Properties of seawater bitterns with regard to liquid-desiccant cooling

G. Lychnos, J.P. Fletcher, P.A. Davies *

School of Engineering and Applied Science, Aston University, Birmingham, B4 7ET, UK

ARTICLE INFO

ABSTRACT

This study concerns the properties of the concentrated bittern solutions occurring as by-product from solar salt works, in relation to their potential use as liquid desiccants in cooling systems. Solutions of compositions similar to those of bitterns have been made up in the laboratory, as have concentrated mixtures of $MgCl_2$–$MgSO_4$–H_2O. Measurements of vapour pressure have been carried out using an isteniscope and are reported together with measurements of density and viscosity. Several theoretical models representing these properties are reviewed and compared against the experimental results; the average agreement between theory and experiment is within 5% for vapour pressure and better for the preferred models of the other two properties. Based on these findings, an expression is provided for the equilibrium relative humidity of bitterns as a function of concentration relative to raw seawater. The vapour pressures of bittern solutions are found to be similar to those of solutions containing only magnesium chloride but having the same mass fraction of total salts. Therefore magnesium chloride solution is a reasonable model for bitterns for the purpose of developing the proposed cooling system.

© 2009 Elsevier B.V. Open access under CC BY-NC-ND license.

1. Introduction

The processes of desalination and salt production yield substantial quantities of reject brines and bitterns. Ahmed and co-authors have drawn attention to the possibility of exploiting these by-products for uses that add value to desalination, in preference to regarding them as waste [1,2]. A potential example is to use hygroscopic solutions of sea salts, in particular magnesium chloride, as liquid desiccants in refrigeration systems. In a previous paper [3] we explored this possibility by comparing the properties of magnesium chloride to those of more conventional liquid desiccants, such as lithium chloride, lithium bromide, calcium chloride and tri-ethylene glycol. Though magnesium chloride is a somewhat weaker desiccant, it has the advantages of low cost, availability and low toxicity — properties which would be valuable in applications requiring large volumes of low-grade cooling [3]. One such example is the cooling of greenhouses for food production in hot and humid climates, such as the Gulf states, by means of systems driven by solar energy, as proposed in references [3], [4] and [5].

Magnesium chloride is abundant in seawater and is the main constituent of bitterns, the concentrated brine occurring in solar salt works. In these works, seawater is concentrated as it passes through a series of lagoons. Sodium chloride crystallises leaving the magnesium-rich solution, referred to as bitterns due to its bitter taste. Besides magnesium and chloride ions, however, bitterns contain

significant impurities including sulphate, sodium, potassium and calcium ions.

The overall aim of the current work is to develop a practical greenhouse cooling system using bitterns. As a first step in this development it is important to have relations for the properties of the working solution. The earlier studies mentioned above concluded that bitterns could serve as useful desiccant, but this conclusion was tentative in that it was based on the published properties of pure magnesium chloride solutions; the effects of the impurities were not taken into account [3,4]. The first objective of the work reported here is to determine more precisely the properties of concentrated seawater bitterns, specifically their vapour pressure (and therefore equilibrium relative humidity, ERH), density and viscosity, these being the properties of greatest interest in the design of a desiccant refrigeration system.

A second objective is to obtain theoretical models to predict these properties as a function of the composition, concentration and temperature. Such models would be needed as a tool in the design of any practical system.

While developing a prototype refrigeration system in the laboratory, it is sometimes convenient to obtain and use pure magnesium chloride reagent as opposed to the multi-component bitterns mixture. A third objective is therefore to quantify the difference between the properties of seawater bitterns and those of pure magnesium chloride solution, and therefore assess the validity of this experimental approach.

For a complex electrolyte solution such as bitterns, published data were not available and a number of competing theoretical models were identified, most of which were originally developed for more

* Corresponding author. Tel.: +44 121 204 3724.
E-mail address: p.a.davies@aston.ac.uk (P.A. Davies).

dilute solutions than those encountered here. Consequently an experimental study was needed.

It is noted that electrolyte solution theory is a well developed field and it is beyond the scope of this work to make any fundamental new contribution in this area. Instead the focus here is on finding results that will be practically useful in the context described above.

2. Theories of electrolyte solutions

The desired characteristics of the theoretical model are that it should be sufficiently accurate for engineering purposes and lead to concise and usable mathematical formulations. Further, an established theory is preferable to one that is entirely novel. Here we will briefly highlight the main features of the theories used in this study. For a more comprehensive review the reader is referred elsewhere [6–9].

Historically, research on modelling thermodynamic properties of electrolyte solutions has developed along two main lines as follows.

1) Fundamental electrolyte solution theories, as discussed thoroughly by Loehe and Donohue [7]. Generally these are too complex and do not lead to formulations that are convenient for the current purpose.
2) Engineering models of the empirical and semi-empirical kinds. These can be sub-divided in different categories according to the underlying physical concepts: (i) local composition-based models [10–13], (ii) adsorption-theory models [14,15], (iii) speciation-based models for mixed-solvent electrolyte systems [16,17], and (iv) empirical and semi-empirical models based on various theories including the Debye–Hückel relation [18–27]. In this study, we focus on the fourth of these options, as already adopted by El Gouendouzi et al., Ha and Chan and by Dinane and Mounir to predict water activity in electrolyte mixture solutions similar to seawater, but at lower concentrations or different compositions than in this study [28–31].

2.1. Vapour pressure and equilibrium relative humidity

In a desiccant refrigeration system, a property of prime importance is the equilibrium relative humidity (ERH) which compares the humidity of air in contact with the desiccant solution, to that of air in contact with pure water at the same temperature. By definition ERH must be in the range $0 < ERH \leq 100\%$. The ERH depends directly on the vapour pressure P of the solution, and in turn on the chemical activity a_w of the water in the solution, which is a fundamental thermodynamic property appearing in many of the standard theories available. In so far as the water vapour can be treated as an ideal gas, and assuming that the solute has zero vapour pressure, these quantities are related by the following expression:

$$ERH = P / P_0 = a_w \tag{1}$$

where P_0 is the vapour pressure of pure water at the temperature of interest.

