Salt Effect on the Isobaric Vapor−Liquid Equilibrium of the Methyl Acetate + Methanol System

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The effect of sodium thiocyanate at constant salt mole fraction from 0.01 to 0.05 and at saturation on the vapor−liquid equilibrium (VLE) of methyl acetate + methanol has been studied at 101.32 kPa using a modified Othmer equilibrium still. The salt exhibited both salting-in and salting-out effects on the methyl acetate, the azeotrope being eliminated at saturation. The results were correlated using the extended UNIQUAC model of Sander et al. and the electrolytic NRTL model of Mock et al.

1. Introduction

The alteration of phase equilibrium of mixed-solvent mixtures by the addition of salts (known as the salt effect) constitutes a possible technique of extractive distillation for the separation of systems of low relative volatility or systems exhibiting azeotropic behavior in the composition regions critical to the separation. However, the salt effect on the vapor−liquid equilibrium (VLE) must be better understood before the extractive distillation processes using this effect can be designed.

Although the molecules of the more polar component are normally preferentially attracted by the electrostatic field of the ions and hence the vapor composition is enriched in the less polar component in which the salt is less soluble, three types of behaviors anomalous to the general predictions have been identified and presented by Meranda and Furter (1974). Moreover, a minimum nonazeotropic point in the temperature−compositions diagram was observed for some azeotropic systems. Iliuta and Thyrion (1995, 1996) and Iliuta et al. (1996) have shown that the minimum in the temperature−compositions diagram corresponds to an apparent intersection point and hence does not represent an azeotropic point. To point out that this behavior is more evident at the smallest azeotropic mole fraction az) ($x'_1(az)$ representing the mole fraction of the more volatile component at the azeotropic point in the salt-free system), the methyl acetate + methanol system was chosen. Sodium thiocyanate is very soluble in methanol and also soluble in methyl acetate so to allow the investigation on a large range of salt concentrations below saturation. Moreover, the azeotropic methyl acetate + methanol system is of industrial importance, being involved in the poly(vinyl alcohol) manufacturing.

Methyl acetate + methanol was experimentally investigated at atmospheric pressure in the presence of $CaCl_2$ (Hashitani and Hirata, 1968) or CH_3COOK and $ZnCl_2$ (Hashitani and Hirata, 1969) at saturation and below saturation. The same system was also investigated at 298.15 K in the presence of $CaCl_2$, CH_3COOK, $Ca(NO_3)_2$, and LiCl only at saturation (Martin et al., 1994). Data concerning the influence of NaSCN on the VLE of this system are not present in the literature.

To calculate VLE for the mixed-solvent salt systems, most of the models are based on the local composition concept taking into account the interactions in the electrolytic systems. To represent the long-range contribution, a Debye−Hückel expression is often used. For the short-range contribution, Mock et al. (1986) used the NRTL model, Sander et al. (1986) and Macedo et al. (1990) used the UNIQUAC model and Kikic et al. (1991) used the UNIFAC group-contribution model.

The aim of this work is to determine the effect of sodium thiocyanate on the VLE of methyl acetate + methanol at different salt concentrations and at saturation. The new set of ion−solvent and salt−solvent interaction parameters obtained from the data correlation with the extended UNIQUAC model of Sander et al. (1986) and salt−solvent interaction parameters obtained from the data correlation with the electrolyte NRTL model of Mock et al. (1986) would be a contribution to the data base. The interaction parameter values involving CH_3COOCH_3 were not found in the literature.

2. Experimental Section

2.1. Chemicals. Methyl acetate (Fluka, HPLC grade) with a stated minimum purity of 99.5 mass % (maximum 0.05 mass % water) and methanol (LAB-SCAN, HPLC grade) with a stated minimum purity of 99.9 mass % (maximum 0.03 mass % water) were used directly without further purification.

Sodium thiocyanate (p.a. grade, minimum 99 mass %, Across) was dried before use and was shown to contain less than 0.1 mass % water, as analyzed by the Karl Fisher method.

