Effect of temperature on the activity coefficient of KCl in the KCl-KOAc-H₂O mixture

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Received 14 May 1990; revised and accepted 29 April 1991

Electromotive-force measurements have been made on KCl-KOAc-H₂O mixtures to find the activity coefficient of KCl at 25, 35 and 45°C and at four different ionic strengths from 0.5 to 3.0 mol/kg. The measurements have been made using a cell containing a potassium ion-selective glass electrode and an Ag/AgCl electrode. The data have been analysed in terms of Pitzer and Scatchard formalism for evaluating the anion-anion interactions (Ω) and anion-cation-anion interactions (Ψ). The osmotic coefficients and excess Gibbs free energies of mixing have been calculated. Also, the heats of mixing for this system have been calculated.

The activity coefficients of multicomponent electrolyte solutions are needed to understand the thermodynamic behaviour of these solutions. The isopiestic vapour pressure measurements were carried out on KCl-KOAc-H₂O system by Jones et al. at 25°C in the total concentration range 0.9426-3.1665 mol/kg. Heats of mixing for KCl-KOAc-H₂O system were reported by Wood et al. at total ionic strengths of 1 mol/kg. However, the activity coefficients of this system have not been measured yet. In continuation of our earlier work, we are now reporting the activity coefficient data of KCl in KCl-KOAc-H₂O system at total ionic strengths of 0.5, 1.0, 2.0 and 3.0 mol/kg and at 25, 35 and 45°C. This paper reports measurements of KCl activity coefficients in aqueous solution containing potassium acetate. The purpose of the present work is to estimate the γKCl values, examine the results in the light of Pitzer's and Scatchard's treatments and calculate the binary and ternary interaction parameters of these theories. The osmotic coefficients, excess free energies and the heats of mixing were also calculated using the Pitzer parameters (Ω and Ψ).

Materials and Methods

Analytical reagent grade potassium chloride (Glaxo, India) was purified by precipitation from a saturated solution with hydrogen chloride gas. AR grade potassium acetate (Glaxo, India) was used after careful drying at 120°C. The stock solution of KCl was standardized by volumetric titrations against standard silver nitrate solution. All the solutions were prepared by weight. Also, all the titrations and dilutions were made using weight burettes.

The cell consisted of a potassium ion-selective electrode and an Ag/AgCl electrode:

\[
\text{KCl} (\text{mA}) + \text{Ag/AgCl} \text{ electrode}
\]

\[
\text{KCl(mA)} + \text{KOAc(mB)}
\]

The potassium ion-selective glass electrode was obtained from M/s Elico, India. The Ag/AgCl electrodes were prepared as described by Ives and Janz. These electrodes were immersed in aqueous KCl (mA) - KOAc (mB) solution placed in a double walled glass vessel whose temperature was maintained constant within ±0.01 K. The electrodes were connected to a high impedance (≈ 10¹²Ω) unit gain amplifier. A Keithley 54 digit electrometer/multimeter (model: DMM 191) was used to measure the output of this amplifier. The accuracy of EMF measurements was ±0.01 mV. The electrodes were first standardised at all the ionic strengths studied. The method of EMF measurements on this type of cell has been described in detail earlier.

Results and Discussion

The EMF values of potassium ion-selective electrode vs Ag/AgCl electrode in KCl-KOAc-H₂O mixtures are given by the relation:

\[
E_{\text{KCl-KOAc}} = E_0 + k \log(m_{\text{KCl}} \gamma_{\text{KCl}}^2 + K' m_{\text{KOAc}} \gamma_{\text{KOAc}}^2) \ldots (1)
\]

where \(K' m_{\text{KOAc}} \gamma_{\text{KOAc}}^2\) term takes into account...
the effect of potassium acetate on the cell EMF. The term $k = 2.303 R \ln F$ represents the Nernst slope and $E_0$ is the EMF of the pure KCl solution at unit activity. The $K$ values at all the ionic strengths and temperatures studied were $\leq 1 \times 10^{-5}$. Therefore, the $K' = 2.303 R T/n F$ term in Eq. 1 could be neglected. Thus, Eq. 1 could be rearranged as,

