# Effect of Inorganic Salts on the Isobaric Vapor−Liquid Equilibrium of the Ethyl Acetate−Ethanol System

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Ⓢ Supporting Information

ABSTRACT: The effect of various salts such as magnesium nitrate, calcium nitrate, zinc nitrate, and magnesium chloride on vapor−liquid equilibrium (VLE) of the ethyl acetate−ethanol system was studied experimentally in a modified Othmer still at atmospheric pressure. The influence of cation and anion of the salts on the VLE of the ethyl acetate−ethanol system was examined. It was observed that the order of effect of salts for breaking the azeotrope was $Zn(NO_3)_2 > Ca(NO_3)_2 > Mg(NO_3)_2 > MgCl_2$. Salting-out coefficients were calculated using the scaled particle theory. The experimental vapor−liquid equilibrium data with salt was compared with that calculated using the scaled particle theory, and the agreement was satisfactory. Thus, it may be seen that the scaled particle theory can be used to estimate the salt effect of polar solvents in nonaqueous systems.
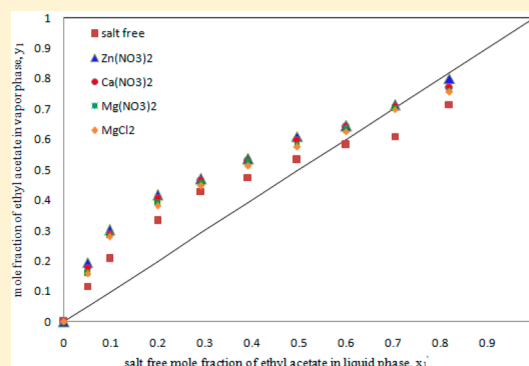
1. INTRODUCTION

Distillation is one of the most common techniques used for the separation of binary liquid mixtures. The separation of azeotropic mixtures by conventional distillation is not possible beyond the azeotropic composition as their liquid and vapor compositions are the same at the azeotropic composition, and special distillation techniques such as extractive distillation are used in such cases.[1−4] Extractive distillation is the addition of salt that alters the relative volatility of the mixture and is usually referred to as the salting-out effect. Therefore the azeotropic composition shifts or breaks toward higher composition of the more volatile compound in the mixture. Hence, the phase equilibria of the mixed-solvent system are of practical interest in the design of distillation columns. The salt effect on the vapor−liquid equilibrium of binary systems has been reported earlier.[5−7]

Different inorganic salts are found to give either salting-out or salting-in effects for the same binary azeotropic systems. The screening of suitable salts for the separation of azeotropic mixtures is very difficult from a theoretical point of view. There are various theories such as hydration of salt ions in solution, internal pressure effect, electrostatic theory, van der Waals force, and scaled particle theory by which the salt effect on vapor−liquid equilibrium can be predicted. While the first four theories require the experimental data to correlate and cannot be extrapolated, scaled particle theory requires only molecular parameters which are readily available. Hence, the scaled particle theory becomes the obvious choice to predict the salting coefficient of ternary systems.[8,9]

Numerous experimental investigations have been performed on the application of scaled particle theory to calculate the salting coefficient of nonpolar aqueous systems.[10,11] The salting coefficients of organic and inorganic electrolyte solutions of nonpolar systems were found to be in good agreement with experimental results. In recent years, scaled particle theory has also been applied to the case of polar systems in aqueous media,[12−15] and a reasonable agreement with experimental data was observed.

Ethyl acetate−ethanol system forms a minimum boiling azeotrope at 0.55 mole fraction of ethyl acetate at a temperature of 346.1 K and 1 atm. The effect of various salts on ethyl acetate−ethanol system has been reported by many investigators.[16−18] Calcium chloride and potassium acetate exhibited salting-out effects, which shifted the azeotropic composition to a modest higher ester composition but could not eliminate the azeotropic composition completely. Zinc chloride was found to have a stronger salting-out effect than lithium nitrate to eliminate the azeotropic composition of mixture completely at lower salt concentrations. However, the literature indicates that the vapor−liquid equilibrium with salt for this binary system has not been reported. The salt effect on vapor−liquid equilibrium is important in extractive distillation when the salt is used as an entrainer. The development of theories of the salt effect requires vapor−liquid equilibrium data over the whole range of concentration for comparison between theory and experiment.

The aim of the present investigation is to experimentally study the salt effect on the ethyl acetate−ethanol system using a modified Othmer still. The isobaric vapor−liquid equilibrium data of the ethyl acetate−ethanol system with different divalent
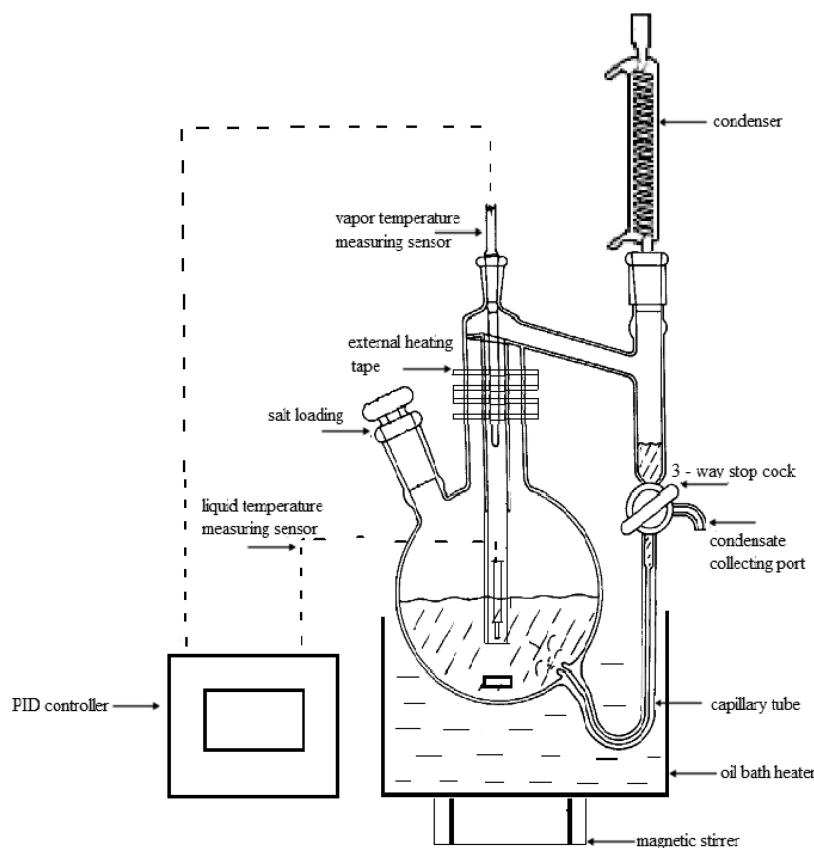
Figure 1. Modified Othmer still.

chloride and nitrate salts at various salt concentrations are obtained in this work. An attempt is made to apply the scaled particle theory to characterize the salting phenomenon of polar nonaqueous systems by inorganic electrolytes. The experimental vapor−liquid equilibrium data with salt are compared with that calculated using the scaled particle theory.

