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REMOVAL OF A SMALL AMOUNT OF METHYLENE CHLORIDE IN ACETONE BY EXTRACTIVE DISTILLATION EMPLOYING SALT AS SEPARATING AGENT*

MASASHI IINO, AKIRA NAKAE**, JIRO SUDOH, MITSUHO HIRATA AND YASUO HIROSE

Chemical Engineering Laboratory, Tokyo Metropolitan University, Tokyo, Japan

Vapor-liquid equilibrium data at one atmosphere are studied for the system methylene chloride-acetone-salt. The salts ZnBr_2 , ZnCl_2 , KSCN , MnCl_2 , NaI , CuCl_2 , CaCl_2 , NH_4NO_3 and LiNO_3 are examined to observe the salt effect on the methylene-chloride-acetone system. Effective salts are ZnBr_2 , ZnCl_2 and KSCN , which are more soluble in acetone than are MnCl_2 , NaI , CuCl_2 , CaCl_2 , NH_4NO_3 and LiNO_3 . An increase of relative volatility of methylene chloride was observed by adding these salts. By extractive distillation with zinc bromide, high-purity acetone with a methylene chloride content of 0.09 (mole %) or less was obtained.

Solutions of acetone containing a small amount of methylene chloride are found in the recovery and reworking of tars in gas manufacture, solvent refining of lubricating oil and separation of close-boiling hydrocarbons by azeotropic distillation. The economical separation of the methylene chloride from such mixtures of acetone by normal distillation methods is precluded by adverse vapor-liquid equilibrium relationships in the usual commercial range of operating pressures and temperatures. There is imposed the further handicap of the existence of a tangent azeotrope³⁾ undesirably high in acetone concentration (about 96.0 mole %) which normally does not yield suitable further enrichment of acetone by simple distillation. It will be found that the separation of methylene chloride-acetone mixtures by atmospheric pressure fractional distillation can be accomplished only at total reflux, with maximum enrichment limited to the tangent azeotrope composition of about 96.0 mole% acetone. Recourse may then be had to separation of these mixtures by extractive distillation. In general the unit operation of extractive distillation employing liquid separating

agents is a well-known technique. However, it has been adequately demonstrated both in theory^{5,7)} and by vapor-liquid equilibrium measurements^{4,6)} that non-volatile, soluble salts also can have quite marked effects on equilibrium vapor compositions in a volatile system. For example, Johnson⁴⁾ reported sodium chloride saturated in ethanol-water system shifts the azeotropic composition from 87 to over 90 mole% ethanol and Hashitani et al.²⁾ also studied calcium chloride saturated in the ethanol-water system eliminates the azeotrope.

In this work, nine salts as separating agent for extractive distillation were examined to observe the salt effect on the methylene chloride-acetone system. The three effective salts tried, as can be seen from **Table 1**, were ZnBr_2 , ZnCl_2 and KSCN . Therefore, isobaric vapor-liquid equilibrium data at atmospheric pressure were measured for the system: methylene chloride-acetone with ZnBr_2 , ZnCl_2 and KSCN . ZnBr_2 was the best salt used as separating agent for extractive distillation to remove a small amount of methylene chloride from acetone. The extractive distillation in which zinc bromide was fed gave good results. Experimental results are presented and discussed.

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** Chemical Engineering Laboratory, Toa Oil Co., Kawasaki, Japan

1. Search of Salts as Separating Agent for Extractive Distillation

At first, an attempt was made to find an effective salt as separating agent for extractive distillation to separate methylene chloride from acetone. Generally, the salt effect on vapor-liquid equilibrium may be predicted by the solubility of salt in each component. If the salt is more soluble in a less volatile component, then the relative volatility will be raised, because of the lowered vapor pressure of the less volatile component. In this case, the salts must be more soluble in acetone, the less volatile component, thus increasing relative volatility. Therefore, isobaric vapor-liquid equilibrium at atmospheric pressure in about 15 mole% of methylene chloride composition was examined to observe the effect due to salt addition for the system; methylene chloride-acetone with ZnBr_2 , ZnCl_2 , KSCN , MnCl_2 , NaI , CuCl_2 , CaCl_2 , NH_4NO_3 and LiNO_3 . These salts were added up to the saturated concentration except for ZnBr_2 (at 50 wt%). The efficacy of the various salts tried is compared in Table 1. According to the results, the three desirable salts are ZnBr_2 , ZnCl_2 and KSCN . The effect is $\text{ZnBr}_2 > \text{ZnCl}_2 > \text{KSCN}$. As for the other salts, little effect is noticed at high acetone concentrations because of slight solubility in acetone. Experimental procedure and analysis are described in the following section.

