Determination of the composition of H₂O/LiBr mixtures using sw-near infrared spectroscopy for absorption chillers

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Abstract

In this work the composition of the water/lithium bromide has been determined by Short-Wave Near Infrared Spectroscopy (SW-NIR). The relationship between the absorbance of the mixture in this spectral region, the lithium bromide mass fraction (0.05 - 0.65) and the temperature (323.15–343.15) K is established using experimental design techniques, consisting of a factorial multilevel in a 22 factorial design. The response measured is a global measure of the absorbance defined as the sum of the absorbance values of the water absorption band between 900 nm and 1050 nm. The significance of the effect of the variables in the response is assessed by ANOVA. Results obtained show that the mass fraction has a quadratic-type influence in the global absorbance, being for the temperature a linear-type influence. The model has been used to estimate the lithium bromide mass fraction in a set of test samples in order to evaluate the error, which was between 3 % and 7 %. The higher values are associated to low salt mass fractions in the mixture. However, the error for the representative samples in absorption chillers (0.35-0.65 in mass fraction range) was better than 3 %.

Keywords

Short-wave near infrared spectroscopy, lithium bromide/water mixtures, composition determination, experimental design.

1. Introduction

Water/lithium bromide mixture is one of the conventional working fluids used in absorption heat pumps and chillers, due to the favorable thermophysical properties of both the refrigerant (water) and the absorbent (aqueous solutions of lithium bromide). However, it also presents some drawbacks, such as its limited solubility, minimum chilled refrigerant temperature of 6 ºC to avoid the freezing of water, and the high corrosiveness of the salt solutions. These drawbacks could be critical for the performance of the systems [1] and limit the applications.

Therefore, the development of techniques for the in-situ determination of the salt solution composition is of great interest to control the working process of the chillers and heat pumps. Usually, the method used to determine the composition is through the measurement of the density using Coriolis flowmeters or vibrating tube densimeters. On the other hand, near-

infrared spectroscopy [2] is one of the more commonly used techniques for the in-situ analysis of samples because presents a low molar absorptivity of the compounds in the spectrum region. In the short-wave near infrared (SW-NIR) spectrum region [3] a strong absorption band around 985 nm associated to the stretching vibration of the OH functional group of the water is obtained.

So, it is expected that SW-NIR spectroscopy could be a good technique to determine the water mass fraction in the water/lithium bromide mixture, and in this work this characteristic is used to establish a methodology, based on the analysis of water-lithium bromide mixture in this region, to correlate the measured absorbance with the lithium bromide mass fraction in the mixture.

The relationship between the absorbance of the mixture, the temperature and the mass mass fraction is established using experimental design techniques [4-6]. The LiBr mass fraction range considered is from 0.05 to 0.65 and the temperature range from 323.15 K to 343.15 K. The experiments have been designed according a multilevel factorial in a 2^2 factorial design. The significance of the effects of the temperature and concentration in the absorbance is evaluated using the analysis of variance ANOVA [7].

2. Experimental Part

2.1 - Samples

26 aqueous solutions of lithium bromide (13 in duplicate) with a salt mass fraction between 0.05 and 0.65 were prepared by diluting an appropriate mass of LiBr previously dried in an oven at 353.15 K for 24 h. Samples were prepared by measuring the desired amount of lithium bromide and water on an analytical balance (Mettler Toledo, mod. HE403). The expanded uncertainty (k=2) was estimated to be less than 0.002 g. The samples were analysed at 323.15 K, 333.15 K and 343.15 K. For the preparation of the mixture, lithium bromide supplied by Sigma Aldrich (purity>99%) and ultrapure-Q water were used.

2.2 - Near infrared spectrum

Near-infrared measurements were taken between 850 nm and 1100nm. For each analyzed sample, the spectrum was acquired using the software of Maya2000 Pro VIS NIR spectrophotometer. The data vector contain 251 values related with the absorption intensity values recorder each 0.4 nm.

