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Experimental Study of Vapor–Liquid Equilibrium of Acetone–Water System Using Headspace Gas Chromatography

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ABSTRACT

Isothermal vapor–liquid equilibrium (VLE) data at 60°C for the acetone–water–salt system were obtained using headspace gas chromatography. Three different salts were investigated in this study; NH_4Cl, NaCl, and $CaCl_2$. The results obtained showed that although the alteration in the VLE of the acetone–water system in the presence of any 0.5 M salt was very small, the three salts had a salting-out effect on acetone. On the other hand, significant alteration in the VLE was obtained when NaCl was added under saturation conditions. Good agreement with the Furter equation was observed for the experimental data with unsaturated NaCl salt. The salt effect parameter, obtained from the Furter equation, was found to be a function of the liquid concentration.

INTRODUCTION

The ease of components separation from a liquid mixture using distillation depends on the vapor–liquid equilibrium (VLE) characteristics of the liquid mixture. Solutions with a maximum or minimum azeotropic point reach a

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state in which boiling does not change the liquid composition. Therefore, azeotropic solutions can not be separated by conventional distillation (1). For these cases, special techniques such as extraction with liquid or salt and azeotropic distillation can be used. The addition of salts to a solvent mixture usually changes the interactions between the ions and the solvent components, which results in altering the VLE of the system (2–17). However, because of the complexity of the interactions of the salt with various solvent mixtures, the thermodynamics and mechanism of this process are still poorly understood.

Accurate VLE data are important in the design of separation processes. Most VLE data available in the literature were obtained either by static still methods or recirculation still methods. However, both methods have their advantages and disadvantages. The main disadvantages of circulation methods involve the difficulty in obtaining steady-state conditions, especially for systems of large relative volatilities where equilibrium is almost impossible to establish, and the difficulty in analyzing the samples of the phases accurately (18). On the other hand, the main problem with static still methods is the need to degas the components, which requires carefully designed apparatus.

The headspace gas chromatography (HSGC) technique is a new technique that can be used to study the VLE of mixtures. The use of HSGC in studying the VLE of binary mixtures is simple, accurate, and fast since equilibrium and sample analysis are done in the same apparatus. Headspace analysis in VLE studies involves sampling of the vapor phase, which is injected into the GC, in equilibrium with its liquid phase (18–23). The liquid composition is determined from the mass of the pure components after correction for evaporation (18). Lepori et al. (21) and Park et al. (22) used the HSGC technique to study the VLE of some binary mixtures. Recently, Wong (23) used this technique to study the VLE of some binary systems in capillary porous plates. The results obtained were in agreement with those reported in the literature.

The objective of this study is to investigate further the practical feasibility of using HSGC in analyzing the VLE of mixtures. Furthermore, this technique will be used to study experimentally the VLE of the acetone–water system in the presence of different salts.

EXPERIMENTAL

A vapor phase in equilibrium with a liquid phase is referred to as the “headspace.” The principle behind headspace analysis is that when a fixed volume of solution is sealed in a fixed-volume vial at any temperature and pressure, there will be only one vapor composition corresponding to that liquid composition. The experiments in this study consisted of analyzing the vapor composition above liquid mixtures of acetone and water. The vapor was

TABLE 1
Headspace Autosampler Specifications

Model	Genesis Headspace Autosampler with 50 position carousel
Injector inlet connection	Septum needle adaptor
Carrier gas	Ultrahigh purity helium (Matheson)
Sample vial size	22 mL vials
Sample loop volume	20 µL

sampled using a headspace autosampler, and the amount of acetone was determined using a gas chromatograph. Specifications for the headspace autosampler and the gas chromatograph are listed in Tables 1 and 2, respectively.

