J. Chem. Eng. Data **2004,** *49,* 407−410

Articles

Effect of Addition of Calcium Chloride on Vapor Pressure of 2-Methyl-1-butanol

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This work describes the “salt effect” due to the addition of calcium chloride on the vapor pressure of 2-methyl-1-butanol. The working pressure was varied from (23.3 to 96.6) kPa, and the boiling temperatures were obtained. Salt concentrations were increased from a very low value up to a concentration close to saturation. Two types of equations were applied for data correlation. The first equation was derived from the Antoine equation, and it takes into account the presence of the dissolved salt, and the second equation was the nonrandom two liquid−electrolyte model. Both models used show good agreement with the experimental data.

Introduction

Presently, isoamyl alcohols (a mixture of 2-methyl-1-butanol and 3-methyl-1-butanol) are routinely obtained as a byproduct during ethyl alcohol production after wine and similar raw material distillation. Because of their low water solubility, they concentrate at the bottom of distillation towers and have to be removed to improve the column operation.[1]

Nevertheless, this situation needs to be radically changed because of an increasing demand for flavor compounds within the food industry.[2] It is therefore of primary interest to design distillation processes that focus on the recovery and use of these byproducts, as well as on optimization of the operating conditions and on the overall yield. In this aspect, the extractive distillation with salts could improve the effectiveness of the process, since the presence of a soluble salt can modify the relative volatility of the system by alteration of the vapor−liquid equilibrium (VLE). It could even produce the inversion of this VLE and/or the formation or destruction of azeotropes.[3−5]

To be able to design any distillation process, it is first necessary to know equilibrium phase data of the system of interest at the different operating conditions. Once the equilibrium data are known, one will be able to develop models that allow the prediction of the system behavior whatever the changes of the operating conditions.

To find the parameters in these proposed models, generally only pure component data and the different involved binary subsystems will be needed. Keeping in mind that wine consists mainly of water, ethanol, and isoamyl alcohols, the different binary subsystems would be water + ethanol, water + isoamyl, and ethanol + isoamyl alcohol. If a calcium chloride salt is also added to perform an extractive distillation, more subsystems such as water + calcium chloride, ethanol + calcium chloride, and isoamyl alcohol + calcium chloride would have to be considered. Among these, just isoamyl + water and isoamyl + calcium chloride data are not available, while the remaining ones have been widely studied.[6−11]

This is the reason that this work was focused on obtaining vapor pressure−temperature data of the 2-methyl-1-butanol + calcium chloride subsystem, at several salt concentrations, ranging from a very low one up to saturation (1.1 to 10.5) mass %. Pressure was increased from (23.3 to 96.6) kPa.

The determination of the $CaCl_2$ solubility in 2-methyl-1-butanol at different temperatures (from 75 to 130) °C has allowed the establishment of the saturation concentration.

The vapor pressure data obtained have been correlated by using two types of equations: one empirical Antoine equation that contemplates the presence of the dissolved salt and a thermodynamic model based on the concept of local composition, the nonrandom two liquid (NRTL)−electrolyte.

Experimental Section

Chemicals. 2-Methyl-1-butanol (99 mass %) was purchased from Aldrich, and anhydrouschloride calcium (95 mass %) was obtained from Panreac. They were used without further purification. $CaCl_2$ was previously dried at 120 °C in an oven.

Apparatus and Procedures. For the determination of the vapor pressure data of the 2-methyl-1-butanol + calcium chloride system, a modified Othmer still that was connected to a vacuum device was used (Figure 1). Auxiliary equipment includes a Crison 621 digital thermometer with six thermowells and an accuracy of ±0.1 °C, two mercury manometers with an accuracy of ±1 mm Hg, two heaters with a magnetic stirrer system from Selecta Agimatic, and a cryothermostatic bath from Hetofrig. The operating method was described in a previous paper.[12] The performance of this equipment was demonstrated by

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10.1021/je0340147 CCC: $27.50

Table 1. Boiling Points of 2-Methyl-1-butanol[a]

P/kPa	23.3	30.0	33.3	36.7	43.3	50.0	56.6	63.3	70.0	76.6	83.3	90.0	96.6
Dejoz et al.	91.4	97.2	99.7	102.0	106.1	109.8	112.9	116.0	118.7	121.2	123.6	125.8	127.8
This paper	91.7	97.3	99.9	102.0	105.9	109.6	112.5	115.8	118.5	121.0	123.5	125.7	127.9

[a] The temperature is expressed in °C.