2.3 Pretreatment data

An off-set correction [8] was applied to each spectrum in order to suppress the vertical shift during the experiment caused by using a NIR spectrophotometer with only one light beam. This pretreatment involves subtracting the lowest value of absorption intensity for each individual spectrum from the values of absorption intensities recorded at each wavelength. Data pretreatment were carried out using MATLAB subroutines [9]**.**

2.4 Software

The spectrum was exported in ASCII format from the instrument software to MATLAB and the analyses were performed using statistical software Statgraphics 5.0 plus [10].

2.5 Plan of the experiments

The experimental design techniques enable to model a representative response of a process and evaluate the influence of the independent variables, minimizing the experimentation. In the present work, the process is the measurement of the water spectrum in the water/lithium bromide mixture in the near infrared region. The variables are the temperature and the LiBr concentration in the mixture, and the response is a global measure of the absorbance (A_G) obtained when the spectrum of each sample were recorded. A multilevel factorial with a 5-level factor and a 3-level factor in a 2^2 design has been chosen. The ranges considered for each variable are from 323.15 K to 343.15 K for the temperature and between 0.05 and 0.65 in salt mass fraction. The coded level for each variable and their experimental values are shown in Table 1.

Table 1. Experimental design for a multilevel factorial 5-level and 3-level factor in a 2^2 design.

	Coded levels				
	-1	*-0.5*	*0*	*+0.5*	*+1*
Independent variables	**Values of the independent variables**				
LiBr (mass fraction)	0.05	0.20	0.35	0.50	0.65
Temperature (K)	323.15		333.15		343.15

The experimental design was employed to obtain a model that explains the relationship between the variables and the response. Using the least squares method, a quadratic model represented by equation 1 was obtained.

$$A_G = a_0 + a_1 \cdot X + a_2 \cdot T + a_{12} \cdot X \cdot T + a_{11} \cdot X^2 + a_{22} \cdot T^2 \tag{1}$$

In this equation a_0 is a constant, a_1 and a_2 are linear coefficients, a_{12} is a cross-product coefficient, a_{11} and a_{22} are quadratic coefficients and X and T are the variables studied, salt mass fraction and temperature, respectively.

Using the analysis of variance (ANOVA) non-significant effects were rejected for the model regression. ANOVA allows determining which effects have significance at a given level. Each effect has a probability (P-value) and F-distribution (F-test) which indicates the significance of the effect. The fit of the model is given by the R^2 (correlation coefficient), which must be near 100%. This model has been used to estimate the lithium bromide concentration in a set test samples using their water spectrum in order to evaluate their deviation versus the experimental values.

3. Results

Figure 1 shows the water spectra registered between 850 nm and 1100 nm when several samples with a different lithium bromide concentration, were analysed at 323.15 K.
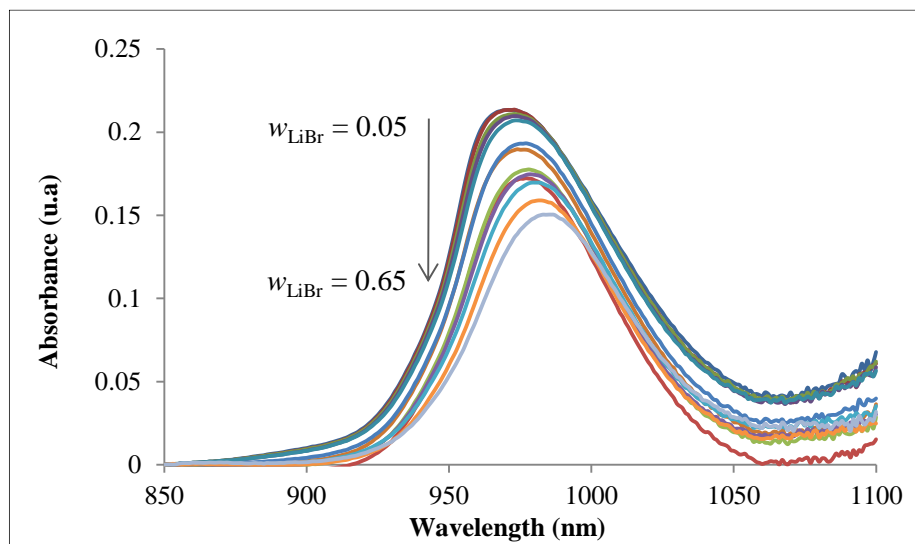
Figure 1. Near-infrared spectra recorded at 323.15 K for several samples of water/lithium bromide mixtures from 0.05 to 0.65 in salt mass fraction.

