Salt-Containing Model for Simulation of Salt-Containing Extractive Distillation

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Three binary vapor–liquid equilibrium (VLE) data were measured: tertbutanol-ethanediol, tertbutanol-KAc, and ethanediol-KAc. Experimental data were correlated with the salt-containing local composition model (SCLCM). For the multicomponent system, VLE data predicted by SCLCM are in agreement with the data in the literature. An industrial plant (3500T/Y) of salt-containing extractive distillation for the tertbutanol/water/ethanediol/potassium acetate system was simulated by SCLCM and improved the Rose relaxation method. Simulation results agree well with industrial data.

Introduction

Extractive distillation is an important method for separating the mixture of compounds with azeotropic behavior, but it has the disadvantage of using large amounts of solvent. A large solvent ratio (> 5) causes not only great energy consumption but also a heavier liquid load in column, leading to a higher operating cost, shorter stay time, lower plate efficiency, and more actual plate number. In order to avoid liquid flood caused by the heavier liquid load, the allowed load of vapor and liquid must be decreased, which results in a lower production capacity. To extend the application field of extractive distillation, it is essential to improve solvent efficiency and reduce solvent consumption.

Salt-containing distillation is a distillation process using salt as the separating agent. For mixtures with binary azeotrope, a certain amount of salt has a more pronounced effect on the relative volatility of the mixtures than solvent does, so it can eliminate the azeotrope entirely. Usually adding even small amounts of salt to the mixtures increases the relative volatility several times. The advantages of the use of salts are that a smaller amount of separating agent is required, and lower energy requirements and equipment costs are needed. The disadvantages are related to the restoration of solvent, the conveyance of salt, and so on, thus limiting the application of salt-containing distillation.

Duan et al. (1980) have developed a new process called salt-containing extractive distillation by combining the advantages of extraction and those of salt-containing distillation. Using mixtures of solvent with salt as the extractive agent, the process overcomes the disadvantages of conventional extrictive distillation, since salt has a pronounced effect on the relative volatility of solvent species and, at the same time, maintains the advantages of conventional processes, such as easy cycling and conveyance of the separating agent. According to the results of their studies on the system of ethanol–water–ethanediol–KAc, they used the process in an industrial plant (2300 T/Y) and produced a top-quality product. Compared with the conventional ethanol extractive distillation process, the solvent ratio is 4–5 times smaller and tower is 3–4 times shorter in the salt-containing extractive distillation process. The satisfactory effects of this process were demonstrated by running the plant for more than 2 years. Regrettably, no data for simulation were reported.

Furthermore, Lei et al. (1982), who studied the tertbutanol–water–ethanediol–KAc system by means of salt-containing extractive distillation in a similar plant (3500 T/Y), reported the data about the plant in detail. This study makes simulation of the columns possible.

One of the aims of this article is to find a simple effective method for simulating a salt-containing extractive distillation column.

To simulate salt-containing extractive distillation, models of vapor–liquid equilibrium are needed; these are reported widely. Sander et al. (1986) give a good review of the earlier models. The main types of these models are $\mathrm{Ln}(\alpha s/\alpha) = KsXs$; the pseudobinary approach; and the model that combines the Debye–Hückel equation with the local composition

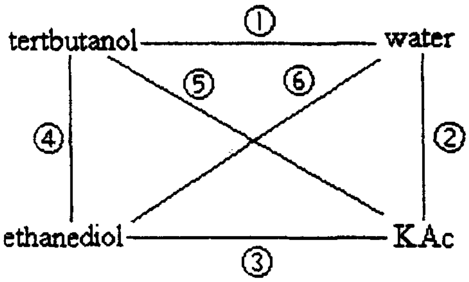

Figure 1. Binary VLE data used for predicting multicomponent salt-containing system.

model. In the last type the activity coefficient of the i component in the solution (solvent and salt) is expressed by a long-range and a short-range item: $\ln\gamma_i = \ln\gamma_{i,D-H} + \ln\gamma_{i,LCM}$. Sander et al. proposed a model, $\ln\gamma_i = \ln\gamma_{i,D-H} + \ln\gamma_{i,\mathrm{UNIQUAC}}$, in which the effects of liquid concentration on the UNIQUAC model parameters are considered.

Using the local composition model, Glugla and Sax (1985) calculated the activity coefficients, $\ln\gamma_i = \ln\gamma_{i,\mathrm{UNIQUAC}}$, and successfully correlated fifteen binary systems (methanol/ethanol/acetone/water and monovalent salts). Using the salt-containing local composition model (SCLCM), Fu (1991) correlated eighteen binary systems (methanol/ethanol/water and monovalent salt/bivalent salt/organic salt) and predicted the results of five ternary systems which are in good agreement with the results predicted by the pseudobinary approach. Fu (1994a) studied ternary and quaternary systems: methanol/ethanol/water and NH_4NO_3/NH_4Cl. Total absolute deviations are $\Delta\overline{T} = 0.34$°C, $\Delta\bar{y} = 0.0171$.

It must be proved whether SCLCM can be used in the system of tertbutanol, ethanediol, water, and organic salt because the materials are different from those in previous works, and concentration and temperature vary greatly in the simulation of the column.

The other aim of this article is to identify the effectiveness of SCLCM through studying the vapor–liquid (VLE) of the quaternary system (tertbutanol/water/ethanediol/KAc) and simulating the salt-containing distillation columns.

The advantage of SCLCM is that salt-containing systems are dealt with by means of a local composition model of a conventional miscible system, in which the salt is assumed "solvent." The software of the model and calculation methods used in the system are well known. For example, to calculate the quaternary system (Figure 1), six binary data are needed: data of saturated vapor pressure containing salt, (2), (3), and (5); and data of binary VLE in a conventional miscible system, (1), (4), and (6). It is well known that binary data are only required to predict multicomponent data by the local composition model, so the quaternary VLE can be predicted when salt is considered as a "solvent."