In total six models of vapour pressure were considered. Their principal features are outlined below.

a) Pitzer's model [18–24,32] which is an extension to the Debye–Hückel theory. Starting from Bronsted's work [33] and improvements by Guggenheim [34] describing the properties of non-ideal gases, Pitzer extended the theory to electrolyte solutions while including the Debye–Hückel term to describe the long range forces (i.e. the electrostatic effects) in addition to the short-range forces of the earlier models. He refined this ion-interaction approach extending its applicability to mixed electrolyte solutions with ionic strength up to 6 m [18]. However, any modification of the model that has been made to date concerns specific electrolyte systems and there is no generalised form applicable to the majority of

strong electrolytes and their mixtures for concentrations higher than 6 m. The mathematical formulation of Pitzer's model is complex and the reader is referred to references [18] and [20] for more details. Based on this model, Harvie and Weare developed a chemical model for predicting mineral solubilities in brines of the seawater system Na–K–Mg–Ca–Cl–SO₄–H₂O at high concentrations [35]. Later on Harvie et al. successfully extended this model to more complex systems [36]. Krumgalz investigated the application of Pitzer's model to natural hypersaline brines and specifically to the Dead Sea based on parameters published by others for similar systems [37]. In this study, we have used the parameterisation of Harvie et al. [36], Harvie and Weare [35], Pengsheng and Yan [38] and Long et al. [39].

b) The model of Zdanovskii–Stokes–Robinson (ZSR) [27,30,40,41]. This is a simple empirical equation, first discovered by Zdanovskii empirically and later by Stokes and Robinson mathematically. The ZSR method can be described briefly by the following relationship:

$$\sum_i \frac{m_i}{m_i^S(a_w^M)} = 1 \tag{2}$$

where m_i represents the molality of each salt in the multi-electrolyte solution in which the water has activity a_w^M, and $m_i^S(a_w^M)$ is the molality of a solution of a single salt i in which the water has the same activity a_w^M.

This model requires the expression of the molality of any single salt in the solution as a function of water activity. Ha and Chan [30] reported the coefficients of the polynomial fits for this function for MgCl₂–H₂O and MgSO₄–H₂O, as shown in Table 1. In this study we additionally report in Table 1 the coefficients of polynomial fits to published experimental data for KCl–H₂O, CaCl₂–H₂O, NaCl–H₂O and LiCl–H₂O from reference [26]. Note that since a_w^M is implicit in Eq. (2), an iterative numerical procedure is used to solve for a_w^M and thus find ERH on the basis of Eq (1). Ha and Chan used the ZSR method to model successfully the properties of solutions containing high concentrations of MgCl₂ and MgSO₄, with application to inorganic aerosols [30].

c) The model of Kusik and Meissner (KM) [42] proposes the following equation for a multi-electrolyte solution containing cations $k = 1, 3, 5,...$ and anions $j = 2, 4, 6,...$

$$\log_{10} a_w^M = \sum_j \sum_k W_{kj} \log_{10}(a_w^s(I_T))_{kj} + \varepsilon \tag{3}$$

in which:

$$W_{kj} = X_k \cdot Z_j \tag{4}$$

where a_w^M is the water activity in the multi-electrolyte solution, X_k and Z_j are the cationic and anionic strength fractions respectively, the a_w^S terms are the activities of water in various single-salt solutions at the total ionic strength I_T of the multi-electrolyte solution, and ε is a residue term which is generally negligible.

Table 1
Coefficients in the polynomial $m = A_0 + A_1 \cdot a_w + A_2 \cdot a_w^2 + A_3 \cdot a_w^3 + A_4 \cdot a_w^4 + A_5 \cdot a_w^5$ for single-salt solutions at 25 °C as required by the ZSR model, obtained by fitting to data from reference [26], except in the case of MgCl₂ and MgSO₄ where the coefficients are those provided in reference [30].

Salt	A_0	A_1	A_2	A_3	A_4	A_5
MgCl₂	11.505	−26.518	34.937	−19.829	0	0
MgSO₄	−0.7776	177.74	−719.79	1174.6	−863.44	232.31
KCl	10.69	24.69	−49.35	13.95	0	0
CaCl₂	15.13	−38.52	49.16	−25.68	0	0
NaCl	55.08	−148.5	163.4	−69.98	0	0
LiCl	24.41	−58.79	72.61	−38.22	0	0

The model requires the expression of the water activities in single-salt solutions as a function of ionic strength. For this purpose, polynomial fits to published experimental data from reference [26] have been used. Note that the ionic strengths represent the stoichiometric values, not taking into account the possible formation of ion pairs or complexes.

Simplified versions of the KM equation were presented by El Guendouzi et al. and have been used here to predict the water activity of the $MgCl_2 \cdot MgSO_4 \cdot H_2O$ solutions [28,29].

d) The Robinson and Stokes (RS) (also known as the Robinson and Bower) relation [43,44],

$$(1-a_w^M) = \sum_i [1-a_{wi}^S(m_T)] \cdot \left(\frac{m_i}{m_T}\right). \tag{5}$$

Where a_{wi}^S represents the water activities of single-salt solutions at the total molality m_T of the multi-electrolyte solution, and m_i is the molality of salt i in the multi-electrolyte solution. This model requires the water activities of single-salt solutions to be expressed as a function of molality. For this purpose polynomial fits to data in reference [26] have again been used.

e) The model of Lietzke and Stoughton [23] [45,46]

$$\phi_M \sum_i \nu_i m_i = \sum_i \nu_i m_i \phi_i(I_T) \tag{6}$$

where ϕ_M is the osmotic coefficient of the multi-electrolyte solution; ν_i is the number of ions released by the complete dissociation of the electrolyte i; and ϕ_i is osmotic coefficient of a single-salt solution having the same total ionic strength I_T as the multi-electrolyte solution, calculated by means of polynomial fits to data in reference [26].