2.2. Apparatus and Procedure. The VLE was measured with a modified recirculation Othmer type still previously used by Sada et al. (1975). The description of the still and the experimental procedure have been described previously (Iliuta and Thyrion, 1995, 1996).

Results were obtained at 101.32 kPa. Atmospheric pressure was measured by a mercury column barometer with an accuracy of ±0.066 kPa. The boiling temperature

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Table 1. Experimental Results for Methyl Acetate (1) + Methanol (2) + NaSCN (3) at 101.32 kPa

	$x_3 = 0.00$			$x_3 = 0.01$			$x_3 = 0.02$			$x_3 = 0.03$		
x'_1	y_1	T/K	α_0[a]	y_1	T/K	α_s[b]	y_1	T/K	α_s	y_1	T/K	α_s
0.000	0.000	337.65		0.000	337.95		0.000	338.50		0.000	339.00	
0.047	0.128	335.30	2.9764	0.135	335.55	3.1646	0.134	336.00	3.1375	0.132	336.50	3.0835
0.095	0.230	333.20	2.8455	0.243	333.40	3.0580	0.243	333.80	3.0580	0.242	334.25	3.0414
0.194	0.368	330.65	2.4192	0.376	330.65	2.5034	0.382	330.85	2.5681	0.393	331.25	2.6899
0.297	0.451	328.95	1.9445	0.470	329.00	2.0990	0.478	329.20	2.1675	0.486	329.45	2.2381
0.397	0.519	327.95	1.6389	0.538	328.00	1.7688	0.544	328.20	1.8120	0.555	328.40	1.8943
0.495	0.575	327.30	1.3803	0.589	327.35	1.4620	0.604	327.50	1.5561	0.617	327.70	1.6435
0.600	0.627	327.05	1.1206	0.644	327.15	1.2060	0.657	327.35	1.2770	0.674	327.60	1.3783
0.670	0.667	327.00	0.9866	0.684	327.20	1.0661	0.702	327.50	1.1603	0.714	327.70	1.2296
0.702	0.683	327.10	0.9146	0.702	327.20	1.0000	0.718	327.55	1.0808	0.735	327.75	1.1774
0.800	0.757	327.30	0.7788	0.773	327.55	0.8513	0.790	327.90	0.9405	0.802	328.25	1.0126
0.900	0.848	328.25	0.6199	0.865	328.65	0.7119	0.872	328.95	0.7569	0.882	329.15	0.8305
0.950	0.913	329.10	0.5523	0.909	329.30	0.5257	0.928	329.50	0.6784	0.935	329.70	0.7571
1.000	1.000	330.15		1.000	330.30		1.000	330.40		1.000	330.55	

	$x_3 = 0.04$			$x_3 = 0.05$			saturation			
x'_1	y_1	T/K	α_s	y_1	T/K	α_s	y_1	x_3	T/K	α_s
0.000	0.000	339.60		0.000	340.30		0.000	0.183	352.65	
0.047	0.128	337.05	2.9764	0.125	337.90	2.8967	0.109	0.182	350.50	2.4805
0.095	0.242	334.85	3.0414	0.238	335.45	2.9754	0.211	0.180	348.25	2.5476
0.194	0.395	331.65	2.7125	0.396	332.20	2.7239	0.396	0.180	345.00	2.7239
0.297	0.494	329.85	2.3109	0.501	330.25	2.3765	0.515	0.179	341.65	2.5134
0.397	0.567	328.70	1.9889	0.578	329.00	2.0804	0.619	0.175	338.85	2.4677
0.495	0.629	327.95	1.7297	0.639	328.30	1.8058	0.702	0.170	336.35	2.4033
0.600	0.687	327.90	1.4633	0.699	328.20	1.5482	0.772	0.163	334.80	2.2573
0.670	0.728	328.00	1.3183	0.735	328.30	1.3661	0.812	0.160	334.00	2.1273
0.702	0.746	328.05	1.2468	0.759	328.35	1.3369	0.825	0.153	333.20	2.0012
0.800	0.812	328.55	1.0798	0.825	328.75	1.1786	0.878	0.117	331.95	1.7992
0.900	0.891	329.45	0.9083	0.902	329.80	1.0227	0.927	0.087	331.60	1.4110
0.950	0.942	329.95	0.8548	0.950	330.15	1.000	0.960	0.079	331.05	1.2632
1.000	1.000	330.75		1.000	330.85		1.000	0.052	330.95	