2. Measurements of Vapor-Liquid Equilibrium

In the previous section, it was obvious that the salts effective as separating agent for extractive distillation to remove a small amount of methylene chloride in acetone were ZnBr_2 , ZnCl_2 and KSCN . Therefore, in a complete range, vapor-liquid equilibrium data were measured to observe the salt effect of ZnBr_2 , ZnCl_2 and KSCN for the system methylene chloride-acetone.

2.1 Materials

Salts used for experiments were commercially available reagents. ZnBr_2 , ZnCl_2 , NaI , CaCl_2 and LiNO_3 were prepared by heating in a furnace to 200 °C in 20 mmHg vacuum, and KSCN , MnCl_2 , CuCl_2 and NH_4NO_3 to 150°C in 10 mmHg vacuum. The dried salts contained less than 0.2 wt% water. A comparison of our values with accepted values for the two starting materials, methylene chloride and acetone, is shown in Table 2. The methods used to purify the materials are described below. The acetone was dried over calcium chloride and then distilled by a 5 ft fractionating packed column three times. The methylene chloride was distilled by the same column twice.

2.2 Experimental procedure and analysis

The apparatus employed was a Smith-Bonner type still⁸. The still was fitted with a ground glass standard-taper thermometer graduated in one-degree increments which could be read within ± 0.5

Table 1 Salt effect of nine saturated salts on methylene chloride(1)-acetone(2) system (1 atm)

No.	Salts	Salt effect		t [°C]
		x_1	y_1	
1	ZnBr_2^*	0.1488	0.4435	66.0
2	ZnCl_2	0.1471	0.2021	55.8
3	KSCN	0.1500	0.1981	57.0
4	MnCl_2	0.1516	0.1900	55.6
5	NaI	0.1509	0.1874	59.7
6	CuCl_2	0.1515	0.1798	54.2
7	CaCl_2	0.1485	0.1775	56.8
8	NH_4NO_3	0.1520	0.1771	56.0
9	LiNO_3	0.1485	0.1715	56.8

* salt: 50 wt%

Table 2 Properties of materials

	Methylene chloride		Acetone	
	Exptl.	Lit.(1)	Exptl.	Lit.(9)
Refractive Index, n_D^{25}	1.4221	1.4212	1.3562	1.3566
Density, d_4^{25}	1.3169	1.3163	0.7847	0.7850
Boiling point, 760 mmHg, °C	40.00	39.75	56.30	56.15

Table 3 Refractive index at 25.0°C of mixtures of methylene chloride and acetone

mole% methylene chloride	n_D^{25}
0.00	1.3562
2.31	1.3575
4.40	1.3591
8.36	1.3613
11.86	1.3635
15.49	1.3653
21.58	1.3684
31.62	1.3730
40.04	1.3791
50.24	1.3857
60.23	1.3919
70.07	1.3988
83.96	1.4093
90.08	1.4142
100.00	1.4221

°C. The volume of the still were approximately 700 ml. At the beginning of the experiments with any given salt, the still was charged with a solution of the salt containing approximately 2 mole% methylene chloride and 98 mole% acetone, salt-free basis. Additional salt was added to provide precipitated salt at the bottom of the still at all times. All solutions except for ZnBr_2 were saturated as it was thought that the greatest effect would thus be observed. Care was taken not to obstruct the circulatory system of the still with salt. Salt in the circulatory system would greatly increase the bumping hazard. All runs were of a minimum duration of 2 hours, which was the time required to reach equilibrium.

The temperatures were then recorded and a 5 ml condensate sample was drawn off through the auxiliary cooler into a weighed 10 ml graduate immersed in ice to prevent evaporation losses. The concentrations of methylene chloride in the equilibrium liquid

Fig. 1 x - y curves of methylene chloride(1)-acetone(2) system with ZnCl_2 at 1 atm

Table 4 Vapor-liquid equilibrium data for methylene chloride(1)-acetone(2) with saturated ZnCl_2 (1 atm)

x_1	y_1	$t[^\circ\text{C}]$
0.0296	0.0310	57.3
0.0303	0.0334	57.2
0.0625	0.0653	57.1
0.1008	0.1290	56.8
0.1471	0.2021	55.8
0.2502	0.3365	55.7
0.3360	0.4518	55.0
0.3632	0.5173	54.0
0.5244	0.7586	50.4
0.7531	0.9245	44.8
0.8680	0.9810	41.7

phase were calculated by mass balance, using the concentration of methylene chloride and acetone in the original charge and the analyzed concentrations of methylene chloride and acetone in the equilibrium vapor condensate samples. The holdup in the vapor phase chamber and condenser was neglected, because it was only 3 to 5 cc, approximately 1 % of the still charge. Only the equilibrium vapor condensate samples were analyzed. Salt concentrations only for ZnBr_2 were calculated by the original charge of each component. The vapor condensate samples were analyzed by refractive index. All refractive index measurements were made in an Abbe refractometer in sodium light at 25°C . Data obtained on refractive index of mixtures of methylene chloride and acetone are given in Table 3.

