Method for determining the composition of aqueous highly concentrated salt mixture solutions by attenuated total-reflectance IR spectrometry

N. Yoshikawa[a], Y. Ueda[a] and H. Ohya[b]

[a] Sea Water Science Research Laboratory, The Salt Industry Center of Japan, 4-13-20 Sakawa, Odawara, Kanagawa 256-0816, Japan

[b] Department of Material Science and Chemical Engineering, Faculty of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya, Yokohama, Kanagawa 240-0067, Japan

In the table-salt manufacturing process, the mother liquid and the concentrated brine in a crystallizer are highly concentrated salt-mixture solutions comprising NaCl, $MgCl_2$, KCl and $CaCl_2$, and a determination of their concentrations plays an important role. A method is proposed to determine the concentration of each component in the mother liquid and the concentrated brine using the absorbance change relative to the water absorption at six wavenumbers by attenuated total-reflectance IR (ATR-IR) spectrometry; an experimental confirmation can be used to accurately determine the composition. In particular, for $MgCl_2$, whose spectral change is larger than that of the other components, its concentration can be quantitatively determined with an accuracy nearly equal to that of a chemical analysis.

1. INTRODUCTION

In Japan, almost all of the commercially available salt is produced by crystallizing NaCl from brine obtained by concentrating seawater using an ion-exchange membrane electrodialyzer [1]. The main component of the mother liquid and the concentrated brine in the crystallizer is NaCl, and their impurities are $CaCl_2$, $MgCl_2$, KCl and so on. This composition varies with the concentrating conditions and affects the quality of the product salt [2]. Therefore, determining the composition plays an important role in the quality control of the product salt. Furthermore, from the view point of automation, labor saving and optimization of the salt manufacturing processes, it will be necessary to research and develop a method of an on-line quantitative determination that can determine the concentrations of the components of the mother liquid and the concentrated brine.

The IR method can be used to identify any organic substance and to quantitatively determine its concentration if its solution to be analyzed has characteristic absorption bands [3]. Particularly, the ATR-IR method can be applied to a quantitative determination of the concentrations of aqueous organic solutions [4]. However, the inorganic components in the mother liquid and the concentrated brine do not show any characteristic IR absorption band. Therefore, the IR and ATR-IR methods can not be applied to identify inorganic substances and to determine their concentrations.

Ions in an aqueous solution are usually hydrated, and change the structure of water [5], thus resulting in changes of the normal vibration, the harmonic tone and the combination tone relative to the absorbance of water. It is well known that due to the sorts and concentrations of ions, the degrees of the changes in the absorbance of each vibraion of water are different. Nightingale measured the IR spectra of some aqueous salt solutions and proved that the wavenumbers of the water absorption are sifted and the width of the mesial magnitude is changed by hydration [6]. Also, Bergley *et al.* determined sodium chloride content in meat by near infrared method [7].

A method is proposed to wisely determine on-line the concentrations of the components of the mother liquid and the concentrated brine using the absorbance changes relative to the pure water absorption at the six wavenumbers by ATR-IR spectrometry.

2. EXPERIMENTAL

2.1. Measurement of the ATR-IR spectra

The ATR-IR spectra of the test solutions on a background of distilled water were measured with a FT-IR spectrometer (Applied Systems Inc. React-IR) and an ATR attachment (ZnS crystal). The measurement conditions were as follows: repetitive number of scanning, 128; measurement wavenumbers, ranging from 4000 to 800 cm^{-1}; resolution, 4cm^{-1}; measurement temperature of single-salt solutions, 20 ℃; and measurement temperatures of model solutions, 20, 40, 60 and 80℃.

2.2. Preparation of test solutions

Twenty kinds of aqueous single-salt solutions were prepared using reagent-grade NaCl, KCl, LiCl, CsCl, $CaCl_2$, $MgCl_2 \cdot 6H_2O$, $SrCl_2 \cdot 6H_2O$ and $BaCl_2 \cdot 2H_2O$ without further purification. The concentrations of the solutions tested are listed in Table 1.

