

# THERMODYNAMICS OF ELECTROLYTE SOLUTIONS: ELECTROMOTIVE FORCE STUDIES ON AQUEOUS SOLUTIONS OF KCl IN KCl + MgCl<sub>2</sub> + H<sub>2</sub>O SYSTEM AT 25°C

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## ABSTRACT

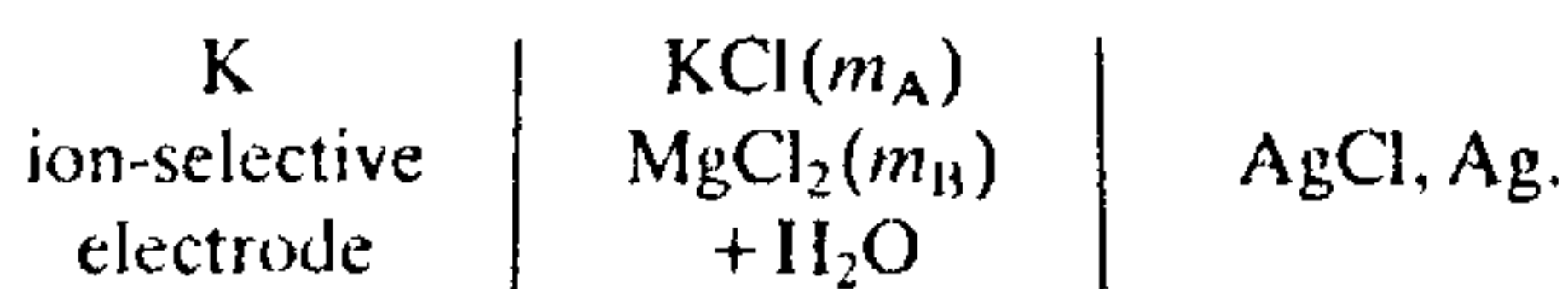
The activity coefficients of aqueous KCl in KCl-MgCl<sub>2</sub>-H<sub>2</sub>O system were obtained at 25°C and at total ionic strengths of 0.5, 1, 2 and 3 m by an emf method using potassium ion-selective electrode and Ag/AgCl electrode. The activity coefficient data were fitted to the Harned equation and the Harned coefficients evaluated. The data were also analysed using the Pitzer equations and the corresponding binary and ternary interaction parameters were estimated.

## INTRODUCTION

THE thermodynamic properties, such as the activity coefficients of multicomponent aqueous electrolyte solutions are useful in several fields such as environmental water pollution studies, oceanography, biological phenomena, and petroleum drilling and therefore, attracted the attention of solution chemists<sup>1</sup>. The activity coefficients of KCl in KCl + MgCl<sub>2</sub> + H<sub>2</sub>O mixtures were estimated<sup>2</sup> at a total ionic strength of 1 and 25°C. Padova and Saad<sup>3</sup> measured the vapour pressures of aqueous KCl and MgCl<sub>2</sub> mixtures isopiesticly and estimated the osmotic coefficients of these solutions. However, a systematic study to estimate the activity coefficients of aqueous KCl in these mixtures over a wide range of ionic strength is still lacking. In the present study, the mean ionic activity coefficients of aqueous KCl solutions were estimated in KCl + MgCl<sub>2</sub> + H<sub>2</sub>O system at 25°C and at total ionic strengths of 0.5, 1, 2 and 3 m using emf studies.

## EXPERIMENTAL

The cell arrangement consisted of a potassium ion-selective electrode (Elico, India) and Ag/AgCl electrode immersed in a mixture of KCl and MgCl<sub>2</sub> aqueous solutions placed in a double-walled glass vessel whose temperature was maintained constant by circulating thermostated water.



The Ag/AgCl electrodes were prepared according to the standard thermal method<sup>4</sup>. The electrodes were connected to a high impedance ( $\approx 10^{12} \Omega$ ) unit gain amplifier. The output of this amplifier was

measured by an electrometer/multimeter (Keithley, Model, DMM 191 digit). The accuracy of emf measurements was  $\pm 0.1$  mV.

Analytical grade potassium chloride (GR: S Merk) and magnesium chloride (AR: Glaxo) were used without further purification. The stock solutions were standardized by volumetric determination of chloride ion with AgNO<sub>3</sub>. All solutions were taken by weight. Also, all titrations and dilutions were made using weight burettes.

