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Short communication

Isothermal vapour–liquid equilibria of 1-propanol–water–salt mixtures

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Abstract

Isothermal vapour–liquid equilibrium data at 60°C for the system 1-propanol–water–salt were obtained using the headspace gas chromatography (HSGC) technique. Three different salts were investigated in this study; NH_4Cl, NaCl and $CaCl_2$. The results obtained showed that while 0.50 M NH_4Cl or 0.50 M $CaCl_2$ had no effect on the vapour–liquid–equilibrium (VLE) of this system, NaCl with the same molarity could alter the VLE of the system and shift its azeotropic point. The azeotropic point of the system was shifted from 40 mol% 1-propanol to about 60 mol% 1-propanol when NaCl was added under saturation conditions. Good agreement with the Furter equation was observed for the experimental data with NaCl under unsaturated conditions. The salt effect parameter calculated from the Furter equation was found to be a function of the liquid concentration. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Vapour-liquid equilibrium; Furter equation

1. Introduction

Distillation is the most common technique used for separation of alcohol–water mixtures. The phase diagram of these mixtures is characterized by the presence of an azeotropic point and the small 'pinch', or closeness of the vapour–liquid equilibrium (VLE) curves between the azeotropic composition and the pure alcohol. This makes conventional distillation in these regions impractical [1]. For these cases special techniques such as extractive, with liquid or salt, and azeotropic distillation can be used. Addition of salts may result in changing the vapour and partial pressures, solubility, thermal conductivity, density, surface tension, etc. These changes, if they occur, will result in altering the VLE of the system [2–24].

Accurate vapour-liquid equilibrium data are important in the design of separation processes. Most VLE data available in the literature are obtained either by static still methods or circulation still methods. Both methods have their advantages and disadvantages. The main disadvantages of circulation methods are 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 [25]. On the other hand, the main problem with static still methods is the need to degas the components which requires carefully designed apparatus.

Headspace gas chromatography (HSGC) is a 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, fast, and can save time, since equilibrium and sample analysis are done in the same apparatus. Headspace analysis in VLE studies involves sampling of the vapour phase, the sample is injected into a GC, in equilibrium with its liquid phase [25–30]. The liquid composition is determined from the mass of the pure components after correction for evaporation [25]. [28,29] used the HSGC technique to study the VLE of some binary mixtures. Recently, [30] 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.

A review of the literature reveals that the VLE of 1-propanol–water mixtures and the effect of some salts on the VLE of these mixtures are widely investigated using the traditional VLE measuring techniques [31,32]. The objective of this study is to investigate further the practical feasibility of using the HSGC technique in measuring the VLE of mixtures with particular emphasis on the effect of different salts such as NH_4Cl, NaCl and $CaCl_2$ on the VLE of 1-propanol–water mixtures.

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Table 1
Headspace autosampler specifications

Model	Genesis headspace autosampler with 50 position carrousel
Injector inlet connection	Septum needle adaptor
Carrier gas	Ultra high purity helium (Matheson)
Sample vial size	22 ml vials
Sample loop volume	20 µl

Table 2
Gas chromatography specifications

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

2. Experimental

The vapour phase in equilibrium with the liquid phase is referred to as the 'headspace'. The principle behind headspace analysis is that at any temperature and pressure when a fixed volume of solution is sealed in a fixed-volume vial, there will be only one vapour composition corresponding to that liquid composition. The experiments in this study consisted of analyzing the vapour composition above liquid mixtures of 1-propanol and water. The vapour was sampled using a headspace autosampler and the amount of 1-propanol was determined using a gas chromatograph. Specifications for the headspace autosampler and the gas chromatograph are listed in Tables 1 and 2, respectively.

2.1. Procedure

Liquid samples of 1-propanol–water mixtures with and without salts were placed in a closed vial and introduced into a 50-position rotating carrousel. 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 portion of the vapour in the vial headspace was automatically transferred with a gas sampling valve and passed through a transfer line into the gas chromatograph where the analysis took place. Reproducibility of data showed that the accuracy of the measurements was within ±0.1%. The experimental set-up and the configuration of the autosampler are schematically illustrated in Figs. 1 and 2, respectively.

By testing various instrument settings, the analytical method which yielded the most reproducible data was determined. Table 3 lists these parameters for the 1-propanol–water system.

2.2. Chemicals

Distilled water and 1-propanol with 99.9% purity (Sigma) were used. The salts used in this study had purities of 99.5+%.