As can be expected, the intensity of the absorption band attributable to the stretching vibration of the OH functional group present in the water decreases when the LiBr concentration increases in the sample. In addition, it is observed a shift of the maximum of the absorption peaks to longer wavelengths. This behaviour is also observed when the samples are analysed at 333.15 K and 343.15 K.

Figure 2 shows the evolution of the intensity of the absorption band at the maximum of the peak, 985 nm, for all samples. It is possible to observe that the temperature affects to the absorbance, although the absorbance profile respect to the concentration seems not vary.
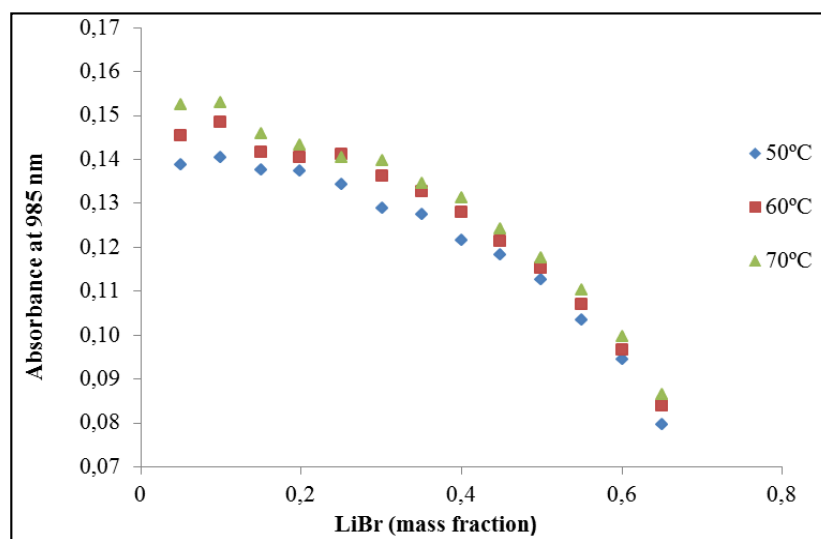

Figure 2. Absorbance profile at 985 nm of the water/lithium bromide mixture with the salt mass fraction, at different temperatures between 323.15 K and 353.15K.

In order to take into account the deformation of the absorption band when the composition changes, a global measurement of the absorbance has been chosen to obtain the statistical model that explains the relationship between the temperature and the composition with the

water absorption band measured. Therefore, the sum of the absorbance values between 900 nm and 1050 nm in the spectrum has been considered as response variable (A_G). The results obtained for the samples involved in the experimental design are shown in Table 2.a

Table 2. Experimental conditions (lithium bromide mass fraction and temperature) and results for (a) the designs experiments and (b) the set test used to validate the model.

Samples	$T = 323.15$ K		$T = 333.15$ K		$T = 343.15$ K	
X_{LiBr}	$A_G{}^*$ Rep*. 1	A_G Rep. 2	A_G Rep. 1	A_G Rep. 2	A_G Rep. 1	A_G Rep. 2
a) Experimental design samples						
0.05	5.0268	5.0345	5.1837	5.2247	5.3462	5.3865
0.20	4.8853	4.8757	4.9628	4.9979	5.0642	5.0172
0.35	4.5439	4.5381	4.6394	4.6532	4.6661	4.6823
0.50	4.0534	4.0425	4.1447	4.1567	4.1996	4.1775
0.65	3.3472	3.3612	3.4366	3.4168	3.5384	3.6382
b) Set test samples						
0.10	5.0209	4.9822	5.2182	5.1322	5.3049	5.2987
0.15	4.9254	4.9078	5.0493	5.0546	5.1592	5.1533
0.25	4.7804	4.7663	4.9435	4.9211	4.9603	4.9879
0.30	4.5952	4.5888	4.7564	4.7793	4.8324	4.8390
0.40	4.2935	4.2808	4.4617	4.4268	4.5327	4.5756
0.45	4,2194	4.2488	4.3311	4.3309	4.3749	4.3915
0.55	3.8277	3.8063	3.9626	3.9815	4.1143	4.0986
0.60	3.6172	3.6206	3.8154	3.8063	3.8116	3.8224