Relative volatility for the salt-free system calculated with relation 1. [b] Relative volatility for the salt system calculated with relation

was measured using a calibrated thermometer with an accuracy of ±0.05 K.

2.3. Sample Analysis. The liquid and vapor compositions were analyzed by gas chromatography using a TCD detector and a 2.4 m × 3.2 mm o.d. Poropak Q column. The optimum operating conditions were the following: carrier gas (hydrogen) flow rate, 30 cm^3/min; oven temperature, 453 K; injection temperature, 473 K; detector temperature, 453 K. Calibration and analysis were carried out in molar fractions by means of an internal standard technique. The gas chromatograph was calibrated using ten standard solutions with known composition that were prepared gravimetrically. An injection volume of 0.2 μL was used. The chromatographic measurements showed a good reproducibility, the mole fractions of alcohol and methyl acetate being calculated from the peak area ratio of the samples with an accuracy of ±0.001 in mole fraction. By evaporation of a known mass of liquid samples, it was possible to determine the salt solubility in different solvent mixtures with an accuracy of ±0.001 in mole fraction.

3. Results and Discussion

3.1. Experimental Data. Isobaric VLE data at 101.32 kPa were measured at $x_3 = 0.00$, 0.01, 0.02, 0.03, 0.04, and 0.05 and at saturation for the system methyl acetate (1) + methanol (2) + NaSCN (3), and the results are presented in Table 1. The liquid concentration is presented on a salt-free basis x' ($x'_1 = n_1/(n_1 + n_2)$ where n_1 and n_2 represent the number of moles of solvents 1 and 2).

The results for the salt-free system are compared with those reported by Dobroserdov and Bagrov (1967) and Nagata (1969) in Figure 1. A good agreement is found with the results of the literature. The azeotropic point was found at $x'_1 = 0.668$ and $T = 327.00$ K.

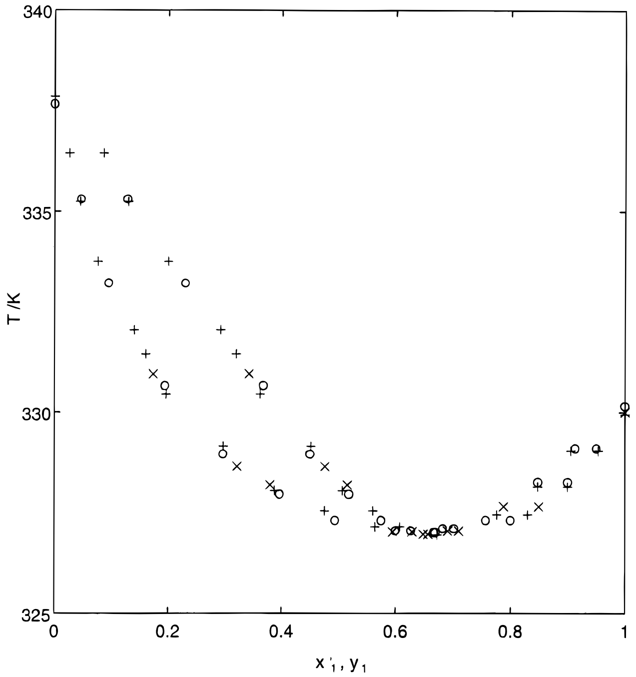

Figure 1. Temperature–composition diagram for methyl acetate (1) + methanol (2) at 101.32 kPa: (○) this work; (×) Dobroserdov and Bagrov (1967); (+) Nagata (1969).