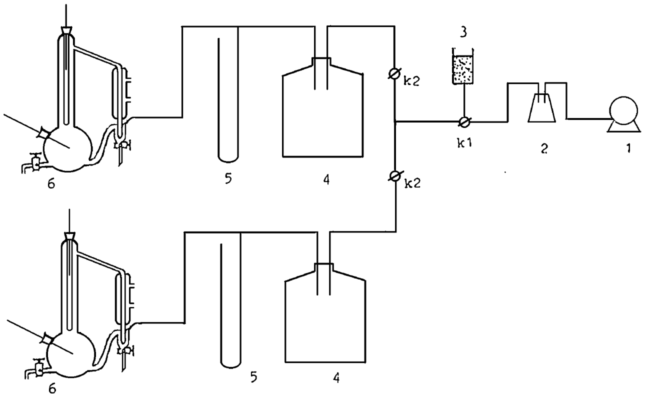

Figure 1. System used for the determination of low-pressure VLE: 1, vacuum pump; 2, trap; 3, drying vessel ($CaCl_2$); 4, pressure-controller vessel; 5, mercury manometer; 6, modified Othmer still.

comparing the experimental data of vapor pressure of pure 2-methyl-1-butanol and published values,[13] as reported in Table 1.

The exact amount of salt present in each one of the series of experiments was determined gravimetrically by weighing a sample taken from the reboiler. After the evaporation of the solvent and the drying of the salt, the sample was weighed again. Each determination was carried out three times. The estimated concentration error was found to be ±0.15%. This number is the standard deviation of the differences in the duplicate determinations of concentration.

Experimental Results

The determination of $CaCl_2$ solubility in 2-methyl-1-butanol at different temperatures allowed us to obtain the salt saturation concentrations in the temperature range studied. The correlation of the experimental data allowed the establishment of the following equation

$$w = -0.0023t^2 + 0.266t + 14.178 \qquad (1)$$

valid from 75 to 130 °C and with a determination coefficient very near to 1 ($R^2 = 0.999$), where t is the temperature in °C and w is the salt concentration in mass %.

The vapor pressure−temperature data of 2-methyl-1-butanol as well as those of different saline solutions are shown in Figure 2.

As expected, for an increasing concentration of salt, the temperature increases slightly. The increase of the latter is less than 2 °C regardless of the amount of added salt.

Empirical Equation. For the experimental data correlation, a modified Antoine equation was applied,[12] where the parameters take into account the salt concentration effect. The parameter (A, B, and C) values, for each salt concentration, have been calculated using a regression method with the objective function

$$F = \sum ((P_v)_{exp} - (P_v)_{cal})^2 \qquad (2)$$

Table 2 gives the A, B, and C parameters for all salt concentrations.

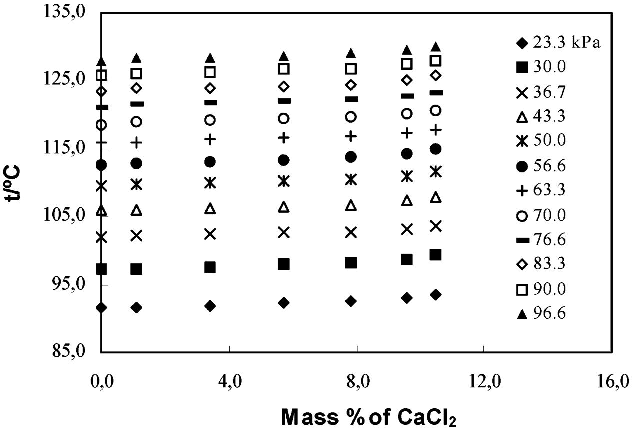

Figure 2. Boiling points of the 2-methyl-1-butanol + $CaCl_2$ (mass %) system, at different operating pressures.