$A_G{}^*$: is the global absorbance calculated by the sum of the absorbance values between 900 nm and 1050 nm.
Rep[*]: Replicate

Table 3. Analysis of variance (ANOVA) for the global absorbance between 900 nm-1050 nm

Source of variation	Sum of squares	Df	Mean Square	F- Ratio	P- Value
LiBr concentration	11.2292	1	11.2292	18030.75	0.0000
Temperature	0.20152	1	0.20152	323.59	0.0000
LiBr concentration²	0.44908	1	0.44908	721.09	0.0000
LiBr concentration·Temperature	0.00496	1	0.00496	7.97	0.1098
Temperature²	0.00072	1	0.00072	1.16	0.5320
Lack-of-fit	0.03283	9	0.00365	5.86	0,4849
Pure error	0.00934	15	0.00062		

$R^2 = 99.57$ %

The influence of the variables in the global absorbance (A_G) was studied by ANOVA. The results at significance level of 95 % are shown in Table 3. The effect of the variables in the

absorbance with F<4.54 and P>0.05 exhibit a statistical significance level lower than 95 % and they must be rejected. This occurs for the interaction between $X \cdot T$ and T^2.

Thus, the obtained parameters for the equation 1 are: $a_0 = 1.88813$; $a_1 = -0.6093$; $a_2 = 0.010038$; $a_{11} = 3.24968$ and $a_{12} = a_{22} = 0$.

The response surface representative of the global absorbance of water/lithium bromide mixture in the experimental domain studied is shown in Figure 3. This plot allows analysing jointly the influence of the both variables (temperature and mass fraction).
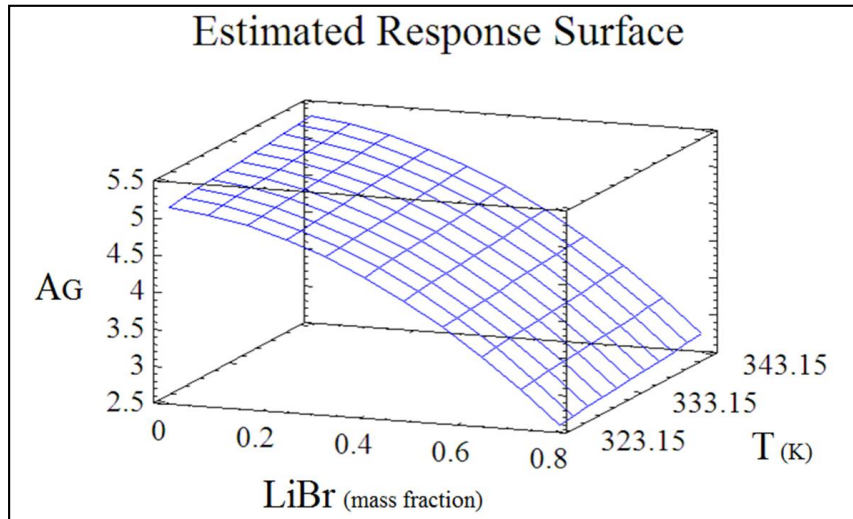

Figure 3. The response surface of the global absorbance of water-lithium bromide mixture in the experimental domain defined by LiBr concentration between (0.05-0.65) at the temperature between 323.15 K and 343.15 K.