Model solutions of the mother liquid and the concentrated brine containing three kinds of chloride salts ($MgCl_2$, KCl and $CaCl_2$) as impurities in a saturated NaCl solution were prepared as follows: ① A mixture of the three salts ($MgCl_2$, KCl and $CaCl_2$) of which the weight ratios are listed in Table 2, were added to the distilled water until the mixture did not dissolve; thus, 900 ml of the saturated impurity solution was prepared. ② One hundred milliliters of the distilled water was added to the solution. ③ NaCl was added to the solution until NaCl did not dissolve even after 10 minutes under solution agitation. ④ The ATR-IR spectrum was measured using 100 ml of the model solution without agitation; the sample solution was then returned and the procedure repeated (② to ④) 10 times, as shown in Fig. 1.

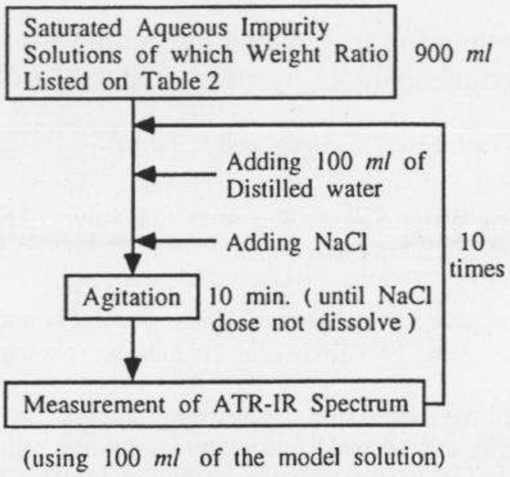

Fig. 1 Flow chart of the preparation method of the model solutions of the mother liquid and the concentrated brine.

Table 2 Concentration of impurities in saturated aqueous NaCl solutions

No.	Weight Ratio		
	$CaCl_2$	$MgCl_2$	KCl
1	1	2	1
2	1	2	2
3	1	2	3
4	1	3	1
5	1	3	2
6	1	3	3
7	1	4	1
8	1	4	2
9	1	4	3

Table 1 Salt species and concentration of aqueous single salt solutions

Concentration / M	NaCl	KCl	LiCl	CsCl	$CaCl_2$	$MgCl_2$	$SrCl_2$	$BaCl_2$
1	O	O	O	O	O	O	O	O
2	O	O	X	X	O	O	X	X
3	O	O	X	X	O	O	X	X
4	O	O	X	X	O	O	X	X

O: prepared; X: not prepared

2.3. Analysis

The concentrations of the components in the model solutions were analyzed using the method proposed by Japan Tobacco inc. [8]. The concentration of Cl^- (C(Cl)) was analyzed by a titration method using a 0.1 M silver nitrate solution and the concentrations of Ca^{2+} and Mg^{2+} (C(Ca) and C(Mg)) were analyzed by a titration method using a 0.01 M EDTA solution. The concentration of K^+ (C(K)) was analyzed by atomic absorption spectrochemical analysis; also, the concentration of Na^+ (C(Na)) was calculated based on the analytical values of other ions using the following equation:

$$C(Na)=C(Cl)-2(C(Mg)+C(Ca))-C(K). \qquad (1)$$

2.4. Identification of the spectra

The ATR-IR spectra of the model solutions of the mother liquid and the concentrated brine are shown in Fig. 2. The spectral absorption shows a H-O-H deformation vibration in a 1500-2200 cm^{-1} band, a harmonic tone of the H-O-H deformation vibration in a 2800-3200 cm^{-1} band, and an O-H stretching vibration in a 3500-3700 cm^{-1} band. The absorbances in these bands change according to the compositional ratio and the concentrations of the impurities.