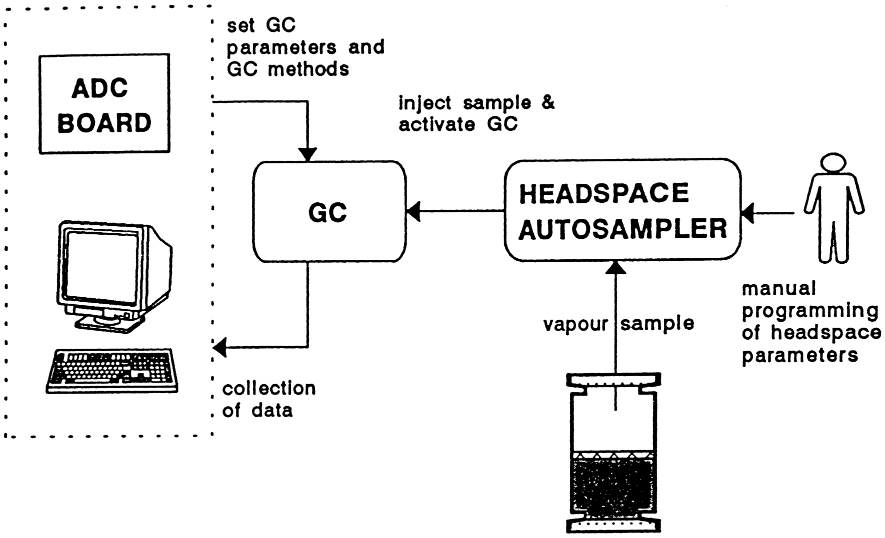

Fig. 1. Experimental set-up used in this study [30].

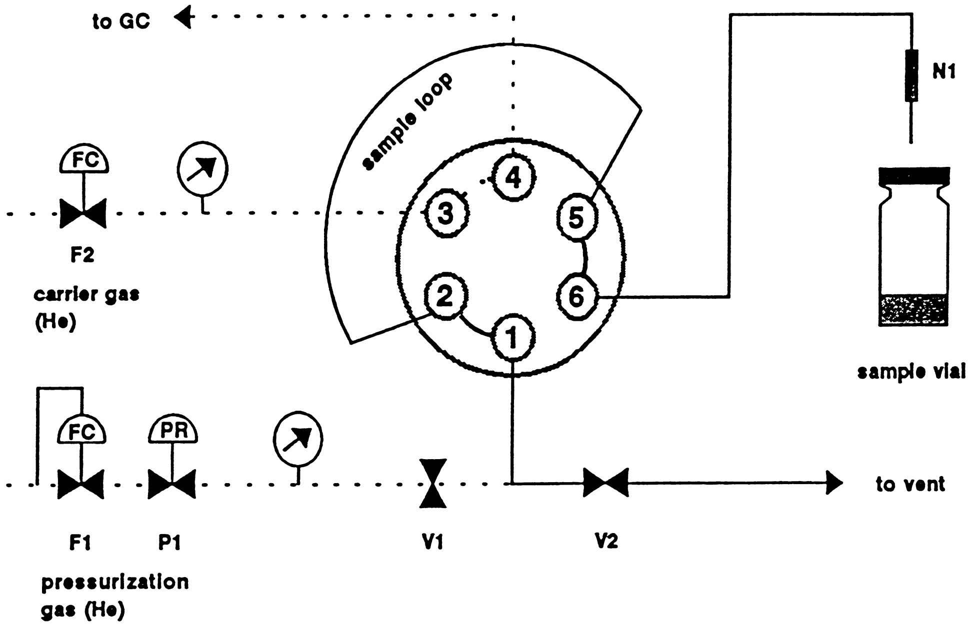

Fig. 2. The autosampler configuration for the filling of sample loop [30].

3. Results and discussion

A check on the technical feasibility of using the HSGC technique to study the VLE of binary mixtures was done by using this technique to study the VLE of 1-propanol–water system at 60°C. The close agreement between the measured and literature data [31], shown in Fig. 3 where the data coincide on each other, proves the feasibility of the method.

Three different salts; namely $CaCl_2$, NaCl and NH_4Cl, were used to investigate the effect of salt addition on the VLE of 1-propanol–water system at 60°C. The experimental results are presented in Table 4 and are shown in Figs. 3 and 4. These results show that the VLE of 1-propanol–water mixtures including the azeotropic point were altered in the presence of NaCl. The increase in the relative volatility of 1-propanol in the 1-propanol rich region in the presence of NaCl indicates that this salt has a salting-out effect on 1-propanol in this region.