In this article, three measured binary data are correlated by SCLCM and VLE data are predicted for the multicomponent system; the results are in good agreement with the literature. In addition, two columns of salt-containing distillation are simulated. Since the simulation results agree very well with the industrial data, SCLCM is suitable for this system and the simulation method is effective. The simulation software of the distillation column, based on the calculation method of the VLE of the conventional miscible system, can be used directly in similar systems.

Experimental Studies

Measurement of VLE binary data

The binary VLE data for the systems of tertbutanol/ethanediol, tertbutanol/KAc, and ethanediol/KAc were measured, since no such data have been published. The reagents used are tertbutanol (> 99.7 wt. %), ethanediol (> 99.8 wt. %), and KAc (> 99.7 wt. %) supplied by the Beijing Chemical Reagent Corporation.

Tertbutanol/Ethanediol. It is difficult to determine binary VLE data for systems of tertbutanol/ethanediol due to the large difference between their boiling points (114.8°C). The improved Dvorak–Boublik still was used because of its good reproducibility. The experimental technique and procedure were the same as those described in earlier articles (Fu and Zhang, 1989; Fu and Gao, 1991; Fu, 1994c,d).

Compositions of the liquid and vapor phases were measured by a five-digit refractometer, and the temperatures were measured with a mercury-in-glass thermometer (1/10°C division).

A device consisting of a 220C pressure gauge and PDRC-1C/2C display supplied by the MKS Corporation (Andover, MA), whose accuracy is 0.013 kPa, was used to measure the equilibrium total pressure. The equilibrium data were determined at 66.665 kPa (± 0.040 kPa). The binary VLE data in the whole concentration range were determined and are presented in Table 1.

Testing of the thermodynamics consistency for the binary VLE data has been done by the point test method (Frenslund et al., 1977), and the result is $\overline{\Delta P} = 2.2202$ kPa, $\overline{\Delta y} = 0.00996$.

Tertbutanol/KAc and Ethanediol/KAc. The salt-containing binary VLE (salt-containing saturated vapor pressure) for systems of tertbutanol/KAc and ethanediol/KAc were measured.

The measurement mode of the temperature and pressure are the same as those given earlier, an ebulliometer (Bao et al., 1990; Fu, 1992) was used instead of the Dvorak–Boublik still. The composition of liquid phase was determined by weight method and the residual volume of the vapor phase was corrected.

Two sets of binary data with different pressure and salt concentrations were determined; they are shown in Tables 2 and 3.

Correlation of binary data and estimation of parameters

The vapor phase was assumed with ideal gas behavior, and the vapor–liquid equilibrium relation is

$$y_i P = P_i^0 \gamma_i x_i \tag{1}$$

for salt-containing binary data, $y_{\mathrm{solvent}} = 1$, $y_{\mathrm{salt}} = 0$, so,

$$P_i^S = P_i^0 \gamma_i x_i, \tag{2}$$

where γ_i was calculated by the NRTL model.

Table 1. Experimental Data and Correlation Results for the Binary System of Tertbutanol/Ethanediol*

No.	P_{measure} (kPa)	ΔP (kPa)	T_{measure} (°C)	ΔT (°C)	$x_{1,\text{measure}}$ (mol %)	Δx_1 (mol %)	$y_{1,\text{measure}}$ (mol %)	Δy_1 (mol %)
1	66.665	0.1000	73.30	−0.16	0.9400	−0.0033	0.9990	−0.0001
2	66.665	0.1986	75.99	−0.31	0.8130	−0.0064	0.9981	0.0010
3	66.665	0.2946	78.62	−0.44	0.6911	−0.0096	0.9970	0.0020
4	66.665	0.1013	81.21	−0.15	0.6069	−0.0035	0.9951	0.0018
5	66.665	0.0027	83.31	0.00	0.5373	−0.0002	0.9942	0.0025
6	66.665	−0.06933	85.82	0.10	0.4587	0.0027	0.9915	0.0018
7	66.665	−0.08933	87.24	0.13	0.4178	0.0039	0.9902	0.0018
8	66.665	−0.0973	89.28	0.14	0.3648	0.0048	0.9900	0.0036
9	66.665	−0.0187	90.70	0.03	0.3252	0.0010	0.9849	0.0001
10	66.665	0.0093	94.00	−0.01	0.2614	−0.0007	0.9820	0.0011
11	66.665	0.0320	96.95	−0.04	0.2168	−0.0033	0.9800	0.0030
12	66.665	0.0040	99.84	0.01	0.1892	0.0004	0.9730	0.0003
13	66.665	0.0040	105.20	0.00	0.1439	−0.0008	0.9640	0.0010
14	66.665	0.0173	109.88	−0.02	0.1135	−0.0036	0.9527	0.0002
15	66.665	0.0040	118.10	0.00	0.0824	−0.0013	0.9285	0.0003
16	66.665	0.0027	125.70	−0.04	0.0593	−0.0032	0.8912	−0.0057
17	66.665	0.0093	136.96	−0.01	0.0385	−0.0028	0.8295	−0.0010
18	66.665	0.0070	146.28	−0.01	0.0343	0.0053	0.7486	−0.0017
19	66.665	0.0054	157.44	0.01	0.0208	0.0028	0.6137	0.0002
20	66.665	0.0240	163.94	−0.03	0.0186	0.0058	0.5043	−0.0019
21	66.665	0.1093	172.34	−0.14	0.0080	0.0011	0.3230	−0.0054
22	66.665	0.1827	175.42	−0.23	0.0044	−0.0005	0.2410	−0.0080
23	66.665	0.2187	177.77	−0.27	0.0031	−0.0003	0.1752	−0.0088
24	66.665	0.1787	179.00	−0.22	0.0026	−0.0001	0.1440	−0.0069
Mean Dev.		0.1240		0.16		0.0037		0.0036

*$\Delta g_{12} = 124.515$ J/mol; $\Delta g_{21} = 2{,}931.338$ J/mol; $\alpha_{12} = 0.30$.

