

THERMODYNAMICS OF EXTRACTION OF Zn^{2+} FROM SULFURIC ACID MEDIA WITH A MIXTURE OF DEHPA AND MEHPA

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Abstract Thermodynamics of extraction of Zn^{2+} from sulfuric acid media contacting to a mixture of DEHPA and MEHPA diluted with 80 wt% aromatic - aliphatic kerosene with a constant DEHPA to MEHPA ratio is investigated at different acidities, concentrations and temperatures. As a result, the extraction reaction is found to be endothermic with a zinc distribution factor that increases with increasing of the temperature, acidity of the solution and the concentration of the extractant. The mechanism of the extraction reaction is shown to be different for $pH > 1$ with that at $pH < 1$. The pH of the aqueous media has also an important influence on progressing of the extraction reaction.

Key Words Solvent Extraction, Zinc, DEHPA, MEHPA, Thermodynamics, Extraction Mechanism

چکیده ترمودینامیک استخراج یون Zn^{2+} از محیط حاوی اسید سولفوریک در تماس با مخلوط دپا DEHPA و مپا MEHPA رقیق شده با ۸۰٪ نفت سفید آروماتیک الیفاتیک با نسبت ثابت دپا به مپا در اسیدیته، غلظت و دماهای مختلف بررسی شده است. در نتیجه معلوم شده است که واکنش استخراج حرارت گیر است و فاکتور توزیع با افزایش دما، اسیدیته محلول و غلظت استخراج گر بزرگ می شود. همچنین نشان داده شده که مکانیزم استخراج در پی اچ بزرگتر از یک با مکانیزم استخراج در پی اچ کوچکتر از یک فرق داشته و پی اچ محیط آبی بر پیشرفت واکنش استخراج تاثیر بسزایی دارد.

1. INTRODUCTION

Solvent extraction is a desirable way for production of high purity metallic by-products from leaching liquor solutions. Although organic solvents are usually expensive materials, they are, however, proved to be eligible for selective extraction of multiple coexisting ions present in the dilute acid media of many commercial systems of interest. Solvent extraction can, therefore, be considered as a capable way for simultaneous production of zinc, copper, cobalt, cadmium and germanium that may be present in leaching liquors

obtained from dissolution of a low-grade ore.

Considerable emphasis has recently been given to the pollution-free hydrometallurgical extraction of nonferrous metals such as zinc. Application of this root to production, up grading and refining of nonferrous metals seems an attractive way for approaching industrial automation and cost effective extractive processes of considerable interest [1-13].

In 1974, for the first time, DEHPA was used for extraction of zinc from leaching liquor solutions produced in a zinc production plant in Soviet Union. Di-Ethyl Hexyl Thiophosphoric Acid

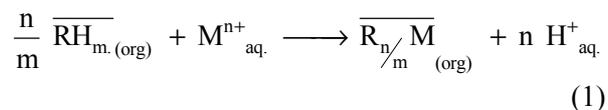
was then used by other investigators for separation of Zn, Cu, Ga, Ge and In from leaching liquor solutions. D. S. Flett, et al. investigated the solvent extraction of zinc, too [14-16]. S. Zielinsky worked to develop an extraction technique for recovery of zinc, cadmium, lead, copper, nickel and cobalt by DEHPA and precipitation stripping of metals, through utilization of oxalic acid, ammonium oxalate and sodium oxalate salty solution [16]. Laboratory scale selective extraction of zinc, nickel, cobalt and cadmium by DEHPA in presence of TBP modifier was also investigated by G. Owusu [17]. T. Zhang, et al. studied the solvent extraction of zinc, cadmium, cobalt, nickel, iron, aluminum and manganese with DEHPA diluted in kerosene [18]. F. J. Alguacil studied the extraction of zinc ions dissolved in an ammonia media with LIX 54 [19]. At present, there is a plant in Espinosa, Spain, that works for extraction of zinc by hydrometallurgical solvent extraction method. S Cole and Sole reviewed the solvent extraction of zinc with different extractants [20]. Synergistic effect of MEHPA on co-extraction of zinc and cadmium with DEHPA also has been investigated by Keshavarz Alamdari and et al. [21].