Procedure

Liquid samples of the acetone–water mixture, with and without salts, were placed in a closed vial and introduced into a 50-position rotating carousel. One at a time, the vials moved onto a platen which heated them to a specified temperature. Sufficient time was allowed for the solutes to diffuse into the vial's atmosphere. The amount of time required to reach equilibrium was determined by plotting an area count for the same sample concentration as a function of time spent on the platen. When the curve levels out, equilibrium has been reached. In addition to residence time on the platen and platen temperature, other parameters of the headspace autosampler, such as loop fill time, loop equilibrium time, injection time, line temperature, and valve temperature, must be established. Following equilibration, an aliquot of the vapor in the vial headspace was automatically transferred with a gas sample valve and passed through a transfer line into the gas chromatograph where the analysis took place. The use of the autosampler significantly reduced the variation in data under the same conditions. Reproducibility of data showed that the accuracy

TABLE 2
Gas Chromatograph Specifications

Model	Varian 3400 Gas Chromatograph
Detector	Flame ionization detector (FID)
Column	DB-624 glass capillary column, length = 75 m, diameter = 530 µm
Make-up gas	Helium

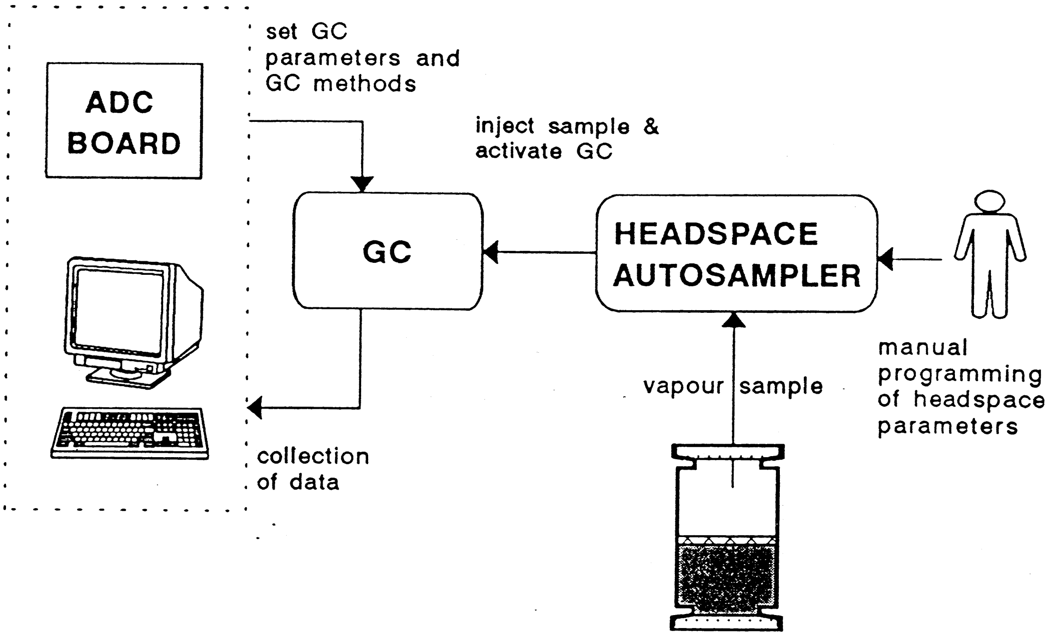

FIG. 1 Experimental setup used in this study.

of the measurements was within ±0.1%. The experimental setup is illustrated in Fig. 1.

When a fixed volume of sample vapor was automatically injected into the gas chromatograph column, a second method involving injector, detector, and oven temperatures was invoked. The gas chromatograph output, in the form of an analog signal, is acquired by a Star Chromatography Workstation through an ADC Board and processed for storage as digitized data. The Star Workstation software was acquired from Varian along with the chromatographic equipment.

By testing various instrument settings, the analytical method which yielded the most reproducible data was determined. Table 3 lists these parameters for the acetone–water system.

Chemicals

Distilled water and acetone of 99.9 purity (Sigma) were used. The salts used in this study had purities of 99.5+%.

RESULTS AND DISCUSSION

The technical feasibility of using the HSGC technique to study the VLE of binary mixtures was checked by using this technique to study the VLE of the acetone–water system at 60°C. The close agreement between the measured and literature data (24), shown in Fig. 2, proves the feasibility of using the HSGC technique to study the VLE of binary mixtures.