There are two definitions of the salt concentration in SCLCM:

1. The mole fraction is defined by the mole number of ions and solvent, and the difference between positive ions and negative ions is neglected:

$$x_{\text{solvent}} = \frac{n_i}{\sum n_i + \sum n_{\text{salt}}^{\pm}} \tag{3}$$

$$x_{\text{salt}} = \frac{\sum n_{\text{salt}}^{\pm}}{\sum n_i + \sum n_{\text{salt}}^{\pm}}, \tag{4}$$

where $n_{\text{salt}}^{\pm}$ is the mole number of ions, and n_i is the mole number of solvent.

2. The mole fraction defined by the mole number of salt and solvent:

$$x_{\text{solvent, salt}} = \frac{n_i}{\sum n_i}, \tag{5}$$

where n_i is the mole number of solvent and salt.

In predicting the multicomponent system VLE by these two

Table 2. Experimental Data and Correlation Results for the Binary System of Tertbutanol-KAc*

No.	P_{measure} (kPa)	ΔP (kPa)	T_{measure} (°C)	ΔT (°C)	$x_{1,\text{measure}}$ (mol %)	Δx_1 (mol %)	$y_{1,\text{measure}}$ (mol %)	Δy_1 (mol %)
1	100.117	−0.1720	81.91	0.17	0.9966	0.0007	1.0000	0.0000
2	93.331	−0.1707	80.14	0.16	0.9966	0.0007	1.0000	0.0000
3	86.645	−0.1693	78.30	0.15	0.9966	0.0006	1.0000	0.0000
4	79.998	−0.1693	76.34	0.14	0.9966	0.0006	1.0000	0.0000
5	73.332	−0.1253	74.22	0.13	0.9966	0.0005	1.0000	0.0000
6	66.665	−0.1640	72.00	0.14	0.9966	0.0005	1.0000	0.0000
7	59.999	−0.1440	69.54	0.13	0.9966	0.0004	1.0000	0.0000
8	53.332	−0.1307	66.85	0.11	0.9966	0.0004	1.0000	0.0000
9	99.998	0.4133	81.38	−0.04	0.9880	0.0007	1.0000	0.0000
10	93.331	0.4040	79.60	−0.05	0.9880	0.0008	1.0000	0.0000
11	86.645	0.3493	77.79	−0.03	0.9880	0.0006	1.0000	0.0000
12	79.998	0.3360	75.84	−0.03	0.9880	0.0005	1.0000	0.0000
13	73.332	0.3067	73.75	−0.02	0.9880	0.0004	1.0000	0.0000
14	66.665	0.2453	71.55	0.00	0.9880	0.0000	1.0000	0.0000
15	59.999	0.2573	69.06	−0.02	0.9880	0.0003	1.0000	0.0000
16	53.332	0.2013	66.42	0.00	0.9880	0.0000	1.0000	0.0000
Mean Dev.		0.2533		0.10		0.0005		0.0000

*$\Delta g_{12} = 31{,}357.039$ J/mol; $\Delta g_{21} = -699.531$ J/mol; $\alpha_{12} = 0.25$.

Table 3. Experimental Data and Correlation Results for the Binary System of Ethanediol-KAc*

No.	P_{measure} (kPa)	ΔP (kPa)	T_{measure} (°C)	ΔT (°C)	$x_{1,\text{measure}}$ (mol %)	Δx_1 (mol %)	$y_{1,\text{measure}}$ (mol %)	Δy_1 (mol %)
1	100.237	−0.0240	193.40	0.02	0.9535	−0.0022	1.0000	0.0000
2	93.331	−0.0253	190.75	−0.01	0.9535	0.0011	1.0000	0.0000
3	86.645	0.0587	187.81	−0.08	0.9535	0.0064	1.0000	0.0000
4	79.998	0.0053	185.20	−0.10	0.9535	0.0076	1.0000	0.0000
5	73.332	0.1987	181.98	−0.18	0.9535	0.0122	1.0000	0.0000
6	100.077	0.0053	192.45	0.04	0.9430	−0.0031	1.0000	0.0000
7	93.331	0.0013	189.66	−0.04	0.9430	0.0026	1.0000	0.0000
8	86.645	0.0653	186.92	−0.10	0.9430	0.0067	1.0000	0.0000
9	79.998	0.1467	183.98	−0.19	0.9430	0.0113	1.0000	0.0000
10	73.332	0.2467	180.84	−0.30	0.9430	0.0162	1.0000	0.0000
11	99.998	−0.0787	192.30	0.07	0.9386	−0.0053	1.0000	0.0000
12	93.331	0.0093	189.51	−0.01	0.9386	0.0005	1.0000	0.0000
13	86.645	0.1173	186.67	−0.09	0.9386	0.0056	1.0000	0.0000
14	79.998	0.1413	183.58	−0.23	0.9386	0.0125	1.0000	0.0000
15	73.332	0.2480	180.54	−0.33	0.9386	0.0165	1.0000	0.0000
16	100.517	−0.1533	192.30	0.21	0.9243	−0.0158	1.0000	0.0000
17	93.331	−0.0800	189.25	0.13	0.9243	−0.0082	1.0000	0.0000
18	86.645	0.0360	186.40	0.04	0.9243	−0.0023	1.0000	0.0000
19	79.998	0.0773	183.40	−0.09	0.9243	0.0042	1.0000	0.0000
20	73.332	0.1613	180.26	−0.24	0.9243	0.0102	1.0000	0.0000
21	100.224	−0.1400	191.85	0.35	0.9104	−0.0234	1.0000	0.0000
22	93.331	−0.2120	188.90	0.25	0.9104	−0.0143	1.0000	0.0000
23	86.645	−0.0827	186.19	0.19	0.9104	−0.0094	1.0000	0.0000
24	79.998	−0.1453	183.41	0.10	0.9104	−0.0046	1.0000	0.0000
25	73.332	0.2000	179.75	−0.25	0.9104	0.0081	1.0000	0.0000
26	100.384	−0.2320	190.78	0.38	0.8970	−0.0183	1.0000	0.0000
27	93.331	−0.0030	187.70	0.19	0.8970	−0.0070	1.0000	0.0000
28	86.645	−0.0280	185.10	0.06	0.8970	−0.0020	1.0000	0.0000
29	79.998	−0.0187	182.59	0.03	0.8970	−0.0009	1.0000	0.0000
30	73.332	0.0133	179.90	0.00	0.8970	0.0000	1.0000	0.0000
Mean Dev.		0.1270		0.18		0.0099		0.0000