In spite of the above endeavors, there is no quantitative data now available on the effect of temperature, concentration of DEHPA, MEHPA and their mixture and pH of the aqueous media on the distribution factor of zinc and other coexisting ions throughout the literature. Simple thermodynamic properties such as enthalpy, entropy and equilibrium constant of the extraction reactions are generally not mentioned anywhere. These information are, however, quite necessary for any detailed scientific study of any industrially important application. It is, therefore, desirable to spend some more time to dig deeper into the proposed extraction systems of interest to obtain pieces of the information necessary for convenient estimation of the distribution factors prevailing under practical commercial extraction conditions.

2. CHEMICAL EQUILIBRIA

The Extraction reaction of a cation with a cationic

extractant has the following general form:



Where RH_m is the cationic extractant as a m capacity organic acid and M^{n+} is the cation being extracted and where n is equal two then m is equal one or two. The equilibrium constant of reaction 1 may be written as:

$$\text{K} = \frac{\overline{a_{\text{R}_{n/m}\text{M}}} \times a_{\text{H}^+}^n}{a_{\overline{\text{RH}}_m}^{n/m} \times a_{\text{M}^{n+}}} = \frac{[\overline{\text{R}}_{n/m} \text{M}] \times [\text{H}^+]^n}{[\overline{\text{RH}}_m]^{n/m} \times [\text{M}^{n+}]}$$

$$\frac{\gamma_{\overline{\text{R}}_{n/m} \text{M}} \times \gamma_{\text{H}^+}^n}{\gamma_{\overline{\text{RH}}_m}^{n/m} \times \gamma_{\text{M}^{n+}}} = \frac{[\overline{\text{R}}_{n/m} \text{M}] \times [\text{H}^+]^n}{[\overline{\text{RH}}_m]^{n/m} \times [\text{M}^{n+}]} \times \text{Q} \quad (2)$$

where Q is the quotient of the activity coefficients and square brackets indicate the molar concentrations. The distribution factor of species M may be written as:

$$\text{D}_M = \frac{\sum [\text{M}]_{\text{org.}}}{\sum [\text{M}]_{\text{aq.}}} \quad (3)$$

By substituting Equation 3 into Equation 2 and considering that solubility of aqueous/organic phases in each other is negligible, thus:

$$\frac{\text{K}}{\text{Q}} = \text{K}' = \frac{\text{D}_M \times [\text{H}^+]^n}{[\overline{\text{RH}}_m]^{n/m}} \quad (4)$$

Re-arranging and taking logarithms yields:

$$\log \text{D}_M = \log (\text{K}') + \frac{n}{m} \log [\overline{\text{RH}}_m] - n \log [\text{H}^+] \quad (5)$$

Since $\log \text{K}'$ is a function of temperature,

Equation 5 can be written as:

$$\log D_M = -\frac{\Delta H_{app}^\circ}{2.303 RT} + \frac{\Delta S_{app}^\circ}{2.303 R} + \frac{n}{m} \log [\overline{RH}_m] + n \text{ pH} \quad (6)$$

Where ΔH_{app}° and ΔS_{app}° are called the apparent standard changes of enthalpy and entropy of the reaction 1, respectively. By measuring the distribution factor of an ion, one can determine the relationship between the stoichiometric coefficients and the apparent standard enthalpy and entropy of the reaction.

3. EXPERIMENTAL

3.1 Materials and Reagents Stock of zinc ion solution (50 gr./lit) was prepared by dissolving analytical grade zinc sulfate heptahydrate $ZnSO_4 \cdot 7H_2O$ produced by Panreac (Madrid-Spain) company - in distilled water. The sulfuric acid solution was prepared by diluting analytical grade sulfuric acid from Baran Chemical Company of Iran in distilled water. Acidic solutions of zinc sulfate were prepared by diluting aliquot solution with 5 M sulfuric acid to produce the required final concentrations. Corresponding quantities of technical grade DEHPA were dissolved in aromatic kerosene both obtained from Fluka AB., Switzerland. This grade of DEHPA has contained up to 40% Mono-2-Ethylhexyl phosphoric acid (MEHPA).

