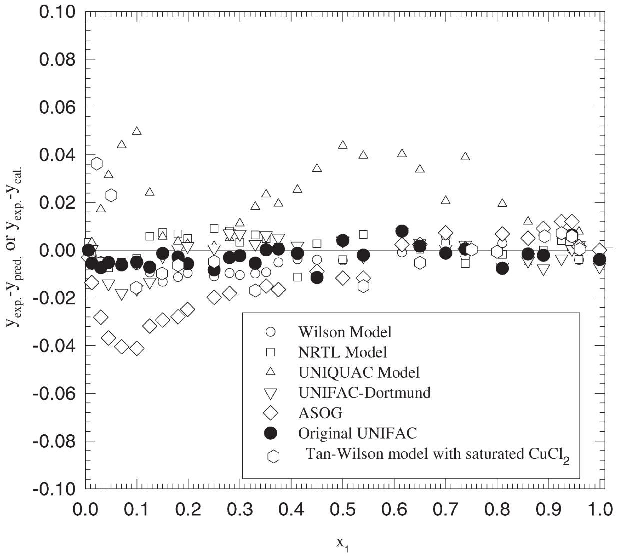

Figure 4. Comparison of vapor-phase deviations of the systems MTBE–ethanol and MTBE–ethanol–copper chloride at 702 mmHg.

temperatures and vapor-phase compositions are the highest with the ASOG method, while the UNIFAC method gave the lowest deviations in both the bubble-point temperatures and vapor-phase compositions predictions. This conclusion is supported using a comparison in terms of root-mean-square-deviations (RMSD) given in Table 4, which lists the RMSD in bubble-point temperatures and vapor-phase compositions prediction using the different prediction methods.

The experimental data were correlated with the Wilson (21), the UNIQUAC (22), and the NRTL (23) models. The parameters of these models were obtained using the gradient search optimization method where the sum of the squares of relative deviations in activity coefficients was minimized. The

Table 4. Root-Mean-Square Deviations in Prediction of Bubble-Point Temperatures and Vapor-Phase Compositions of MTBE–Ethanol Mixtures at 702 mmHg

Method	*T*-RMSD	y_1-RMSD
ASOG	1.30	0.0197
Original UNIFAC	0.16	0.0049
UNIFAC–Dortmund	0.38	0.0070

Table 5. Adjustable Parameters and RMSD in Caclulation of Bubble-Point Temperatures and Vapor-Phase Compositions of MTBE–Ethanol Mixtures at 702 mmHg

Model	Δg_{12} (J/mol)	Δg_{21} (J/mol)	α_{12}	T-RMSD	$-y_1$ RMSD
Wilson	−798.8	4321.7	—	0.14	0.0055
NRTL	923.5	1064.7	−2.0	0.31	0.0084
UNIQUAC	484.199	508.68	—	0.77	0.0190

optimum values of these parameters, listed in Table 5, are used to calculate the VLE of MTBE–ethanol mixtures at 702 mmHg, and the results are shown in Figs. 1, 3, and 4. The corresponding RMSD in bubble-point temperatures and in vapor-phase compositions calculations is also shown in Table 5. The results listed in Table 5 and presented in Figs. 3 and 4 show that both the Wilson and NRTL interaction parameters, found in this study, can be adequately represent the VLE data of the MTBE–ethanol mixtures.

Effect of Salt Addition on the Vapor–Liquid Eqilibrium of Methyl *tert*-Butyl Ether–Ethanol Mixtures

The effect of salt addition on the VLE of the MTBE–ethanol mixtures was investigated by studying the VLE of these mixtures in the presence of either calcium chloride or copper chloride. These salts were used in saturation conditions, i.e., ethanol was saturated with either of these salts. The experimental data in the presence of these salts are tabulated in Table 6 and are shown in Fig. 5. These results show that MTBE was salted-out in the presence of both salts and the azeotropic point was shifted from 94.0 to 96.0 mol% MTBE.