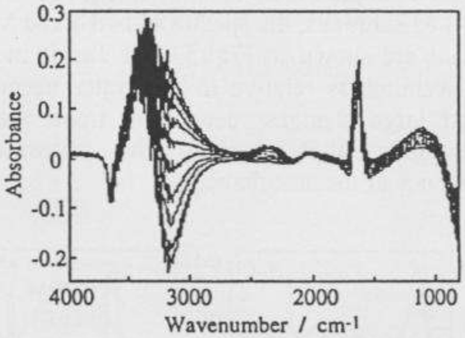

Fig. 2 ATR-IR spectra of the model solutions of the mother liquid and the concentrated brine in the crystallizer

3. RESULT AND DISCUSSION

3.1. Spectral changes of aqueous single-salt solutions

The spectra of 1 M aqueous chloride solutions of some monovalent and divalent cations are shown in Fig. 3. The spectral change of a LiCl solution was larger than that of the other monovalent cation solutions. The reason might have been due to the larger hydration energy of Li^+ than that of the other monovalent cations. The hydration Gibbs energies ($-\triangle Gh^0$) of monovalent cations become larger in the order $Li^+(510 kJmol^{-1}) > Na^+(410) > K^+(337) > Cs^+(283)$ [9]. On the other hand, the absorbance at 1710 cm^{-1} originates from the H-O-H deformation vibration, and that at 3150 cm^{-1} from the harmonic tone of the H-O-H deformation vibration. The values of the absorbance became larger in the order LiCl>NaCl>KCl>CsCl with the same tendency as the hydration energies of these cations.

The spectra of $SrCl_2$ and $BaCl_2$ solutions showed the same tendency, whereas the spectral changes of $MgCl_2$ and $CaCl_2$ solutions appeared to be larger than those of other divalent cation chloride solutions. The reason might be due to the larger hydration energies of Mg^{2+} and Ca^{2+} than those of other divalent cations. The vaues of the absorbances at 1710 cm^{-1} and around 3150-3160 cm^{-1} became larger in the order $MgCl_2 > CaCl_2 > SrCl_2 > BaCl_2$ with the same tendency as the hydration energies of cations.

Regarding the effect of the valences of the cations, the hydration energies of the divalent cations are larger than those of the monovalent cations; also, the spectral changes of the divalent cation chloride solutions were larger than those of the monovalent cation chloride solutions.

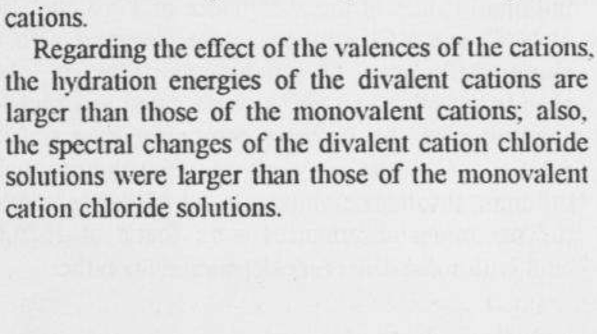

Fig. 3 ATR-IR spectra of some aqueous chloride 1 M solutions for studying the spectral changes of aqueous single-salt solutions.

These results suggest that the spectra of aqueous single-salt solutions change respectively due to the sorts of salts, thus making it possible to determine the concentrations of the components of the mother liquid and the concentrated brine using the absorbance changes at the wavenumbers relative to the water absorption.

