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Recovery of Mineral Salts and Potable Water from Desalting Plant Effluents by Evaporation. Part I. Evaluation of the Physical Properties of Highly Concentrated Brines

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Recovery of Mineral Salts and Potable Water from Desalting Plant Effluents by Evaporation. Part I. Evaluation of the Physical Properties of Highly Concentrated Brines

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Abstract

The main theme of this study is the recovery of a salt (in particular, magnesium chloride) from rejected brines of desalination plants through the simulation of a modified Multistage Flash (MSF) evaporation system. Such a proposal is attractive for countries highly dependent on water desalination. Saudi Arabia and other Arab Gulf states are good examples. A basic assumption underlying this study (both Part I and Part II) is that desalination effluents are assumed to contain only the two most abundant salts in seawater: sodium and magnesium chlorides. In this paper and equilibrium relationship describing the solubility of NaCl in aqueous solutions of $MgCl_2$ is first developed. This generalized correlation is based on the solubility data available in the literature. The correlation is valid for the temperature range 15–200°C and for a concentration of $MgCl_2$ up to 30 g/100 g saturated solution. Next, calculations of the specific gravity and viscosity of highly concentrated brines are presented, and then compared with experimental data. Research findings presented in this paper serve as a prerequisite for the reclamation of mineral salt to be considered in Part II.

INTRODUCTION

Different salts are obtained from various sources in various ways, but the main source remains seawater. Shingley (*1*) reported that each cubic

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mile of seawater contains 165 million tons of dissolved solids, and from the sea comes 29% of the world's salt, 70% of its bromide, 61% of its magnesium metal, 6% of its magnesium compounds, and 59% of "manufactured" water. Abdel-Aal (*2*)—in an economic study—elaborated on the importance of a new process for the production of magnesium chloride from seawater.

The composition of seawater as shown in Table 1 clearly indicates that sodium chloride and magnesium chloride are the predominant salt components of seawater.

Seawater contains 78.0% sodium chloride and 10.5% magnesium chloride, so these two salts total 88.5% of the entire salt content. Accordingly, seawater can be approximated by a ternary solution containing sodium chloride and magnesium chloride in water in the right proportion. Before the recovery of mineral salts from desalination plant effluents is considered, a knowledge of the physical properties of concentrated brines has to be established. This is the scope of the present work.

2. DEVELOPMENT OF THE SOLUBILITY CORRELATION FOR NaCl IN AQUEOUS SOLUTION WITH $MgCl_2$

A knowledge of the composition of the components present and quantitative data on phase equilibria is a prerequisite for the reclamation of mineral salts from brine. A solubility equation is necessary to develop and perform stage-to-stage material an heat balance calculations, and to determine the composition of the streams leaving the different stages.

Experimental data on the solubilities of sodium chloride in aqueous magnesium chloride solutions is either not available or scattered in the

TABLE 1
Composition of Seawater

Ion	ppm
Na^+	10,561
Mg^{2+}	1,272
Ca^{2+}	400
K^+	380
Cl^-	18,980
SO_4^{2-}	2,649
HCO_3^-	141
Br^-	65
Other solids	34

literature, because magnesium chloride is one of the most difficult salts to work with due to its strongly hygroscopic behavior. Published tabulations show major deviations between the data from different sources. Seidell (*3*) gives the solubilities of sodium chloride–magnesium chloride solutions for temperatures ranging from 0 to 105°C. Clynne (*4*) gives the solubilities of sodium chloride in aqueous electrolyte solutions over the range of 10 to 100°C. D'Ans and Sypiena (*5*) give the solubilities of sodium chloride in aqueous magnesium chloride solution up to 200°C. Achoumov and Wassilijew (*6*) give data on solubilities for the sodium chloride–magnesium chloride–water system from 100 to 200°C. Meissner (*7*) gives the solubility of sodium chloride in aqueous magnesium chloride solutions at 25 and 105°C.