The goodness of this model to estimate the salt composition in the water/lithium bromide mixture was assessed by comparing the values estimated by the model with the experimentally obtained values for the test samples (Table 2b). The results and deviations are shown in Table 4.

4. Conclusions

In this work has been probed that near infrared spectroscopy can be used to determine the lithium bromide composition in aqueous solutions.

In the considered mixtures, the absorbance measurement is representative of the water content in the mixture which is related with the lithium bromide concentration and with the temperature.

The global absorbance of the mixture follows a second order equation because the lithium bromide mass fraction has a quadratic-type influence in the global absorbance.

The near infrared spectroscopy can be incorporated to the in-situ analysis of these mixtures. So, this methodology could be used in the absorption refrigeration system in order to control their performance.

It is necessary remark that the present methodology only can be considered to determine lithium bromide in aqueous mixture.

Table 4. Comparison between the experimental and estimated lithium bromide mass fraction (X) using equation 2.

		T = 323.15 K		T = 333.15 K		T = 343.15 K	
	X experimental	X estimated	Deviation	X estimated	Deviation	X estimated	Deviation
Rep.1	0.10	0.12	0.02	0.02	0.08	0.03	0.07
	0.15	0.18	0.03	0.16	0.01	0.15	0.00
	0.25	0.25	0.00	0.22	0.03	0.26	0.01
	0.30	0.33	0.03	0.30	0.00	0.31	0.01
	0.40	0.42	0.02	0.40	0.00	0.41	0.01
	0.45	0.45	0.00	0.44	0.01	0.46	0.01
	0.55	0.55	0.00	0.54	0.01	0.52	0.03
	0.60	0.60	0.00	0.57	0.03	0.60	0.00
Rep.2	0.10	0.14	0.04	0.11	0,01	0.04	0.06
	0.15	0.19	0.04	0.16	0,01	0.16	0.01
	0.25	0.26	0.01	0.23	0,02	0.24	0.01
	0.30	0.33	0.03	0.29	0,01	0.31	0.01
	0.40	0.41	0.01	0.41	0,01	0.40	0.00
	0.45	0.44	0.01	0.44	0,01	0.45	0.00
	0.55	0.55	0.00	0.53	0.02	0.53	0.02
	0.60	0.60	0.00	0.58	0.02	0.59	0.01

The individual deviation for all the experiments ranges between 3 % and 7 %. The higher deviation values are associated to the lowest salt concentration in the mixture. However, the deviations for the samples representatives of the absorption chillers (0.35-0.65 in LiBr mass fraction) are better than 3 %.

Acknowledgments

References

[1] Herold K.E., Radermacher R., Klein S.A., Absorption Chillers and Heat Pumps, 1996, CRC Press.

[2] Hildrum K.I., Isaksson T., Naes. T., Tandberg A., Near infrered spectroscopy. Brinding the gap between data analysis and NIR applications, England: Ellis Horwood, 1992

[3] Burns D.A., Ciurczak E.W., Practical spectroscopy. Handbook of Near-Infrared Analysis. CRC Press 2008; 35(3): 521.

[4] Blackwell D., Solomon H., Introduction to experimental statistics. McGraw-Hill, 1964.

[5] Box G.E.P., Hunter W. G., Hunter J.S., Statistics for experimenters: an introduction to design, data analysis, and model building. John Wiley & Sons, 1978.

[6] Lazic Z R., Design of experiments in chemical engineering. Weinheim: Wiley-VCH, 2004.

[7] Massart D.L., Vandeginste B.G.M., Buydens L.M.C., De Jong. S., Lewi. P.J., Smeyers-Verbeke., Handbook of chemometrics and Qualimetrics Part A, Amsterdam: Elsevier, 1997.

[8] Kelly J.J., Barlow C.H., Jinnguji T.M., Callis J.B., Prediction of gasoline octane numbers from near-infrared spectral features in the range 660-1215 nm. Anal. Chem 1989; 61: 313-320.

[9] Matlab, The Mathworks, south Natick, MA, USA. http://www.mathworks.com/products/

[10] Statgraphics 5.0 plus: http://www.statgraphics.com