2. EXPERIMENTAL SECTION

To develop isobaric vapor−liquid equilibrium data for various salt concentrations, a modified Othmer still[19] was fabricated as shown in Figure 1. A modified Othmer still provides accurate vapor−liquid equilibrium data in a relatively short experimental period. It is a continuous distillation still that recirculates the vapor phase only. The still has a salt loading port which facilitates the addition of salt and cleaning the still pot. The boiling of the still was achieved by an oil bath heater, and the Pt100 RTD (resistance temperature detector) sensor was inserted into the still to measure the equilibrium temperature with an accuracy of ± 0.1 °C. It was necessary to heat the space above the vapor (2 to 3) °C above the solution boiling point to prevent refluxing. To accomplish this, the vapor jacket was wrapped with an external electrical heating tape. Both liquid and vapor temperatures were controlled with PID controller. A graduated condensate chamber fitted with a three-way stock was provided to control the volume of holdup and sample size. To ensure a rapid approach to steady state, constant boiling was necessary. The positioning of the return line in the bottom of the still pot provides mixing action during still operation.

In each experimental run, an initial solution of about 300 mL was prepared gravimetrically using an electronic analytical balance (Sartorius BSA 224S-CW) with a standard uncertainty

of 0.0001 g. The salt was added to the feed and was introduced into the still through the loading port. The heater was turned on to boil the solution in the still. Initial condensate was recirculated through a capillary tube to provide uniform mixing throughout the solution. The attainment of steady state was observed through constant temperature of liquid mixture. After (10 to 15) min at constant holdup, the vapor and liquid temperatures were recorded, and the sample of the condensate was quickly withdrawn into a sample vial. The samples were sealed and cooled to attain room temperature. After the sample was taken, the power source was turned off. The experiments were repeated as described above for various salt concentrations and feed compositions. The vapor condensate and liquid phase compositions were analyzed using automatic refractometer (Rudolph J357) with an uncertainty of 0.0002 mole fraction. The liquid phase composition was measured for different combinations of ethyl acetate−ethanol as reported in Table 5. When we conduct the experiment with a particular proportion, the corresponding liquid phase composition which was analyzed (binary system) earlier was used to describe the ternary system compositions as well which are given in Tables 6 to 9.

The ethyl acetate and ethanol used in this work were analytical reagent grade with a minimum purity of 99.99 wt %. The purity was verified using a refractometer. Salts of magnesium nitrate, calcium nitrate, and magnesium chloride (Rankem) with a minimum assay of 98 % pure and zinc nitrate (S-d fine chemicals) with an assay of 99 wt % pure were used. They were of analytical grade and dried before use, and the water content was less than 0.1 % as analyzed by the Karl

Fischer method. The physical properties of chemicals are given in Table 1.

Table 1. Physical Properties of Chemicals Used

compound	boiling temperature/°C		density/kg·m^{-3} at 25 °C		refractive index at 25 °C	
	exptl	lit.[a]	exptl	lit.[a]	exptl	lit.[a]
ethyl acetate	77.3	77.1	894.72	894.62	1.3696	1.3698
ethanol	79.6	78.30	785.22	785.12	1.3599	1.3593

[a]From Murti and Winkle.[20]

The densities of known molalites of magnesium, calcium, and zinc nitrates and magnesium chloride in ethanol solution were measured using a Rudolph automatic density meter (DDM 2910) at 25 °C with a precision of $\pm$ 1·10^{-2} kg·m^{-3} and are presented in Tables 2 to 4. The density of double-distilled water is measured as a reference fluid for calibrating each experiment.

Table 2. Experimental Values of Density ρ and Apparent Molal Volume Φv at Molality m for the System of Zn(NO$_3$)$_2$ in Ethanol Solution at 25 °C[a]

m	ρ/kg·m^{-3}	Φv/m^3·mol^{-1}
0.0053	785.90	32.4957
0.0106	786.55	37.2671
0.0159	787.20	38.9672
0.0212	787.84	40.6619
0.0265	788.49	41.1330
0.0292	788.78	43.2633
0.0319	789.09	44.0356
0.0346	789.38	45.6355
0.0372	789.70	45.7148
0.0399	789.99	47.0076
0.0426	790.29	47.7679
0.0453	790.60	48.0904
0.0480	790.89	49.0580
0.0507	791.19	49.6121
0.0533	791.49	50.1177
0.0804	794.55	52.3710

[a]m is the molality of Zn(NO$_3$)$_2$ salt in ethanol solution. Standard uncertainties u are $u(m)$ = 0.0001 and $u(T)$ = 0.03 °C, and the combined standard uncertainties is $u_c(\rho)$ = 0.01 kg·m^{-3}.

Table 3. Experimental Values of Density ρ and Apparent Molal Volume Φv at Molality m for the System of Mg(NO$_3$)$_2$ in Ethanol Solution at 25 °C[a]

m	ρ/kg·m^{-3}	Φv/m^3·mol^{-1}
0.0067	782.90	24.9185
0.0135	783.59	23.8537
0.0203	784.17	32.4383
0.0271	784.79	34.3742
0.0339	785.43	34.6214
0.0373	785.75	34.7284
0.0407	786.06	35.2280
0.0441	786.43	33.4462
0.0475	786.74	33.9844
0.0510	787.05	34.4586
0.0544	787.34	35.4789
0.0578	787.64	36.1040
0.0612	787.92	37.1965
0.0647	788.22	37.6765
0.0681	788.49	38.8295

[a]m is the molality of Mg(NO$_3$)$_2$ salt in ethanol solution. Standard uncertainties u are $u(m)$ = 0.0001 and $u(T)$ = 0.03 °C, and the combined standard uncertainties is $u_c(\rho)$ = 0.01 kg·m^{-3}.

Table 4. Experimental Values of Density ρ and Apparent Molal Volume Φv at Molality m for the System of MgCl$_2$ in Ethanol Solution at 25 °C[a]

m	ρ/kg·m^{-3}	Φv/m^3·mol^{-1}
0.0105	782.98	3.9579
0.0211	783.73	4.8442
0.0317	784.5	4.1853
0.0423	785.26	4.2987
0.0530	786.01	4.7190
0.0583	786.38	5.0264
0.0636	786.75	5.2913
0.0689	787.12	5.5237
0.0743	787.49	5.7305
0.0796	787.86	5.9168
0.0850	788.23	6.0864
0.0903	788.57	6.7809
0.0957	788.93	7.0643

[a]m is the molality of MgCl$_2$ salt in ethanol solution. Standard uncertainties u are $u(m)$ = 0.0001 and $u(T)$ = 0.03 °C, and the combined standard uncertainty is $u_c(\rho)$ = 0.01 kg·m^{-3}.