At every ionic strength the potassium ion-selective electrode was first calibrated using the aqueous KCl solutions at various molalities. Next, its selectivity towards Mg<sup>2+</sup> ions was estimated by measuring the cell emfs with pure MgCl<sub>2</sub> solutions at several molalities. The third set consisted of the emf measurements in KCl + MgCl<sub>2</sub> + H<sub>2</sub>O mixtures. For this set the potentials were first measured by starting with pure KCl solution and adding aliquots of MgCl<sub>2</sub> solution. Next, starting with pure MgCl<sub>2</sub> solution aliquots of KCl were successively added. The overlapping portion between these two experiments was used to test the reproducibility and accuracy of the measurements. Also, all the three sets were repeated at least twice to get consistent and reproducible results.

## RESULTS AND DISCUSSION

The emfs of potassium ion-selective electrode vs the Ag/AgCl electrode in KCl-MgCl<sub>2</sub> mixtures are given by the relation

$$E_{\text{KCl-MgCl}_2} = E_o + k \log (a_K a_{\text{Cl}^-} + K' a_{\text{Mg}^{2+}}^2 a_{\text{Cl}^-}), \quad (1)$$

where  $K'$  = selectivity coefficient of potassium electrode for Mg<sup>2+</sup> ions and  $k = 2.303 RT/nF$  which is the Nernst slope.

In pure KCl solutions,  $a_{Mg} = 0$  and therefore

$$E_{KCl} = E_o + k \log a_K a_{Cl} \quad (2)$$

In pure  $MgCl_2$  solutions  $a_K = 0$  and therefore the rearranged equation is

$$K' = (1/a_{MgCl_2}^3) 10^{(E_{MgCl_2} - E_o)/k} \quad (3)$$

At each ionic strength the emf data obtained in the calibration run was fitted to (2) using a least-squares procedure to find the  $E_o$  and  $k$  values. Next, the emf data obtained in the second set i.e. with pure  $MgCl_2$  solutions along with these  $E_o$  and  $k$  values were substituted in (3) to find the selectivity coefficient ( $K'$ ) values. The activity coefficients of potassium chloride<sup>5</sup> and magnesium chloride<sup>6</sup> were taken from the NBS data. The values of the selectivity coefficients at all the ionic strengths studied were  $\leq 1 \times 10^{-4}$ . Therefore, the second term within brackets on the RHS of (1) was neglected. The cell emfs for aqueous KCl- $MgCl_2$  mixtures could be described by the relation

$$E_{KCl-MgCl_2} = E_o + k \log a_K a_{Cl}. \quad (4)$$

Equation (4) could be rearranged as

$$\gamma_{\pm}^2 = (1/m_K m_{Cl}) 10^{(E_{KCl-MgCl_2} - E_o)/k} \quad (5)$$

Thus, the activity coefficients of KCl in aqueous KCl- $MgCl_2$  mixtures were calculated by substituting the cell emfs ( $E_{KCl-MgCl_2}$ ) in (5). These experimental mean activity coefficients ( $\gamma_{\pm}$ ) of KCl in aqueous KCl- $MgCl_2$  mixtures at the total ionic strengths of 0.5, 1, 2 and 3 are given in table 1 at different values of  $y_B$  i.e. the ionic strength fraction of  $MgCl_2$ .

$$y_B = 3m_{MgCl_2}/(m_{KCl} + 3m_{MgCl_2}). \quad (6)$$

The  $\log \gamma_{\pm}$  vs  $y_B$  plots shown in figure 1 are all linear. These  $\gamma_{\pm}$  values at each ionic strength were fitted to the Harned equation<sup>7</sup>.