3. PROPOSED CORRELATION

A correlation of the solubility of sodium chloride in aqueous magnesium chloride solutions has been developed using regression analysis. In this correlation the solubility of sodium chloride is calculated as a function of brine temperature and magnesium chloride composition. It is valid for the temperature range from 15 to 200°C and for a magnesium chloride concentration in the brine up to 30 g/100 g saturated solution.

The correlation is represented by the polynomial

$$Y = A_0 + A_1T + A_2T^2 + A_3X + A_4TX + A_5X^2 \tag{1}$$

where Y = composition of NaCl (g/100 g saturated solution)
X = composition of $MgCl_2$ (g/100 g saturated solution)
T = temperature (°C)

The constants in Eq. (1) were determined for a set of 73 data points as follows:

$$\begin{aligned} A_0 &= 26.28357 \\ A_1 &= 2.82775 \times 10^{-2} \\ A_2 &= 2.44604 \times 10^{-5} \\ A_3 &= -1.27383 \\ A_4 &= -3.85590 \times 10^{-4} \\ A_5 &= 1.42452 \times 10^{-2} \end{aligned} \tag{2}$$

A comparison between the values calculated by Eq. (1) and experimental data is shown in Figs. 1–4 for different temperatures. The final correlation has also been tested over the entire range as presented graphically in Fig. 5. Moreover, data from other sources (*8*) were used to test and verify the accuracy of this correlation, as shown in Figs. 6 and 7.

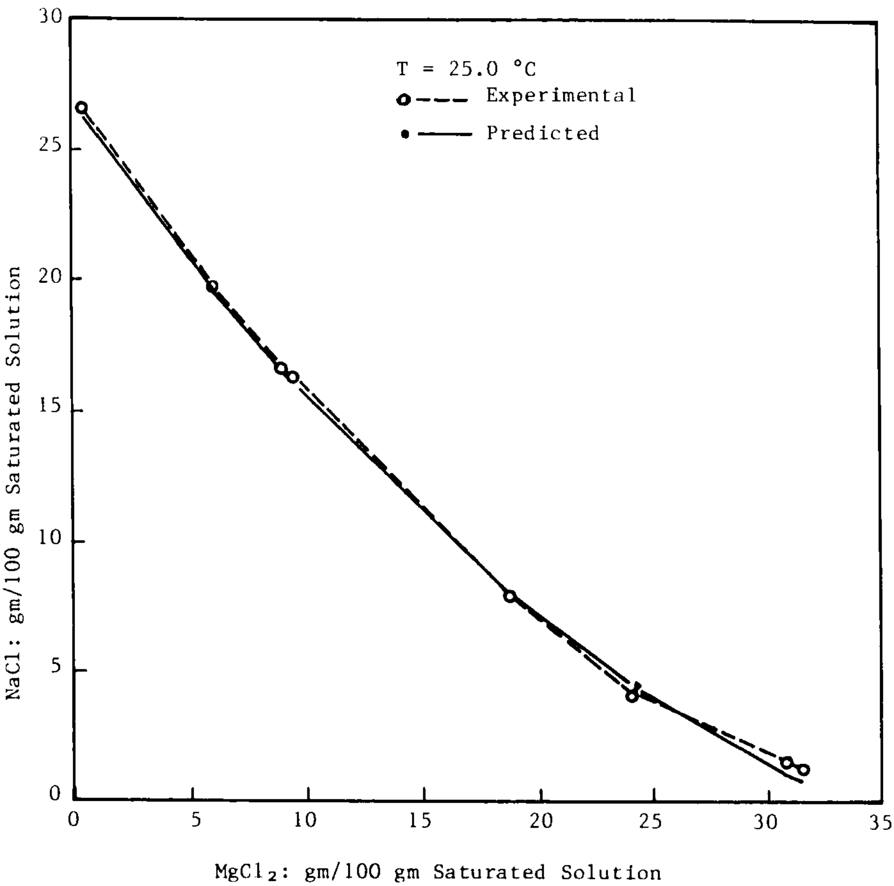

FIG. 1. Solubility of NaCl in $MgCl_2$ solutions at 25°C.