3. RESULTS AND DISCUSSION

To check the performance of the modified Othmer still, the binary vapor−liquid equilibrium data of the ethyl acetate−ethanol system measured at 1 atm, shown in Table 5, is compared with the data of Topphoff et al.[18] and Tu et al.[21] in Figure 2. Since there is a good agreement between the present experimental and literature data, the still has been benchmarked to generate ternary salt-effect data of vapor−liquid equilibrium.

3.1. Effect of Type of Salts on the Vapor−Liquid Equilibrium. The ternary isobaric vapor−liquid equilibrium data are obtained for the ethyl acetate (1) + ethanol (2) + salt (3) system with various nitrate salts and magnesium chloride at a constant salt concentration in each experimental run and are listed in Tables 6 to 9. The liquid-phase mole fraction of ethyl acetate is expressed on salt-free basis. It is observed that both

vapor phase mole fraction and temperature increase with the addition of salt to the binary system.

The effect of the salts on the vapor−liquid equilibrium of the ethyl acetate−ethanol system is shown in Figure 3. At constant salt concentration, all of the three nitrate salts, namely, calcium, zinc, and magnesium nitrates, exhibited a salting-out effect. Even though magnesium chloride exhibited a salting-out effect, it could not eliminate the azeotrope completely. However, zinc nitrate is the best entrainer, since the vapor-phase mole fraction of ethyl acetate increased significantly when compared to that of calcium and magnesium nitrates. The increase in vapor-phase mole fraction of ethyl acetate causes a shift in the azeotropic point toward higher ethyl acetate concentrations.

3.2. Effect of Salt Concentration on Vapor−Liquid Equilibrium. Figures 4 to 7 show the effect of salt concentration on VLE data for different salts. The salt-free data is also included in these figures. It can be seen from these

Table 5. Experimental Vapor−Liquid Equilibrium Data for Temperature *T*, Liquid-Phase Mole Fraction *x*, and Gas-Phase Mole Fraction *y* for the System of Ethyl Acetate (1) + Ethanol (2) at Pressure *p* = 1 atm[a]

$T/°C$	x_1	y_1
79.6	0.0000	0.0000
77.1	0.0502	0.1173
76.2	0.0968	0.2071
74.3	0.1990	0.3313
74.1	0.2923	0.4288
73.5	0.3913	0.4750
73.2	0.4962	0.5317
73.3	0.6000	0.5817
73.6	0.7038	0.6096
74.9	0.8192	0.7154
77.3	1.0000	1.0000

[a]The standard uncertainty u is $u(T)$ = 0.1 °C, and the combined expanded uncertainty U_c is $U_c(x_1') = U_c(y_1)$ = 0.0384 (95 % level of confidence).

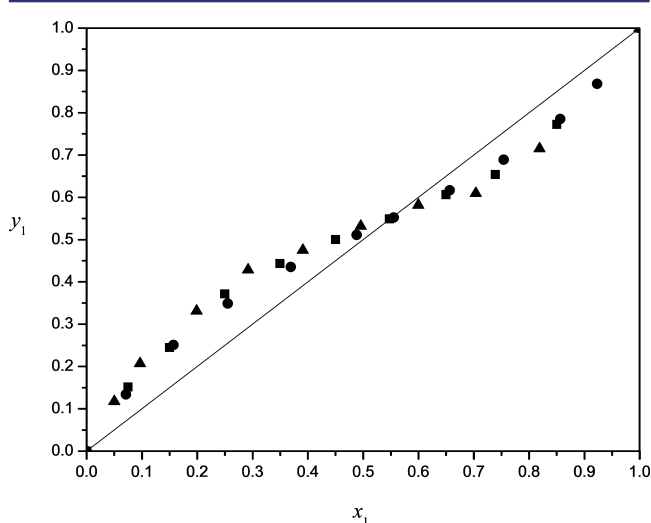**Figure 2.** Equilibrium phase diagram of the ethyl acetate (1) + ethanol (2) system at 1 atm: ▲, present work; ■, Tu et al. ; ●, Topphoff et al.

figures that the addition of salt to the liquid phase causes an increase in the vapor-phase mole fraction of ethyl acetate. The nonideality of a ternary system calculated using an activity coefficient (γ) of a mixture is defined as follows:

$$\gamma_i = y_i P / x_i p_i^s \tag{1}$$

where P is the total pressure and p_i^s is the vapor pressure of a pure component i in liquid phase. The vapor pressure of a pure component i is estimated using the Antoine equation, and the constants of Antoine equation are obtained from Orchilles et al.[22] It is observed that the activity coefficient of ethyl acetate increases with increasing salt concentration and consequently increases the vapor-phase mole fraction of ethyl acetate. As the salt concentration increases, the azeotropic point disappears and causes a rise in the concentration of ethyl acetate. The salt concentration at which the azeotrope disappears is 7 wt %, 10 wt %, and 12 wt % for zinc, calcium, and magnesium nitrates, respectively. This shows that zinc nitrate is more effective than calcium nitrate and magnesium nitrate to eliminate the azeotrope of the binary system. It is also found that zinc nitrate has a greater salting-out effect at lower salt

concentrations compared to calcium and magnesium nitrates. Magnesium nitrate requires a higher salt concentration for the complete elimination of the azeotrope of the mixture (Figure 6). It is observed that the vapor phase mole fraction of magnesium chloride increases in the ethyl acetate rich region but did not break the azeotrope of the mixture even at higher salt concentrations due to its insolubility in the mixture (Figure 7). Therefore, magnesium chloride produces a similar salt effect to that of calcium and lithium chlorides at the same salt concentration of 10 wt % as reported by Hashitani and Hirata.[16,17]

3.3. Effect of Salt on Relative Volatility. The salts considered in the present study are preferentially soluble in ethanol and sparingly in ethyl acetate. Therefore, the relative volatility of ethyl acetate to ethanol shifts by adding salt to the binary system. Thus, the azeotrope shifts to the ethyl acetate rich region. The relative volatility of ethyl acetate to ethanol is calculated using the following equation:

$$\alpha_s = \frac{y_1/x_1}{y_2/x_2} \tag{2}$$

where x_1 and x_2 are mole fractions of ethyl acetate and ethanol in the salt solution. y_1 and y_2 are vapor-phase mole fractions of the salt solution, and α is the polarizability of the nonelectrolyte.

The effect of different salts on relative volatility at 5 wt % concentration of salt is shown in Figure 8. The best entrainer among the various salts is chosen on the basis of relative volatility. The higher the relative volatility, the better is the separation of the azeotrope. The breaking of the azeotrope enhances by increasing the relative volatility and subsequently increasing the concentration of ethyl acetate. This is brought about by salts that are highly soluble in ethanol. The solubility of salts in ethanol follows the order $Zn(NO_3)_2 > Ca(NO_3)_2 > Mg(NO_3)_2 > MgCl_2$.

When salt concentration increases in a binary system, the interaction between salt and ethanol becomes much stronger since salts possess greater attraction toward ethanol than that with ethyl acetate. This is because ethanol is highly polar. Thus ethyl acetate concentration moves from azeotropic composition to higher composition. It was further observed that the separation of the azeotrope is better as the salt concentration increases. This observation can be attributed to the combined effect of the cation and anion of the salt.