2.3 Data and results

The data for the methylene chloride-acetone systems saturated with zinc chloride and potassium thiocyanate are shown in Figs. 1 and 2 and presented in Tables 4 and 5. The data for the system with zinc bromide, at 10 to 50 wt% salt are shown in Fig. 3 and presented in Table 6. It was impossible to obtain a complete range of data for a saturated zinc bromide solution as zinc bromide decomposes at 97.5°C .

A comparison of the data obtained in this work with the available published data³⁾ at atmospheric

Fig. 2 x - y curves of methylene chloride(1)-acetone(2) system with KSCN at 1 atm

Fig. 3 x - y curves of methylene chloride(1)-acetone(2) system with ZnBr_2 at 1 atm

pressure and in the absence of salts is illustrated in Fig. 1, 2 and 3. Concentrations of methylene chloride are expressed in mole fraction of the binary mixture (salt-free basis). Concentrations of zinc bromide are expressed in weight percent in the solution. Figs. 1 and 2 show that the presence of the salt does not affect so remarkably the vapor-liquid data as zinc bromide. However, Fig. 3 shows relative volatility of methylene chloride to acetone increases markedly with increasing zinc bromide concentrations at high acetone concentrations.

It is obvious from these equilibrium data that a mixture in which concentration of acetone is higher than that of the tangent azeotrope may be easily obtained by the extractive distillation of reflux containing zinc bromide. The mixture may also be obtained when a tangent azeotrope containing zinc bromide undergoes a simple distillation. The elimination of the tangent azeotrope suggests that the salt effect of zinc bromide may be utilized effectively for the separation of a small amount of methylene chloride from acetone. The distillations for the removal of methylene chloride from acetone with various concentrations of zinc bromide are described in the following section.

Table 6 Vapor-liquid equilibrium data for methylene chloride(1)-acetone(2) with ZnBr_2 (1 atm)

about 10 wt%			Concentrations of zinc bromide about 30 wt%			about 50 wt%		
x_1	y_1	t [°C]	x_1	y_1	t [°C]	x_1	y_1	t [°C]
0.0258	0.0275	57.0	0.0254	0.0403	60.3	0.0301	0.0764	69.7
0.0535	0.0593	57.0	0.0372	0.0647	60.3	0.0422	0.1090	69.0
0.0860	0.1028	56.6	0.0550	0.0936	60.0	0.0527	0.1986	69.0
0.0907	0.1072	56.6	0.0823	0.1404	59.9	0.0929	0.3024	67.9
0.1431	0.1700	56.5	0.1218	0.2202	59.5	0.1152	0.3582	67.2
0.1849	0.2442	56.0	0.1945	0.3701	58.5	0.1488	0.4435	66.0
0.2124	0.2968	56.0	0.2522	0.4730	57.1	0.1818	0.5261	64.9
0.2793	0.4005	55.2	0.3130	0.5798	55.9	0.2426	0.6400	62.2
0.3779	0.5083	53.9	0.4195	0.6869	54.0	0.3075	0.7693	58.7
0.4831	0.7101	51.9	0.5531	0.8525	50.5	0.4004	0.8760	53.5
0.6800	0.8729	47.1	0.6814	0.9433	46.5	0.5280	0.9435	47.5
0.8524	0.9754	42.5	0.7893	0.9807	42.1	0.6491	0.9832	43.3
0.9212	0.9967	41.0	0.8495	0.9852	41.1	0.7003	0.9884	41.7

Table 5 Vapor-liquid equilibrium data for methylene chloride(1)-acetone(2) with saturated KSCN (1 atm)

x_1	y_1	t [°C]
0.0133	0.0175	58.0
0.0450	0.0652	57.4
0.0604	0.0860	57.2
0.0862	0.1229	57.1
0.1098	0.1350	57.0
0.1500	0.1981	57.0
0.1766	0.2459	56.8
0.2695	0.3553	56.5
0.3751	0.4691	53.2
0.4800	0.6064	51.3
0.6472	0.7970	47.5
0.7852	0.8905	44.1
0.9111	0.9563	41.3

3. Experimental of the Batch Distillation Column

3.1 Apparatus and methods

All of the distillations were made in a 2 inch diameter glass distillation column having a 5 ft packed section of $1/4 \times 1/4$ inch Raschig rings. The apparatus is shown in Fig. 4. This column showed the equivalent of 9 theoretical plates when tested at total reflux with an isopropanol-water mixture.