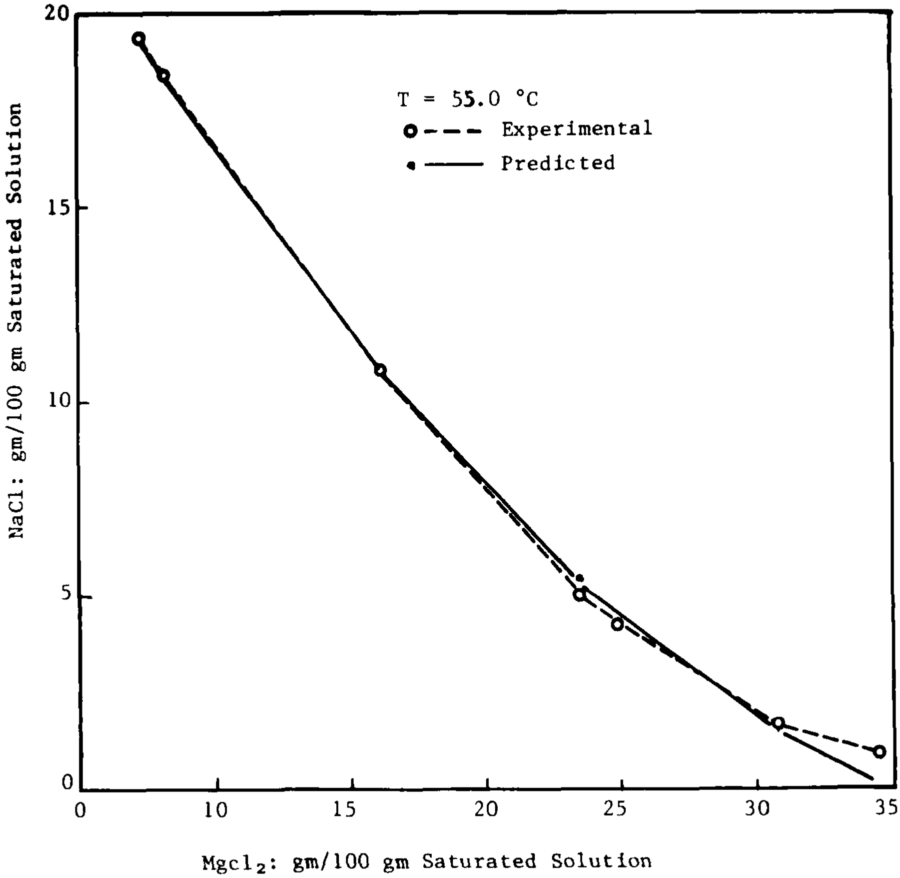

FIG. 2. Solubility of NaCl in $MgCl_2$ solutions at 55°C.