3.2 Experimental Procedure Batch experiments were carried out in a flask containing equal volumes (20 ml) of aqueous and organic phases. The mixture was agitated at a constant temperature with a mechanical shaker. The experiments were allowed to run for one hour, even though equilibrium could be obtained within less than 20 minutes [17,23,24]. The samples were retained for

three more hours to allow complete separation of phases and the two phases were then removed with a separation funnel. Equilibrium was attained at different temperatures (25, 40 and 60 ± 0.5 °C).

The initial concentration of zinc in the aqueous phase in all experiments was 5 g/L. Zinc content of the aqueous phase was analyzed by the titration method using EDTA and Erio-chrome black T as Indicator. Chemical composition of the organic phase was determined through mass balance calculations.

4. RESULTS AND DISCUSSION

4.1 Effect of pH Effect of pH on the distribution factor of Zn was determined by changing the equilibrium pH value while keeping temperature, organic extractant concentration. It is seen from Figure 1 that D_{Zn} increases with increasing of the pH. It is also observed that at 25°C, the value of the slope for $pH < 1$ is different from that at $pH > 1$.

The values of the slopes at different extractant concentrations and temperatures are given in Table 1. It is seen that the average value of the slopes, is 1.29 for $pH < 1$ and 0.84 for $pH > 1$. Based on these results at 25°C and lower pH values, MEHPA and DEHPA can extract zinc simultaneously, while at higher pH values, only DEHPA can extract zinc from the aqueous extractant concentrations of 5%, 10%, 20% and 30%, respectively. On the other hand, decreasing of pH (increasing of H^+ concentration) could be activates the organic extractant of lower acid capacity, i.e. DEHPA.

4.2 Effect of Extractant Concentration

Equation 6 indicates that at constant temperature, pH and metal concentration of the aqueous phase, the logarithm of the distribution factor of zinc must be proportional to the logarithm of the concentration of DEHPA, MEHPA and mix of them. For extractant concentrations ranging from 5 to 30 vol. % mix of DEHPA and MEHPA, this effect is shown in Figure 2 for 25 °C and is summarized in Table 2 for other temperatures.