$$\gamma^2 = 1/(m_0 m_{Cl}) 10^{(E_{KCI KOAc} - E_0)/k}$$  

Hence, the mean activity coefficients ($\gamma^2$) of KCl can be calculated by substituting the EMFs of the cell with aqueous KCl-KOAc mixtures ($E_{KCI KOAc}$) in Eq. 2. All the calculations were done using a computer. The experimental mean activity coefficient data determined at $I = 0.5, 1.0, 2.0$ and $3.0$ mol/kg and at 25, 35 and 45°C are listed in Table 1 as a function of $\gamma_B$, the ionic strength.

<table>
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<th>$\gamma_B$</th>
<th>$-\log \gamma$</th>
<th>$\gamma_B$</th>
<th>$-\log \gamma$</th>
<th>$\gamma_B$</th>
<th>$-\log \gamma$</th>
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〈-contd〉
Table 1 – Activity coefficient of KCl in the KCl-KOAc-H₂O system – Continued

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<tr>
<th>Temp. = 45°C</th>
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<th>I = 3.0</th>
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<td>y_B</td>
<td>-log y</td>
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</table>

The activity coefficients and osmotic coefficients of pure potassium chloride\(^{12}\) and potassium acetate\(^{13,14}\) solutions were calculated using the Pitzer equations given below at all the experimental temperatures studied.

\[
\ln \gamma_A = -\frac{A_0}{[1 + b_1 \sqrt{I}] + 2 \sqrt{I}} \ln [1 + b_1 \sqrt{I}] + m [2 \beta^0 + 2 \beta^{11} / (4 \sqrt{I})] [1 - (1 + 2 \sqrt{I} - 2 \sqrt{I})] \exp (-2 \sqrt{I}) + 1.5 m^2 C^0
\]

\[
\phi^0 = 1 - \frac{A_0}{[1 + b_1 \sqrt{I}] + 2 \beta^0 + 2 \beta^{11} \exp (-2 \sqrt{I})] + m^2 C^0
\]

According to Guggenheim\(^{15}\), an electrolyte mixture involves the pair-wise interactions of only oppositely charged ions, and for two univalent electrolytes with a common ion, such as KCl (\(m_a\)) and KOAc (\(m_b\)) the following expression can be written.

\[
\ln \gamma_A = (\phi_A^0 - \phi_A^1) y_B
\]

where \(\gamma_A\) is the activity coefficient of pure component A at the same ionic strength as in the mixture. The possibility of interactions between the charges of same sign was recognised by Pitzer\(^5\).
Table 2 - Harned coefficients for the system KCl-KOAc-H2O

<table>
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<tr>
<th>Temp.</th>
<th>I</th>
<th>α_{AB}</th>
<th>β_{AB}</th>
<th>log γ_A^k (exp.)</th>
<th>log γ_A^k (calc.)</th>
<th>RMSD × 10^4</th>
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<tr>
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<td>-0.2184</td>
<td>4.42</td>
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<td>2.45</td>
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<tr>
<td></td>
<td>3.0</td>
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<td>0.0059</td>
<td>-0.2438</td>
<td>-0.2438</td>
<td>2.87</td>
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<td>35°C</td>
<td>0.5</td>
<td>-0.0260</td>
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<td>-0.1875</td>
<td>-0.1875</td>
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<td>—</td>
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<td>-0.2370</td>
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Hence, the binary interaction (\(\Theta\)) and ternary interaction (\(\Psi\)) terms were included in the electrolyte mixture equation. The Pitzer equation for the three-ion mixtures such as KCl-KOAc-H2O can be written as,

\[
\ln(\frac{\gamma_{KCl}}{\gamma_{KCl}^0}) = y_B(\phi_B^0 - \phi_A^0) + y_B\Theta_{Cl-OAc} + 0.5 y_B^2(2 - y_B)\Psi_{Cl-OAc-K} \quad \cdots (8)
\]