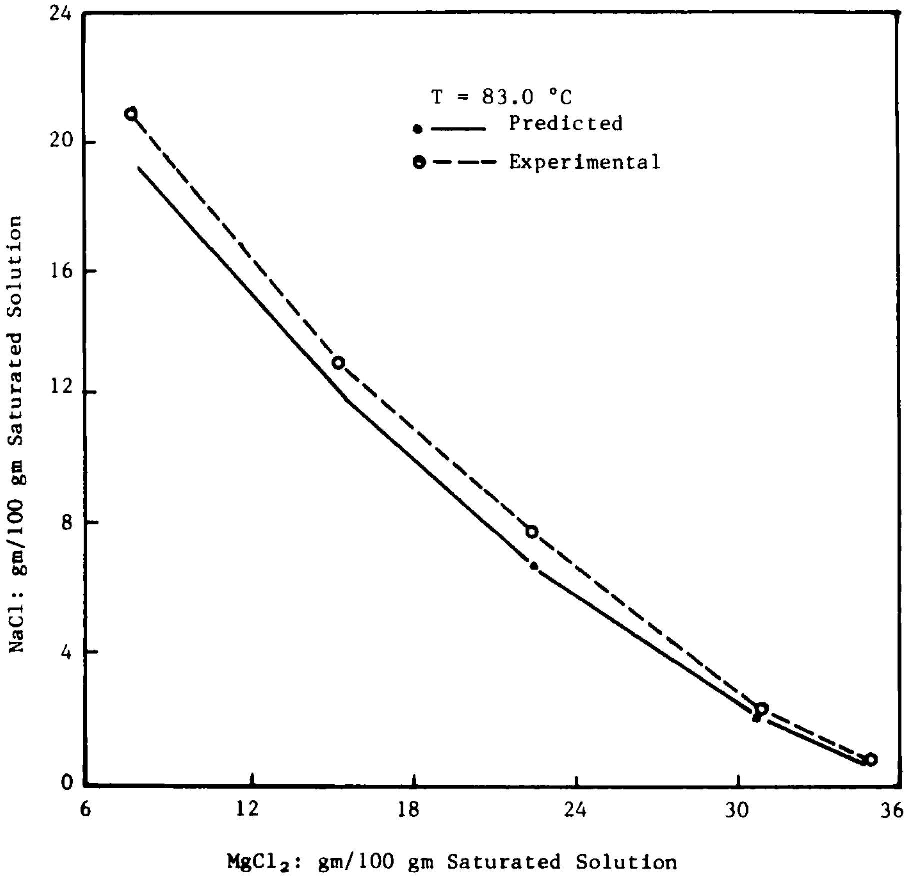

FIG. 3. Solubility of NaCl in $MgCl_2$ solutions at 83°C.

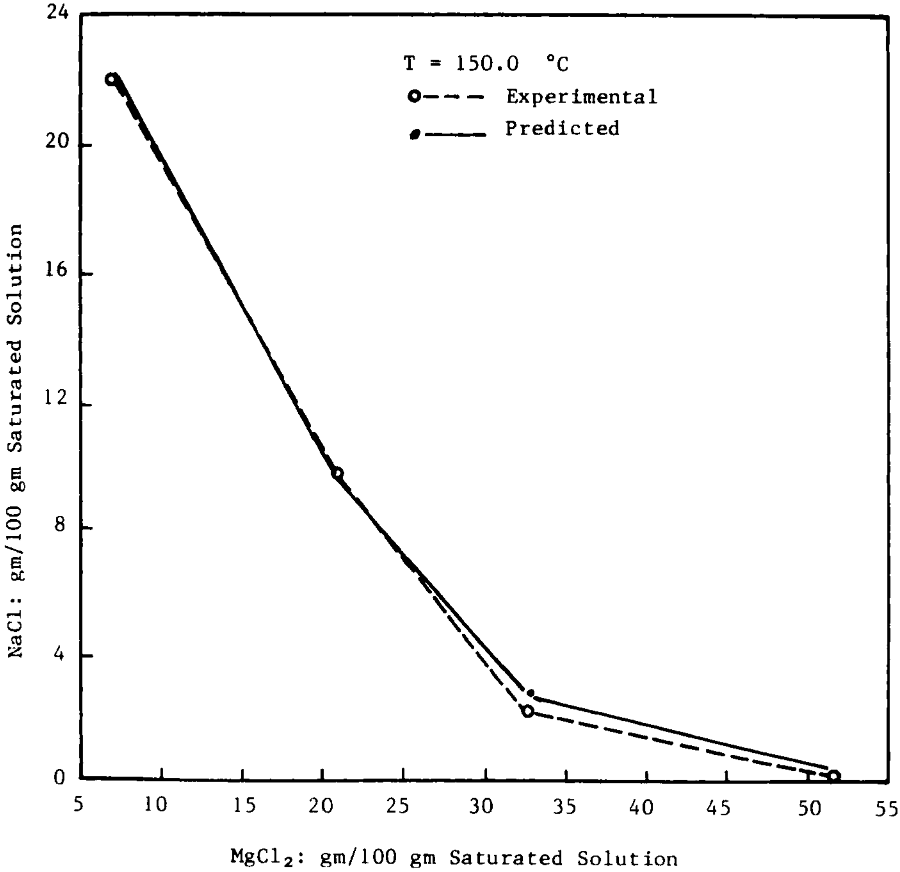

FIG. 4. Solubility of NaCl in $MgCl_2$ solutions at 150°C.