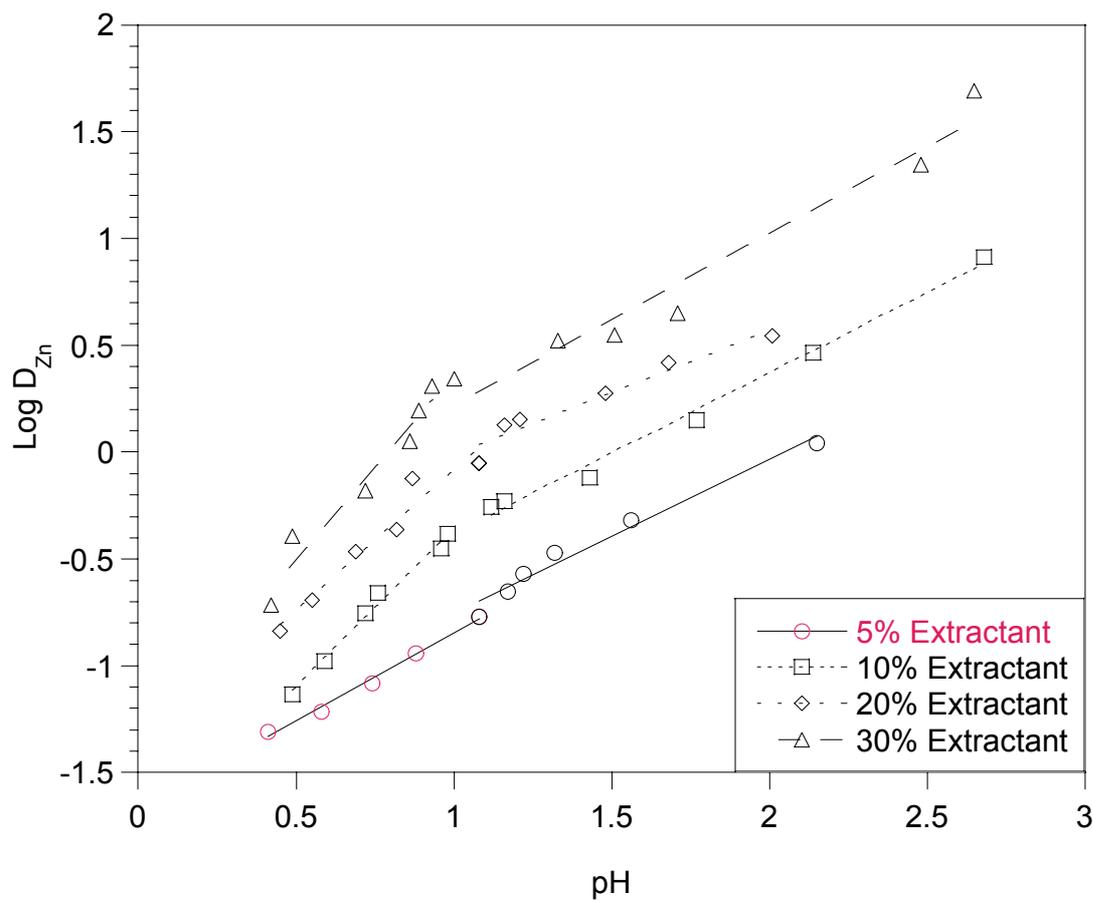


Figure 1. Effect of equilibrium pH on the distribution factor of zinc at 25 °C.

TABLE 1. Values of the Slopes of $\log D_{Zn}$ versus pH Evaluated at Different Temperatures and Extractant Concentrations.

% DEHPA + % MEHPA	Temperature °C					
	25		40		60	
	pH < 1	pH > 1	PH < 1	pH > 1	pH < 1	pH > 1
5	0.82	0.72	0.84	0.64	1.43	0.84
10	1.49	0.75	1.34	0.99	1.35	1.03
20	1.31	0.58	0.99	0.81	1.47	1.30
30	1.74	0.80	1.34	0.77	1.37	0.83
Average	1.34	0.71	1.13	0.80	1.40	1.00
	For pH < 1		1.29	For pH > 1		0.84