*$\Delta g_{12} = 55{,}043.022$ J/mol; $\Delta g_{21} = -4{,}583.081$ J/mol; $\alpha_{12} = 0.20$.

definitions, a small difference in the accuracy of the calculation exists (Fu, 1994b). The definition for the mole fraction of salt and solvent was chosen to calculate the enthalpy of salt conveniently.

The binary data were correlated by the maximum likelihood method (Anderson et al., 1978), and the correlated binary parameters give the "best" overall representation of both the experimental results and an optimal prediction result (Sutton and Macgregor, 1977).

The object function is

$$F = \sum_{j}^{m} \left[\frac{(P_j^c - P_j^e)^2}{\sigma_{P_j}^2} + \frac{(T_j^c - T_j^e)^2}{\sigma_{T_j}^2} + \frac{(x_{1j}^c - x_{1j}^e)^2}{\sigma_{x_{1j}}^2} + \frac{(y_{1j}^c - y_{1j}^e)^2}{\sigma_{y_{1j}}^2} \right]. \quad (6)$$

To the salt-containing binary system, $y_1 = 1$, $y_2 = 0$, the salt was regarded as a nonvolatile component, so the last item on the righthand side of Eq. 6 is zero; and $\sigma_{P_j}^2$, $\sigma_{T_j}^2$, $\sigma_{x_{1j}}^2$, and $\sigma_{y_{1j}}^2$ are the error variances of P, T, x, and y. In this work, the standard deviation values are the following: $\sigma_P = 0.133$ kPa, $\sigma_T = 0.05$ K, $\sigma_{x_1} = 0.001$, and $\sigma_{y_1} = 0.003$.

The correlation results using the NRTL model for the tertbutanol(1)/ethanediol(2), tertbutanol(1)/KAc(2), and ethanediol(1)/KAc(2) systems are shown in Tables 1, 2, and 3.

The data of (1) and (6) (Figure 1) and the optimal binary parameters were obtained from Gmehling and Onken (1977), while the data of (2) (Figure 1) were obtained from Li et al. (1986).

Prediction of the Multicomponent System VLE and the X-Y Diagram of the Tertbutanol(1)/Water(2) Binary System

Lei et al. (1982) have published eight points of X-Y data (ethanediol + KAc free) for the tertbutanol(1)/water(2)/ethanediol(3)/KAc(4) system. But the concentration of ethanediol and KAc for each point has not been reported because it is difficult to measure the concentration of KAc. It is therefore impossible to compare each datum predicted by SCLCM with the experimental one. But the changeable range of the mole fraction for ethanediol and KAc in the liquid phase can be estimated from their description of the experiment. The ethanediol (x_3) range is from 0.437 to 0.443, and the KAc (x_4) range is from 0.008 to 0.012. In this work, their average values ($x_3 = 0.440$; $x_4 = 0.010$) are used as constants for predicting. The boiling points at isobaric (101.33 kPa) have been calculated by SCLCM for the quaternary system; thus

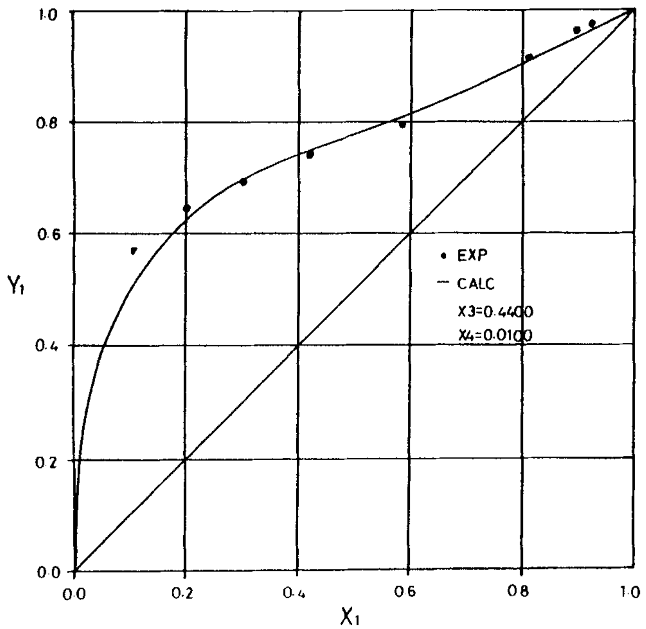

Figure 2. Predicted vs. experimental value for the system tertbutanol/water/ethanediol/KAc.