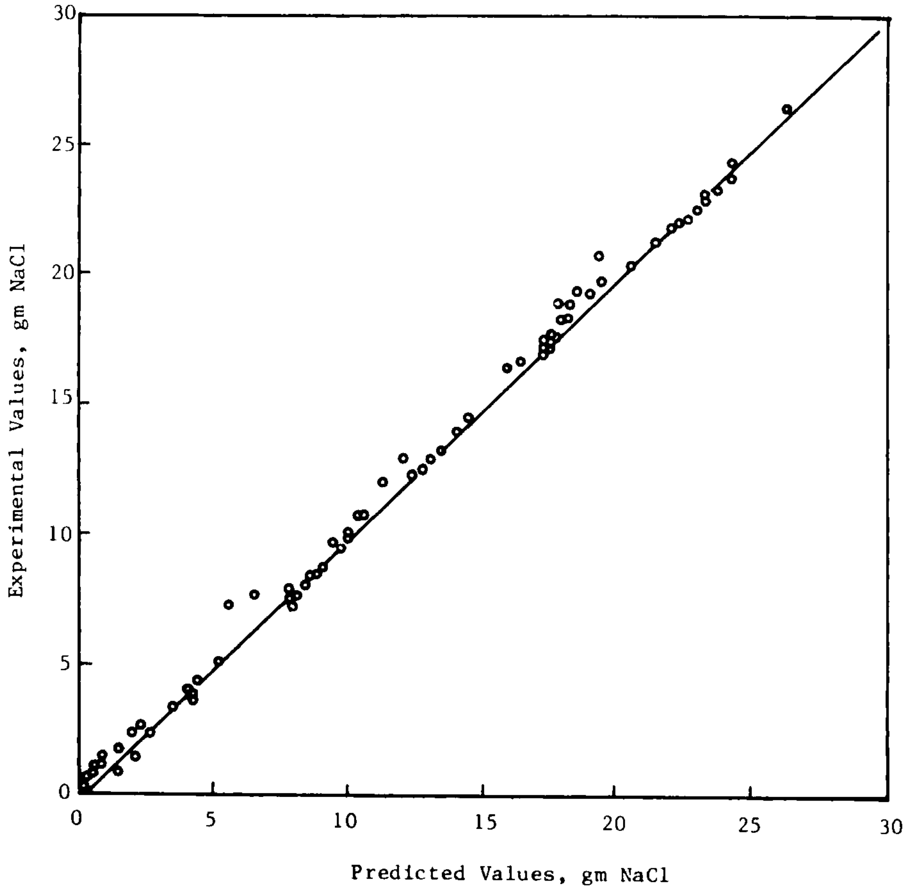

FIG. 5. Comparison between predicted and experimental values of NaCl solubility in $MgCl_2$ solutions.