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TABLE 3
Parameters Used for Acetone Composition Determination

Headspace autosampler:	
Platen temperature	60.0 ± 0.1°C
Equilibrium time	90 minutes
Loop fill time	0.25 minutes
Loop equilibrium time	0.3 minute
Inject time	2.00 minutes
Line temperature	150.0 ± 0.1°C
Valve temperature	150.0 ± 0.1°C
Gas chromatograph:	
Column temperature	65.0 ± 0.1°C. The column was ramped to 75.0 ± 0.1°C and held for 3.5 minutes at that temperature after each 10-minute run to prevent carry-over between samples
Injector temperature	140 ± 0.1°C
Detector temperature	250 ± 0.1°C

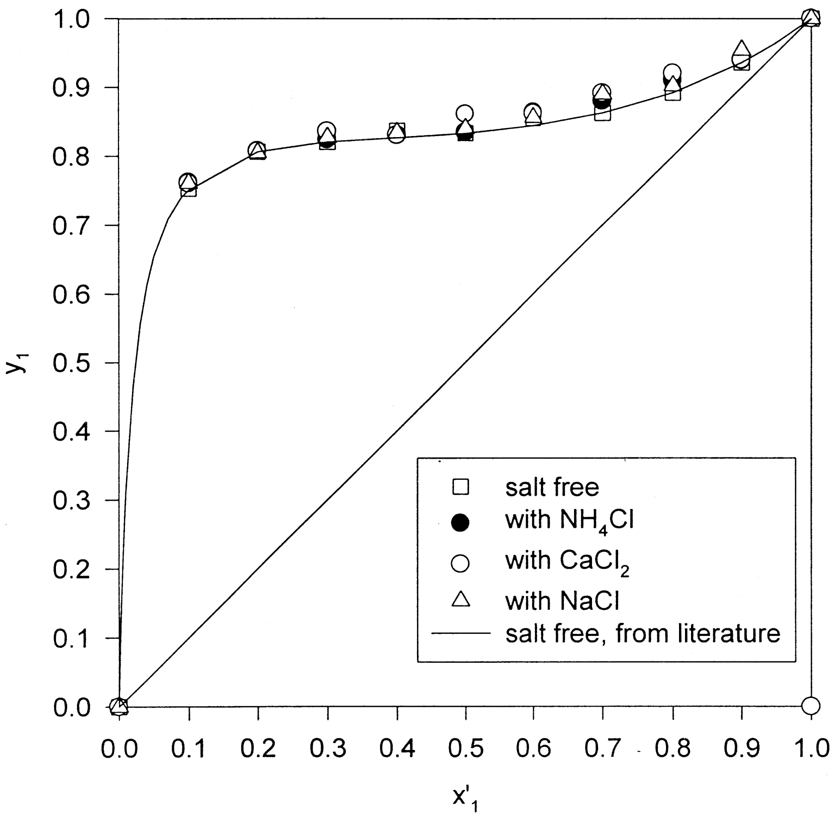

FIG. 2 x'_1–y_1 diagram (isothermal) for acetone–water system at 60°C.

TABLE 4
VLE Data for Acetone (1)–Water (2)–Salt System at 0.50 M Salt

x'_1	y_1		
	Salt-free	With 0.5 M NH_4 Cl	With 0.5 M $CaCl_2$
0.0000	0.0000	0.0000	0.0000
0.1000	0.7531	0.7621	0.8606
0.2000	0.8062	0.8078	0.8070
0.3000	0.8203	0.8241	0.8336
0.4000	0.8365	0.8331	0.8364
0.5000	0.8338	0.8341	0.8611
0.6000	0.8440	0.8636	0.8617
0.7000	0.8626	0.8801	0.8911
0.8000	0.8918	0.9101	0.9120
0.9000	0.9357	0.9392	0.9401
1.0000	1.0000	1.0000	1.0000

The effect of salt addition on the VLE of the acetone–water system at 60°C was investigated for three different salts: $CaCl_2$, NaCl, and NH_4 Cl. The experimental results of the VLE are presented in Tables 4 and 5 and plotted in Figs. 2 and 3. These results show that the VLE of the acetone–water system was altered significantly in the presence of NaCl at saturation conditions.