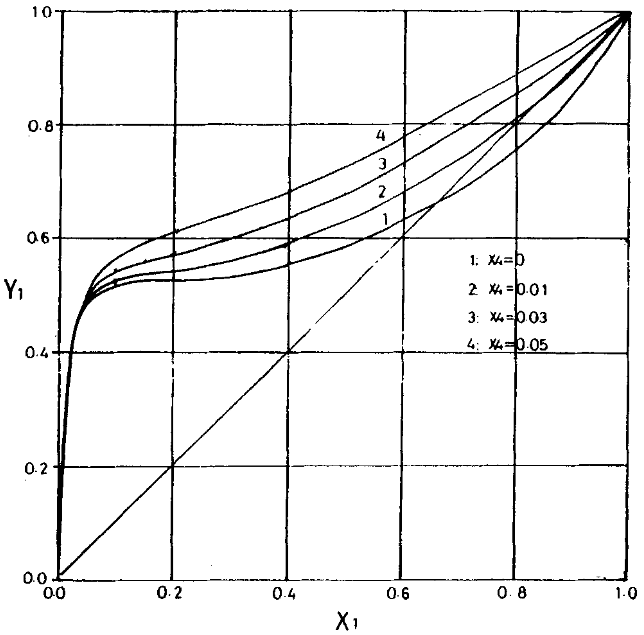

Figure 3. *X*-*Y* diagram for the system tertbutanol/water at different concentrations of KAc (salt-free).

the *X*-*Y* equilibrium relationship for the tertbutanol(1)/water(2)/(ethanediol + KAc free) system can be calculated after processing the boiling point *x*-*y* data. Figure 2 compares the predicted values with the experimental ones. It shows that they are in good agreement. This confirms that SCLCM is appropriate for the quaternary system. To research the influence of different KAc concentrations, ternary VLE data ($x_3 = 0$) for the tertbutanol(1)/water(2)/KAc(4) system were predicted at four constant x_4 values ($x_4 = 0$, 0.01, 0.03, and 0.05). The *X*-*Y* equilibrium relationships (KAc free) are illustrated in Figure 3. It is shown that the relative volatility between components 1 and 2 increases with the increase in the KAc concentration, and that the azeotropic composition is a function of salt concentration. The azeotrope can be eliminated only by adding some amount of KAc.

Similar work has been done for the system of tertbutanol(1)/water(2)/ethanediol(3), at $x_3 = 0.0$, 0.1, 0.3, and 0.5 in order to study the influence of different ethanediol concentrations. The *X*-*Y* equilibrium relationships are reported in Figure 4. It can be seen that again the azeotrope can only be eliminated by ethanediol, but the concentration of ethanediol is higher.

Figure 5 shows the experimental and predicted VLE *x*-*y* data for the binary system of tertbutanol(1)/water(2) and the *X*-*Y* relationship at $x_3 = 0.4206$, $x_4 = 0.0296$ (advantage of the mole fraction of the mixed solvent within column 1), and at $x_3 = 0.45$, $x_4 = 0.0$. It can be clearly seen from curves 1 and 2 that the relative volatility of tertbutanol(1)/water(2) with mixed solvent of ethanediol and KAc is higher than that with pure ethanediol, when the concentration of the agent is the same. It therefore takes fewer theoretic trays for salt-containing extractive distillation when the separation demand is the same. In other words, it takes less solvent than the pure agent extractive distillation with the same number of trays.

Simulation of Salt-Containing Extractive Distillation

The process of salt-containing extractive distillation is similar to conventional extractive distillation, as illustrated in Figure 6. Here, the system is tertbutanol(1)/water(2)/ethanediol(3)/KAc(4).

Column I is the salt-containing extractive distillation col-

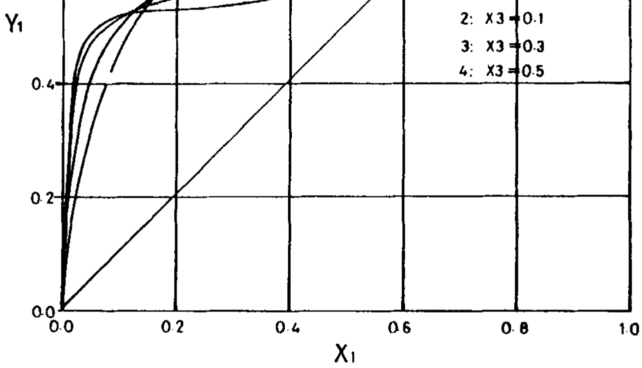

Figure 4. *X*-*Y* diagram for the system tertbutanol/water at different concentrations of ethanediol (solvent-free).

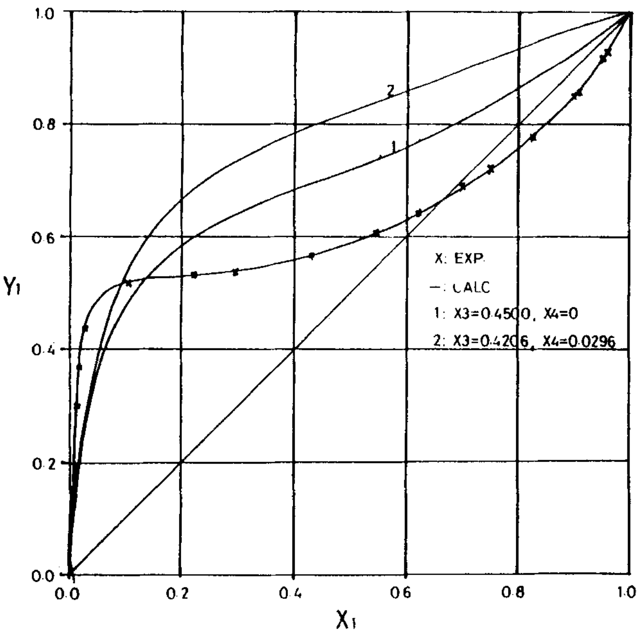

Figure 5. X-Y diagram for the system tertbutanol/water at different agents.

umn. The materials with azeotrope (tertbutanol and water) are fed in at location F, and the mixed extractive agent (ethanediol and KAc) is charged at point S. The pure light component (tertbutanol) is separated from the mixture with solvent (ethanediol) by several trays from point S to the top, and the liquid at the bottom (water + ethanediol + KAc) is fed to column II, the extractive-agent-restoring column.