where \(\phi_A^0\) and \(\phi_B^0\) are the osmotic coefficients of pure KCl and KOAc solutions at the same ionic strength as the mixture. The activity coefficient data at all the four ionic strengths at one temperature were fitted into a single least-squares program and common \(\Theta\) and \(\Psi\) values were evaluated. The evaluated \(\Theta\) values are \(-0.00533\), \(-0.00434\) and \(-0.00334\) and \(\Psi\) values are \(-0.00299\), \(-0.00301\) and \(-0.00304\) at 25, 35 and 45°C respectively.

Scatchard\(^6\) introduced the neutral electrolyte treatment for electrolyte mixtures which was later elaborated by Rush and Johnson\(^7\) who obtained the expression:

\[
\ln(\frac{\gamma_A}{\gamma_A^0}) = y_B(\phi_B^0 - \phi_A^0) + 0.5 y_B(b_{01}I + b_{02}I^2 + b_{03}I^3)
+ b_{12}I^2 + b_{13}I^3 - 0.5y_B^2(1/2)b_{01}I^2
+ (2/3)b_{01}I^2 + (3/2)b_{12}I^2 + 2b_{13}I^3]
+ (1/3)I^3y_B^2b_{13} \quad \cdots (9)
\]

where \(\phi_A^0\) and \(\phi_B^0\) are the osmotic coefficients of the pure components A and B at the ionic strength of the mixture and can be calculated using the Pitzer equation \(6\). The coefficients \(b_{mn}\) are the mixing parameters accounting for the ion-ion interactions specific to the mixture. The experimental data could be fitted accurately, using the two parameters, \(b_{01}\) and \(b_{02}\). Of these two, \(b_{01}\) represents the binary interaction between Cl-OAc, and \(b_{02}\) the ternary interaction K-Cl-OAc. The experimental activity coefficient data at all the four ionic strengths were fitted into a single least-squares program in order to find these \(b_{01}\) and \(b_{02}\). The estimated values are \(b_{01} = -0.01047\), \(-0.00886\) and \(-0.0066\) and \(b_{02} = -0.00609\), \(-0.00591\) and \(-0.00609\) at 25, 35 and 45°C respectively. Jones et al\(^2\) reported \(b_{01} = -0.0156\) assuming \(b_{02}\) as zero at 25°C. The different treatments of uni-univalent three ion mixtures are equivalent and the mixing parameters of Pitzer\(^5\) and Scatchard\(^6\) models are related. Thus, \(b_{01} = 2\Theta_{Cl-OAc}\) and \(b_{02} = 2\Psi_{Cl-OAc-K}\), when only two mixing interaction parameters are considered in each of the treatments. This comparison is shown in Table 3. By combining equations 3, 8 and 9 it is evident that when the excess free energy of mixing can be accounted for satisfactorily in terms of only \(\Theta_{Cl-OAc}\) or \(b_{01}\), the Harned rule is obeyed and these parameters are related to the Harned slope \(\alpha_{AB}\) as,

\[
\alpha_{AB} = \frac{(\phi_A^0 - \phi_B^0 - I^2\Theta_{Cl-OAc})}{(\phi_A^0 - \phi_B^0 - 0.5Ib_{01})}
\]

\[
= \frac{2.3026}{2.3026} \quad \cdots (10)
\]
Table 3 – Pitzer and Scatchard parameters for the system KCI-KOAc-H2O

<table>
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<th>T°C</th>
<th>( \Theta )</th>
<th>( \Psi )</th>
<th>RMSD ( \times 10^5 )</th>
<th>( b_{01} )</th>
<th>( b_{02} )</th>
<th>RMSD ( \times 10^5 )</th>
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Table 4 – Osmotic coefficients for the system KCI-KOAc-H2O

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<th>( I = 0.5 )</th>
<th>( I = 1.0 )</th>
<th>( I = 2.0 )</th>
<th>( I = 3.0 )</th>
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</table>