Table 4 and Fig. 2 show that under the same molarity, 0.50 M, all of the salts used resulted in a small increase in the relative volatility of acetone, thus hav-

TABLE 5
VLE Data for Acetone (1) Water (2)–NaCl System

x'_1	y_1		
	With 0.167 M NaCl	With 0.50 M NaCl	With saturated NaCl
0.0000	0.0000	0.0000	0.0000
0.1000	0.7611	0.7701	0.8518
0.2000	0.8090	0.8102	0.8725
0.3000	0.8261	0.8274	0.8751
0.4000	0.8342	0.8349	0.8762
0.5000	0.8404	0.8408	0.8781
0.6000	0.8502	0.8566	0.8800
0.7000	0.8709	0.8754	0.8954
0.8000	0.9000	0.9025	0.9161
0.9000	0.9395	0.9500	0.9550
1.0000	1.0000	1.0000	1.0000

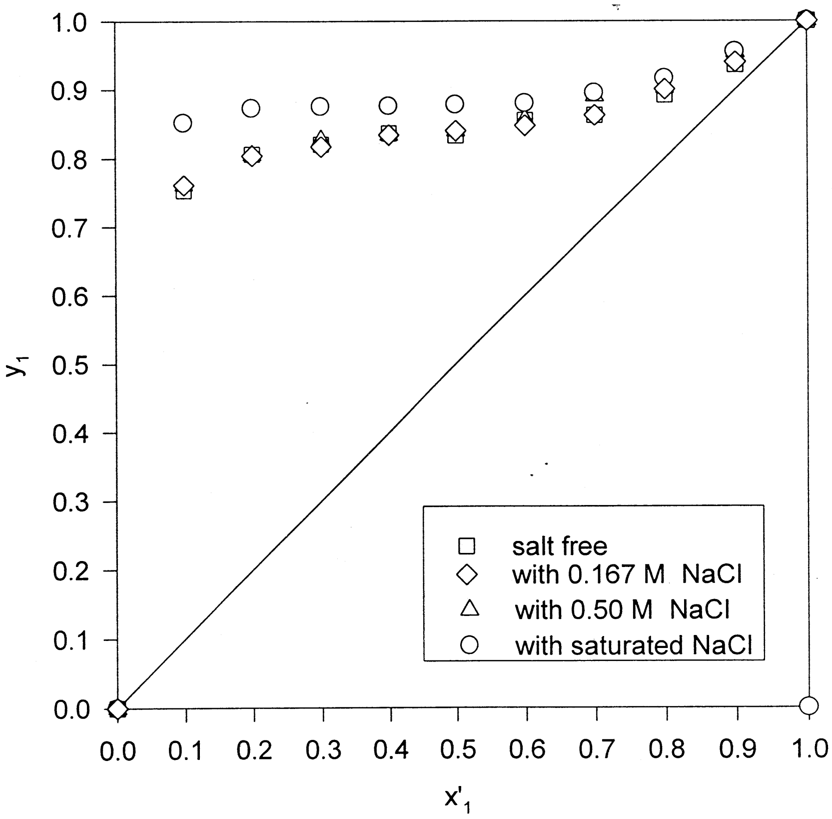

FIG. 3 Effect of NaCl concentration on the VLE data of acetone–water system at 60°C.

ing a salting-out effect. The salting-out effect occurs as a result of the formation of salt–liquid phase complexes with one species in the liquid more than the other. The formation of these complexes reduces the activity of the more attracted component in the solution and increases the activity of the less attracted component, which results in expelling or salting out the latter from the liquid solution, hence increasing its relative volatility.

The effect of salt concentration on altering the VLE of acetone–water was studied for the case of NaCl, where experiments with saturation, 0.50 M, and 0.167 M NaCl were conducted. The results are presented in Table 5 and plotted in Fig. 3. As expected, the alteration in the VLE “increases” as the salt concentration increases. This is due to the fact that as the salt molality increases, the intermolecular forces between the highly polar component in the mixture increase, thus decreasing its composition. Thus, the salting-out effect of the component of less polarity, acetone, increases as the salt molality increases.