According to Reichardt (1988), methanol is much more polar than methyl acetate, as shown by the values of the normalized spectroscopic solvent polarity parameter, E_T^N (0.762 and 0.287, respectively). This parameter, based on the intramolecular CT absorption of the pyridinium *N*-phenoxide betaine dye, consitutes a more comprehensive measure of solvent polarity than the dielectric constant or

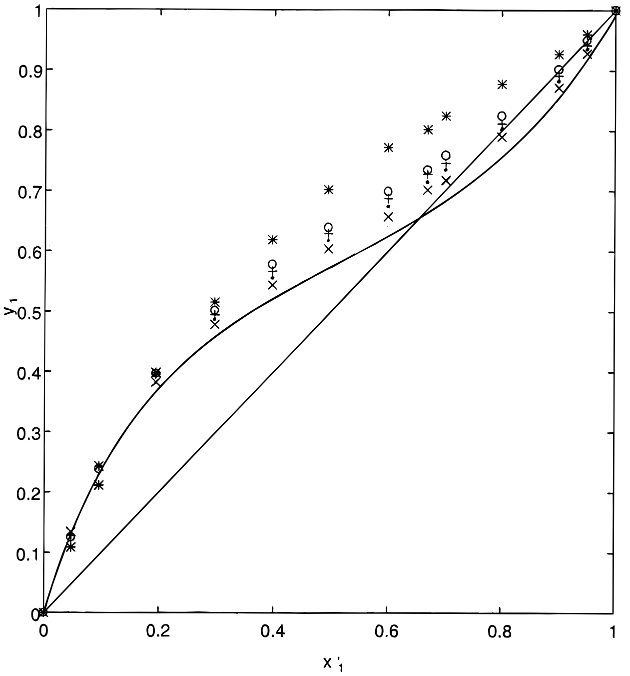

Figure 2. Effect of NaSCN on the VLE of methyl acetate (1) + methanol (2), y_1 versus x'_1: (—) salt-free system; (×) x_3 = 0.02; (·) 0.03; (+) x_3 = 0.04; (○) x_3 = 0.05; (∗) saturation.

any other single physical characteristic, since it reflects more reliably the complete picture of all intermolecular forces acting between solute and solvent molecules. Moreover, the large difference in the relative permittivities (dielectric constant) for methanol and methyl acetate (32.66 and 6.68, respectively) could be linked to the large difference between the salt solubilities in pure solvents (Table 1). Hence, methyl acetate is expected to be salted-out from the mixed solvent over the whole range of the liquid concentration. To point out the modifications in the vapor-phase concentrations, the results are presented in Figure 2 at various salt concentrations. At all salt concentrations the salting-out effect on methyl acetate increases with increasing salt concentration, as predicted by the relationship of the relative volatility as a function of the salt mole fraction, x_3 (Johnson and Furter, 1960). As shown previously (Iliuta and Thyrion, 1996), this can be explained by the decrease of the escaping tendency of methanol molecules due to the stronger interaction of this solvent, mainly with ion pairs. However, an anomalous crossover between salting-in and salting-out effects on methyl acetate was observed at $x_3 = 0.05$ and at saturation, both salting-in and salting-out effects being much stronger at saturation. This is due perhaps to the rather large difference between the salt solubility in pure methyl acetate (0.052) and that in the liquid mixture with mole fractions extending from x'_1 0 to about 0.70 (Figure 3).

The azeotropic point was changed to about $x'_1 = 0.702$, 0.73, 0.80, 0.88, and 0.95 at $x_3 = 0.01$, 0.02, 0.03, 0.04, and 0.05, respectively. Moreover, the azeotrope of the mixed solvent system disappears at saturation.