The heavy component of the system with azeotrope is removed at top of column II, and the mixed agent (ethanediol and KAc) at the bottom is fed back to column I again.

The salt solution of ethanediol and KAc at the bottom of column II can be used again by transporting it in the liquid state after the water is removed. Thus the difficulty of the transportation and restoration of solid salt in conventional salt-containing distillation is overcome.

Simulation method

The simulation method of multicomponent distillation has been widely reported (Henley and Seader, 1981; Guo, 1983). The following group of equations can be solved in simulation methods based on the equilibrium stage: vapor–liquid phase equilibrium equations, material balance equations, enthalpy balance equations, and equations of mole fraction summation. The main three methods are (1) the matrix method, (2) the tray-by-tray calculation, and (3) the nonstable equation method.

The matrix method is widely used because of its fast convergence, but it needs a strict initial value. The improved Rose relaxation method (Guo, 1983) was adopted because of the existence of salt and a large variance in the boiling points between the components. The flow rates of vapor and liquid phase at each plate were also obtained by calculating the mixing enthalpy.

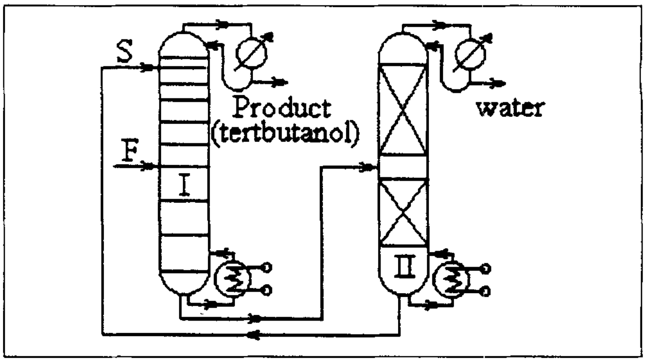

Figure 6. Industrial process for salt-containing extraction distillation.

For simulation the operating equation is

$$x_j^{(K+1)} = x_j^{(K)} + U_j\Big[(V_{j+1}y_{j+1})^{(K)} + (L_{j-1}x_{j-1})^{(K+1)} - (V_jy_j)^{(K)} - (L_jx_j)^{(K+1)}\Big]. \quad (7)$$

However, the operating equations for condenser, feeding plate, and reboiler are slightly different from Eq. 7.

It is suitable for the adopted phase-equilibrium model (SCLCM), because the molar fraction (x) is solved in the liquid phase. In the simulation of the column, the salt concentration in the vapor phase equals zero ($y_4 = 0$). The corresponding items disappear, which has no obvious effect on the new x solution. But in the matrix method, the phase-equilibrium constant (K_4) became zero at $y_4 = 0$ and it had bad effects on the new x solution.

To calculate the flow rates of both phases by the heat balance equation, the enthalpies of the vapor-and-liquid-phase mixture must be computed. The ideal solution mixing enthalpy, Eqs. 8 and 9, was used in this work:

$$H_{mj}^{v} = \sum_{i}^{c} (H_{ij}^{v} y_{ij}^{v}) \quad (8)$$

$$H_{mj}^{L} = \sum_{i}^{C} \left(H_{ij}^{L} x_{ij}^{L}\right). \quad (9)$$

To calculate the enthalpy by the $C_p \sim t$ relationship, simplified salt processing is used: the heat capacity C_p of salt in the vapor phase is zero, and the C_p of salt in the liquid phase was replaced by the C_p of solid salt.

The convergence criteria are:

$$\sum_{i=1}^{C} \sum_{j=2}^{N} \left[\frac{x_{ij}^{(K+1)} - x_{ij}^{(K)}}{x_{ij}^{(K+1)}}\right]^2 \le \epsilon_x \quad (10)$$

and

$$\sum_{j=3}^{N} \left|\frac{V_j^{(K+1)} - V_j^{(K)}}{V_j^{(K+1)}}\right| \le \epsilon_V. \quad (11)$$

Table 4. Simulation Result for Distillation Column I*

Tray No.	T (°C)	P (kPa)	V (kmol/h)	L (kmol/h)	x_1 (mol %)	x_2 (mol %)	x_3 (mol %)	x_4 (mol %)
1	50.00	101.33	0.00	5.92	0.9997	0.0000	0.0003	0.0000
2	84.07	106.40	10.58	6.53	0.9838	0.0000	0.0162	0.0000
3	94.23	107.45	11.20	13.10	0.5177	0.0000	0.4512	0.0311
4	94.49	108.42	11.56	13.11	0.5180	0.0001	0.4508	0.0311
5	94.75	109.44	11.57	13.12	0.5182	0.0002	0.4505	0.0311
6	95.00	110.45	11.58	13.13	0.5181	0.0005	0.4503	0.0311
7	95.24	111.46	11.59	13.14	0.5175	0.0015	0.4500	0.0310
8	95.47	112.48	11.59	13.14	0.5156	0.0037	0.4497	0.0310
9	95.65	113.49	11.60	13.14	0.5103	0.0091	0.4496	0.0310
10	95.76	114.50	11.60	13.13	0.4975	0.0216	0.4498	0.0311
11	95.79	115.52	11.59	13.08	0.4700	0.0477	0.4511	0.0312
12	95.80	116.53	11.54	12.98	0.4182	0.0961	0.4543	0.0314
13	96.16	117.54	11.44	12.77	0.3300	0.1763	0.4618	0.0319
14	98.18	118.56	11.23	12.53	0.2027	0.2927	0.4720	0.0326
15	102.76	119.57	10.99	12.78	0.1010	0.4091	0.4580	0.0319
16	97.76	120.58	11.24	19.82	0.0748	0.6065	0.2981	0.0206
17	113.04	121.60	10.69	20.59	0.0075	0.6844	0.2883	0.0198
18	117.04	122.61	11.47	20.82	0.0006	0.6942	0.2856	0.0196
19	117.89	123.62	11.70	20.76	0.0000	0.6902	0.2901	0.0197
20	122.14	124.64	11.63	19.64	0.0000	0.6174	0.3618	0.0208
21	151.06	125.65	10.52	9.12	0.0000	0.3194	0.6359	0.0447