The effect of the salt on the relative volatility for unsaturated systems can be analyzed using the simple correlation (15)

$$\ln \alpha_s = m \ln \alpha + c \tag{1}$$

where α_s and α are the relative volatility in the presence of constant salt concentration and in the absence of the salt, respectively, and m and c are constants characterizing the system. Figures 4 and 5 show a plot of the relative volatilities for the different salts used in this study. The values of m and c are shown in Table 6. Values of m close to unity along with values of c close to zero indicate a "poor" effect of the salt on the VLE of the system. Thus, as is shown in Table 6, the effect of the salts investigated in this study at 0.5 M on the VLE of the acetone–water system at 60°C is expected to be poor.

Another equation that can be used to study the effect of salt on the VLE is that proposed by Furter (15):

$$\ln(\alpha_s/\alpha) = kz \tag{2}$$

This equation correlates the ratio of relative volatility in the presence of salt to that in the absence of salt to the salt concentration z in the liquid phase by the salt effect parameter, k, which depends on system and solvent composition.

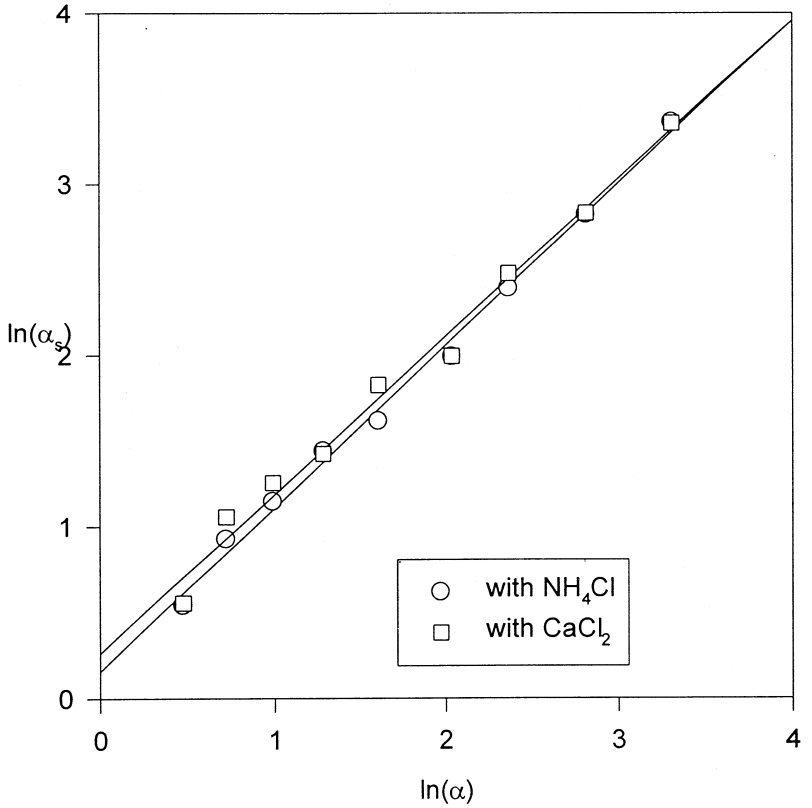

FIG. 4 Plot of ln α_s against ln α for acetone–water system at 60°C with 0.50 M NH_4Cl and 0.50 M $CaCl_2$.