Table 2. Antoine Equation Parameters[a] for the 2-Methyl-1-butanol + $CaCl_2$ System at Different Salt Concentrations (Mass %)

% $CaCl_2$	A	B	C
0.0	11.46	1454.03	−189.99
1.1	11.50	1490.10	−186.57
3.4	11.65	1555.16	−182.23
5.7	11.71	1572.44	−181.73
7.8	11.61	1533.81	−184.27
9.6	11.37	1427.60	−192.54
10.5	11.17	1354.47	−197.93

[a] $\ln(P_v/\text{kPa}) = A - \{B\}/\{(C + (T/\text{K}))\}$.

Table 3. Cubic Equation Coefficients for 2-Methyl-1-butanol + $CaCl_2$ System

2-methyl-1-butanol + $CaCl_2$	E_0	E_1	E_2	E_3	R^2
A	11.454	0.0458	0.0077	−0.0014	0.9987
B	1453.7	34.301	−0.0814	−0.3902	0.9994
C	−189.8	2.7997	−0.0927	−0.0236	0.9967

A dependence of the modified Antoine equation parameters (Table 2) on the amount of salt added was established. This relationship can be represented through a general equation give by

$$E = E_0 + E_1C_{sal} + E_2{C_{sal}}^2 + E_3{C_{sal}}^3 \qquad (3)$$

where C_{sal} is the salt concentration (%) and E is a parameter of the Antoine equation. The coefficient values of the cubic equation (eq 3) for each of the parameters (A, B, or C) are depicted in Table 3.

When the parameters have been included in the modified Antoine equation, it is possible to calculate the boiling temperature of the system for any pressure and salt concentration within the interval studied. These values, experimental and calculated, are given in Table 4.

When the calculated results are compared to the experimental ones, the standard deviation for the whole data set is $\sigma_m = 0.15$ °C. This result shows that the method applied

Table 4. Experimental and Calculated by Means of the Modified Antoine Equation Boiling Temperature Data of 2-Methyl-1-butanol + $CaCl_2$ System[a]

	2-methyl-1-butanol + $CaCl_2$											
	1.1%		3.4%		5.7%		7.8%		9.6%		10.5%	
P/kPa	t_{exp}	t_{cal}	t_{exp}	t_{cal}	t_{exp}	t_{cal}	t_{exp}	t_{cal}	t_{exp}	t_{cal}	t_{exp}	t_{cal}
23.3	91.7	91.9	91.9	92.0	92.2	92.0	92.5	92.5	93.1	93.2	93.6	93.6
30.0	97.3	97.5	97.6	97.7	97.9	97.6	98.2	98.1	98.6	98.7	99.4	99.1
33.3	99.9	99.9	100.1	100.1	100.3	100.1	100.6	100.5	101.3	101.1	101.6	101.5
36.7	102.2	102.2	102.4	102.4	102.6	102.4	102.7	102.8	103.2	103.4	103.7	103.8
43.3	106.1	106.2	106.2	106.4	106.4	106.4	106.8	106.8	107.4	107.4	107.9	107.8
50.0	109.8	109.8	110.0	110.1	110.2	110.1	110.4	110.4	111.0	111.1	111.6	111.4
56.6	112.9	113.1	113.1	113.4	113.4	113.3	113.7	113.7	114.3	114.3	114.9	114.7
63.3	116.0	116.1	116.3	116.4	116.7	116.4	116.8	116.7	117.2	117.3	117.7	117.7
70.0	119.0	118.9	119.2	119.3	119.5	119.2	119.6	119.5	120.1	120.1	120.6	120.5
76.6	121.5	121.5	121.8	121.9	122.0	121.8	122.2	122.1	122.7	122.7	123.1	123.1
83.3	123.8	124.0	124.0	124.3	124.2	124.2	124.5	124.5	125.0	125.2	125.7	125.5
90.0	126.0	126.3	126.2	126.7	126.7	126.5	126.8	126.8	127.5	127.5	128.0	127.9
96.6	128.3	128.4	128.5	128.8	128.7	128.7	129.0	129.0	129.5	129.6	130.0	130.0
σ^b	0.148		0.220		0.203		0.080		0.126		0.138	
$\sigma_m{}^c$	0.153											

[a] The temperature is expressed in °C and the salt concentration in mass %. [b] $\sigma = (\sum (t_{exp} - t_{cal})\ ^2/N)^{1/2}$ where N = number of data points. [c] σ_m is the mean of standard deviations.