*$C = 4$, $N = 21$; $N_F = 16$; $N_S = 3$; $R = 1.268$; $F = 7.58$ kmol/h; $T_F = 352.97$ K; $z_{F,1} = 0.6200$ mol %; $z_{F,2} = 0.3800$ mol %; $F_S = 6.21$ kmol/h; $T_S = 368.55$ K; $z_{S,3} = 0.9343$ mol %, $z_{S,4} = 0.0657$ mol %; $Q_1 = 4.773 \times 10^5$ kJ/h; $Q_n = 5.447 \times 10^5$ kJ/h; $z_1 = 0.3504$ mol %; $z_2 = 0.2093$ mol %; $z_3 = 0.4206$ mol %; $z_4 = 0.0296$ mol %; $U = 7.252 \times 10^{-3}$.

Simulation of salt-containing extractive column I

The system is tertbutanol(1)/water(2)/ethanediol(3)/KAc(4).

Column I was simulated under the conditions reported by Lei et al. (1982). The initial value of x of each plate is the average concentration of the feed, and the initial value of the temperature is the linear distribution of the temperature at the top and the bottom of the column. The initial values of the flow rate of the vapor–liquid phase are the constant molar flow rates. The relaxation factor is $U = 0.10/(Fs + F)$ and the convergence accuracies are $\epsilon_x \leq 5 \times 10^{-6}$ and $\epsilon_V = 10^{-2}$.

The simulation results are shown in Table 4, and the comparison with industrial data for the distillation column is shown in Table 5.

The comparison shows that the simulation result agrees with the actual value. This confirms that SCLCM is applicable to the simulation of the distillation column for this quaternary system, and it is suitable to simplify the processing for the enthalpy calculation of salt. Thus we can determine the optimum operating conditions for column I by the simulation method. For example, from Table 4 we can see that there is a constant concentration zone within the column. The plates in the zone have no separation effect, so the optimum number of plates may be redetermined.

In this work optimization of the number of plates has been done under the same conditions listed in Table 4. The simulated result showed that the required production accuracy can be achieved with only 12 theoretical plates. The results of optimum simulation are presented in Figures 7–9.

Table 5. Comparison of Simulation Result and Industrial Data for Distillation Column I

	Temperature (°C)			Comp. of Top Product (mol %)			
Value	Bottom	Middle	Top	x_1	x_2	x_3	x_4
Obs.	150.00	93.00	82.50	0.9910	0.0038	0.0052	0.0000
Cal.	151.06	95.76	84.07	0.9997	0.0000	0.0003	0.0000

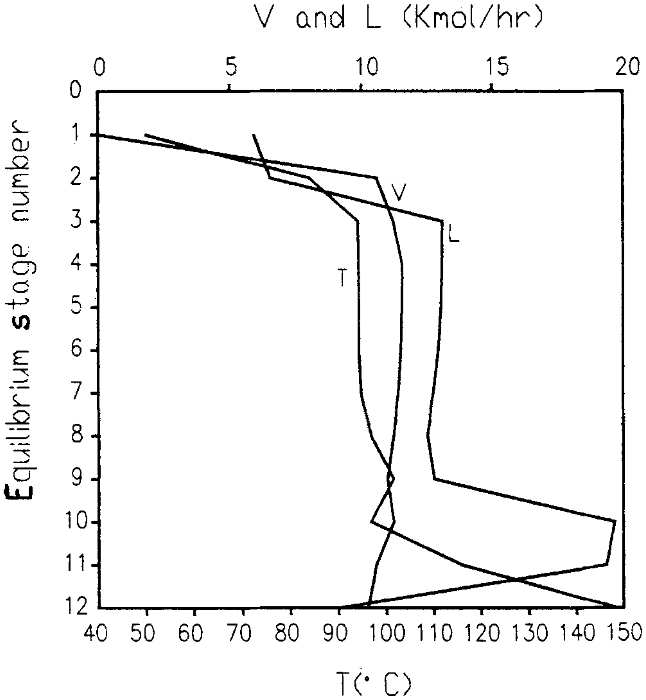

Figure 7. Converged temperature and flow rates of vapor–liquid phase for optimum column I.

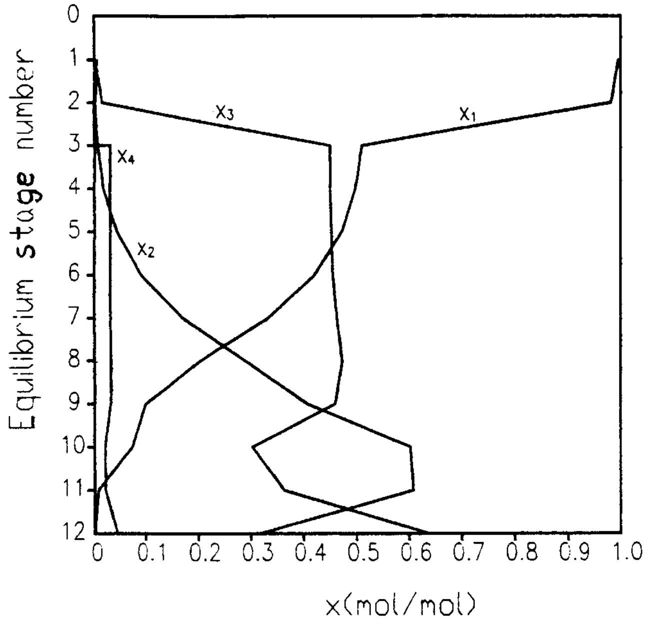

Figure 8. Converged liquid-phase composition for optimum column I.