3.4. Calculation of Salting Coefficient Using Scaled Particle Theory. The solubility of an electrolyte in an aqueous salt solution at low salt concentrations can be estimated by the Setschenow equation:[9]

$$\log S_o/S = k_s c \tag{3}$$

where S_o is the solubility in pure ethanol, S is the solubility in a salt solution of concentration c (mol·L^{-1}), and k_s is the salting coefficient, which has a characteristic value for a given salt−electrolyte pair. A positive value of k_s corresponds to salting-out ($S_o > S$), and salting-in is observed ($S_o < S$) if k_s is negative. The salting coefficient can be expressed by the following equation:[12]

$$k_s = -\left(\frac{d(\log S)}{d(c)} \right)_{c \to 0} \tag{4}$$

Shoor and Gubbins[8] derived the following expression for log S

Table 6. Isobaric Ternary Vapor−Liquid Equilibrium Data of Ethyl Acetate (1) + Ethanol (2) + Zn(NO₃)₂ (3) at $p = 1$ atm[a]

x_1'	y_1	$T/°C$	γ_1	γ_2	α_{12}	y_1	$T/°C$	γ_1	γ_2	α_{12}
			2 wt % Zn(NO₃)₂					5 wt % Zn(NO₃)₂		
0.0502	0.1535	77.1	3.0538	0.9377	3.4277	0.1962	77.3	3.8777	0.8833	4.6140
0.0968	0.2625	76.2	2.7912	0.8907	3.3193	0.3024	76.6	3.1731	0.8291	4.0426
0.1990	0.3698	74.4	2.0316	0.9232	2.3611	0.4171	75.0	2.2461	0.8332	2.8797
0.2923	0.4648	74.4	1.7389	0.8873	2.1027	0.4697	74.6	1.7453	0.8721	2.1442
0.3913	0.5296	73.8	1.5101	0.9292	1.7511	0.5360	73.9	1.5231	0.9129	1.7963
0.4962	0.5688	73.3	1.3012	1.0502	1.3398	0.6095	73.5	1.3848	0.9434	1.5850
0.6000	0.6029	73.5	1.1327	1.2083	1.0123	0.6433	73.5	1.2085	1.0855	1.2022
0.7038	0.6827	73.6	1.0897	1.2988	0.9053	0.7123	74.1	1.1179	1.1538	1.0418
0.8192	0.7933	75.5	1.0206	1.2832	0.8467	0.8008	75.9	1.0166	1.2168	0.8869
			7 wt % Zn(NO₃)₂					10 wt % Zn(NO₃)₂		
0.0502	0.2265	77.3	4.4784	0.8500	5.5381	0.2587	77.9	5.0134	0.7954	6.5971
0.0968	0.3144	76.9	3.2667	0.8050	4.2770	0.3865	77.5	3.9372	0.7033	5.8760
0.1990	0.4123	75.5	2.1834	0.8233	2.8232	0.4721	76.0	2.4589	0.7247	3.5990
0.2923	0.4831	75.3	1.7536	0.8262	2.2625	0.5365	75.7	1.9218	0.7289	2.8028
0.3913	0.5550	74.5	1.5458	0.8542	1.9400	0.6183	75.1	1.6876	0.7152	2.5190
0.4962	0.6250	74.2	1.3868	0.8804	1.6925	0.6606	75.2	1.4174	0.7651	1.9763
0.6000	0.6854	74	1.2661	0.9380	1.4523	0.7283	75.3	1.2879	0.7684	1.7867
0.7038	0.7452	74.2	1.1656	1.0178	1.2304	0.7798	76.0	1.1485	0.8176	1.4901
0.8192	0.8396	76.1	1.0589	0.9719	1.1549	0.8587	76.5	1.0686	0.8427	1.3405

[a] x_1' is the mole fraction of ethyl acetate in the liquid phase expressed on a salt-free basis. The standard uncertainty u is $u(T) = 0.1$ °C, and the combined expanded uncertainty U_c is $U_c(x_1) = U_c(y_1) = 0.0384$ (95 % level of confidence).

Table 7. Isobaric Ternary Vapor−Liquid Equilibrium Data of Ethyl Acetate (1) + Ethanol (2) + Ca(NO₃)₂ (3) at 1 atm[a]

x_1'	y_1	$T/°C$	γ_1	γ_2	α_{12}	y_1	$T/°C$	γ_1	γ_2	α_{12}
			2 wt % Ca(NO₃)₂					5 wt % Ca(NO₃)₂		
0.0502	0.1462	77.1	2.9084	0.9458	3.2366	0.1794	77.4	3.5353	0.8981	4.1344
0.0968	0.2577	76.2	2.7400	0.8965	3.2374	0.2915	76.8	3.0389	0.8353	3.8376
0.1990	0.3606	74.5	1.9744	0.9328	2.2693	0.4090	75.1	2.1948	0.8415	2.7845
0.2923	0.4413	74.4	1.6511	0.9262	1.9127	0.4645	74.5	1.7319	0.8842	2.1000
0.3913	0.5019	73.7	1.4360	0.9879	1.5673	0.5301	73.7	1.5168	0.9320	1.7549
0.4962	0.5471	73.5	1.2430	1.0941	1.2268	0.5999	73.6	1.3583	0.9627	1.5225
0.6000	0.5971	73.4	1.1256	1.2310	0.9881	0.6419	73.6	1.2019	1.0853	1.1949
0.7038	0.6481	74.0	1.0206	1.4171	0.7749	0.7120	74.5	1.1025	1.1364	1.0402
0.8192	0.7394	75.2	0.9609	1.6371	0.6261	0.7690	76.0	0.9730	1.4052	0.7345
			7 wt % Ca(NO₃)₂					10 wt % Ca(NO₃)₂		
0.0502	0.1942	77.5	3.8145	0.8784	4.5579	0.2048	77.9	3.9697	0.8532	4.8700
0.0968	0.3100	77.0	3.2102	0.8070	4.1901	0.3760	77.4	3.8421	0.7183	5.6184
0.1990	0.4209	76.1	2.1848	0.7918	2.9246	0.4529	76.9	2.2894	0.7244	3.3311
0.2923	0.4844	75.8	1.7294	0.8076	2.2748	0.5029	76.2	1.7716	0.7662	2.4491
0.3913	0.5502	75.0	1.5067	0.8462	1.9021	0.5702	75.7	1.5255	0.7860	2.0633
0.4962	0.6001	74.4	1.3226	0.9313	1.5236	0.6394	75.0	1.3813	0.8194	1.8008
0.6000	0.6613	74.1	1.2176	1.0055	1.3019	0.7194	74.8	1.2937	0.8097	1.7094
0.7038	0.7418	75.0	1.1295	0.9984	1.2086	0.7763	76.0	1.1434	0.8304	1.4606
0.8192	0.7998	76.4	0.9987	1.1983	0.8816	0.8350	76.8	1.0289	0.9719	1.1167

[a] x_1' is the mole fraction of ethyl acetate in the liquid phase expressed on a salt-free basis. The standard uncertainty u is $u(T) = 0.1$ °C, and the combined expanded uncertainty U_c is $U_c(x_1) = U_c(y_1) = 0.0384$ (95 % level of confidence).

$$-\log S = \frac{\bar{g}_1^h}{2.3kT} + \frac{\bar{g}_1^s}{2.3kT} + \log kT \sum_{j=1}^{4} \rho_j \quad (5)$$

where g_1^h is the free energy change when a cavity large enough to hold the nonelectrolyte molecule is formed in the solution, g_1^s is the free energy change when the nonelectrolyte molecule is introduced into the cavity, and ρ_j is the number density (particles/cc) of a solution species.