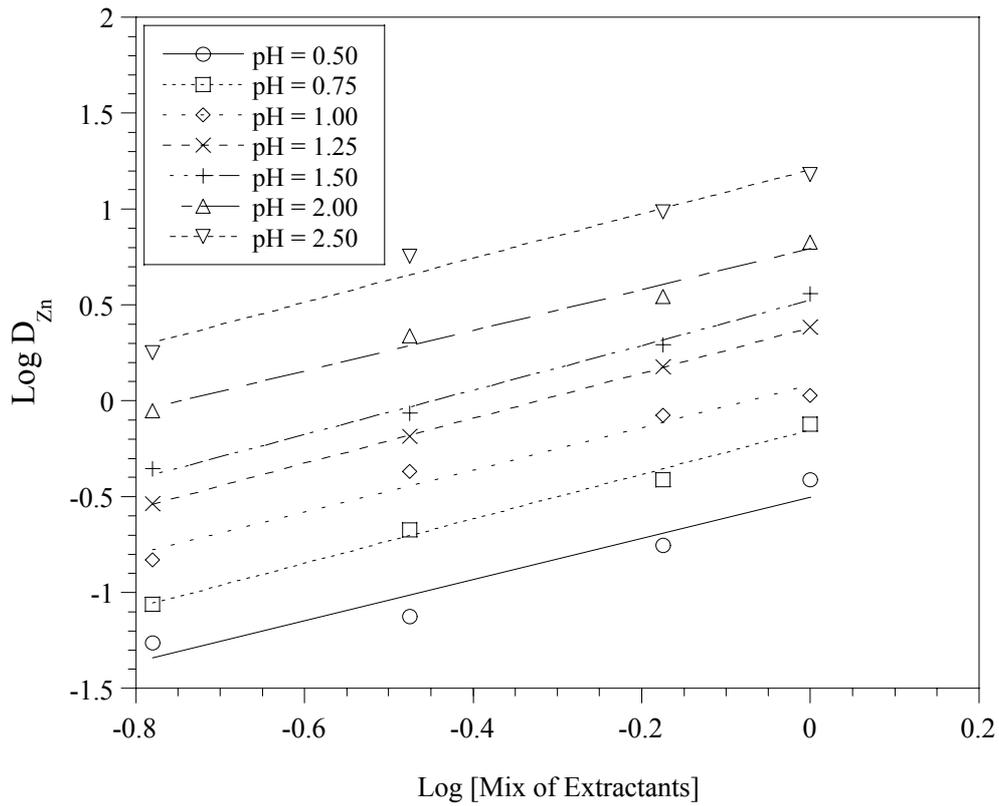


Figure 2. Effect of equilibrium extractant mixture on the distribution factor of zinc at 25°C and different equilibrium pH.

TABLE 2. Slopes of $\log D_{Zn}$ versus $\log [\text{Extractant}]$ Evaluated at Different Temperatures and Equilibrium pH Values.

Equilibrium pH value	Temperature °C			
	25	40	60	Mean
0.5	1.08	1.05	1.06	1.06
0.75	1.16	0.99	0.92	1.02
1.00	1.10	1.02	0.92	1.01
1.25	1.18	1.12	0.94	1.08
1.50	1.16	1.07	0.97	1.07
2.00	1.06	1.11	1.15	1.11
2.50	1.15	-	-	-
Mean value for pH<1	1.11	1.02	0.97	1.03
Mean value for pH>1	1.14	1.10	1.02	1.09
Overall mean value	1.13	1.06	0.99	1.06