$$\log \gamma'_A = \log \gamma_A^0 - \alpha_{AB} y_B, \quad (7)$$

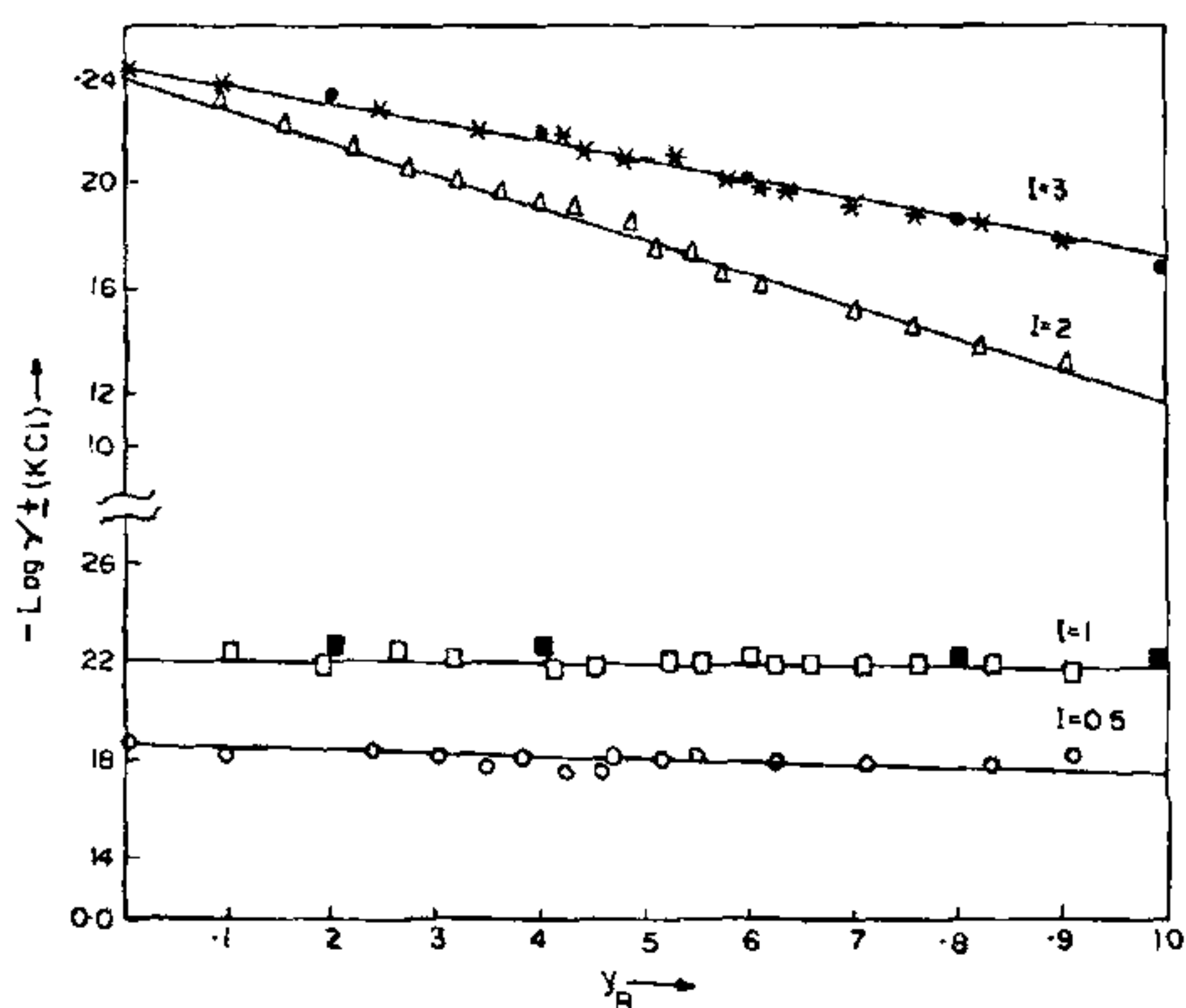
where  $\gamma_A^0$  is the activity coefficient of pure KCl at the same ionic strength as the mixture. The values of Harned coefficients i.e.  $\alpha_{AB}$  are listed in table 2. All the calculations were done on a VAX computer.

Table 1 Mean activity coefficients of KCl in KCl +  $MgCl_2$  +  $H_2O$  system at 25°C

|       | $I = 0.5$              | $I = 1$                | $I = 2$                | $I = 3$                |
|-------|------------------------|------------------------|------------------------|------------------------|
| $E_o$ | 0.1990                 | 0.1979                 | 0.2068                 | 0.2024                 |
| $k$   | 0.05915                | 0.05916                | 0.05914                | 0.05915                |
| $K'$  | $2.217 \times 10^{-5}$ | $3.621 \times 10^{-5}$ | $7.760 \times 10^{-5}$ | $6.413 \times 10^{-5}$ |