As shown previously for acetone (1) + methanol (2) + NaI or NaSCN (3) (Iliuta and Thyrion, 1996) and 1-propanol (1) + water (2) + $CaCl_2$ (3) systems (Iliuta et al., 1996), methyl acetate (1) + methanol (2) + NaSCN (3) also presents a nonazeotropic minimum in the temperature. The existence of this minimum in bubble points at a salt concentration below saturation is shown in Table 1 where y_1 is higher than x'_1 up to the azeotropic point on each side of the temperature minimum. This is illustrated in Figure 4 for $x_3 = 0.04$. This behavior was shown to be less evident for acetone (1) + methanol (2) + NaI or NaSCN (3) than for 1-propanol (1) + water (2) + $CaCl_2$ (3). As supposed previously, the lowest the $x'_1(az)$ value, the most evident appears this phenomenon.

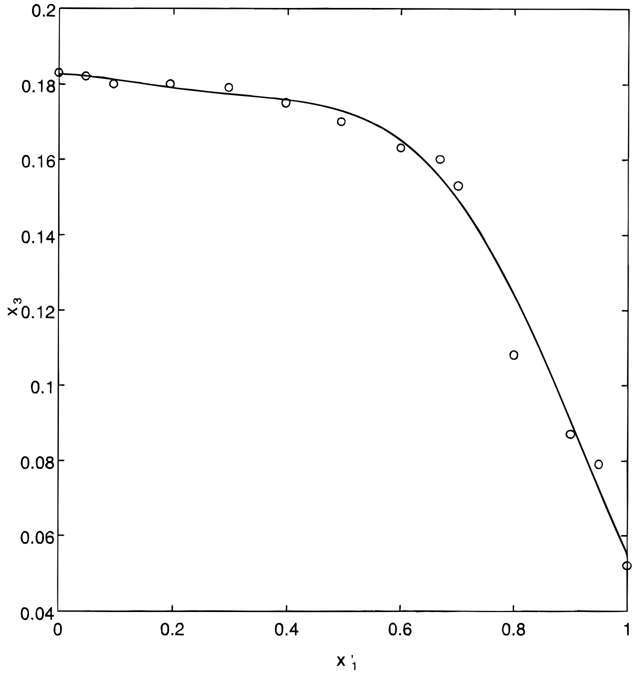

Figure 3. Saturation salt mole fraction, x_3, versus liquid mole fraction (salt-free basis), x'_1.

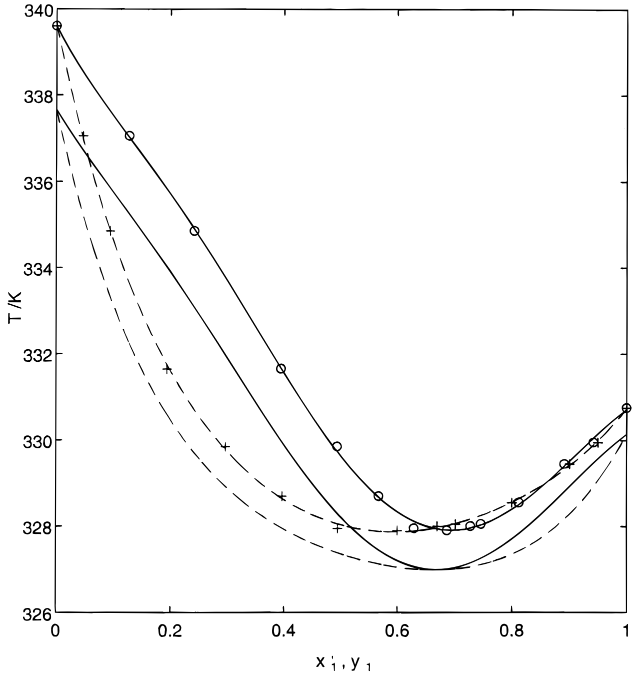

Figure 4. VLE of methyl acetate (1) + methanol (2) + NaSCN (3) at x_3 = 0.00 [*T*, *x*′ (– –), *T*, *y* (—)] and at x_3 = 0.04 [*T*, *x*′ (– – + – –), *T*,*y* (–○–)].