Combining eqs 4 and 5

$$k_s = \left[\frac{d(\bar{g}_1^h/2.3kT)}{d(c)} \right]_{c \to 0} + \left[\frac{d(\bar{g}_1^s/2.3kT)}{d(c)} \right]_{c \to 0} + \left[\frac{d(\log \sum \rho_j)}{d(c)} \right]_{c \to 0} \quad (6)$$

or

$$k_s = k_\alpha + k_\beta + k_\gamma \quad (7)$$

Table 8. Isobaric Ternary Vapor−Liquid Equilibrium Data of Ethyl Acetate (1) + Ethanol (2) + Mg(NO$_3$)$_2$ (3) at p = 1 atm[a]

x_1'	y_1	T/°C	γ_1	γ_2	α_{12}	y_1	T/°C	γ_1	γ_2	α_{12}
		2 wt % Mg(NO$_3$)$_2$						5 wt % Mg(NO$_3$)$_2$		
0.0502	0.1234	77.1	2.4562	0.9710	2.6626	0.1601	77.5	3.1436	0.9157	3.6035
0.0968	0.2507	76.5	2.6388	0.8942	3.1194	0.2830	76.9	2.9402	0.8419	3.6809
0.1990	0.3543	75.0	1.9080	0.9230	2.2083	0.3925	75.4	2.0854	0.8545	2.5999
0.2923	0.4360	74.8	1.6092	0.9200	1.8713	0.4585	75.0	1.6810	0.8762	2.0496
0.3913	0.4914	74.0	1.3919	0.9964	1.5029	0.5277	74.5	1.4696	0.9067	1.7377
0.4962	0.5338	73.8	1.2007	1.1124	1.1630	0.5809	74.2	1.2891	0.9838	1.4078
0.6000	0.5913	73.5	1.1109	1.2437	0.9645	0.6370	74.0	1.1768	1.0822	1.1700
0.7038	0.6383	74.0	1.0051	1.4566	0.7424	0.7024	74.5	1.0877	1.1741	0.9932
0.8192	0.7290	75.0	0.9537	1.7166	0.5935	0.7600	75.7	0.9713	1.4777	0.6987
		7 wt % Mg(NO$_3$)$_2$						10 wt % Mg(NO$_3$)$_2$		
0.0502	0.1822	77.5	3.5780	0.8915	4.2123	0.1977	78.0	3.8188	0.8574	4.6585
0.0968	0.3016	77.0	3.1227	0.8169	4.0264	0.3300	77.4	3.3720	0.7712	4.5923
0.1990	0.4132	76.0	2.1521	0.8056	2.8338	0.4421	76.5	2.2649	0.7506	3.1895
0.2923	0.4790	75.5	1.7273	0.8260	2.2261	0.4919	76.0	1.7446	0.7894	2.3443
0.3913	0.5461	74.8	1.5057	0.8608	1.8715	0.5685	75.4	1.5363	0.7987	2.0490
0.4962	0.5962	74.6	1.3054	0.9325	1.4997	0.6284	75.2	1.3485	0.8375	1.7176
0.6000	0.6582	74.1	1.2118	1.0150	1.2836	0.6973	74.9	1.2498	0.8700	1.5358
0.7038	0.7340	74.8	1.1252	1.0368	1.1611	0.7759	75.5	1.1619	0.8490	1.4568
0.8192	0.7804	75.8	0.9941	1.3466	0.7842	0.8189	76.2	1.0294	1.0925	0.9981

x_1'	y_1	T/°C	γ_1	γ_2	α_{12}
		12 wt % Mg(NO$_3$)$_2$			
0.0502	0.2245	78.1	4.3239	0.8254	5.4753
0.0968	0.3341	77.6	3.3919	0.7604	4.6789
0.1990	0.4674	76.8	2.3707	0.7080	3.5318
0.2923	0.5137	76.2	1.8096	0.7496	2.5573
0.3913	0.5899	75.9	1.5677	0.7439	2.2369
0.4962	0.6367	75.4	1.3570	0.8124	1.7794
0.6000	0.7231	75.0	1.2916	0.7927	1.7407
0.7038	0.7979	75.6	1.1908	0.7628	1.6608
0.8192	0.8294	76.4	1.0356	1.0212	1.0727

[a] x_1' is the mole fraction of ethyl acetate in the liquid phase expressed on a salt-free basis. The standard uncertainty u is $u(T)$ = 0.1 °C, and the combined expanded uncertainty U_c is $U_c(x_1) = U_c(y_1)$ = 0.0384 (95 % level of confidence).

Table 9. Isobaric Ternary Vapor−Liquid Equilibrium Data of Ethyl Acetate (1) + Ethanol (2) + MgCl$_2$ (3) at 1 atm[a]

x_1'	y_1	T/°C	γ_1	γ_2	α_{12}	y_1	T/°C	γ_1	γ_2	α_{12}
		2 wt % MgCl$_2$						5 wt % MgCl$_2$		
0.0502	0.1205	77.1	2.3977	0.9743	2.5904	0.1579	77.4	3.1109	0.9217	3.5451
0.0968	0.2499	76.3	2.6481	0.9023	3.1065	0.2799	76.7	2.9277	0.8523	3.6256
0.1990	0.3469	74.5	1.8993	0.9528	2.1370	0.3808	75.0	2.0507	0.8851	2.4752
0.2923	0.4247	74.2	1.5995	0.9616	1.7871	0.4474	74.9	1.6460	0.8977	1.9603
0.3913	0.4851	73.5	1.3972	1.0298	1.4651	0.5131	74.5	1.4291	0.9347	1.6392
0.4962	0.5248	73.5	1.1923	1.1481	1.1214	0.5760	74.0	1.2868	1.0035	1.3796
0.6000	0.5868	73.6	1.0986	1.2524	0.9466	0.6266	73.8	1.1653	1.1225	1.1185
0.7038	0.6247	74.0	0.9837	1.5114	0.7002	0.6990	74.4	1.0861	1.1923	0.9773
0.8192	0.7134	75.0	0.9334	1.8151	0.5494	0.7564	75.4	0.9765	1.5179	0.6853
		7 wt % MgCl$_2$						10 wt % MgCl$_2$		
0.0502	0.1791	77.8	3.4835	0.8842	4.1263	0.1992	78.0	3.8490	0.8557	4.7044
0.0968	0.2907	77.0	3.0107	0.8295	3.8229	0.3198	77.4	3.2679	0.7830	4.3839
0.1990	0.4004	75.1	2.1487	0.8537	2.6869	0.4387	75.6	2.3152	0.7832	3.1446
0.2923	0.4676	75.0	1.7147	0.8613	2.1267	0.5438	75.3	1.9742	0.7291	2.8865
0.3913	0.5352	74.8	1.4756	0.8815	1.7908	0.5582	75.0	1.5287	0.8312	1.9648
0.4962	0.5862	74.6	1.2833	0.9558	1.4384	0.6132	74.8	1.3335	0.8861	1.6099
0.6000	0.6480	74.3	1.1850	1.0367	1.2273	0.6873	74.5	1.2484	0.9135	1.4651
0.7038	0.7091	74.5	1.0980	1.1478	1.0256	0.7681	75.0	1.1697	0.8965	1.3938
0.8192	0.7791	75.9	0.9891	1.3491	0.7783	0.8081	76.5	1.0057	1.1442	0.9291