Table 5. Parameters of the NRTL−Electrolyte Model

	2-methyl-1-butanol + $CaCl_2$												
P/kPa	23.3	30.0	33.3	36.7	43.3	50.0	56.6	63.3	70.0	76.6	83.3	90.0	96.6
α^a	1.123	1.149	1.143	1.094	1.073	1.111	1.090	1.094	1.109	1.102	1.121	1.151	1.116
$\tau_{i,ca}{}^b$	2.703	2.545	2.425	2.373	2.758	2.472	2.662	2.284	2.168	2.162	2.337	2.261	2.189
$\tau_{ca,i}{}^b$	8.989	8.992	8.985	9.123	8.976	9.168	8.968	8.899	9.024	9.090	9.162	8.993	9.100

[a] Dimensionless. [b] In units of J·mol^{-1}.

Table 6. Experimental and Calculated (by Means of the NRTL−Electrolyte Model) Boiling-Temperature Data of the 2-Methyl-1-butanol + $CaCl_2$ System[a]

	2-methyl-1-butanol + $CaCl_2$											
	1.1%		3.4%		5.7%		7.8%		9.6%		10.5%	
P/kPa	t_{exp}	t_{cal}	t_{exp}	t_{cal}	t_{exp}	t_{cal}	t_{exp}	t_{cal}	t_{exp}	t_{cal}	t_{exp}	t_{cal}
23.3	91.7	91.9	91.9	92.0	92.2	92.2	92.5	92.5	93.1	93.0	93.6	93.2
30.0	97.3	97.5	97.6	97.6	97.9	97.8	98.2	98.2	98.6	98.6	99.4	98.9
33.3	99.9	100.0	100.1	100.0	100.3	100.2	100.6	100.6	101.3	101.1	101.6	101.4
36.7	102.2	102.3	102.4	102.3	102.6	102.5	102.7	102.9	103.2	103.4	103.7	103.7
43.3	106.1	106.3	106.2	106.4	106.4	106.6	106.8	107.0	107.4	107.5	107.9	107.8
50.0	109.8	109.9	110.0	110.0	110.2	110.2	110.4	110.6	111.0	111.1	111.6	111.4
56.6	112.9	113.2	113.1	113.2	113.4	113.4	113.7	113.9	114.3	114.4	114.9	114.7
63.3	116.0	116.1	116.3	116.2	116.7	116.4	116.8	116.9	117.2	117.4	117.7	117.7
70.0	119.0	118.9	119.2	118.9	119.5	119.2	119.6	119.6	120.1	120.2	120.6	120.5
76.6	121.5	121.4	121.8	121.5	122.0	121.7	122.2	122.2	122.7	122.7	123.1	123.1
83.3	123.8	123.8	124.0	123.9	124.2	124.1	124.5	124.6	125.0	125.2	125.7	125.5
90.0	126.0	126.0	126.2	126.1	126.7	126.3	126.8	126.8	127.5	127.4	128.0	127.7
96.6	128.3	128.2	128.5	128.2	128.7	128.5	129.0	129.0	129.5	129.5	130.0	129.9
σ^b	0.147		0.171		0.206		0.118		0.130		0.230	
$\sigma_m{}^c$	0.167											

[a] The pressure is expressed in kPa, the temperature in °C, and the salt concentration in mass %. [b] $\sigma = (\sum (t_{exp} - t_{cal})^2/N)^{1/2}$ where N = number of data points. [c] σ_m is the mean of standard deviations.

is not only quite simple but also suitable for the study of extractive distillation.