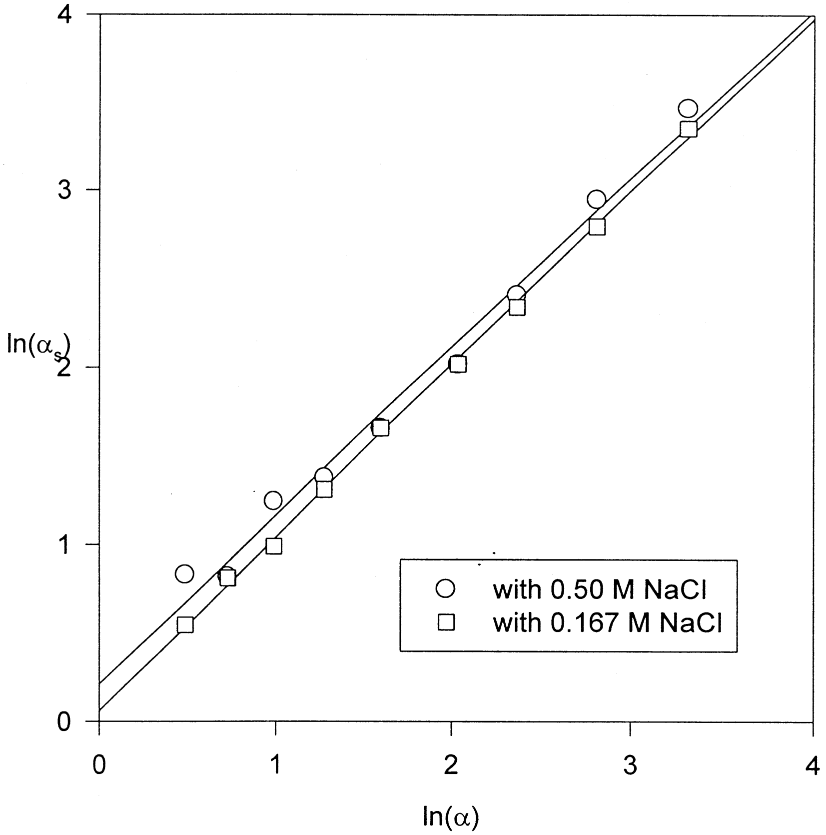

FIG. 5 Plot of ln α_s against ln α for acetone–water system at 60°C with 0.167 M and 0.50 M NaCl.

Figure 6 shows $\ln(\alpha_s/\alpha)$ against NaCl concentration, z, at different acetone compositions. This figure shows that the Furter equation fits our data under unsaturated conditions. The values of the salt effect parameter are shown in Table 7 and Fig. 7 against acetone composition in the liquid phase. It is evi-

TABLE 6
Constants of Eq. (1) for the Salts Used

Salt	m	c
NH_4Cl	0.946	0.1567
$CaCl_2$	0.922	0.262
NaCl with 0.50 M	0.960	0.210
NaCl with 0.167 M	0.980	0.06

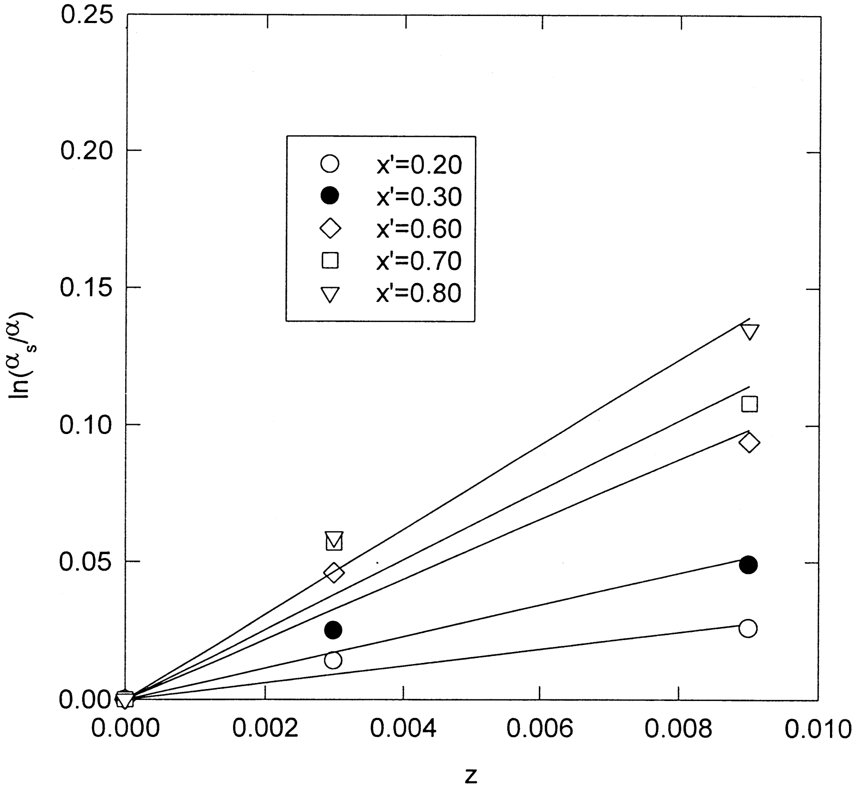

FIG. 6 Salt effect of unsaturated NaCl on acetone–water system at 60°C.