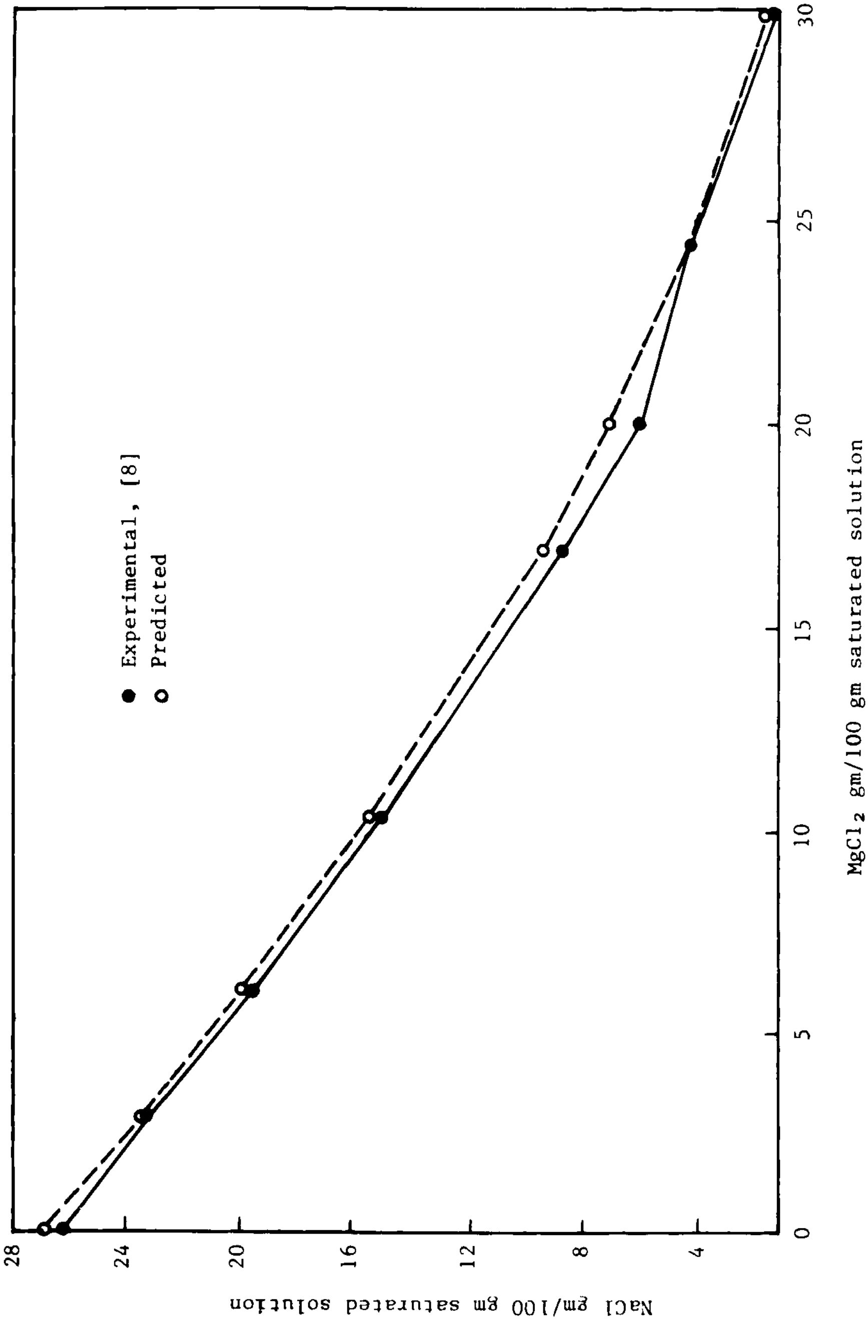

FIG. 6. Comparison between experimental and predicted values of NaCl solubility in $MgCl_2$ solutions at 25°C.