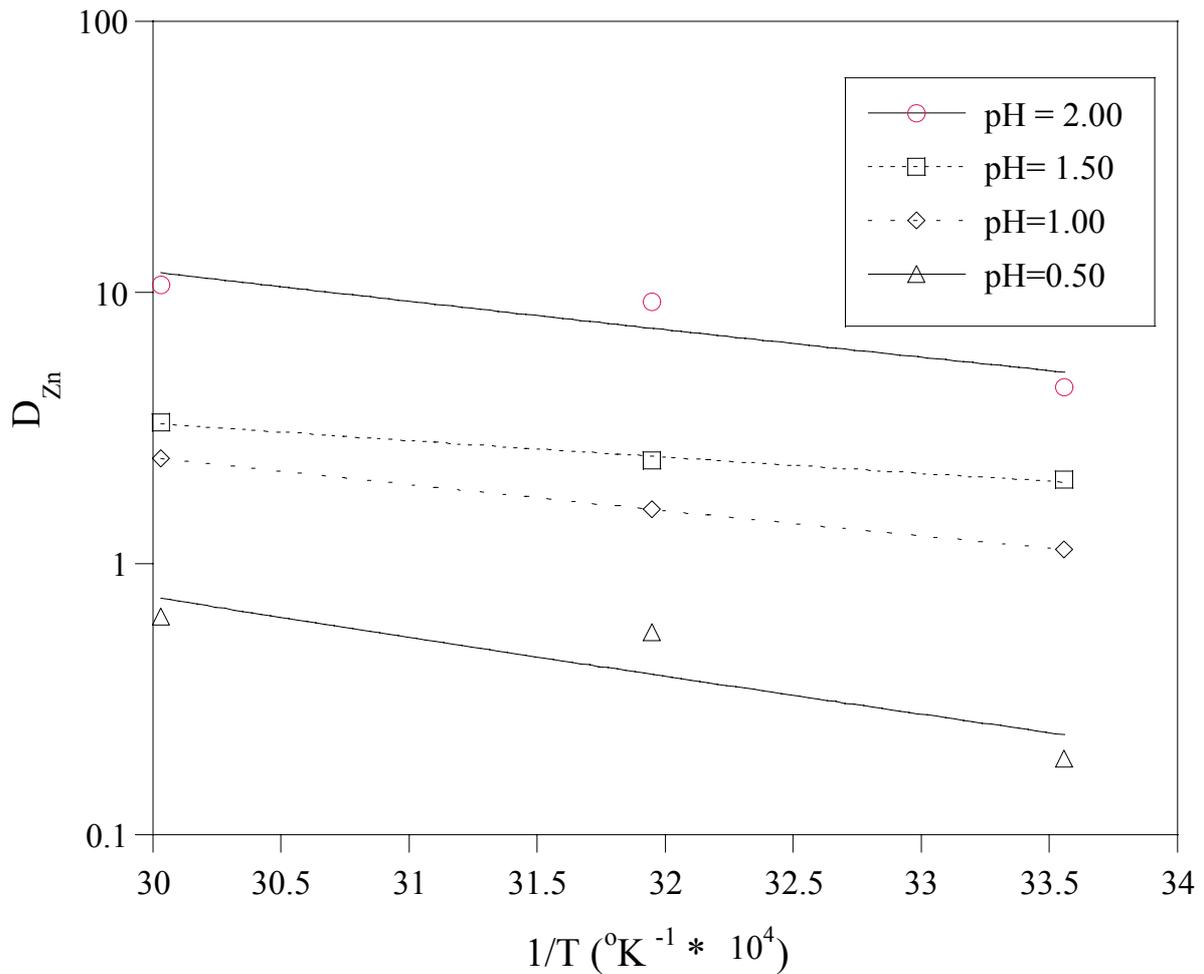


Figure 3. Effect of temperature on zinc distribution factor with 30 vol.% of extractant in kerosene.

These results indicate a constant slope at different temperatures, $\log [\text{DEHPA} + \text{MEHPA}]$ vs $\log [\text{Zn}]$. The average slopes at 25°C, 40°C and 60°C are 1.11, 1.02 and 0.97 for $\text{pH} < 1$ and 1.14, 1.10 and 1.02 for $\text{pH} > 1$, respectively. The overall slope at the temperature range 25 to 60 °C is 1.06.

4.3 Effect of Temperature Effect of temperature on the extraction of zinc was concentration. It can be seen from Figure 3 that D_{Zn} increases with increasing of the temperature.

Similar effect is observed at all acid and Extractant concentrations. The values of the slopes for determined by changing temperature between 25 °C and 60 °C at a constant extractant different extractant concentrations and acid molarities are given in Table 3. These values are -1796.23, -1503.62, -1624.17 and -1383.77 for 5%, 10%, 20% and 30% extractant concentrations, respectively. The overall slope at the extractant concentrations range 5 to 30 is -1576.95. The apparent standard enthalpy

TABLE 3. Values of the Slopes of log D_{Zn} versus $1/T$ Evaluated at Different Extractant Concentrations and Equilibrium pH Values .

Initial pH value	Extractant (%)				Mean
	5	10	20	30	
0.5	-1202.4	-1391.8	-1583.6	-1076.7	-1313.6
0.75	-1938.5	-1551.5	-1699.6	-1230.7	-1605.1
1.00	-2019	-1406.5	-1450.8	-1552.2	-1607.1
1.25	-1692.4	-1146.6	-1107.5	-1082.9	-1257.4
1.50	-1865.2	-1373.3	-1661.5	-1271.8	-1543.0
2.00	-2059.9	-2152	-2242	-2088.3	-2135.6
Mean value for pH<1	-1719.97	-1449.93	-1578	-1286.53	-1508.6
Mean value for pH>1	-1872.5	-1557.3	-1670.33	-1481	-1645.3
Overall mean value	-1796.23	-1503.62	-1624.17	-1383.77	-1576.9

TABLE 4. Results of Regression Analysis of Data with SPSS for Both Conditions of pH < 1 and pH > 1.