dent from the results that the salt effect parameter is a strong function of the liquid phase composition on a salt-free basis. This is due to the fact that the degree of disassociation of NaCl and the intermolecular interactions between the components of the liquid phase are composition-dependent.

TABLE 7
Salt Effect Parameter of NaCl at Different Liquid Compositions

x'_1	Salt effect parameter, z
0.20	3.06
0.30	5.73
0.60	10.9
0.70	12.7
0.80	15.4

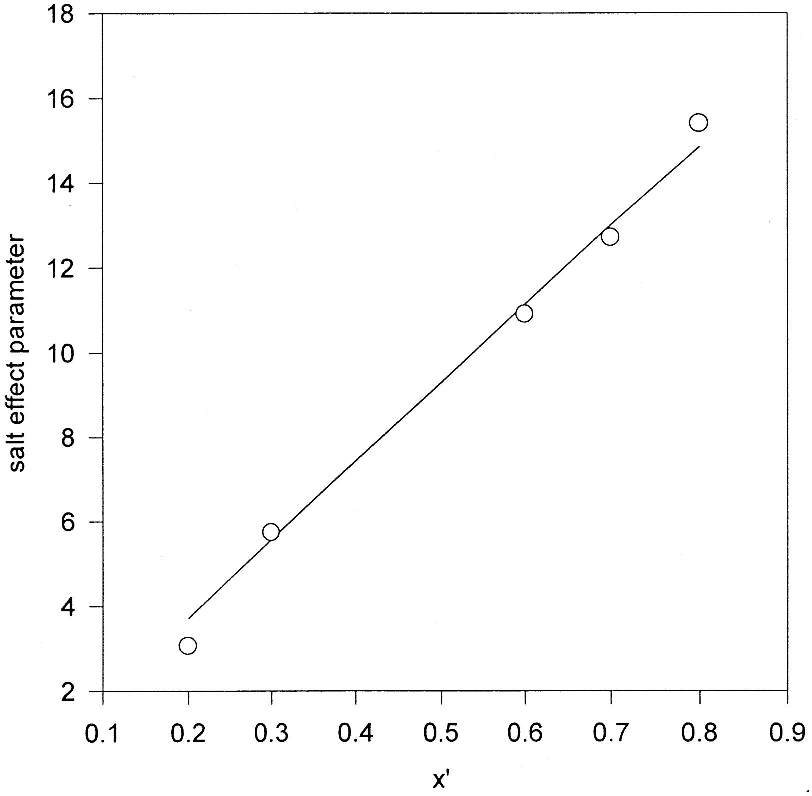

FIG. 7 Variation of the salt effect parameter with acetone composition for acetone–water system at 60°C.

CONCLUSIONS

The VLE of the acetone–water system at 60°C was studied in the presence of NaCl, $CaCl_2$, and NH_4Cl salts using the HSGC technique. The results showed that only NaCl, when added in saturation conditions, had a significant effect in altering the VLE of the acetone–water system under the experimental conditions. The degree of alteration in the VLE was found to increase by increasing the salt molality. The experimental VLE results in the absence and in the presence of NaCl under unsaturation conditions were correlated successfully by the Furter equation, with the salt parameter effect found to be strongly liquid-composition-dependent.

NOTATION

c	empirical constant for a given constant salt concentration
k	salt effect parameter

m	empirical constant for a given constant salt concentration
x	mole fraction in the liquid phase
y	mole fraction in the vapor phase
z	salt concentration

Greek Letter

α	relative volatility

Subscripts

i	species i
s	in presence of salt

Superscript

$'$	salt-free

Abbreviations

HSGC	headspace gas chromatography
VLE	vapor–liquid equilibrium

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