[a] x_1' is the mole fraction of ethyl acetate in the liquid phase expressed on a salt-free basis. The standard uncertainty u is $u(T)$ = 0.1 °C, and the combined expanded uncertainty U_c is $U_c(x_1) = U_c(y_1)$ = 0.0384 (95 % level of confidence).
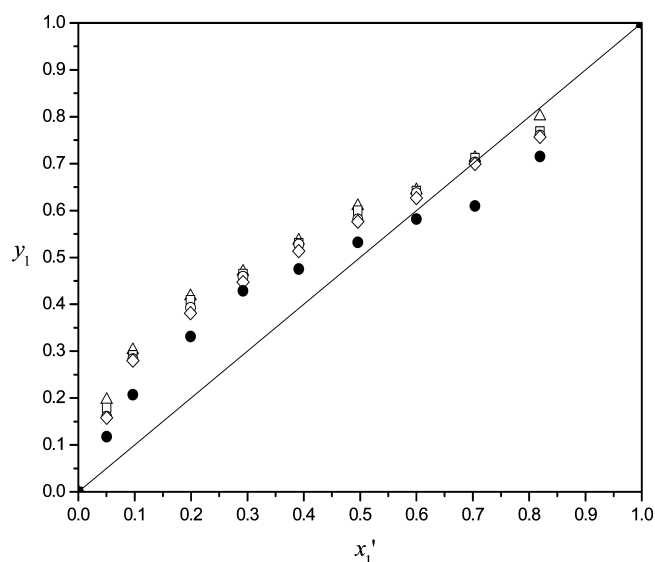
Figure 3. Isobaric VLE diagram of ethyl acetate (1) + ethanol (2) + salt (3) at 1 atm for various salts at $z_3 = 0.05$ (z is the salt mole fraction): ●, salt free; ◇, magnesium chloride; ○, magnesium nitrate; □, calcium nitrate; △, zinc nitrate.
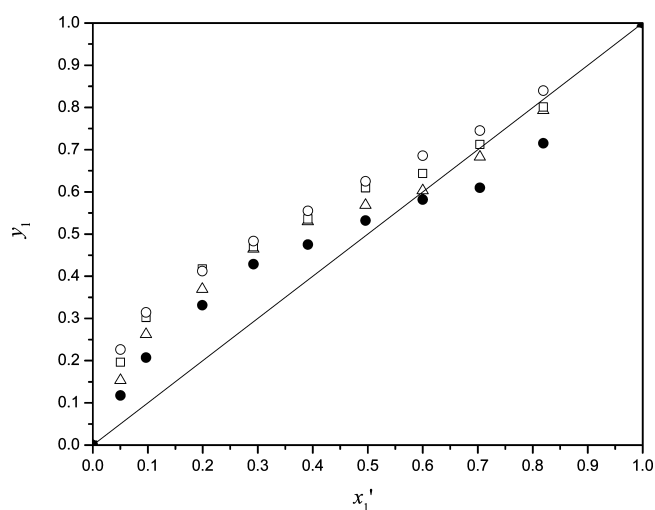

Figure 4. Isobaric VLE diagram of ethyl acetate (1) + ethanol (2) + $Zn(NO_3)_2$ (3) for different salt concentrations at 1 atm; ●, salt free; △, $z_3 = 0.02$; □, $z_3 = 0.05$; ○, $z_3 = 0.07$.

Figure 5. Isobaric VLE diagram for ethyl acetate (1) + ethanol (2) + $Ca(NO_3)_2$ (3) with varying salt concentrations: ●, salt free; △, $z_3 = 0.02$; □, $z_3 = 0.05$; ○, $z_3 = 0.07$; ◇, $z_3 = 0.10$.

Figure 6. Salt effect on the VLE diagram for ethyl acetate (1) + ethanol (2) + $Mg(NO_3)_2$ (3) at 1 atm with salt concentrations: ●, salt free; △, $z_3 = 0.02$; □, $z_3 = 0.05$; ○, $z_3 = 0.10$; ◇, $z_3 = 0.12$.

where k_α, k_β, and k_γ represent the contributions to the salting coefficient and they can be either positive or negative. If k_s is positive, the system exhibits a salting-out effect, and salting-in occurs for negative values of k_s. The salting coefficient of polar nonaqueous system is derived for 1:1 and 1:2 electrolytes using scaled particle theory. The expressions for k_α, k_β, and k_γ are given in terms of known molecular parameters of the polar molecules and ions of the salt by Lei et al.[15] and are presented in the Supporting Information. To find k_s for a particular system, it is necessary to know: (1) the apparent molal volume of the salt at infinite dilution, (2) the diameters and polarizabilities of the cation and anion, and (3) the diameter, energy parameter, and polarizability of polar molecule.