3.2. Selection of the characteristic absorption band

The spectra of 1 M NaCl, KCl, $CaCl_2$ and $MgCl_2$ solutions are shown in Fig. 4. As for the absorbance of the 3650-3660 cm^{-1} band, which shows the O-H stretching vibration and the 3140-3160 cm^{-1} band, which represents the harmonic tone of the H-O-H deformation vibration, although a slight difference was observed only between KCl and NaCl solutions, a large difference was observed between monovalent and divalent cation chloride solutions. In particular, as for the absorbance of the 3140-3160 cm^{-1} band, a $MgCl_2$ solution had a positive value, whereas the other solutions had negative values. The absorbance of the 1500-2200 cm^{-1} band, which shows a H-O-H deformation vibration, varied largely depending upon each sort of cation. The minimun values of the absorbance of 1710 cm^{-1}, as in NaCl and KCl solutions, were observed with a slight difference. The minimum value of the absorbance of 1657.5 cm^{-1} was observed in a $MgCl_2$ solution, and the highest absorbance in a $CaCl_2$ solution. At 2230 cm^{-1}, all of the solutions had different absorbance values. In all of the solutions the maximum absorbances were found at 1626.6 cm^{-1} with some difference depending upon the valence of the cations. On the basis of the above discussion on the spectra of the aqueous single-salt solutions, the six measurement and reference wavenumbers given in Table 3 were selected. The wavenumbers is the best selection at present, but not critical. The difference in the absorbance of the measurement and reference wavenumbers will be offered for calculating the concentration of each salt. The details of the calculation will be discussed later.

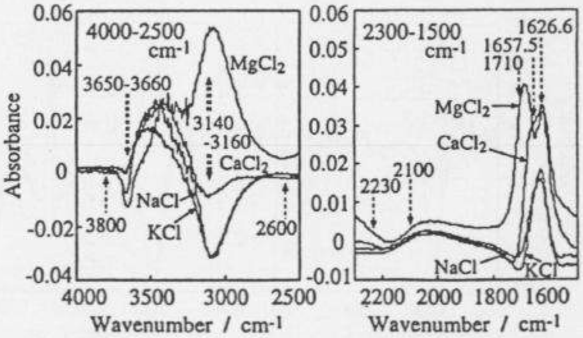

Fig. 4 ATR-IR spectra of aqueous chloride 1 M solutions for selecting the measurement and reference wavenumbers.

Table 3 Measurement and reference wavenumbers

No.	Wavenumber / cm^{-1}		Assignment
	Measurement	Reference	
1	3650-3660	3800	O-H stretching
2	3140-3160	2600	harmonic tone of H-O-H deformation
3	2230	2100	H-O-H deformation
4	1710	2100	H-O-H deformation
5	1657.5	2100	H-O-H deformation
6	1626.6	1657.5	H-O-H deformation

3.3. Effects of the concentration of aqueous single-salt solutions

As an example of the spectra of aqueous single-salt 1-4 M solutions, the spectra of NaCl and $MgCl_2$ solutions are shown in Fig. 5. The absorbances at the wavenumbers relative to the water absorption showed large changes, depending upon the salt concentration, thus showing the concentration dependency of the absorbance.

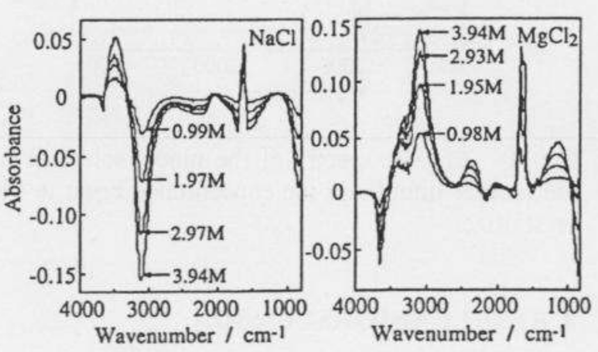

Fig. 5 ATR-IR spectra of aqueous chloride 1-4 M solutions for studying the effects of the concentration of aqueous single-salt solutions.

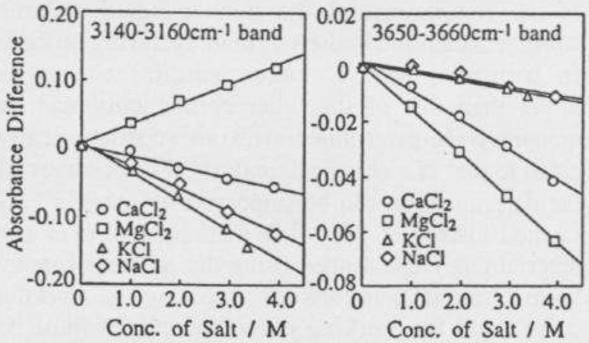

Fig. 6 Correlation between the salt concentration and the absorbance difference.