To illustrate the salt effect in the salt-containing mixture, the relative volatility of methyl acetate (1) to methanol (2), α, defined as

$$\alpha = y_1 x'_2 / y_2 x'_1 \qquad (1)$$

was used. In Figure 5, the relative volatility for the salt-free system (α_0) and at various salt molar fractions (α_s) is plotted against x'_1. It can be observed that the relative

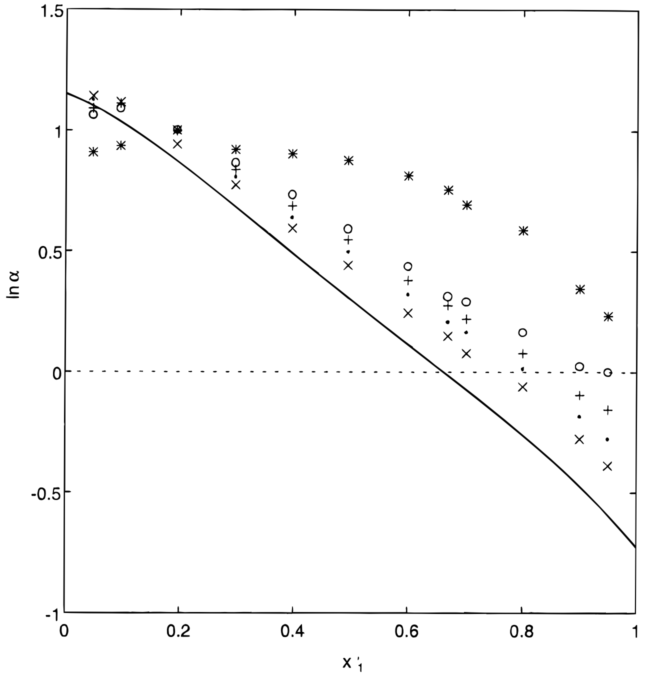

Figure 5. Relative volatility of methyl acetate (1) + methanol + NaSCN (3) at different salt mole fractions: (—), salt-free system; (×) x_3 = 0.02; (·) x_3 = 0.03; (+) x_3 = 0.04; (○) x_3 = 0.05; ( ) saturation.

Table 2. Results of the Correlation with NRTL, UNIQUAC, and Wilson Models for Methyl Acetate (1) + Methanol (2)

model type	ΔT^a/K	Δy^b	model params	units
NRTL	0.05	0.003	g12 − g22 = 178.06	K
			g21 − g11 = 190.27	K
			α12 = α12 = 0.47	
UNIQUAC	0.05	0.003	u12 − u22 = 304.6	K
			u21 − u11 = −41.97	K
Wilson	0.09	0.003	λ12 − λ22 = −55.03	K
			λ21 − λ11 = 423.35	K

$\Delta T = (1/N)\sum_i^N |T_i^{\rm exp} - T_i^{\rm calc}|$. ^{b} $\Delta y = (1/N)\sum_i^N |y_{1,i}^{\rm exp} - y_{1,i}^{\rm calc}|$, where N represents the number of data points.

volatility is generally higher for salt systems due to the salting-out effect on methyl acetate. However, at low ester mole fraction ($x'_1 < 0.15$), α becomes lower than for the salt-free system as far as $x_3 \geq 0.05$. This is an indication of the salting-in effect on methyl acetate under these conditions.