Analysis of the Salt Effect on the Vapor–Liquid Eqilibrium of Methyl *tert*-Butyl Ether–Ethanol Mixtures

The salt effect on VLE can be analyzed using different empirical and semi-theoretical approaches. One of these approaches is that of Tan and coworkers, which is based on the solute–solvent interaction parameter, A_{si}, which is defined by (24,25)

$$A_{si} \equiv \frac{p_i^s}{P} \text{ evaluated at } T_{\text{salt},i} \tag{6}$$

where p_i^s is the saturation vapor pressure of the pure solvent at the given bubble point of the solvent–salt mixture, $T_{\text{salt},i}$ is the bubble point of the solvent component i saturated with dissolved solute or having the same solute concentration at the given

Table 6. Isobaric Vapor–Liquid Eqilibrium Data for MTBE(1)–Ethanol(2)–Salt Systems at 702 mmHg

Saturated with Copper Chloride			Saturated with Calcium Chloride		
T (K)	x_1	y_1	T (K)	x_1	y_1
350.40	0.0000	0.0000	353.60	0.0000	0.0000
347.50	0.0221	0.1561	349.55	0.0210	0.1741
344.45	0.0501	0.2614	347.61	0.0500	0.2801
341.10	0.0989	0.3699	342.61	0.1000	0.4251
338.12	0.1488	0.4776	339.15	0.1512	0.5121
336.95	0.1801	0.5291	335.60	0.2500	0.6302
335.01	0.2502	0.6101	332.00	0.3511	0.6984
332.89	0.3301	0.6598	330.90	0.4491	0.7391
329.68	0.4510	0.7041	328.12	0.6001	0.7884
328.20	0.5401	0.7593	325.70	0.9601	0.9601
327.46	0.6500	0.8065	325.95	1.000	1.0000
326.90	0.7999	0.8652			
325.92	0.8919	0.9168			
325.78	0.9250	0.9394			
325.67	0.9451	0.9531			
325.66	0.9601	0.9600			
325.95	1.0000	1.0000			

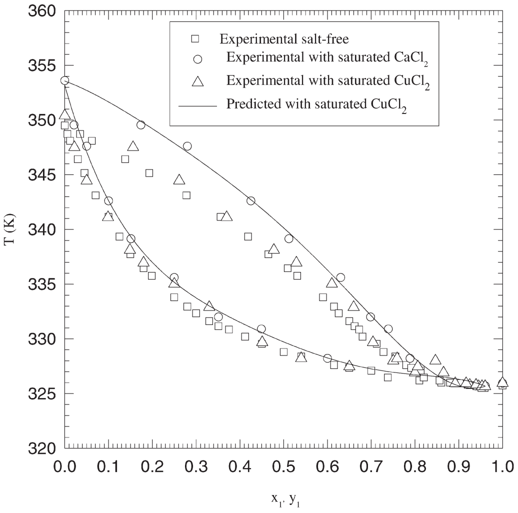

Figure 5. Isobaric T–x–y data of the MTBE–ethanol–salt mixtures at 702 mmHg.

Table 7. Correlation Parameters and RMSD in Caclulation of Bubble-Point Temperatures and Vapor-Phase Compositions of Methyl *tert*-Butyl Ether–Ethanol–Salt Mixtures at 702 mmHg

Salt	Δg_{12} (J/mol)	Δg_{21} (J/mol)	A_{s1}	A_{s2}	A_{21}^{s}	T-RMSD	$-y_1$ RMSD
Calcium chloride	−798.8	4321.7	1.0	1.20	1.20	0.73	0.0193
Copper chloride	−798.8	4321.7	1.0	1.11	1.11	0.92	0.016

system according to whether the system is saturated or unsaturated but containing a constant solute concentration over the whole mole fraction range. The values of the salt–solvent interaction parameters were calculated for MTBE and ethanol in the presence of each salt and are listed in Table 7. For a binary mixture, the ratio of the solute–solvent interaction parameters for both solvents, A_{21}^{s}, is found to be an effective indication of the effect of the solute, where

$$A_{21}^{s} \equiv \frac{A_{s2}}{A_{s1}^{s}} \tag{7}$$

Values of A_{21}^{s} greater than one indicate salting-out effect of the lighter component, values less than one indicate salting-in of the lighter component, and values equal to one indicate that the dissolved solute has an effect on either component. The values of A_{21}^{s} are listed in Table 7. These values were greater than 1.0, which indicates salting-out of the MTBE in the presence of either of the salts.