Fig. 3 shows that at the same molarities, considerable alteration in the VLE in the presence of 0.50 M NaCl was obtained, while no alteration in the VLE was observed in the presence of either 0.50 M NH_4Cl or 0.50 M $CaCl_2$. This indicates that, under these conditions, only NaCl has the ability to change the intermolecular interactions between 1-propanol–water mixture. In another words, the magnitude of

Table 3
Parameters used for 1-propanol composition determination

Headspace autosampler	
Platen temperature	60°C
Equilibrium time	120 min
Loop fill time	0.25 min
Loop equilibrium time	0.3 min
Inject time	2.00 min
Line temperature	150°C
Valve temperature	150°C
Gas chromatograph	
Column temperature	75°C The column was ramped to 85°C and held for 5 min at that temperature after each 10 min run to prevent carry over between samples
Injector temperature	140°C
Detector temperature	250°C

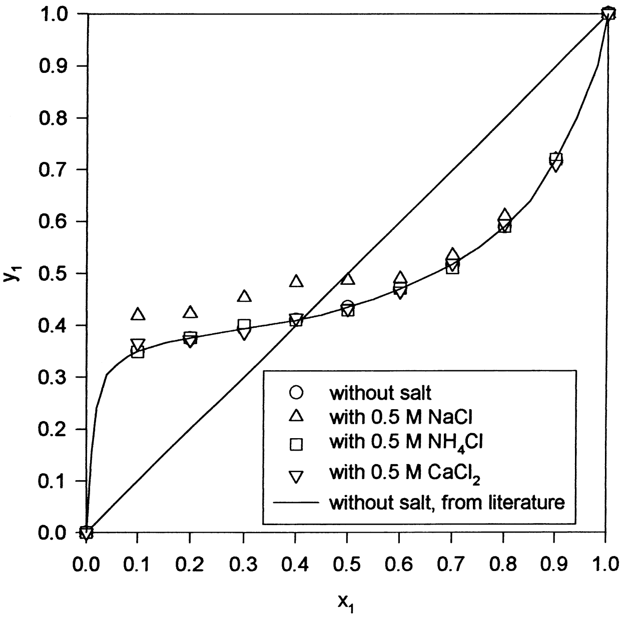

Fig. 3. x_1–y_1 diagram (isothermal) for 1-propanol–water system at 60°C.

Table 4
Vapour–liquid equilibria data of 1-propanol–water–salt systems

x_1	y_1 (salt-free)	y_1 (with 0.50 M NH_4Cl)	y_1 (with 0.50 M $CaCl_2$)	y_1 (with 0.50 M NaCl)	y_1 (with 0.167 M NaCl)	y_1 (with saturated NaCl)
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.000 0
0.1000	0.3501	0.3492	0.3659	0.4190	0.3850	0.4902
0.2000	0.3751	0.3760	0.3720	0.4223	0.4100	0.5894
0.3000	0.3940	0.4001	0.3864	0.4533	0.4230	0.5910
0.4000	0.4100	0.4100	0.4143	0.4822	0.4532	0.5984
0.5000	0.4350	0.4289	0.4314	0.4867	0.4596	0.5988
0.6000	0.4702	0.4701	0.4654	0.4900	0.4762	0.5990
0.7000	0.5170	0.5099	0.5189	0.5342	0.5230	0.6274
0.8000	0.5900	0.5902	0.5945	0.6104	0.6101	0.6514
0.9000	0.7201	0.7200	0.7100	0.7200	0.7200	0.7964
1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

the intermolecular forces of either $CaCl_2$ or NH_4Cl with 1-propanol is similar to that with water. Hence, no alteration in the VLE is expected.

The effect of salt concentration on alteration of the VLE of 1-propanol–water was studied for the case of NaCl, where experiments with saturated, 0.50 M and 0.167 M NaCl were conducted. The results are shown in Fig. 4. 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 salt and the highly polar component in the mixture increases and accordingly increases the composition of the component of less polarity in the vapour phase. Thus, the salting-out effect of the component of less polarity 1-propanol, increases as the salt molality increases. Moreover, Fig. 4 shows that the azeotropic point of this system was shifted from about 40 mol% 1-propanol to about 60 mol% 1-propanol when the NaCl was added at saturation conditions. These results show clearly the usefulness of using NaCl in shifting the azeotropic composition of 1-propanol–water mixtures, and thus enhancing the separation in these mixtures.