Figure 6 shows a correlation between the salt concentration and the absorbance difference of the 3140-3160 cm^{-1} band and the 3650-3660 cm^{-1} band. The concentration of each component had a linear correlation with the absorbance difference, with large differences in its slope. The gradient of the slope of the 3140-3160 cm^{-1} band depended upon the degree of hydration energy of each cation. The slopes of the 3650-3660 cm^{-1} band of NaCl and KCl solutions were slightly different, while the slopes of $CaCl_2$ and $MgCl_2$ solutions largely differed.

At other wavenumbers, some components were found to have linear correlations, and the other components secondary curvilinear correlations and sometimes non-linear correlations. Also, the differential coefficient of the absorabance to the concentration varied according to the components.

3.4. Analytical results

In a material comprising many components, the IR spectra of each component are generally affected by the other components in proportion to the contents of the respective components owing to mutual interference. Therefore, the concentrations of the respective components cannot be calculated from the absorbance of only one wavenumber as an independent variable. In such a case, a multiple-regression (MLR) method which takes account of the effects of the components is used for a quantitative determation of the concentrations of the components [10].

Aqueous multicomponent salt solutions do not have any characteristic absorption. However, the wavenumbers relative to the water absorption of such a solution changes characteristically, depending upon its components and their concentrations. Therefore, the regression coefficients of the MLR equation for model solutions of the mother liquid and the concentrated brine (as explained in previous paragraph) were calculated using the concentrations of the respective components taken as dependent variables and the values of the absorbance difference of six measurement and reference wavenumbers as independent variables:

$$C(i)=a(i,0)+\sum_{j=1}^{6}(a(i,j)A(j)), \qquad (2)$$

where C(i) is the concentration (%) of the i component (i=$CaCl_2$, $MgCl_2$, KCl, NaCl), A(j) is the absorbance difference (j=1,2,3,4,5,6), a(i,j) is a

Table 4 Regression coefficient and t-value calculated by the multiple-regression equation (Eq.(2)) at 20℃

j	C(CaCl2)		C(MgCl2)		C(KCl)		C(NaCl)	
	a(CaCl2,j)	t-value	a(MgCl2,j)	t-value	a(KCl,j)	t-value	a(NaCl,j)	t-value
0	5.50		4.01		15.20		-2.97	
1	151.82	5.15	-125.23	-7.15	-187.55	-5.42	-38.31	-0.91
2	48.29	3.76	4.84	0.63	60.06	3.98	-98.56	-5.35
3	-216.26	-1.35	-101.01	-1.07	-674.19	-3.60	800.63	3.50
4	-157.16	-3.50	55.26	2.07	-275.83	-5.24	258.66	4.02
5	11.90	0.77	10.51	1.14	-239.88	-13.16	155.29	6.97
6	137.13	7.37	-49.49	-4.48	14.63	0.67	-104.94	-3.94

C(i): concentration of i component; a(i,j): coefficient; i: component; j: no. of measurement and reference wavenumbers corresponding to No. in Table 3.

coefficient, and j is the No. of measurement and reference wavenumbers corresponding to No. in Table 3.

Table 4 gives the regression coeffcient and the t-value calculated by the MLR equation (eq.(2)) at 20℃. The t-value shows the contribution of the respective measurement wavenumbers based on the reference wavenumbers in determining the components. Each component had a different coefficient and t-value.

3.5. Calculation of concentrations

Figure 7 shows plots of the values of the concentration calculated using the regression coefficients shown in paragraph 3.4 versus the analytical values of the components. The plots of $CaCl_2$ and $MgCl_2$ were almost within the range of ±1.0 % dispersion, and the plots of KCl and NaCl were almost within the range of ±1.5 % dispersion. Also, the estimated values of the variances at 20℃ were 0.201 for $CaCl_2$, 0.071 for $MgCl_2$, 0.276 for KCl and 0.412 for NaCl.