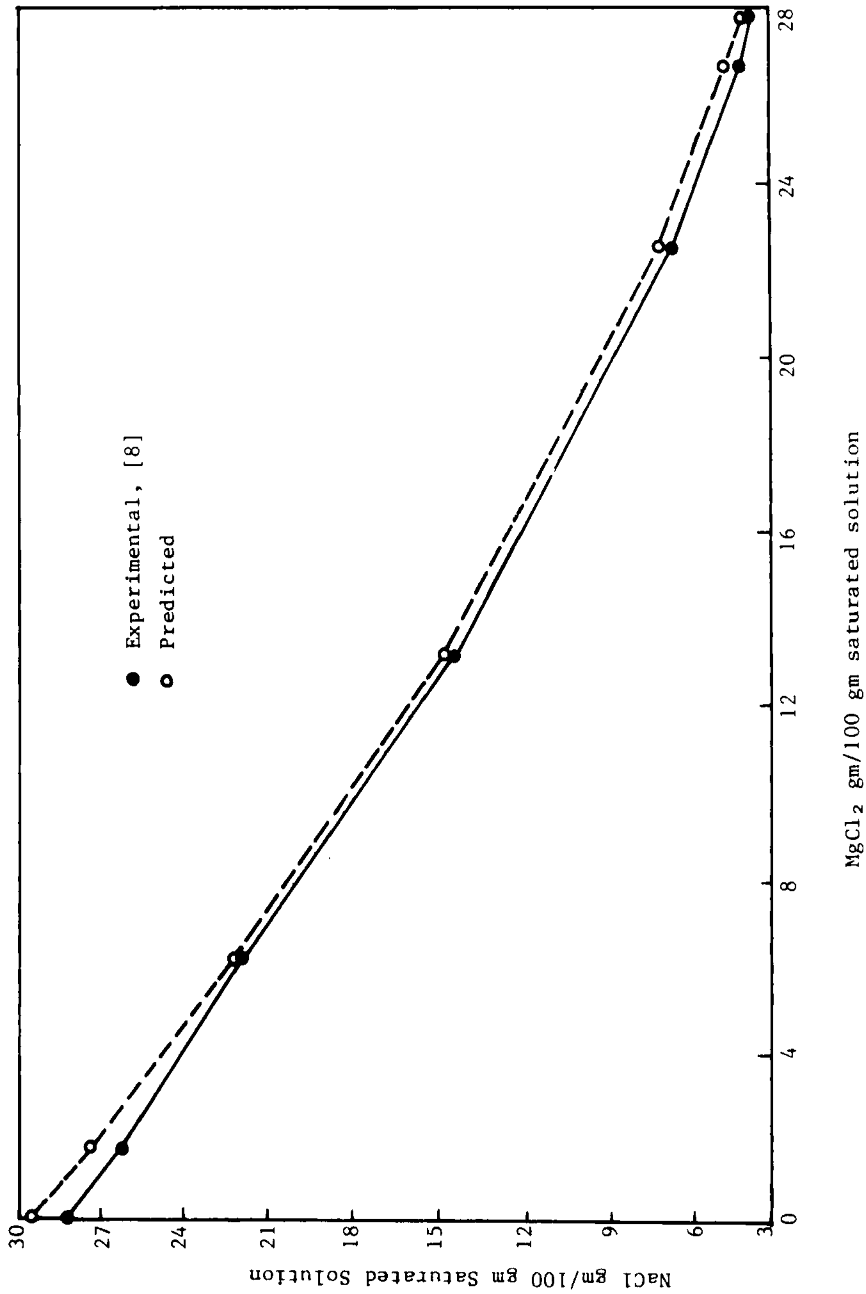

FIG. 7. Comparison between experimental and predicted values of NaCl solubility in $MgCl_2$ solutions at 105°C.

4. OTHER PHYSICAL PROPERTIES

In order to confirm the reliability of the calculation methods for the physical properties of saline water, in particular the viscosity and density as reported in the literature (*9, 10*), the following procedure was executed.