<table>
<thead>
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<th>Temp. = 25°C</th>
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<td>0.2</td>
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</table>

<table>
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<tr>
<th>Temp. = 35°C</th>
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<table>
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<th>Temp. = 45°C</th>
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<td>1.0</td>
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</tbody>
</table>

Osmotic coefficients of this system were calculated by substituting the \( \Theta \) and \( \Psi \) values listed in Table 3 in the Pitzer equation:

\[
\phi = -A_{\text{Cl-OAc}} L_{1} / \left( 1 + b_{1} L_{1} \right) + A_{\text{Cl-OAc}} B_{\text{KCl}}^{\ast} + y_{\text{B}} B_{\text{KCl}}^{\ast} + y_{\text{B}} B_{\text{KCl}}^{\ast}
\]

\[
+ y_{\text{B}} \left( 1 - y_{\text{B}} \right) \Theta_{\text{Cl-OAc}} + \left( 1 - y_{\text{B}} \right) C_{\text{KCl}}^{\ast} + y_{\text{B}} C_{\text{KCl}}^{\ast}
\]

\[
+ y_{\text{B}} \left( 1 - y_{\text{B}} \right) W_{\text{Cl-OAc-K}} + 1
\]

By substituting the \( \Theta \) or \( b_{01} \) values listed in Table 3 in the above equation the \( \alpha_{AB} \) value could be calculated; it was found to be \(-0.0284\) and \(-0.0496\) at \( I = 0.5 \) and \( I = 1.0 \) respectively. These values are in good agreement with the experimentally determined \( \alpha_{AB} \) values of \(-0.0282\) and \(-0.0490\) (cf. Table 2).

The resulting data are listed in Table 4 at all the temperatures and ionic strengths studied. Our estimated osmotic coefficients at 25°C are in agreement with experimental values of Jones et al.\(^2\) with an RMSD = 1.615 \( \times \) 10\(^{-3}\).

Then the excess Gibbs free energies of mixing were calculated using the equation

\[
\Delta_{m} G^{E} = 2 y_{\text{B}} \left( 1 - y_{\text{B}} \right) / 2 R T \left( \Theta_{\text{Cl-OAc}} + 4 \Psi_{\text{Cl-OAc-K}} / 2 \right)
\]

\[\ldots \] (12)

The values obtained are listed in Table 5. It is evident that our values are in good agreement with those reported by Jones et al.\(^2\) at 25°C.

Using the \( \Theta \) and \( \Psi \) values listed in Table 3,
their temperature derivatives were calculated as 
\[ \frac{\partial \Theta}{\partial T} = 9.9 \times 10^{-5} \] and 
\[ \frac{\partial \Psi}{\partial T} = -2.2 \times 10^{-6} \].

Then the heats of mixing of aqueous KCl with
KOAc could be calculated by substituting these
temperature derivatives in the following equa­
tions\textsuperscript{14,17,18}:

\[ R\Delta H = n_w I^2 y_B (1 - y_B) |R\Delta T_0| \quad \ldots (14) \]

The resulting heats of mixing values are \(-2.17, -8.65, -34.2\) and 76.1 cal/kg at total ionic
strengths of 0.5, 1.0, 2.0 and 3.0 mol/kg respect­
ively and at \( y_A = y_B = 0.5 \) and temp. = 25\(^\circ\). The
heat of mixing value (-8.65 cal/kg) at \( I = 1 \) is
in good agreement with the value of \(-8.58 \) cal/kg
reported earlier by Wood \textit{et al.}\textsuperscript{3}.

Therefore, it can be concluded that the Pitzer
formalism accurately represents the thermodyna­
mic properties of the aqueous KCl-KOAc system
over the temperature range 25-45\(^\circ\).  

\textbf{Acknowledgement}

The authors wish to thank Prof. T. Navaneeth
Rao, Vice-Chancellor, Osmania University,
Hyderabad, for constant encouragement and help­
ful discussions. One of the authors (S.M.) is
thankful to the CSIR, New Delhi for the award of
a fellowship.

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