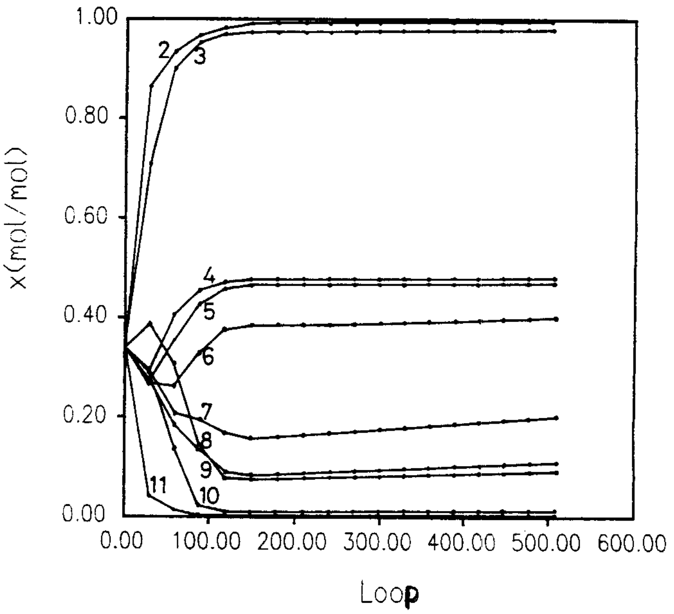

Figure 9. Convergence trend.

Simulation of extractive-agent-restoring column II

The system is water(1)/ethanediol(2)/KAc(3).

The actual column is a packed column and the height of the packing equivalent to one theoretical stage adopted in this work is 0.57 m.

The simulation method and equilibrium model are the same as before, and the convergence criterion are $\epsilon_x \leq 1.0 \times 10^{-4}$ and $\epsilon_v \leq 10^{-2}$.

The simulation results are shown in Table 6, and the comparison with industrial data for distillation column II is shown in Table 7.

Comparison of the simulation values with the industrial data shows satisfying results.

Conclusion

Measured binary data are accurate enough to be used as base data. SCLCM fits the calculation of the vapor–liquid equilibrium and simulation of the salt-containing extractive distillation system presented in this article. The simplification for calculating salt ethalpy is feasible for simulating the distillation column. Some software for calculating the phase equilibrium of a miscible system and simulating the distillation column can be directly used for salt-containing extractive distillation. Thus, a simple and effective method for the optimal design of salt-containing extractive distillation is given.

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Table 6. Simulation Result for Distillation Column II*

Plates No.	T (°C)	P (kPa)	V (kmol/h)	L (kmol/h)	x_1 (mol %)	x_2 (mol %)	x_3 (mol %)
1	30.00	4.00	0.00	2.91	1.0000	0.0000	0.0000
2	34.12	5.33	5.83	2.91	1.0000	0.0000	0.0000
3	39.13	7.00	5.83	2.90	0.9964	0.0036	0.0000
4	47.23	8.66	5.81	2.33	0.8120	0.1880	0.0000
5	85.99	10.34	5.25	1.56	0.1674	0.8326	0.0000
6	110.92	12.00	4.48	1.56	0.0596	0.9404	0.0000
7	116.13	13.67	4.47	1.57	0.0539	0.9461	0.0000
8	117.63	15.33	4.48	9.12	0.1283	0.8263	0.0454
9	131.70	17.00	2.82	9.17	0.0718	0.8833	0.0449
10	139.76	18.66	2.87	9.22	0.0411	0.9143	0.0446
11	144.51	20.34	2.92	9.26	0.0245	0.9310	0.0445
12	147.82	22.00	2.96	9.30	0.0147	0.9410	0.0443
13	150.45	23.67	3.00	9.34	0.0085	0.9474	0.0441
14	151.35	25.33	3.04	6.30	0.0044	0.9302	0.0654

*$C = 3$; $N = 14$; $N_F = 8$; $R = 1$; $F = 9.12$ kmol/h; $T_F = 424.32$ K; $z_{F,1} = z_1 = 0.3194$ mol %; $z_{F,2} = z_2 = 0.6359$ mol %; $z_{F,3} = z_3 = 0.0447$ mol %; $Q_1 = 2.681 \times 10^5$ kJ/h; $Q_n = 2.360 \times 10^5$ kJ/h; $U = 1.086 \times 10^{-2}$.

Table 7. Comparison of Simulation Result and Industrial Data for Distillation Column II

	Temperature (°C)			Comp. of Bottom Product (mol %)		
Value	Bottom	Middle	Top	x_1	x_2	x_3
Obs.	150.00	109.00	34.80	0.0040	—	—
Cal.	151.39	110.92	34.12	0.0044	0.9302	0.0654

Notation

B = total flow rate of bottom product
C = number of components
D = total flow rate of overhead product
F = flow rate of feed
Δg = NRTL model parameter
H = enthalpy
L = flow rate of liquid phase
m = number of experimental points
N = number of equilibrium stages
P = pressure
Q = flow rate of heat
R = actual reflux
T = temperature
U = relaxation factor
V = flow rate of vapor phase
x = liquid-phase molar fraction
y = vapor-phase molar fraction
X = liquid-phase mole fraction at KAc, or ethanediol, and/or ethanediol + KAc free
Y = vapor-phase mole fraction at KAc, or ethanediol, and/or ethanediol + KAc free
Z = feed mole fraction

Superscripts and subscripts

c = calculated value
e = experimental value
L = liquid phase
V = vapor phase
S = agent
F = feed

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