For unsaturated systems, the effect of salt on the relative volatility 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 mixture. Figs. 5 and 6 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 5. The results in Fig. 6 and in Table 5

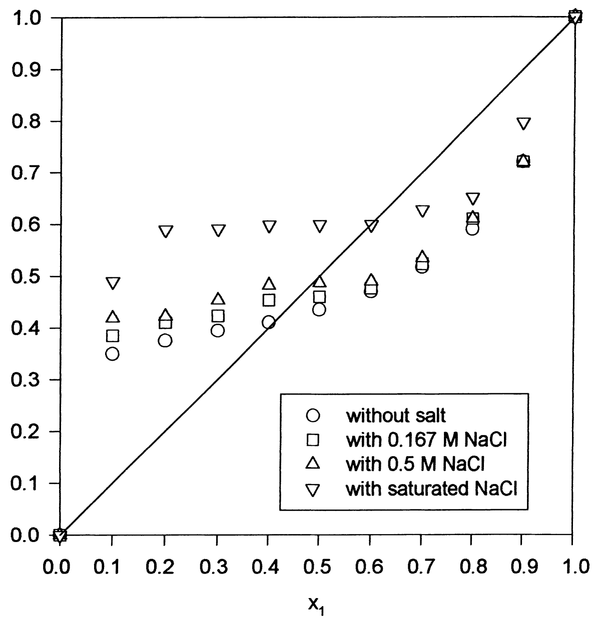

Fig. 4. Effect of NaCl concentration on the VLE data of 1-propanol–water system at 60°C.

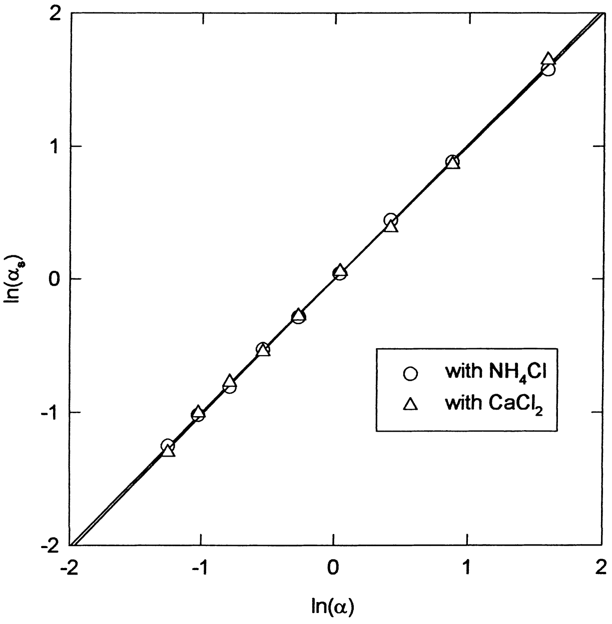

Fig. 5. Plot of ln α_s against ln α for 1-propanol–water system at 60°C with 0.50 M NH_4Cl and 0.50 M $CaCl_2$.

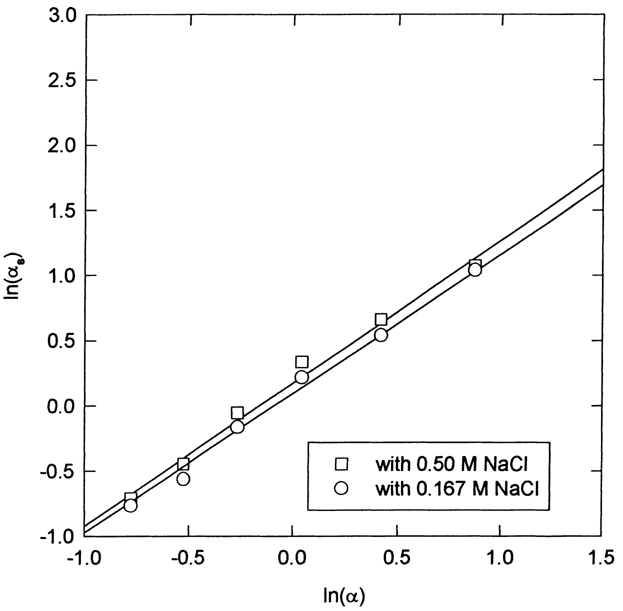

Fig. 6. Plot of ln α_s against ln α for 1-propanol–water system at 60°C with 0.167 M and 0.50 M NaCl.

show that the constant c equals zero for the salts $CaCl_2$ and NH_4Cl while the constant m equals unity. These values indicate that these salts had no effect on the VLE of the system. The results shown in Table 5 and Fig. 6 show that for NaCl salt, while the value of m was a weak function of salt concentration for the two salt concentrations (other than the saturated) the value of c was salt concentration dependent, thus parallel straight lines were obtained for different salt concentrations.