3.2. Calculation of Phase Equilibrium. Experimental data for methyl acetate (1) + methanol (2) were correlated using Wilson (1964), NRTL (Renon and Prausnitz, 1968), and the UNIQUAC (Abrams and Prausnitz, 1975) models for liquid-phase activity coefficients. The bubble point temperature, T, and vapor composition, y, under isobaric conditions were calculated from the models using a Newton−Raphson iterative method. The pure solvent's vapor pressures were obtained with excellent precision from the Antoine constants reported by Reid et al. (1977), the difference between experimental and calculated boiling points at atmospheric pressure being much less than the experimental error. Model parameter values, mean absolute deviations in vapor phase composition (Δy) and bubble points (ΔT) are presented in Table 2. Good results are obtained especially using the NRTL and UNIQUAC models.

In the case of a mixed solvent−salt system, the results were correlated using two reliable electrolytic models, in which the molar excess Gibbs energy, $G^{\rm E}$, was considered as a sum of the long-range ion−ion interaction contribution ($G^{\rm E}_{\rm LR}$) and the short-range ion−ion, ion−solvent, salt−solvent, and solvent−solvent interaction contributions ($G^{\rm E}_{\rm SR}$).

Table 3. Results of the Correlation with the Electrolytic NRTL Model of Mock et al.^{a} and the Extended UNIQUAC Model of Sander et al.^{b}

		ΔT/K		Δy	
N	x_3	NRTL model	UNIQUAC model	NRTL model	UNIQUAC model
14	0.01	0.34	0.25	0.005	0.008
14	0.02	0.37	0.38	0.007	0.010
14	0.03	0.38	0.54	0.008	0.016
14	0.04	0.48	0.69	0.011	0.018
14	0.05	0.62	0.83	0.014	0.028
14	sat	1.16	1.85	0.022	0.030
		0.56	0.75	0.011	0.018

^{a} NRTL salt−solvent interaction parameters for the system methyl acetate (m) + methanol (m') + NaSCN (ca): $\tau_{m,{\rm ca}} = 31.233$, $\tau_{{\rm ca},m} = -18.892$, $\alpha_{{\rm ca},m} = 0.024$, $\tau_{m',{\rm ca}} = 5.170$, $\tau_{{\rm ca},m'} = -3.475$, $\alpha_{{\rm ca},m'} = 0.2$. The first three parameters were obtained using the present data; the last three were taken from Iliuta and Thyrion (1996). ^{b} UNIQUAC interaction parameters are given in Table 4.

Electrolyte NRTL Model of Mock et al. (1986). This model was developed to represent the phase equilibrium of mixed-solvent electrolyte systems by the extension of those used for the aqueous electrolyte systems (Chen et al., 1982; Chen and Evans, 1986). Having in mind that the long-range interaction contribution (Pitzer, 1980) was found to have little effect on the phase equilibrium of water, only the local interaction contribution term derived from the NRTL equation (Renon and Prausnitz, 1968) was used and the long-range interaction contribution term was dropped. The model binary adjustable parameters are associated with the solvent−solvent pairs, solvent−salt pairs, and salt−salt pairs. For a system with two solvents, m and m', and one salt, ca, there are nine binary adjustable parameters: the energy parameters ($\tau_{{\rm ca},m}$, $\tau_{m,{\rm ca}}$, $\tau_{{\rm ca},m'}$, $\tau_{m',{\rm ca}}$, $\tau_{m,m'}$, $\tau_{m',m}$) and the nonrandomness factors ($\alpha_{{\rm ca},m}$, $\alpha_{{\rm ca},m'}$, $\alpha_{m,m'}$).

In order to make the parameter determination tractable, the binary solvent−solvent parameters were first determined from phase equilibrium data of the salt-free system (Table 2). Moreover, the binary NaSCN−methanol parameters were determinated previously (Iliuta and Thyrion, 1996). Values for the other parameters were determined through data regression using the following objective function:

$$F = \sum_{k=1}^{N} W_{U_k}(U_k^{\rm exp} - U_k^{\rm calc})^2/\sigma_{U_k}^{\;2} \qquad (2)$$

where U are the state variables (T and y), W is a weight factor for data type U chosen to obtain close values for these quantities, and σ is the standard error of measurements taken from the original paper (Mock et al., 1986).