Thermocouples for temperature measurement are located at various points throughout the apparatus. The boil-up rate is about 1.5 liter per hour. 1.0 liter of methylene chloride-acetone mixture is charged to a glass still equipped with the column to startup. The reflux stream is returned to the top of the column through the salt feed apparatus, which is fitted with a reflux heater and a condenser.

In the present apparatus, operation is transient until salt concentration in the still balances with that of the reflux stream. When steady-state operation has been achieved, 10 ml samples are withdrawn from the overhead product. Simultaneously, vapor samples instead of liquid samples of the bottom are withdrawn into sampling traps equipped with overflow-final condenser tubes and immersed in ice-water slurries, because it is very burdensome to separate salt from liquid samples of the bottom by means of complete vaporization. All samples are stoppered and chilled immediately on withdrawal from the

Fig. 4 Apparatus of distillation with reflux containing salt

column to prevent loss of vapor. Analysis of samples is made by refractive index.

3.2 Experimental results

The data reported in Table 7 are all taken at total reflux. 10 runs were made both with salt at various concentrations, and without salt for comparative purposes. Of these, all runs in which salt was fed (Runs 4,5,6,8,9 and 10) successfully broke the methylene chloride-acetone tangent azeotrope (which occurs at about 4 mole% methylene chloride), despite the fact that in each case the feed composition to the column was higher in methylene chloride than for each of the control runs without salt (Runs 1, 2 and 3). The composition is even more striking with Runs 7-10. Run 3 (without salt) and Runs 4, 5 and 6 (with salt) have quite similar feed compositions, and so do Run 7 (without salt) and Runs 8, 9 and 10 (with salt). The large effects of even modest salt concentrations on the composition of the overhead product stream are clearly evident. In none of these experiments were any traces of entrained salt detected in the overhead product.

Table 7 Extractive distillation with reflux containing zinc bromide

Run No.	Feed composition mole% methylene chloride	Salt concentration C [wt%]	Vapor composition of bottom product, mole% methylene chloride
1	12.00	0	6.50
2	5.35	0	4.55
3	4.65	0	4.50
4	4.65	about 10	1.75
5	4.65	about 30	0.72
6	4.65	about 50	0.41
7	3.20	0	2.75
8	3.20	about 10	0.31
9	3.20	about 30	0.11
10	3.20	about 50	0.09

Conclusions

Vapor-liquid equilibrium data at atmospheric pressure of the system: methylene chloride-acetone with zinc bromide, zinc chloride and potassium thiocyanate are measured. The increase of relative volatility of methylene chloride at high acetone concentrations is noticed when zinc bromide is added in the methylene chloride-acetone mixtures. Moreover, the addition of zinc bromide is confirmed to eliminate the tangent azeotrope. By extractive distillation employing zinc bromide as separating

agent, the methylene chloride content of acetone can be reduced to 0.09 mole% or less.

Nomenclature

C = salt (wt%) in methylene chloride-acetone-salt liquid phase

x_1 = mole fraction of methylene chloride in liquid phase (salt-free basis)

y_1 = mole fraction of methylene chloride in vapor phase

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CALCULATION OF MULTICOMPONENT DISTILLATION ACCOMPANIED BY A CHEMICAL REACTION*

ISAO SUZUKI, HIROSHI YAGI, HIROMASA KOMATSU AND MITSUHO HIRATA

Department of Industrial Chemistry, Faculty of Engineering, Tokyo Metropolitan University, Tokyo, Japan

Iterative method for the determination of stage temperatures, stage reaction rates and interstage flow rates in the problem of multicomponent distillation accompanied by a simultaneous chemical reaction is discussed, and the use of a modified Muller's method for the convergence of the column temperature profile is proposed. Derivation of the equation is simplified by using matrix notation, which also has the advantage that any interstage flow pattern is allowed. For the solution of the linearized material balance equation, the tridiagonal matrix algorithm is employed. Some problems are discussed to demonstrate the feasibility of the calculations and the fact that quadratic convergence is obtained.

The distillation column reactor in which reactions occur during the rectification, is used in the continuous production of esters. The theoretical basis for its design problems has been proposed by Othmer and coworkers^{3,7)}, Marek⁸⁾ and Belck²⁾. But as there

are considerable difficulties in solving a exact design problem, they used manual plate-to-plate calculations with very rough approximations in vapor-liquid equilibrium and reaction rate relations.

In the previous paper⁶⁾, we described experimental results for the continuous production of ethyl acetate

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