Finally, The VLE data of MTBE–ethanol–calcium chloride and MTBE–ethanol–copper chloride will be predicted using the Tan–Wilson model. This model describes the VLE of a solute-containing solvent mixture with two sets of interaction parameters; one set describes the solvent–solvent interaction parameters, which are the same as those of Wilson parameters for the solute-free system, and the other set describes the solute–solvent interactions, as discussed above. The excess Gibbs energy of the Tan–Wilson model is given by (24)

$$G^{\mathrm{E}} = RT\sum_{i} x_i \ln\left[(A_{si} - 1)x_i + \sum A_{ij}x_j\right] \tag{8}$$

where A_{ij}andA_{si} are the solvent–solvent and solute–solvent interaction parameters, respectively.

$$A_{ij} = \frac{v_j}{v_i}\exp\left[-\frac{g_{ji} - g_{ii}}{RT}\right] \tag{9}$$

$$A_{si} = \frac{v_{si}}{v_i}\exp\left[-\frac{g_{si} - g_{ii}}{RT}\right]$$

where g_{ij} and g_{si} are the solvent–solvent and solute–solvent interaction energies, respectively, and v_i and v_{si} are the molar volume of the pure solvent i and its molar volume in the presence of the dissolved solute, respectively. The solute–solvent interaction parameters, A_{si}, can be also calculated using Eq. (6). The predicted VLE data using the interaction parameters listed in Table 7 are shown in Fig. 5 which indicates that the predicted results using the Tan–Wilson model are in good agreement with the experimental data. This result is more evident in Figs. 3 and 4 and Table 7.

CONCLUSIONS

Experimental VLE data were obtained for the MTBE–ethanol, MTBE–ethanol–calcium chloride, and MTBE–ethanol–copper chloride mixtures. A salting-out effect on the MTBE was observed in the presence of either of the salts. The azeotropic point was shifted in the presence of both salts from 94.0 to 96.0 mol% MTBE.

The experimental data of the salt-free system were found to be very well correlated using the Wilson and NRTL models. While the ASOG predictive method failed to predict the VLE data of the salt-free system, the predictive results by both the original UNIFAC and UNIFAC–Dortmund predictive methods were in good agreement with the experimental ones. The Tan–Wilson predictive model gave a good prediction of the salt effect on the VLE of MTBE–ethanol mixtures.

NOTATIONS

A, B, C	Antoine parameters
A_{ij}	solvent–solvent interaction parameter between solvent (i) and solvent (j)
A_{si}	solute–solvent interaction parameter between solute (s) and solvent (i)
A_{21}^{s}	ratio of the solute–solvent interaction parameters of both solvents
B_{ij}	the second varial coefficient
g_{ij}, g_{si}	the solvent–solvent and solute–solvent interaction energies
D, J	terms in Herington test
G	molar Gibbs energy
P	total system pressure, mmHg
P_i^0	vapor pressure of ith component, mmHg
p_i^s	is the saturation vapor pressure of the pure solvent at the given bubble point of the solvent–salt mixture
T	temperature (K)

v_i, v_{si}	the molar volume of the pure solvent i and its molar volume in the presence of the dissolved solute, respectively
x	mole fraction in the liquid phase
y	mole fraction in the vapor phase

Greek Letters

ΔT_{max}	the overall range of boiling points of the system
γ_i	activity coefficient of the ith component

Subscripts

1	MTBE
2	ethanol
i	ith component

Superscripts

E	excess property
m	property due to mixing

Abbreviations

RMSD	root-mean-square-deviations
VLE	vapor liquid equilibrium

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Received December 2000
Revised July 2001