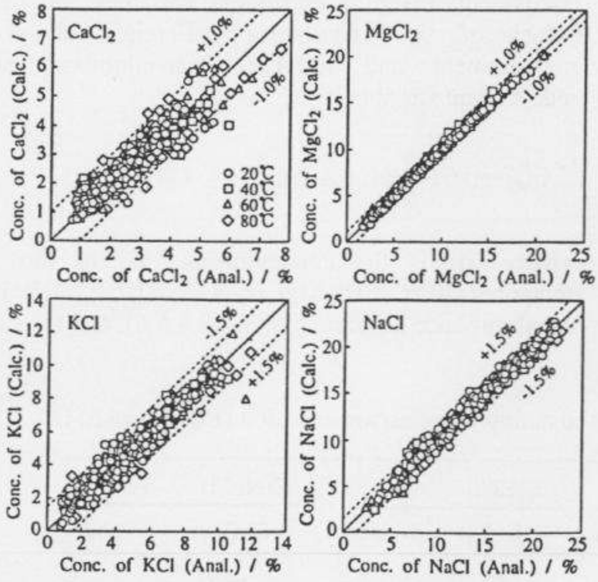

Fig. 7 Plots of the values of the concentration calculated using the regression coefficient shown in Table 4 versus the analytical values of the concentration of the components.

4. CONCLUSION

The results mentioned above prove that this method can accurately determine the concentrations of the components of the mother liquid and the concentrated brine in the salt manufacturing process. In particular, $MgCl_2$, whose spectral change is larger than that of the other components, can be quantitatively determined with an accuracy nearly equal to that of a chemical analysis. The accuracy of the determination can be improved by using a PLS method instead of the MLR method. However our determining method need using the spectra of many kinds of model solutions for preparing the working curve. And the working curve sometimes must be calibrated. For calibration using at most two or three kinds of standard solutions is desired. Therefore applying the PLS method to our determining method is difficult. Since the ZnS crystal used in the ATR attachment has a high water resistance, it can be adapted to long-run applications to the salt manufacturing process for an on-line quantitative determination by using the ATR attachment of flow cell type or probe type. Furthermore, considering the capability of this method for determining the concentrations of the components in aqueous inorganic salt solutions that do not show characteristic absorption, this method will be applicable to other aqueous inorganic and/or organic solutions.

REFERENCES

1. M. Hasegawa, H. Nishimura, K. Soga and S. Sugita, Bull. Soc. Sea Water Sci. Jpn., 39, 94 (1985).
2. N. Yoshikawa and M. Hasegawa, Bull. Soc. Sea Water Sci. Jpn., 45, 353 (1991).
3. R. O. Allen and P. Sanderson, Appl. Spectrosc. Rev., 24, 175 (1988).
4. D. K. Morgan, N. D. Danielson and J. E. Katon, Anal. Lett., 18, 1979 (1985).
5. H. S. Frank and W. Y. Wen, Disc. Faraday Soc., 24, 133 (1957).
6. E. R. Nightingale, "Chemical Physics of Ionic Solution", ed. B. E. Conway, p.95, John Wiley & Sons, New York, 1966.
7. T. M. Begley, E. Lanza, K. H. Morris and W. R. Hruschka, J. Agric. Food. Chem.,1984, 984.
8. Japan Tobacco inc. Salt Administration Headquarters, "Methods for salt analysis", 1989.
9. D. R. Rosseinsky, Chem. Rev., 65, 467 (1965).
10. M. Iwamoto, J. Jpn. Soc. Food Sci. Tech., 27, 464 (1980).

Salt Markets and applications

Chlor – Alkali Markets

Winter road maintenance

Salt in food and agriculture