Parameters	Value	
	pH<1	pH>1
$\frac{\Delta S_{app}^{\circ}}{2.303 R}$	3.38	4.74
$-\frac{\Delta H_{app}^{\circ}}{2.303 R}$	-1223.09	-1509.06
$\frac{n}{m}$	1.13	1.22
n	1.25	0.82

of the extraction reaction 1 is, therefore, -13.1 KJ/mol. Therefore, the extraction of zinc sulfate from sulfuric aqueous media with a mixture of DEHPA and MEHPA is an endothermic reaction.

4.4 Approximate Equation for Computation of the Distribution Factor In order to compute the unknown coefficients of Equation 6 from Tables 1 to 3, Equation 6 may be rewritten for $\text{pH} > 1$ as:

$$\log D_M = - \frac{1508.6}{T} + \frac{\Delta S_{\text{app.}}}{2.303 R} + 1.03 \log [\overline{\text{RH}}_m] + 0.84 \text{ pH} \quad (7)$$

and for $\text{pH} < 1$ as:

$$\log D_M = - \frac{1645.3}{T} + \frac{\Delta S_{\text{app.}}}{2.303 R} + 1.09 \log [\overline{\text{RH}}_m] + 1.29 \text{ pH} \quad (8)$$

where all of the constants are substituted with figures except $\Delta S_{\text{app.}} / R$. It should be noted that the constants are defined for a special case where one parameter is being changed while the others are fixed. It is, however, more appropriate to assign new values to all parameters specified in the equation. In order to determine these coefficients, we gathered a data bank with different pH values and analyzed the data with SPSS for windows V. 8.0. The results are shown in Table 4 for both conditions of $\text{pH} < 1$ and $\text{pH} > 1$. The final equation for the zinc distribution is:

$$\log D_{\text{Zn}} = 3.38 - \frac{1223.09}{T} + 1.13 \log [\overline{\text{RH}}_m] + 1.25 \text{ pH} \quad (9)$$

for $\text{pH} < 1$ and:

$$\log D_{\text{Zn}} = 4.74 - \frac{1509.06}{T} + 1.22 \log [\overline{\text{RH}}_m] + 0.82 \text{ pH} \quad (10)$$

for $\text{pH} > 1$.

5. SUMMARY

The zinc extraction reaction with a mixture of DEHPA and MEHPA is an endothermic reaction. The apparent standard enthalpy of the extraction reaction for pH less than one is 23.4 KJ/mol. and for pH greater than one is 28.9 KJ/mol. Based on regression analysis of the experimental data, the zinc distribution factor depends on temperature, H^+ concentration and Mixture concentration according to:

$$\log D_{\text{Zn}} = 3.38 - \frac{1223.09}{T} + 1.13 \log [\overline{\text{RH}}_2] + 1.25 \text{ pH} \quad (11)$$

for $\text{pH} < 1$ and:

$$\log D_{\text{Zn}} = 4.74 - \frac{1509.06}{T} + 1.22 \log [\overline{\text{RH}}] + 0.82 \text{ pH} \quad (12)$$

for $\text{pH} > 1$.

The apparent standard enthalpies of zinc extraction with a mixture of DEHPA and MEHPA from aqueous sulfuric acid media at $\text{pH} < 1$ and $\text{pH} > 1$ are found to be equal to 23.4 and 28.9 KJ/mol, respectively. The apparent standard entropies of zinc extraction with a mixture of DEHPA and MEHPA from aqueous sulfuric acid media at $\text{pH} <$

1 and $\text{pH} > 1$ are found to be equal to 64.7, and $90.7 \frac{J}{\text{mol.deg}}$, respectively.

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