f) The Reilly, Wood and Robinson (RWR) [25] model:

$$\phi_M = f(\phi_i) + g(interaction\,term). \tag{7}$$

Simplifying the model by neglecting the solute–solute interactions (which require experimental data from ternary solutions that are not readily available) leads to the following relation:

$$\phi_M = 1 - \frac{\sum_i [m_i(1-\phi_i(I_T))]}{m_T}. \tag{8}$$

Like the previous model, this model requires the osmotic coefficients of single-salt solutions to be expressed as a function of ionic strength; therefore the same data has been used. The expression that relates osmotic coefficient and water activity is as follows [6]:

$$\phi = \frac{-55.1 \cdot \ln(a_w)}{\sum_i \nu_i \cdot m_i}. \tag{9}$$

2.2. Viscosity and density

These properties are of secondary but significant importance in a liquid-desiccant refrigeration system. For example, they will influence how much power is needed to pump the liquid and how the liquid will behave in a device such as a heat or mass exchanger. Hefter et al. [47] have reviewed the theories and models used for predicting viscosities in electrolyte mixtures. According to their study, Young's rule is suitable for predicting viscosity η_M in concentrated multi-electrolyte solutions i.e.

$$\eta_M = \sum_i \left[\left(\frac{I_i}{I_T}\right) \cdot \eta_i(I_T)\right] \tag{10}$$

where η_i is the viscosity of a solution of the single salt i at the total ionic strength I_T, calculated by means of polynomial fits to data in reference [48], and I_i is the ionic strength of each salt in the multi-electrolyte solution.

Based on the linear isopiestic relation for multicomponent solutions, the density d_M of a multi-electrolyte solution can be calculated by the following equation as presented by Hu [49]:

$$d_M = \sum_i Y_i / \sum_i [Y_i / d_i(m_T)] \tag{11}$$

where d_i represents the density of a single-salt solution at the total molality m_T, and the term Y_i is as defined by Hu [49]. The values of d_i have been calculated using polynomial fits to data published in reference [48].

Tang et al. [30,50] used the following additive rule for density:

$$\frac{1}{d_M} = \sum_i \frac{x_i}{d_i(c_T)} \tag{12}$$

where d_i represents the density of a single-salt solution at the total mass fraction c_T of the solution (based again on reference [48]) and x_i is the mass fraction of each salt per total mass of dry solute.

Zaytsev and Aseyev [51] reported modified Ezrokhi equations for calculating density and viscosity in multi-electrolyte solutions based on data from single-salt solutions:

$$\log_{10} d_M = \log_{10} d_0 + \sum_i (G_i c_i) \tag{13}$$

where d_0 is the density of pure water and G_i are coefficients for each salt as shown in Table 2; and

$$\log_{10} \eta_M = \log_{10} \eta_0 + \sum_i (H_i c_i) \tag{14}$$

where η_M is the viscosity of the multi-electrolyte solution, η_0 is the viscosity of pure water, H_i are the coefficients for each salt given in Table 2, and c_i is the mass fraction of each salt per mass of solution. In this work Eq. (14) was further modified as follows to extend its applicability to concentrated brines:

$$\log_{10} \eta_M = \log_{10} \eta_0 + \sum_i (H_i c_i) + K_1 c_T + K_2 c_T^2 + K_3 c_T^3 \tag{15}$$

where c_T is the total mass of solute per mass of solution. The values of K_1, K_2 and K_3 are given in Table 3.

3. Experimental equipment and methods

To verify the above models, solutions of sea salts were made up at concentrations varying from that of raw seawater to 37% by mass, following compositions reported from Mediterranean solar salt works [52]. Analar reagents of $MgCl_2$, $MgSO_4$, $NaCl$, KCl, $CaCl_2$ and $LiCl$ were

Table 2
Coefficients G and H in the Ezrokhi models for density and viscosity (Eqs. (13)–(15)) at 25 °C.

	Salt					
	$MgCl_2$	$MgSO_4$	KCl	NaCl	LiCl	$CaCl_2$
G	0.3515	0.4464	0.2744	0.3112	0.2452	0.3628
H	2.013	2.595	−0.003	0.8077	1.744	1.444

Table 3
Coefficients K in the modified Ezrokhi model for viscosity (Eq. (15)) at 25 °C.

K_1	K_2	K_3
−0.4838	3.502	2.673

Table 4
The chemical compositions of the brine samples made up in the laboratory based on the compositions reported from solar salt works and on the phase diagram for $MgCl_2 \cdot MgSO_4 \cdot H_2O$.

Sample number	Composition (moles per kg of solution)						
	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	Li^+
1	0.548	0.012	0.072	0.0118	0.656	0.0273	0.00003
2	1.740	0.324	1.444	0.00474	4.373	0.406	0.000594
3	0.160	0.082	3.281	0.0014	6.346	0.298	0.00188
4	1.976	0.308	1.373	0.00555	4.212	0.531	0.000565
5	0.072	0.021	3.733	0.00153	7.790	0.247	0.00250
6	Zero	Zero	3.342	Zero	6.328	0.178	Zero
7	Zero	Zero	3.493	Zero	6.895	0.046	Zero
8	Zero	Zero	3.545	Zero	6.837	0.126	Zero
9	Zero	Zero	3.399	Zero	6.404	0.197	Zero
10	Zero	Zero	3.266	Zero	5.832	0.350	Zero

added to deionised water in that sequence and stirred. Any salt residue remaining was removed by filtration. Samples were diluted 1000 times with analar water, before being sent to an accredited laboratory, where the compositions were determined using inductively coupled plasma mass spectrometry and photometry based on turbidimetric and colorimetric principles. These dilutions should be sufficient to avoid interference from complexes that form at high concentrations. These compositions are shown against the samples numbered 1 to 5 in Table 4 in moles per kg of solution.

The composition of bitterns is dominated by the $MgCl_2 \cdot MgSO_4 \cdot H_2O$ system therefore further samples containing only these two salts were made up at nearly saturated concentrations as indicated by the phase diagram of Fig. 1. The gravimetrically-determined compositions of these samples, numbered 6 to 10, are also shown in Table 4.