Another equation that can be used to study the effect of salt on VLE is that proposed by Furter. The Furter equation given as [15]

$$\ln\left(\frac{\alpha_s}{\alpha}\right) = kz \tag{2}$$

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

Fig. 7 shows $\ln(\alpha_s/\alpha)$ against NaCl concentration, z, at different compositions of 1-propanol. This figure shows that the Furter equation fits the experimental data very well under unsaturated salt conditions. The values of the salt

Table 5
Constants of Eq. (1)

Salt	m	c
NH_4Cl with 0.50 M	1.0	0.0
$CaCl_2$ with 0.50 M	1.0	0.0
NaCl with 0.50 M	1.10	0.18
NaCl with 0.167 M	1.08	0.10

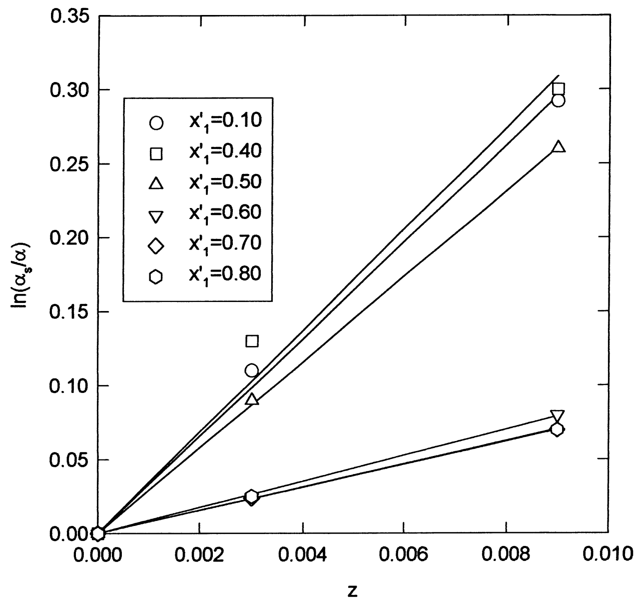

Fig. 7. Salt effect of on 1-propanol–water system at 60°C with NaCl under unsaturated conditions.

Table 6
Salt effect parameter of NaCl

x'_1	Salt effect parameter, k
0.10	32.9
0.40	32.6
0.50	31.0
0.60	8.8
0.70	7.8
0.80	7.8

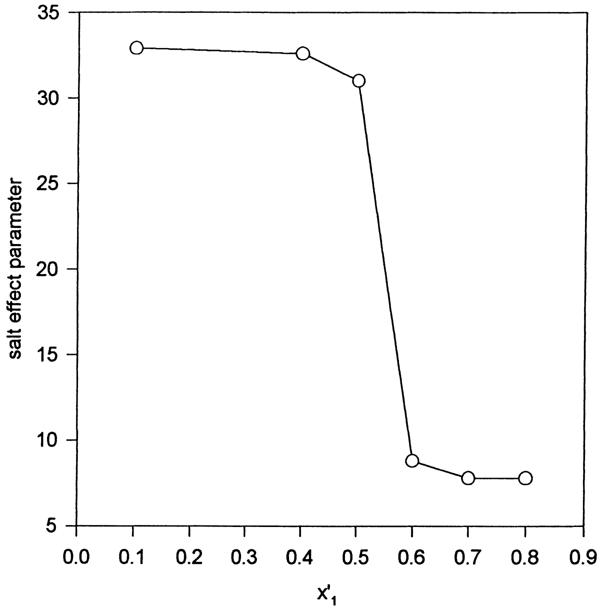

Fig. 8. Variation of the salt effect parameter with 1-propanol composition for 1-propanol–water system at 60°C.

effect parameter, calculated using linear regression, are shown in Table 6 and in Fig. 8 against 1-propanol composition in the liquid phase. It is evident 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 dissociation of NaCl and the intermolecular interactions between the components of the liquid phase are composition dependent.