| $y_B$  | $-\log \gamma_{\pm}$ | $y_B$  | $-\log \gamma_{\pm}$ | $y_B$  | $-\log \gamma_{\pm}$ | $y_B$  | $-\log \gamma_{\pm}$ |
|--------|----------------------|--------|----------------------|--------|----------------------|--------|----------------------|
| 0.0949 | 0.1851               | 0.1035 | 0.2212               | 0.0870 | 0.2335               | 0.0939 | 0.2390               |
| 0.1734 | 0.1833               | 0.1877 | 0.2191               | 0.1601 | 0.2224               | 0.2372 | 0.2294               |
| 0.2394 | 0.1854               | 0.2573 | 0.2198               | 0.2223 | 0.2134               | 0.3413 | 0.2205               |
| 0.2956 | 0.1810               | 0.3160 | 0.2193               | 0.2760 | 0.2062               | 0.4204 | 0.2170               |
| 0.3441 | 0.1784               | 0.4093 | 0.2175               | 0.3227 | 0.2005               | 0.4372 | 0.2134               |
| 0.3863 | 0.1813               | 0.4471 | 0.2171               | 0.3638 | 0.1961               | 0.4826 | 0.2093               |
| 0.4234 | 0.1775               | 0.5187 | 0.2169               | 0.4001 | 0.1929               | 0.5327 | 0.2095               |
| 0.4563 | 0.1787               | 0.5480 | 0.2158               | 0.4326 | 0.1906               | 0.5740 | 0.2035               |
| 0.4687 | 0.1811               | 0.6179 | 0.2158               | 0.4847 | 0.1840               | 0.6085 | 0.1998               |
| 0.5188 | 0.1804               | 0.6599 | 0.2169               | 0.5110 | 0.1766               | 0.6379 | 0.1980               |
| 0.5481 | 0.1810               | 0.7080 | 0.2174               | 0.5404 | 0.1731               | 0.6997 | 0.1916               |
| 0.5809 | 0.1785               | 0.7638 | 0.2161               | 0.5733 | 0.1666               | 0.7565 | 0.1892               |
| 0.6179 | 0.1803               | 0.8291 | 0.2158               | 0.6305 | 0.1623               | 0.8233 | 0.1849               |
| 0.7081 | 0.1807               | 0.9066 | 0.2153               | 0.6529 | 0.1584               | 0.9031 | 0.1793               |
| 0.7638 | 0.1798               |        |                      | 0.7016 | 0.1524               |        |                      |
| 0.8291 | 0.1787               |        |                      | 0.7582 | 0.1453               |        |                      |
| 0.9066 | 0.1826               |        |                      | 0.8247 | 0.1379               |        |                      |
|        |                      |        |                      | 0.9039 | 0.1310               |        |                      |



**Figure 1.**  $\text{Log } \gamma_{\text{KCl}}$  vs  $y_{\text{MgCl}_2}$ . ■ Christenson and Gieskes<sup>2</sup> data at  $I = 1$ ; ● Padova and Saad<sup>3</sup> data at  $I = 3$ .

The activity coefficient data were further analysed using the Pitzer formalism<sup>8-11</sup>. The NBS data<sup>5,6</sup> on the activity coefficients of pure KCl and  $\text{MgCl}_2$  solutions were fitted to the Pitzer equation<sup>9,11</sup> and the corresponding coefficients are

$$\begin{aligned} \beta_{\text{KCl}}^0 &= 0.04808, \beta'_{\text{KCl}} = 0.21875, C_{\text{KCl}}^\phi \\ &= -0.00079, \\ \beta_{\text{MgCl}_2}^0 &= 0.3524, \beta'_{\text{MgCl}_2} = 1.740, C_{\text{MgCl}_2}^\phi \\ &= 0.005192. \end{aligned}$$

**Table 2** Harned coefficients of KCl in  $\text{KCl-MgCl}_2\text{-H}_2\text{O}$  system at 25°C

| $I$ | $\log \gamma_A^0$ | $\alpha_{AB}$ | $\text{RMSD} \times 10^3$ |
|-----|-------------------|---------------|---------------------------|
| 0.5 | -0.1872           | -0.0130       | 2.70                      |
| 1.0 | -0.2184           | -0.00186      | 1.29                      |
| 2.0 | -0.2408           | -0.1236       | 1.96                      |
| 3.0 | -0.2438           | -0.0701       | 1.71                      |

RMSD = Root mean square deviation.