The vapour pressures (needed to determine ERH) of the samples were measured using an isoteniscope arrangement following reference [53] and a manometer filled with dibutyl phthalate, which is a fluid having low surface tension and extremely low vapour pressure

as explained in reference [54]. The brine samples were filtered and then introduced to the isoteniscope where they were degassed following reference [53]. A control experiment showed that the mass loss of the sample as a result of degassing was less than 1%. The error in measuring a_w was ± 0.02, based on the random error of reading the manometer scale ($\pm 1\,mm$) and the systematic error of the isoteniscope arrangement. The latter was estimated to be $\pm 0.06\,kPa$ from comparison of the measured vapour pressure of pure water at 25 °C with published data [55] and from comparison of the measured vapour pressure of a pure $MgCl_2$ solution (4.5 m) with published data [26].

The measurement of density was carried out according to reference [56] using a 50ml pyknometer flask and a constant temperature water bath with an accuracy of ± 0.1 °C. The viscosity measurements were based on reference [57] following the detailed procedure for U-tube viscometers for direct flow, using a BS/U viscometer and a constant temperature bath of ± 0.1 °C accuracy. All experiments were carried out at 25 °C.

4. Results and discussion

Table 5 compares the measured values of a_w to those predicted by the six theoretical models. The agreement of the models is, on average, within 5% of the experimental results. The difference in errors among the models is not sufficient to select any one as being more accurate than the others. However, the ZSR model is both accurate and simple in formulation and therefore adopted for further use in this study.

Similarly, Tables 6 and 7 show the results for density and viscosity respectively. The most accurate models prove to be those based on Ezrokhi giving errors of 1.5% for density and 0.4% for viscosity.

Though the data and experimental verification reported here are for 25 °C only, note that substantial data for the properties of $MgCl_2$ solution at temperatures up to 100 °C are also available [48,58,59].
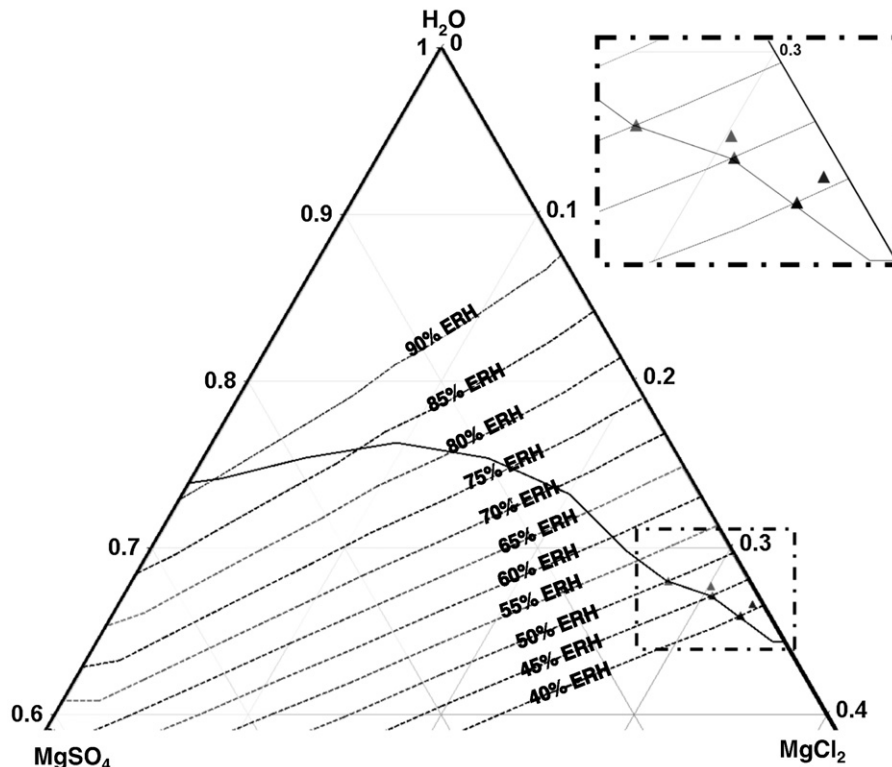

Fig. 1. Phase diagram for $MgCl_2 \cdot MgSO_4 \cdot H_2O$ systems indicating brines 6–10 used for the property-measurement experiments.

Table 5
Measured values of water activity a_w of the brine samples of Table 4, compared to the predictions of six models.

Sample number	Measured a_w	Model											
		Pitzer		ZSR		KM		RS		LS		RWR	
		Pred.	Error%	Pred.	Error %	Pred.	Error %	Pred.	Error %	Pred.	Error %	Pred.	Error %
1	0.981	0.978	0.4	0.977	0.4	0.977	0.4	0.977	0.4	0.977	0.4	0.973	0.8
2	0.668	0.696	4.1	0.729	9.1	0.719	7.6	0.700	4.7	0.707	5.8	0.714	6.8
3	0.424	0.420	1	0.448	5.7	0.435	2.6	0.447	5.6	0.432	2.0	0.439	3.7
4	0.658	0.704	7	0.729	10.8	0.718	9.2	0.699	6.3	0.703	6.8	0.709	7.8
5	0.346	0.299	13.6	0.340	1.6	0.306	11.5	0.328	5.2	0.309	10.5	0.314	9.2
6	0.458	0.482	5.1	0.455	0.8	0.445	2.8	0.462	0.8	0.451	1.6	0.461	0.7
7	0.399	0.413	3.5	0.401	0.6	0.395	1.1	0.408	2.2	0.401	0.4	0.404	1.2
8	0.406	0.411	1.1	0.393	3.4	0.379	6.8	0.396	2.6	0.385	5.3	0.393	3.4
9	0.445	0.468	5	0.439	1.4	0.427	4	0.446	0.1	0.433	2.8	0.444	0.2
10	0.479	0.534	11.5	0.490	2.3	0.473	1.2	0.495	3.4	0.478	0.2	0.496	3.5
	Average error %		5		4		5		3		4		4

The lowest measured ERH among the brines investigated here was 34.6%, compared to the lowest reported value of 32.8% for pure saturated MgCl$_2$ solution at 25 °C [60]. The maximum density and viscosity measured here were 1339 kg/m^3 and 13.2 mPa s respectively, compared to reported values for saturated MgCl$_2$ solution of 1330 kg/m^3 and 12.8 mPa s [48]. These comparisons tend to confirm the similarity between bitterns and solutions of pure MgCl$_2$.