Thermodynamic Model. When the NRTL−electrolyte[14] model is used with systems constituted by a solvent + salt, the equilibrium condition has to do solely with the solvent, since it is the only species present in both phases. For pressures equal or less than atmospheric, the following expression applies

$$P = \gamma_i P_i^{\circ} x_i \tag{4}$$

where P_i° is the vapor pressure of the pure solvent, γ_i is the activity coefficient of the solvent, and x_i is mole fraction of the solvent in the liquid phase. The vapor pressure of 2-methyl-1-butanol is given by the Antoine equation, whose coefficients are given in Table 2 while the activity coefficient, according to the NRTL−electrolyte model, is given by the expression

$$\ln \gamma_i = \frac{G_{ca,i}{}^2 \tau_{ca,i}(X_a + X_c)^2}{(G_{ca,i}(X_a + X_c) + X_i)^2} + \frac{G_{i,ca}\tau_{i,ca}X_cX_a}{(X_a + X_iG_{i,ca})^2} + \frac{G_{i,ca}\tau_{i,ca}X_aX_c}{(X_c + X_iG_{i,ca})^2} \tag{5}$$

where the subscripts ca, c, and a represent the salt, the cation, and the anion, respectively. In the following expressions, r indicates the number of ions (cations or anions) that are present in $CaCl_2$. Z_a and Z_c are the charge the of the anion and cation, respectively

$$G_{\mathrm{ca},i} = \exp(-\alpha\tau_{\mathrm{ca},i}) \tag{6a}$$

$$G_{i,\mathrm{ca}} = \exp(-\alpha\tau_{i,\mathrm{ca}}) \tag{6b}$$

$$X_i = \frac{x_i}{x_i + x_{\mathrm{ca}}(r_\mathrm{a} + r_\mathrm{c})} \tag{6c}$$

$$X_\mathrm{a} = X_\mathrm{c} = \frac{r_\mathrm{a}Z_\mathrm{a}x_{\mathrm{ca}}}{x_i + x_{\mathrm{ca}}(r_\mathrm{a} + r_\mathrm{c})} = \frac{r_\mathrm{c}Z_\mathrm{c}x_{\mathrm{ca}}}{x_i + x_{\mathrm{ca}}(r_\mathrm{a} + r_\mathrm{c})} \tag{6d}$$

Therefore, the activity coefficient depends on the composition of the liquid phase and on the three model parameters α, $\tau_{i,\mathrm{ca}}$, and $\tau_{\mathrm{ca},i}$. The disorder factor, α, in this model does not have the same physical meaning as that in the NRTL model; for that reason, it has been considered as a third adjustable parameter. The application of this model to experimental data has been carried out in a regression method with the objective function

$$F = \sum ((T)_{\mathrm{exp}} - (T)_{\mathrm{cal}})^2 \tag{7}$$

The equilibrium temperature is calculated with eq 4. In fact, this temperature is related to vapor pressure in the Antoine equation ($P°$).

The values of the adjustable parameters of 2-methyl-1-butanol + calcium chloride system, for each pressure, are given in Table 5.

Because none of the three parameters follows a clear dependence with pressure and because these values are quite close to each other, their arithmetic average was taken as a mean value for each parameter. Thus, the values found are

$$\tau_{i,\mathrm{ca}} = 2.411 \qquad \tau_{\mathrm{ca},i} = 9.036 \qquad \alpha = 1.113$$

With these three parameters of the model, the activity coefficient can be calculated for any composition of the liquid phase (eq 5). Then, the boiling temperature are calculated again at the operating pressure (eq 4).

By comparison of the boiling temperature experimental data with those calculated by means of the NRTL−electrolyte model, it was found that the standard deviation of all the data is σ_m = 0.17 °C (Table 6). This is an acceptable deviation, which indicates that the model is in good agreement with experimental data.

Summary

According to the results obtained, we can conclude that both models (the modified Antoine as well as the NRTL−electrolyte model) are suitable to fit the equilibrium data for 2-methyl-1-butanol + calcium chloride system with great precision. This is the reason we can use either model to predict this system behavior for any operating condition as well as for any salt concentration within the interval studied.

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Received for review January 16, 2003. Accepted March 19, 2004.

JE0340147