3.4.1. Salt Effect Using Scaled Particle Theory. The scaled particle theory is used in this work to understand the salting-out and salting-in effect of chloride and nitrate salts. The salting coefficient is calculated for different salts using eq 7. The
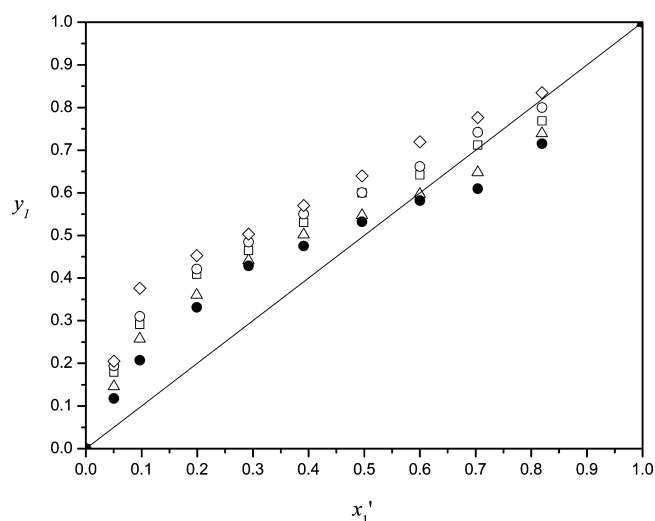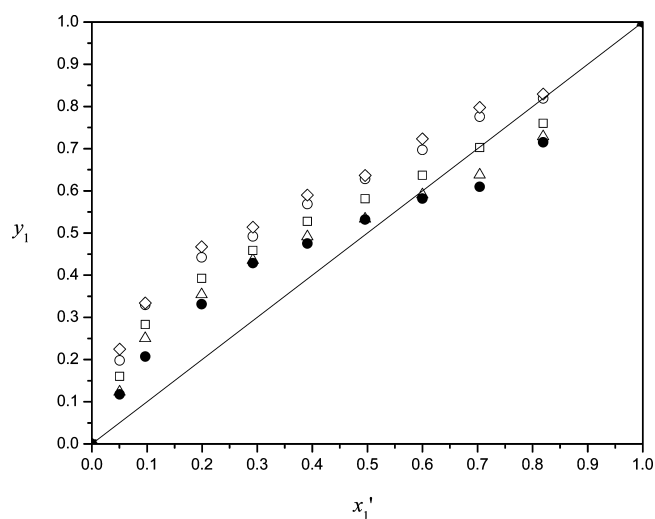
required molecular parameters are presented in Tables 10 and 11. The apparent molal volume of salt in ethanol at infinite dilution is required to estimate the salting coefficient of a ternary system. The apparent molal volume of univalent salts are reported Krumgalz et al.[24] and Marcus and Hefter.[25] For bivalent salts, on the other hand, it is limited to $Ca(NO_3)_2$ and $CaCl_2$. Therefore the apparent molal volumes of chloride and nitrate salts which are bivalent salts have been estimated using the Redlich−Meyer method.

From the density data, the apparent molal volume (ϕ_v) of bivalent salts in the dilute region ($m < 0.1$ mol·kg^{-1}) is calculated using the following equation:

$$\phi_v = \frac{M_1}{d} + \frac{1}{m}\left(\frac{1}{d} - \frac{1}{d_0}\right) \tag{8}$$

where M is the molecular weight (g·mol^{-1}).

The data thus obtained are fitted with the following Redlich−Meyer equation:

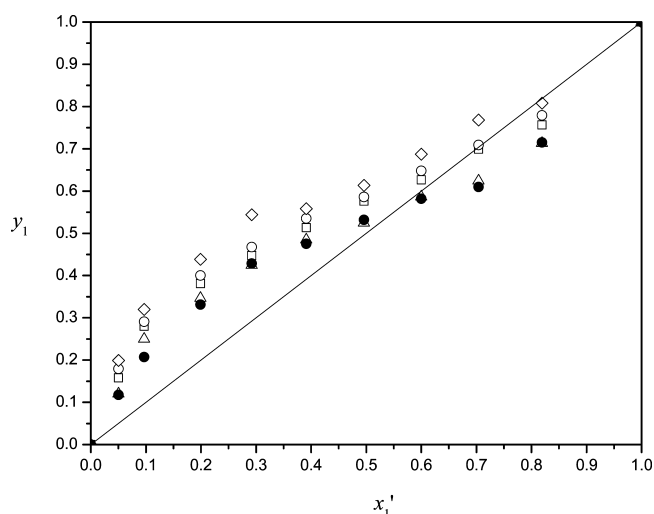**Figure 7.** Effect of $MgCl_2$ on the VLE diagram of ethyl acetate (1) + ethanol (2) at different concentrations: ●, salt free; △, $z_3 = 0.02$; □, $z_3 = 0.05$; ○, $z_3 = 0.07$; ◇, $z_3 = 0.10$.

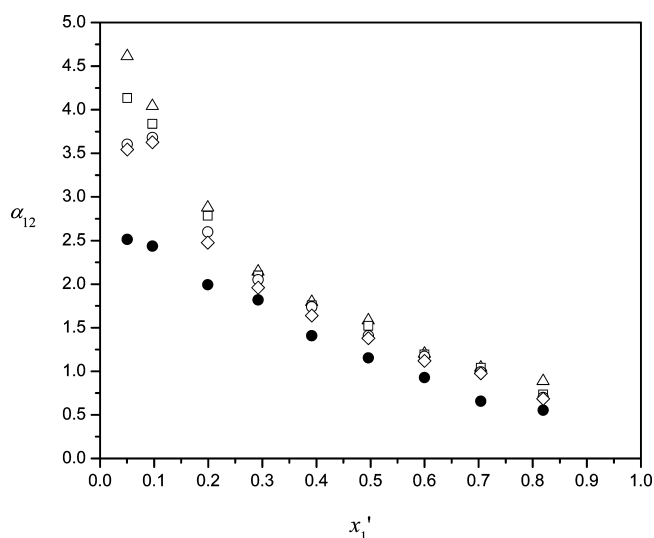**Figure 8.** Relative volatility of ethyl acetate to ethanol for different inorganic salts at $z_3 = 0.05$: ●, salt free; ◇, magnesium chloride; ○, magnesium nitrate; □, calcium nitrate; △, zinc nitrate.

Table 10. Physical Properties of Polar Molecules

molecule[a]	σ[b]/Å	$\alpha \cdot 10^{-24}$/cc	ε/κ[c]/K
ethyl acetate	5.65	10.99	372
ethanol	4.34	5.11	450

[a]From Treiner.[13] [b]Molecule size or ion diameter. [c]Interaction energy parameter.

$$\phi_v = \phi_v^0 + S_v \sqrt{m} + b_v m \qquad (9)$$

The apparent molal volume for calcium nitrate in ethanol at infinite dilution is estimated to benchmark and is compared with the data reported by Sardroodi and Zafaran Moattar[26] with a deviation of only 5.78 %. A similar procedure is followed to calculate the apparent molal volumes for magnesium and zinc nitrates and magnesium chloride in ethanol at infinite dilution and are presented in Table 12. The density of pure ethanol measured in this work is 785.22 kg·m^{-3}. The apparent molal volume of magnesium chloride is smaller than that of

Table 11. Ionic Parameters Required for Scaled Particle Theory

ion[a]	σ/Å	$\alpha \cdot 10^{-24}$/cc	Z_j
Li^+	1.42	0.075	2
Ca^{2+}	1.98	0.510	18
Mg^{2+}	1.30	0.120	10
Zn^{2+}	1.48	0.112	28
NO^{3-}	4.05	4.365	30
Cl^-	3.62	3.020	18

[a]From Xu and Hu.[23]

Table 12. Apparent Molal Volumes of Salt in Ethanol at Infinite Dilution

salt	m/mol·kg^{-1}	$\Phi_o \cdot 10^6$/m^3·mol^{-1}
$Zn(NO_3)_2$	0.0105−0.8040	24.70
$Mg(NO_3)_2$	0.0135−0.0681	15.40
$MgCl_2$	0.0105−0.0956	−8.81

magnesium nitrate because the size of the anion decreases which leads to the increase in apparent molal volume of the salt that was observed. Similarly, the apparent molal volume of chloride and nitrate salts also increase as the size of the cation increases due to their electrostatic interactions in the ethanol solution.