In a practical refrigeration system, water will be continually added to and removed from the desiccant solution during the processes of dehumidification and regeneration. To replicate this situation, solutions were made up with the same relative salt concentrations as concentrated bitterns (based on the brine L4 in reference [52]) but with varying amounts of water added, and the vapour pressure was measured. The results are plotted against mass fraction in Fig. 2 along with the corresponding curve for pure MgCl$_2$ solution as reported from the literature [26]. It can be seen that the difference between these two curves is small. The average relative error between the interpolated values of ERH of pure MgCl$_2$ (by a quadratic polynomial with correlation coefficient $r^2 = 0.98$) and the experimental values for the bitterns is just 5.1%.

In salt works it is conventional and convenient to measure concentration according to the lithium ion which, in the form of lithium chloride, is highly soluble in bitterns [52]. The lithium concentration factor C_{Li} refers to the final concentration of lithium in the bitterns divided by that in raw seawater. Application of the ZSR model to the compositions of various brines and bitterns reported in

reference [52] gives the data points shown in Fig. 3. It is useful to fit the following semi-empirical relation to these points:

$$ERH\% = 97.75 - 66.88\{1 - \exp[-0.0715(C_{Li} - 1)]\}. \tag{16}$$

It has been suggested [3] that a liquid desiccant should achieve ERH below 50% in order to be effective for greenhouse cooling. This corresponds to $C_{Li} \geq 20$ approximately, since $C_{Li} = 20$ gives ERH = 48% in Eq. (16), based on Mediterranean seawater. Where salinity is lower, slightly higher values of C_{Li} will be needed to yield the same ERH.

It is possible to use these models to assess how the presence of minor constituents, besides MgCl$_2$, influences the properties of bitterns. For example, Fig. 4 shows the values for ERH (again based on the ZSR model) as progressively minor impurities are added to pure MgCl$_2$ solution, corresponding to the compositions of the most concentrated (L4, for which $C_{Li} = 80$) and second most concentrated brine (S4, for which $C_{Li} = 59$) reported in [52]. For S4 the minor constituents cause an appreciable depression in ERH, but for L4 the depression is smaller. Moreover, we have seen in Fig. 2 that concentrated bitterns with relative composition like L4 do in fact have similar ERH compared to pure MgCl$_2$ solutions containing equal mass fraction c_T of total dissolved salts.

Note that in addition to the impurities considered in Fig. 4, numerous ions including bromide and fluoride are also present in seawater in very small quantities. Since in total these make up less than 0.7% of the total mass of sea salt, they are reasonably neglected [61].

Table 6
Measured values of density $d/(10^3 \text{ kg m}^{-3})$ of the brine samples of Table 4, compared to the predictions of three models.

Sample number	Measured density	Model					
		Hu		Ezrokhi		Tang's rule	
		Prediction	Error %	Pred.	Relative error %	Prediction	Error %
1	1.025	1.031	0.57	1.028	0.28	1.030	0.46
2	1.255	1.255	0.03	1.240	1.18	1.345	7.14
3	1.317	1.323	0.43	1.315	0.15	1.506	14.4
4	1.264	1.268	0.30	1.252	0.95	1.365	8.01
5	1.339	1.347	0.59	1.349	0.75	1.593	18.9
6	1.301	1.309	0.63	1.300	0.07	1.309	0.63
7	1.307	1.313	0.52	1.307	0.01	1.313	0.52
8	1.315	1.322	0.57	1.317	0.15	1.322	0.57
9	1.308	1.315	0.51	1.306	0.12	1.315	0.51
10	1.296	1.312	1.21	1.302	0.47	1.312	1.21
	Average error %		0.5		0.4		5.2

The calculation of average error for each model shows that of Ezrokhi to be the most accurate.

Table 7
Measured values of dynamic viscosity η/mPa s of the brines samples of Table 4, compared to the predictions of two models.

Sample number	Measured viscosity	Model			
		Young's rule		Ezrokhi	
		Prediction	Error %	Prediction	Error %
1	1.00	0.98	2.4	0.95	5.1
2	3.49	3.68	5.5	3.49	0.0
3	8.99	10.2	13.2	9.00	0.0
4	3.69	4.08	10.5	3.75	1.6
5	13.21	15.5	17.6	13.36	1.1
6	8.37	8.89	6.2	8.10	3.2
7	8.95	10.0	12.0	8.94	0.2
8	9.93	11.0	11.0	9.78	1.6
9	8.99	9.56	6.4	8.66	3.7
10	7.93	8.78	10.6	8.08	1.8
	Average error %		10		1.5

The calculation of the average relative error for each model shows that the modified Ezrokhi model is the most accurate.
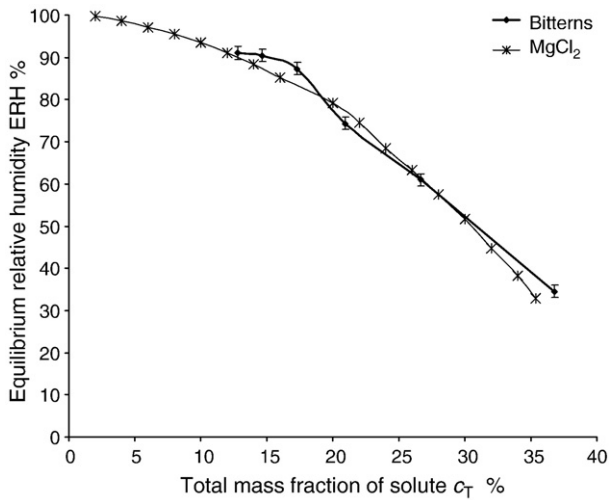
Fig. 2. Measured ERH vs. total mass fraction for bittern solutions with constant relative salt concentrations but with varying amounts of water added; together with the corresponding curve for pure magnesium chloride solution.