The values of model parameters and the mean absolute deviations between the calculated and the experimental values of the temperatures and the vapor mole fractions are given in Table 3. The model represents experimental data with good accuracy, especially the vapor phase composition. The errors in bubble point were shown to be rather high at high salt concentrations, especially at saturation.

Extended UNIQUAC Model of Sander et al. (1986). In this local composition model, the solvent activity coefficients are calculated as a sum of a long-range interaction

Table 4.

UNIQUAC Reference Interaction Parameters

	a^*_{kl}/K			
species	CH_3COOCH_3	CH_3OH	Na^+	SCN^-
CH_3COOCH_3	0.0	304.60[a]	1760.21[a]	1000.0[a]
CH_3OH	−41.97[a]	0.0	558.0[b]	1047.15[c]
Na^+	−447.48[a]	283.8[b]	0.0	0.0[c]
SCN^-	−447.49[a]	−790.98[c]	0.0[c]	0.0

UNIQUAC $\delta_{ij,m}$/K Parameters; $\delta_{ij,m} = \delta_{ji,m}$

	$j = SCN^-$ m	
i	C_3H_6O	CH_3OH
Na^+	−1549.69[a]	1455.58[c]

[a] Estimated from the data of this work. [b] Sander et al. (1986). [c] Iliuta and Thyrion (1996).

contribution given by a generalized Debye−Hückel equation for the mixed solvents and a short-range interaction contribution given by an extended UNIQUAC equation with concentration-dependent parameters. The model parameters are ion specific ones, and no ternary parameters are required. For a binary solvent−salt system, 14 parameters are needed to describe the VLE:2 solvent−solvent interaction parameters, 2 ion−ion interaction parameters, 8 ion−solvent reference interaction parameters, and 2 salt−solvent interaction parameters. The results of the calculations using Sander's model are presented in Table 3. The UNIQUAC volume (r_k) and surface area (q_k) parameters were taken from the original paper of Sander et al. (1986). The UNIQUAC reference interaction parameters, a^*_{kl}, and the $\delta_{ij,m}$ parameters are given in Table 4. Fortunately, some ion−ion, ion−solvent, and −solvent interaction parameters existed in the literature (Sander et al., 1986; Iliuta and Thyrion, 1996). Moreover, the solvent−solvent parameters were given by the salt-free system correlation. The other model parameters were estimated by minimization of the following objective function:

$$F = \sum_{k=1}^{N}\left(\sum_{m=1}^{NS}(\ln \gamma_{km}^{\mathrm{exp}} - \ln \gamma_{km}^{\mathrm{calc}})^2\right) \tag{3}$$

Data correlation is presented in Table 3. Generally, like for the first model used, this model can represent the experimental data with good accuracy, except the bubble points at high salt concentrations. The deviations in bubble points are slightly higher than those obtained with Mock's model, but the objective functions used in correlation were different.

4. Conclusions

The addition of sodium thiocyanate in the methyl acetate + methanol mixture at atmospheric pressure results in a large increase of the mole fraction of the ester in the vapor phase, especially at saturation, when compared with the salt-free system. The azeotrope of the mixed-solvent system disappears at saturation. However, at salt mole fractions higher than 0.05 the system displays an anomalous salting-in effect on methyl acetate in the methanol rich region.

The nonazeotropic minima in the T, x', y curves in this salt system below saturation appear to be more pronounced than for the acetone + methanol + NaI or NaSCN but less pronounced than for the 1-propanol + water + $CaCl_2$ systems previously studied. This behavior is linked to the position of the azeotropic point in the salt-free systems.

The calculated vapor-phase mole fractions using the electrolytic NRTL model of Mock et al. and the extended UNIQUAC model of Sander et al. show good agreement with the experimental results. The errors in bubble points are rather high at high salt concentrations, especially at saturation.

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