The relative contributions of k_α, k_β, and k_γ on the salting coefficient are given in Table 13. It may be noted that k_γ is

Table 13. Salting Coefficients of Univalent and Divalent Salts for the Ethyl Acetate−Ethanol System Using Scaled Particle Theory at 25 °C

salt	k_α	k_β	k_γ	k_s
LiCl	0.6474	−0.4001	0.0531	0.3004
$MgCl_2$	1.9099	−0.7569	0.0800	1.2330
$CaCl_2$	2.0151	−0.8666	0.0788	1.2274
$ZnCl_2$	2.0970	−0.7883	0.0827	1.3913
$LiNO_3$	0.6642	−0.3786	0.0488	0.3344
$Mg(NO_3)_2$	2.0395	−0.6815	0.0698	1.4278
$Ca(NO_3)_2$	2.1690	−0.8073	0.0694	1.4311
$Zn(NO_3)_2$	2.0296	−0.5822	0.0658	1.5133

always small. In all cases, k_α is found to be positive. Physically, this can be interpreted to the free energy change for cavity formation becoming more positive as the concentration of the salt increases. It is therefore more difficult to form a cavity in a nonaqueous solution of salt than in ethanol itself. k_β values are negative which can be interpreted as, once a cavity is formed in a salt solution, it is easier to introduce a polar molecule than it is in pure ethanol. The salting coefficient k_s can be positive or negative depending on the relative magnitudes of k_α and k_β.

It is found that all salts give a positive salting coefficient and this implies that they exhibit a salting-out effect. The magnitude of salting coefficient is higher when the salting-out effect is greater in separation of binary systems. The order of decreasing salting coefficient is zinc nitrate < calcium nitrate < magnesium nitrate. The opposite trend is observed with the apparent molal volumes of the respective cation, as the cation has a preferential affinity toward ethanol molecules and therefore expels the ethyl acetate molecules from the ionic regions in the remaining solution. From the electrostatic theory it is known that, the smaller the cation the salt is, the better the entrainer, but on the

contrary the larger cation proves to be a better entrainer: Zn^{2+} > Ca^{2+} > Mg^{2+}. Similarly, the larger the size of the anion, the better the separation, and hence nitrate aids separation when compared to chloride. The size of anion follows the order NO_3^- > Cl^-.

The number of ions in the salt molecule can also affect the effectiveness of the salt. This investigation uses the scaled particle theory for univalent salts. The salting coefficient of a univalent cation ($LiNO_3$) is 0.3344, and it is compared with its experimental vapor−liquid equilibrium data Topphoff et al.[18] It is found that the azeotrope can be broken at 15 mol % of salt which is higher than the bivalent cation of salt. In addition, salting coefficient is lower than the bivalent cation of salts as given in Table 8. This variation of univalent and bivalent cations can be attributed to the charge of the cation and the number of ions it furnishes in the solution. This kind of behavior has been reported for other systems as well, like in Banat et al.[27] It also appears that the increase in ϕ_o, which makes a negative contribution to k_a, outweighs the effect of the increase in σ_3 and σ_4 in eq 8. This trend has been observed experimentally, showing that a zinc nitrate is more effective than calcium nitrate in breaking the azeotrope formed by the ethyl acetate−ethanol mixture. The vapor-phase mole fraction increases significantly higher for zinc nitrate compared to calcium and magnesium nitrate for the same salt concentrations. This concurs with the trend obtained in the calculated salting coefficients of zinc, calcium, and magnesium nitrates.

The salt effect on vapor−liquid equilibrium can be described using Furter's[11] equation as given below:

$$\ln(\alpha_s/\alpha_o) = Kz \tag{10}$$

where K is the salt effect parameter and z is the concentration of the salt. This equation is applicable to low salt concentrations and at a fixed liquid composition. Using the above equation, the experimental salt effect parameter is estimated for all of the inorganic salts and is reported in Table 14. The salt effect parameter is proportional to salt

Table 14. Comparison of Experimental and Theoretical Salting Coefficients of Nitrate and Chloride Based Salts for the Ethyl Acetate−Ethanol System from Scaled Particle Theory at 25 °C

salt	k_{exp}	k_{SPT}
$Zn(NO_3)_2$	3.395	1.513
$Ca(NO_3)_2$	2.196	1.431
$Mg(NO_3)_2$	1.001	1.427
$MgCl_2$	1.994	1.233

concentration and also varies with respect to liquid composition in the mixture which is shown in Figure 9. The experimental salt effect parameter is compared with that calculated using salting coefficient. It is found that the deviation is quite high due to limitations of the scaled particle theory. This theory predicts the salting coefficient for the entire range of liquid compositions. The selection of molecular parameters of polar molecules and ions in nonaqueous solutions causes an uncertainty in the calculation of the salting coefficient using scaled particle theory.

4. CONCLUSION

It has been shown that VLE data for the binary ethyl acetate−ethanol system can be generated using a modified Othmer still.
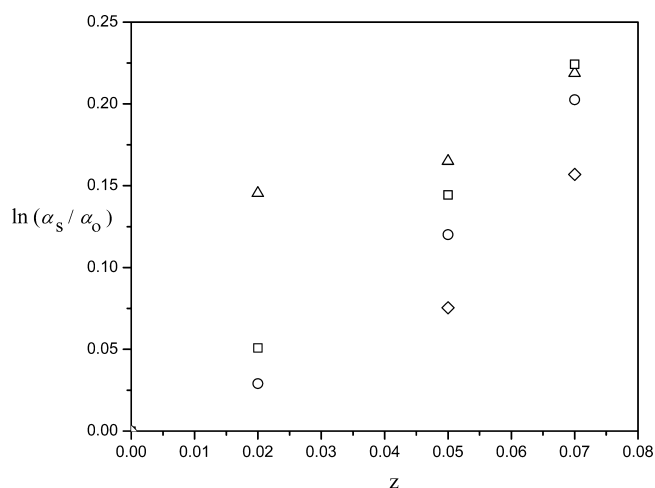

Figure 9. Salt effect of various inorganic salts on the ethyl acetate (1) + ethanol (2) isobaric system at fixed liquid composition: ◇, magnesium chloride; ○, magnesium nitrate; □, calcium nitrate; △, zinc nitrate.

It is also found that zinc nitrate is more effective than calcium and magnesium nitrates at lower concentrations. Scaled particle theory is used to predict the salt effect for the ethyl acetate−ethanol system in inorganic salt solutions. The experimental salt effect parameter is compared with predictions of scaled particle theory, and it shows some deviation. However, the use of scaled particle theory for the estimation of the salt effect on polar nonaqueous systems is possible. Furthermore, it is shown that the effect of anion is in the order of NO_3^- > Cl^-.

■ ASSOCIATED CONTENT

ⓈSupporting Information

Scaled particle theory for the ethyl acetate (1) + ethanol (2) + salt (3) system. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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