5. Conclusions and further work

The properties (vapour pressure, density and viscosity) of seawater salt solutions at concentrations of up to 37% by mass, corresponding to bitterns concentrated about 80 times (as indicated by the lithium ion: $C_{Li} = 80$) relative to raw seawater, have been measured. Six models for the prediction of vapour pressure have been compared and found all to give similar agreement with experiment. Typically this agreement is within 5%. Within the limits of experimental accuracy of this study, no one model for vapour pressure is proven to be more accurate than the others. However, the Zdanovskii–Stokes–Robinson model is preferred on the grounds of simplicity. For density and viscosity, models based on Ezrokhi's work are recommended as giving respectively 1.5% and 0.4% agreement with experiment. Concise formulae and numerical coefficients presented here will enable researchers to apply these models to the design of desiccant cooling systems in which such solutions are used.

To obtain sufficiently hygroscopic solutions for this application will require bitterns to be concentrated at least 20 times relative to raw seawater ($C_{Li} \geq 20$) based on the Mediterranean seawater studied here, and slightly more less saline seawater. At high concentrations
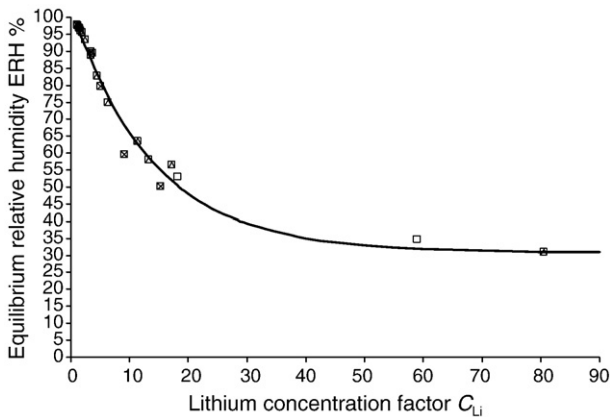

Fig. 3. Equilibrium relative humidity (ERH) of concentrated seawater as a function of the lithium concentration factor C_{Li}. The point data are calculated from the ZSR model applied to the compositions reported in reference [52]. The solid line is the curve fit using Eq. (16).
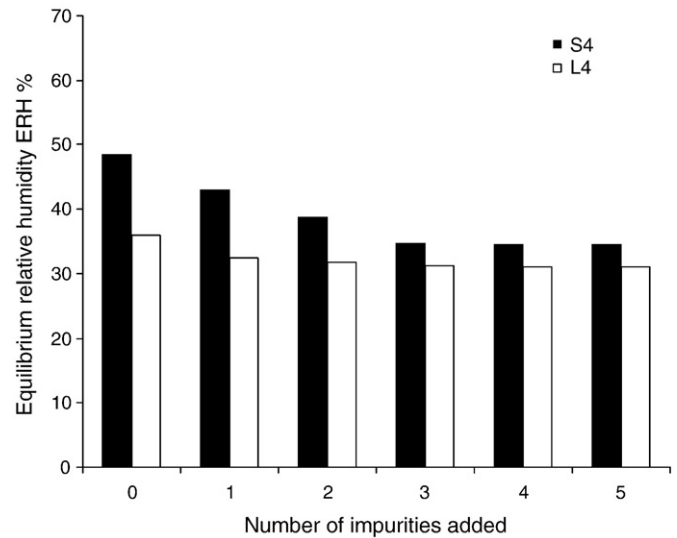

Fig. 4. Histogram showing the effect on ERH of adding 1, 2, 3, 4 and 5 impurities to the $MgCl_2$ solution, calculated from the ZSR model applied to the compositions for brines S4 and L4 of reference [52]. For S4 the impurities are as follows: 0 is pure $MgCl_2$, 1 is 0+ $MgSO_4$, 2 is 1+ NaCl, 3 is 2+ KCl, 4 is 3+ LiCl, 5 is 4+ $CaCl_2$. For L4: 0 is pure $MgCl_2$, 1 is 0+ $MgSO_4$, 2 is 1+ NaCl, 3 is 2+ KCl, 4 is 3+ $CaCl_2$, 5 is 4+ LiCl.

(C_{Li} of approximately 80), the properties of bitterns become very similar to those of aqueous solutions of pure $MgCl_2$; therefore similar behaviour can be expected in a cooling system.

To provide additional results and improve on the accuracy of these studies, further experiments could be carried using alternative methods such as the isopiestic method, as reported elsewhere (for example, Königsberger et al. [62]).

This study supports the conclusion of reference [3]: in principle, liquid-desiccant cooling systems using bitterns could be employed for the cooling of greenhouses in hot, humid climates. Having now studied the properties of the bitterns, we will focus future work on the sizing and detail design of system components such as the solar regenerator and the dehumidifier.

List of symbols	Units	
a		chemical activity
c		mass fraction
C		concentration factor
d	kg m^{-3}	density
ERH		equilibrium relative humidity
I	mol kg^{-1}	ionic strength
m	mol kg^{-1}	molality
P	Pa	vapour pressure of the solution
X		cationic strength fraction
x		mass fraction per total dry mass of solute
Z		anionic strength fraction
Greek variables		
ε		residue term
η	mPa s	viscosity
v		number of ions released
ϕ		osmotic coefficient
Superscripts		
M		in a multi-electrolyte solution
s		in a single-salt solution
Subscripts		
i		single salt
j		anion
k		Cation
Li		Lithium
M		of a multi-electrolyte solution
T		Total
w		Water
0		pure water

Acknowledgements

References

[1] M. Ahmed, A. Arakel, D. Hoey, M. Coleman, Integrated power, water and salt generation: a discussion paper, Desalination 134 (2001) 37–45.

[2] M. Ahmed, A. Arakel, D. Hoey, M.R. Thumarukudy, M.F.A. Goosen, M. Al-Haddabi, A. Al-Belushi, Feasibility of salt production from inland RO desalination plant reject brine: a case study, Desalination 158 (2003) 109–117.