First: Several samples of the effluents from the Al-Khobar Desalination Plant in eastern Saudi Arabia were collected and subjected to laboratory evaporation.
Second: The specific gravity and density of these samples were then determined using the correlations reported by Homing (*9*) as described below:

(*a*) *Density:* The density is given by Homing (*9*) as a function of temperature over the range 0 to 180°C and for a concentration up to 16 g/100 g saturated solution. The correlation used in this work is given by

$$\rho = 1/2\alpha_0 + \alpha_1 Y \alpha_2(2Y^2 - 1) + \alpha_3(4Y^3 - 3Y) \tag{3}$$

where

$$\begin{aligned} \alpha_0 &= 2.016110 + 0.115313\sigma + 0.000326(2\sigma^2 - 1) \\ \alpha_1 &= -0.0541 + 0.001571\sigma - 0.000423(2\sigma^2 - 1) \\ \alpha_2 &= -0.006124 + 0.00174\sigma - 0.000009(2\sigma^2 - 1) \\ \alpha_3 &= 0.000346 + 0.000087\sigma - 0.000053(2\sigma^2 - 1) \end{aligned} \tag{4}$$

$$Y = \frac{2T - 200}{160}, \qquad \sigma = \frac{2s - 150}{150}$$

ρ = density (g/cm³)
T = temperature (°C)

and s is the concentration (g/kg).

(*b*) *Viscosity:* This property is reported by Homing (*9*) in a functional form. Viscosity has been correlated to the brine temperature and concentration for a temperature range of 10 to 150°C and for a concentration up to 13 g/100 g saturated solution by the following formula:

$$\mu = \mu_w \mu R \tag{5}$$

$$\ln \mu_w = -3.79418 + \frac{604.129}{139.18 + T} \tag{6}$$

where μ is the dynamic viscosity (cP), μ_w is the viscosity of pure water, and μ_R is the relative viscosity. Note that μ_R is equal to unity for pure water at all temperatures and greater than unity for salt solutions:

$$\mu_R = 1 + Q_1 S + Q_2 S^2 \tag{7}$$

$$Q_1 = (1.474 \times 10^{-3}) + (1.5 \times 10^{-5} T) - (3.929 \times 10^{-8} T^2) \tag{8}$$

$$Q_2 = (1.0374 \times 10^{-5}) - (8.5 \times 10^{-8} T) + (2.23 \times 10^{-10} T^2) \tag{9}$$

where T is the temperature (°C) and S is the brine concentration in g/1000 g saturated solution.

Third: Calculated values were then compared with the experimental ones (as determined by the chemical laboratory of the plant). The values checked reasonably well as shown in Table 2. The analysis of Al-Khobar Desalination Plant blowdown is given in Table 3.

TABLE 2
Comparison between Experimental and Calculated Values of Brine Specific Gravity and Viscosity at 27°C

Salinity	Experimental specific gravity	Calculated values	Deviation (%)	Experimental viscosity (cP)	Calculated viscosity (cP)	*Deviation (%)[a]
6.45	1.042	1.045	0.288	0.948	0.985	3.9
8.045	1.057	1.057	0.000	0.993	1.038	3.5
10.914	1.075	1.079	0.372	1.030	1.113	8.1
17.654	1.126	1.132	0.476	1.212	1.331	9.8
25.336	1.185	1.194	0.759	1.610	1.576	2.11

[a] $^*\text{Deviation} = \dfrac{\text{Experimental value} - \text{calculated value}}{\text{Experimental value}}.$

TABLE 3
Analysis of Al-Khobar Desalination Plant Blowdown at 27°C

Evaporation (%)	Specific gravity	Cl^- (ppm)	Salinity (ppm)	Mg^{2+} (ppm)	Na^+ (ppm)	Viscosity (cP)
0	1.042	37,151.8	64,410.963	2,381.890	21,800	0.948
22	1.057	47,361.2	80,446.4294	3,038.125	27,700	0.993
43	1.075	64,944.4	109,139.8193	4,204.765	38,200	1.030
67	1.126	110,036.8	176,542.6119	7,024.125	64,000	1.212
79	1.185	166,189.6	253,358.499	10,961.555	104,000	1.610
93	1.230	—	—	—	—	—

CONCLUSIONS

The solubility correlation that was developed is valid for predicting the solubility of NaCl in aqueous $MgCl_2$ solution for the indicated temperature and concentration ranges. An average deviation of less than 8% was calculated, except for a few points which probably had inherent experimental errors. For these specific points, the deviation was extremely high.

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