The activity coefficient of aqueous KCl in constant ionic-strength mixtures of  $\text{KCl-MgCl}_2$  is described by the equation

$$\begin{aligned} \ln \gamma_{\text{KCl}} &= \ln \gamma_{\text{KCl}}^0 - (4/3)Iy_B B_{\text{KCl}} \\ &+ (Iy_B/3)B_{\text{MgCl}_2} + (I^2/18) \\ &+ (7y_B^2 - 30y_B)C_{\text{KCl}}^\phi + (I^2y_B/3\sqrt{2}) \\ &+ (1 - y_B/3)C_{\text{MgCl}_2}^\phi + (Iy_B/3)\theta_{\text{KMg}} \\ &+ (I^2y_B/3)(1 - 2y_B/3)\psi_{\text{KMgCl}} \\ &+ (I^2y_B/3)(y_B - 4)B'_{\text{KCl}} \\ &+ (I^2y_B/3)(1 - y_B/3)B'_{\text{MgCl}_2} \\ &+ (I^2y_B/3)(1 - y_B)\theta'_{\text{KMg}}, \end{aligned} \quad (8)$$

where

$$\theta_{\text{KMg}} = s_{\theta_{\text{KMg}}} + E_{\theta_{\text{KMg}}}$$

$$\theta'_{\text{KMg}} = E_{\theta'_{\text{KMg}}}$$

$E_\theta$  and  $E_{\theta'}$  are called higher order electrostatic terms and were calculated as described by Pitzer<sup>12</sup>.

The experimental activity coefficient data were fitted to (8), to evaluate the binary interaction coefficient ( $s_{\theta_{\text{KMg}}}$ ) and the ternary interaction coefficient ( $\psi_{\text{KMgCl}}$ ) at each ionic strength. These values are listed in table 3.

From figure 1 it is evident that our results are in close agreement with the results of Christenson and Gieskes<sup>2</sup> at  $I = 1$  and also with the indirectly estimated values of Padova and Saad<sup>3</sup> at  $I = 3$ . The  $s_\theta$  and  $\psi$  values given in table 3 show that these values are not totally independent of ionic strength. But according to Pitzer<sup>12</sup> these values should be independent of ionic strength. Also, the activity coefficient data at all the four ionic strengths were fitted into a single least-square program and the common  $s_\theta$  and  $\psi$  values were evaluated. These  $s_\theta$

**Table 3**  $s_\theta$  and  $\psi$  values obtained from the activity coefficient data of KCl

| $I$ | $s_{\theta_{\text{KMg}}}$ | $\psi_{\text{KMgCl}}$ | RMSD ( $\times 10^{-3}$ ) | RMSD for $\theta = -0.3426$ $\psi = 0.2253$ | RMSD for $\theta = 0$ and $\psi = -0.022$ |
|-----|---------------------------|-----------------------|---------------------------|---|---|
| 0.5 | -0.3115                   | 0.8056                | 1.53                      | $7.56 \times 10^{-3}$                       | $3.88 \times 10^{-3}$                     |
| 1.0 | -0.1428                   | -0.0729               | 1.16                      | $4.25 \times 10^{-3}$                       | $1.36 \times 10^{-2}$                     |
| 2.0 | 0.2666                    | -0.0041               | 2.02                      | $5.37 \times 10^{-2}$                       | $4.36 \times 10^{-2}$                     |
| 3.0 | 0.0181                    | -0.0079               | 1.46                      | $2.05 \times 10^{-2}$                       | $1.02 \times 10^{-2}$                     |

and  $\psi$  values are  $-0.3426$  and  $0.2253$  respectively. The corresponding RMSD values are also given in table 3. Harvie and Weare<sup>13</sup>, from an analysis of solubility data, evaluated  $\psi = -0.022$  by fixing  $\theta = 0$ . The RMSD values corresponding to these  $s_\theta$  and  $\psi$  values are also given in table 3. By comparing the RMSD values in the last two columns of table 3 it is evident that  $\theta = 0$  and  $\psi = -0.022$ . The values of Harvie and Weare<sup>13</sup> may also be used to describe the data obtained in the present work.

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## ANNOUNCEMENT

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### 3RD EUROPEAN ELECTRIC STEEL CONGRESS

Organised by the Institute of Metals and co-sponsored by a number of other European bodies, 'The 3rd European Electric Steel Congress' will be held in October 1989 at the Bournemouth International Centre.

With simultaneous interpretation in English, French and German, the programme will comprise a number of Keynote Papers, together with technical sessions investigating the following areas: Design, development, commissioning, operation and economics of electric steelmaking plant and related equipment; Development of steelmaking practices for rolled, forged and cast products to meet the developing demands of the market and the competi-

tion from other processes and materials; Recycling of waste materials and development of techniques to improve environmental control and conserve energy; Research and development aimed at a better understanding of the technology involved and improved performance of electric steelmaking routes, covering raw materials aspects through to the teeming of the liquid steel. Authors are invited to submit an abstract of c.250 words by 1st July 1988. These and general requests for further information should be sent to Ms J Butler, The Institute of Metals, 1 Carlton House Terrace, London SW1Y 5DB.

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