[3] P.A. Davies, P.R. Knowles, Seawater bitterns as a source of liquid desiccant for use in solar-cooled greenhouses, Desalination 196 (2006) 266–279.

[4] P.A. Davies, I. Harris, P.R. Knowles, Cooling of Greenhouses using Seawater: a Solar-driven Liquid Desiccant Cycle for Greenhouse Cooling in Hot Climates, International Symposium on Greenhouse Cooling, Almería, 2006.

[5] P.A. Davies, A solar cooling system for greenhouse food production in hot climates, Sol. Energy 79 (2005) 661–668.

[6] J.F. Zemaitis, Handbook of Aqueous Electrolyte Thermodynamics: Theory and Application, Design Institute for Physical Property Data, New York, 1986.

[7] J.R. Loehe, M.D. Donohue, Recent advances in modeling thermodynamic properties of aqueous strong electrolyte systems, AIChE J. 43 (1997) 180–195.

[8] H. Renon, Electrolyte solutions, Fluid Phase Equilib. 30 (1986) 181–195.

[9] S.I. Sandler, Models for Thermodynamic and Phase Equilibria Calculations, Marcel Dekker, New York, 1994.

[10] D.S. Abrams, J.M. Prausnitz, Statistical thermodynamics of liquid mixtures: a new expression for the excess Gibbs energy of partly or completely miscible systems, AIChE J. 21 (1975) 116–128.

[11] H. Renon, J.M. Prausnitz, Local compositions in thermodynamic excess functions for liquid mixtures, AIChE J. 14 (1968) 135–144.

[12] C.-C. Chen, H.I. Britt, J.F. Boston, L.B. Evans, Local composition model for excess Gibbs energy of electrolyte systems. Part I: single solvent, single completely dissociated electrolyte systems, AIChE J. 28 (1982) 588–596.

[13] C.-C. Chen, L.B. Evans, A local composition model for the excess Gibbs energy of aqueous electrolyte systems, AIChE J. 32 (1986) 444–454.

[14] M. Abraham, M.C. Abraham, Electrolyte and water activities in very concentrated solutions, Electrochim. Acta 46 (2000) 137–142.

[15] M.R. Ally, J. Braunstein, Statistical mechanics of multilayer adsorption: electrolyte and water activities in concentrated solutions, J. Chem. Thermodyn. 30 (1998) 49–58.

[16] P. Wang, R.D. Young, A speciation-based model for mixed-solvent electrolyte systems, Fluid Phase Equilib. 203 (2002) 141–176.

[17] P. Wang, A. Anderko, R.D. Young, Modeling electrical conductivity in concentrated and mixed-solvent electrolyte solutions, Ind. Eng. Chem. Res. 43 (2004) 8083–8092.

[18] K.S. Pitzer, Thermodynamics of electrolytes. I. Theoretical basis and general equations, J. Phys. Chem. 77 (1973) 268–277.

[19] K.S. Pitzer, Characteristics of very concentrated aqueous solutions, Phys. Chem. Earth 13–14 (1981) 249–272.

[20] K.S. Pitzer, Activity Coefficients in Electrolyte Solutions, 2nd edition, CRC Press, Boca Raton, 1991.

[21] K.S. Pitzer, M. Guillermo, Thermodynamics of electrolytes. III. Activity and osmotic coefficients for 2–2 electrolytes, J. Solution Chem. 3 (1974) 539–546.

[22] K.S. Pitzer, J.J. Kim, Thermodynamics of electrolytes. IV. Activity and osmotic coefficients for mixed electrolytes, J. Am. Chem. Soc. 96 (1974) 5701–5707.

[23] K.S. Pitzer, J. Olsen, J.M. Simonson, R.N. Roy, J.J. Gibbons, L. Rowe, Thermodynamics of aqueous magnesium and calcium bicarbonates and mixtures with chloride, J. Chem. Eng. Data 30 (1985) 14–17.

[24] K.S. Pitzer, W. Peiming, A.R. Joseph, L.C. Simon, Thermodynamics of electrolytes. 13. Ionic strength dependence of higher-order terms; equations for $CaCl_2$ and $MgCl_2$, J. Solution Chem. 28 (1999) 265–282.

[25] P.J. Reilly, R.H. Wood, R.A. Robinson, Prediction of osmotic and activity coefficients in mixed-electrolyte solutions, J. Phys. Chem. 75 (1971) 1305–1315.

[26] R.A. Robinson, R.H. Stokes, Electrolyte Solutions, 2nd edition, Butterworths Scientific Publications, London, 1959.

[27] R.H. Stokes, R.A. Robinson, Interactions in aqueous nonelectrolyte solutions. I. Solute–solvent equilibria, J. Phys. Chem. 70 (1966) 2126–2131.

[28] M. El Guendouzi, R. Azougen, A. Benbiyi, Thermodynamic properties of the mixed electrolyte systems {$yMgCl_2$+(1−y)NaCl}(aq) and {$yMgCl_2$+(1−y)$CaCl_2$}(aq) at 298.15 K, Calphad 29 (2005) 114–124.

[29] M. El Guendouzi, A. Benbiyi, A. Dinane, R. Azougen, Thermodynamic properties of multicomponent NaCl–LiCl–H_2O aqueous solutions at temperature 298.15 K, Calphad 28 (2004) 97–103.

[30] Z. Ha, C.K. Chan, The water activities of $MgCl_2$, $Mg(NO_3)_2$, $MgSO_4$, and their mixtures, Aerosol Sci. Tech. 31 (1999) 154–169.

[31] A. Dinane, A. Mounir, Water activities, osmotic and activity coefficients in aqueous mixtures of sodium and magnesium chlorides at 298.15 K by the hygrometric method, Fluid Phase Equilib. 206 (2003) 13–25.

[32] K.S. Pitzer, Thermodynamics of electrolytes. V. Effects of higher-order electrostatic terms, J. Solution Chem. 4 (1975) 249–265.