4. Conclusions

The VLE of 1-propanol–water mixtures 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 had a significant effect in altering the VLE of 1-propanol–water mixtures under the experimental conditions. The degree of alteration in the VLE was found to increase by increasing the salt molality. The azeotropic point of 1-propanol–water system was shifted in the presence of saturated NaCl from about 40 mol% 1-propanol to about 60 mol% 1-propanol. 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 effect parameter found to be strongly liquid–composition dependent.

5. Notation

c	empirical constant for a given constant salt concentration
k	salt effect parameter
m	empirical constant for a given constant salt concentration
x_1	mole fraction of 1-propanol in the liquid phase
y_1	mole fraction of 1-propanol in the vapour phase
z	salt concentration

Greek letters

α	relative volatility

Subscripts

1	1-propanol
i	species i
s	in presence of salt

Superscripts

$'$	salt-free

Abbreviations

HSGC	headspace gas chromatography
VLE	vapour–liquid equilibrium

References

[1] F.A. Abu Al-Rub, J. Akili, R. Datta, Sep. Sci. and Technol. 33 (1998) 1529.
[2] A.I. Johnson, W.F. Furter, Can. J. Technol. 35 (1957) 413.
[3] R.A. Cook, W.F. Furter, Can. J. Chem. Eng. 46 (1968) 119.
[4] M. Hashitani, M. Hirata, J. Chem. Eng. Jpn. 1 (1968) 116.
[5] M. Hashitani, M. Hirata, J. Chem. Eng. Jpn. 2 (1969) 149.
[6] S. Ohe, K. Yokoyama, S. Nakamura, J. Chem. Eng. Jpn. 2 (1969) 1.
[7] S. Ohe, K. Yokoyama, S. Nakamura, J. Chem. Eng. Data 16 (1971) 70.
[8] D. Jaques, W.F. Furter, AIChE J. 18 (1972) 343.
[9] D. Meranda, W.F. Furter, AIChE J. 20 (1974) 103.
[10] E. Sada, T. Morisue, J. Chem. Eng. Jpn. 8 (1975) 191.
[11] E. Sada, T. Morisue, K. Miyahara, J. Chem. Eng. Data 20 (1975) 283.
[12] D.S. Abrams, J.N. Prausnitz, AIChE J. 21 (1975) 116.
[13] W.F. Furter, Can. J. Chem. Eng. 55 (1977) 2775.
[14] W. Wang, K.C. Cao, Chem. Eng. Sci. 38 (1983) 1483.
[15] T. Subbaiah, J. Chem. Tech. Biotechnol. 57 (1993) 163.
[16] T.A. Al-Sahhaf, N.J. Jabbar, J. Chem. Eng. Data 38 (1993) 522.
[17] F. Gironi, L. Lamberti, Fluid Phase Equilibria 105 (1995) 273.
[18] T.C. Tan, Chem. Eng. Res. Dev. 65 (1987) 355.
[19] T.C. Tan, Chem. Eng. Res. Dev. 65 (1987) 421.
[20] T.C. Tan, W.K. Teo, H.C. Ti, Chem. Eng. Res. Dev. 66 (1988) 75.
[21] T.C. Tan, H.C. Ti, Chem. Eng. Res. Dev. 67 (1988) 79.
[22] T.C. Tan, H.C. Ti, Fluid Phase Equilibria 43 (1988) 91, and references cited therein.
[23] T.C. Tan, Fluid Phase Equilibria 55 (1990) 59.
[24] N.A. Darwish, Z.A. Al-Anbar, Fluid Phase Equilibria 131 (1997) 259.
[25] K.N. Marsh, Fluid Phase Equilibria 52 (1989) 169.
[26] L.S. Ettre, B. Kolb, S.G. Hurt, Am. Lab. 15 (1983).
[27] H. Hachenberg, A.P. Schmidt, Gas Chromatographic Headspace Analysis, Heyden and Son, London, England, 1977.
[28] L. Lepori, E. Matteoli, B. Marongiu, Fluid Phase Equilibria 42 (1988) 229.
[29] S.J. Park, B.H. Chol, B.S. Rhee, Hwahak Konghak 25 (1987) 512.
[30] N.S.J. Wong, The Effects of Capillary Plates on Vapour–Liquid Equilibrium in Aqueous Alcohol Systems, M.Sc. Thesis, Dept. Chem. Eng., McGill University, Montreal, 1997.
[31] S. Ohe, Vapour–Liquid Equilibrium Data, Elsevier, 1989.
[32] S. Ohe, Vapour–Liquid Equilibrium Data-Salt Effect, Elsevier, 1990, and references cited therein.