[33] J.N. Bronsted, Calculation of the osmotic and activity functions in solutions of univalent salts, J. Am. Chem. Soc. 45 (1922) 938–948.

[34] E.A. Guggenheim, The specific thermodynamic properties of aqueous solutions of strong electrolytes, Phil. Mag. 19 (1935) 588–643.

[35] C.E. Harvie, J.H. Weare, The prediction of mineral solubilities in natural waters: the Na–K–Mg–Ca–Cl–SO_4–H_2O system from zero to high concentration at 25 deg.C, Geochim. Cosmochim. Acta 44 (1980) 981–997.

[36] C.E. Harvie, N. Møller, J.H. Weare, The prediction of mineral solubilities in natural waters: the Na–K–Mg–Ca–H–Cl–SO_4–OH–HCO_3–CO_3–CO_2–H_2O system to high ionic strengths at 25 °C, Geochim. Cosmochim. Acta 48 (1984) 723–751.

[37] B.S. Krumgalz, Application of the Pitzer ion interaction model to natural hypersaline brines, J. Mol. Liq. 91 (2001) 3–19.

[38] S. Pengsheng, Y. Yan, Thermodynamics and phase diagram of the salt lake brine system at 298.15 K: V. model for the system Li^+, Na^+, K^+, Mg_2^{2+}/Cl^-, SO_4^{2-}–H_2O and its applications, Calphad 27 (2003) 343–352.

[39] Y.Y. Guang-Ming Long, Feng-Qin Wang, Rui-Ling Wang, Isopiestic determination of activity coefficients of LiCl and $CaCl_2$ in LiCl–$CaCl_2$–H_2O system at 298.15K, Acta Phys. Chim. Sin. 15 (1999) 956–960.

[40] S.L. Clegg, J.H. Seinfeld, Improvement of the Zdanovskii–Stokes–Robinson model for mixtures containing solutes of different charge types, J. Phys. Chem. A 108 (2004) 1008–1017.

[41] S.L. Clegg, J.H. Seinfeld, E.O. Edney, Thermodynamic modelling of aqueous aerosols containing electrolytes and dissolved organic compounds. II. An extended Zdanovskii–Stokes–Robinson approach, J. Aerosol Sci. 34 (2003) 667–690.

[42] C.L. Kusik, H.P. Meissner, Electrolyte activity coefficients in inorganic processing, AIChE Symp. Ser. 173 (1978) 14.

[43] R.A. Robinson, R.H. Stokes, Electrolyte Solutions: the Measurement and Interpretation of Conductance, Chemical Potential and Diffusion in Solutions of Simple Electrolytes, 2nd edition, Butterworths, London, 1970.

[44] J. Sangster, F. Lenzi, On the choice of methods for the prediction of the water-activity and activity coefficient for multicomponent aqueous solutions, Can. J. Chem. Eng. 52 (1974) 392–396.

[45] M.H. Lietzke, R.W. Stoughton, A simple empirical equation for the prediction of the activity-coefficient value of each component in aqueous electrolyte mixtures containing a common ion, J. Solution Chem. 1 (1972) 299–308.

[46] M.H. Lietzke, R.W. Stoughton, Extension of a two-structure model for electrolyte solutions to aqueous mixed electrolyte systems, J. Inorg. Nucl. Chem. 37 (1975) 2503–2506.

[47] G. Hefter, P.M. May, P. Sipos, A. Stanley, Viscosities of concentrated electrolyte solutions, J. Mol. Liq. 103–104 (2003) 261–273.

[48] V.M.M. Lobo, Handbook of Electrolyte Solutions, Elsevier, Parts A & B, 1989.

[49] Y.Y.-F. Hu, A new equation for predicting the density of multicomponent aqueous solutions conforming to the linear isopiestic relation, Phys. Chem. Chem. Phys. 2 (2000) 2379–2382.

[50] I.N. Tang, A.C. Tridico, K.H. Fung, Thermodynamic and optical properties of sea salt aerosols, J. Geophys. Res. 102 (1997) 23269–23275.

[51] I.D. Zaytsev, G.G. Aseyev, Properties of Aqueous Solutions of Electrolytes, CRC Press, Boca Raton, 1992.

[52] R. Amdouni, Chemical Study of Free Brine in Solar Salt Works of Sfax Saline (E.S of Tunisia), 8th World Salt Symposium, Elsevier, Arnhem, 2000.

[53] ASTM, D 2879–97 Standard Test Method for Vapor Pressure–Temperature Relationship and Initial Decomposition Temperature of Liquids by Isoteniscope, 1997 (Reapproved 2002).

[54] J.V. McAllan, Oil manometer for the range 0–100 Torr, J. Scient. Instrum. 42 (1965) 290–291.

[55] G.F.C. Rogers, Y.R. Mayhew, Thermodynamic and Transport Properties of Fluids, 5th edition, Blackwell, Oxford, 1995.

[56] British Standards Institute, BS 4522:1988 Method for determination of absolute density at 20 °C of liquid chemical products for industrial use.

[57] British Standards Institute, BS 188:1977 Methods for determination of the viscosity of liquids.

[58] I.D. Aseyev, G. Georgievich, Properties of Aqueous Solutions of Electrolytes, CRC Press, Boca Raton, 1992.

[59] H.F. Holmes, R.E. Mesmer, Aqueous solutions of the alkaline-earth metal chlorides at elevated temperatures. Isopiestic molalities and thermodynamic properties, J. Chem. Thermodyn. 28 (1996) 1325–1358.

[60] OIML, The Scale of Relative Humidity of Air Certified against Saturated Salt Solutions, Bureau Internationale de Mètrologie Lègale, Paris, 1996.

[61] K. Grasshoff, K. Kremling, M. Ehrhardt, Methods of Seawater Analysis, 3rd edition, Wiley-VCH, Weihheim, 1999.

[62] E. Königsberger, P.M. May, G. Hefter, Comprehensive model of synthetic Bayer liquors part 3: sodium aluminate solutions and the solubility of gibbsite and boehmite, Monatsh. Chem. 137 (2006) 1139–1149.