

Isopiestic determination of osmotic coefficients and evaluation of activity coefficients of aqueous mixtures of sodium and potassium chloride at 45°C

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Abstract

The osmotic coefficients of aqueous mixtures of potassium chloride and sodium chloride were evaluated at 45°C by the isopiestic method, varying the total molal concentration between 1 and 5 moles kg⁻¹ in the whole range of reduced molar fraction. The results obtained were correlated by the Pitzer equation and by that derived by Pan and Han, for the application of the McKay–Perring method. From these correlations, the activity coefficients of both salts in the mixture were calculated. A comparative analysis of the results obtained were also made. © 1997 Elsevier Science B.V.

Keywords: Osmotic and activity coefficients; Isopiestic method; Aqueous halide mixtures

1. Introduction

The experimental study of the system NaCl–KCl–H₂O by the isopiestic method has only a few antecedents. The more accurate data at 25°C were reported by Robinson [1], which were used for the evaluation of the mixture parameters (Θ_{NaK} , Ψ_{NaKCl}) of the Pitzer equation [2,3]. Other measurements at this temperature were made by Kirgintsev and Lukyanov [4] and by Covington et al. [5]. At elevated temperatures, the unique results are those of Holmes et al. [6], which were obtained over the temperature range 110°C to 201°C. On the basis of this study, the authors established the dependence of the interaction parameter Θ_{NaK} on temperature.

The present work reports the results obtained by the application of the isopiestic method to aqueous

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mixtures of potassium chloride and sodium chloride at 45°C. The isopiestic apparatus used in the experimental measurements is a modified version of that developed by Grjotheim et al. [7] and it has been previously used for the study of the system KCl–H₂O at the same temperature [8].

2. Experimental

The isopiestic apparatus used in this work was similar to that described elsewhere [7], with several modifications oriented to decrease the time needed to achieve the equilibrium state. The main changes to the original design were: (i) the cups were made of thin Pyrex glass; (ii) a glass stirring bead of 15 mm diameter was added to each cup and (iii) an agitation system was used, consisting in a platform suspension shaker which provided a two dimensional rocking motion to the stirring bead. The conjunction of this kind of agitation and the glass beads produced a substantial increase in the equilibration rate at the working temperature.

The experimental procedure was essentially the same as that described in the previous work [8]. The main difference consisted in the preparation of concentrated stock solutions with different relationships between the molal concentration of potassium and sodium ions. They were prepared by weighing from the dry salts. In order to characterize that relationship, a reduced molar fraction was defined as $y = m_{\text{KCl}}^{\circ} / m^{\circ}$, being $m^{\circ} = m_{\text{KCl}}^{\circ} + m_{\text{NaCl}}^{\circ}$, where the superscript $^{\circ}$ indicates stock solution. The mixtures used for the isopiestic measurements were prepared by dilution of samples obtained from the corresponding stock solutions. Under these conditions, the relationship y does not change either with dilution or during the equilibration process. Consequently, the isopiestic molalities of the components are $m_{\text{KCl}} = my$ and $m_{\text{NaCl}} = m(1 - y)$, being $m = m_{\text{KCl}} + m_{\text{NaCl}}$ the total isopiestic molality at equilibrium.

Six experimental runs were carried out, each of them consisting in five mixture samples of different y values, all in duplicate, and one duplicate sample of pure sodium chloride solution, which was used as reference solution. The equilibration time was generally of about two weeks, being a little longer for the solutions of lower concentrations. It has been considered that the equilibrium condition was reached when the difference between the concentration of each couple of samples was less than 0.1% and in all cases the average between these two duplicates are reported as the total isopiestic molality.

3. Results and discussion

Table 1 displays a summary of the experimental results, where the values of the isopiestic total molality are tabulated as a function of the reduced molar fraction for the different experimental runs. The first column ($y = 0$) corresponds to the solution of pure NaCl used as reference and the last one ($y = 1$) corresponds to the solution of pure KCl, obtained from the correlation of the experimental values of the isopiestic ratio determined previously [8].

Osmotic coefficients ϕ were calculated from the isopiestic molalities by means of the relationship:

$$\phi = \frac{m_{\text{NaCl}(y=0)}}{m} \phi_{\text{NaCl}(y=0)} \quad (1)$$

The $\phi_{\text{NaCl}(y=0)}$ values, used as reference, were calculated by the correlation expressions and

Table 1

Experimental values of the isopiestic total molality at different reduced molar fraction at 45°C

Exp. No.	y = 0.0000	y = 0.1699	y = 0.3367	y = 0.5012	y = 0.6672	y = 0.8333	y = 1.0000
2	4.3593	4.4810	4.5966	4.7038	4.8148	4.9019	4.9722
3	1.9672	2.0059	2.0301	2.0510	2.0763	2.0922	2.1106
4b	1.0911	1.1013	1.1134	1.1189	1.1288	1.1383	1.1408
5	3.2536	3.3268	3.3953	3.4600	3.5177	3.5752	3.6055
6	3.8686	3.9645	4.0531	4.1428	4.2134	4.3024	4.3543
7	2.6415	2.6903	2.7363	2.7822	2.8146	2.8512	2.8835

constants obtained from Pitzer and Silvester [9]. The experimental osmotic coefficients, evaluated with Eq. (1), are summarized in Table 2.

The correlation of the experimental osmotic coefficients, as well as the evaluation of the corresponding activity coefficients, was carried out using the Pitzer equation and that proposed by Pan and Han [10] for the implementation of the McKay–Perring method [11]. The Pitzer equation for the osmotic coefficient can be written as:

$$\phi - 1 = -A^\phi \{m^{1/2} / (1 + bm^{1/2})\} + m \{ (1 - y) B_{\text{NaCl}}^\phi + y B_{\text{KCl}}^\phi + (1 - y) y \Theta_{\text{NaK}} \} + m^2 \{ (1 - y) C_{\text{NaCl}}^\phi + y C_{\text{KCl}}^\phi + (1 - y) y \Psi_{\text{NaKCl}} \} \quad (2)$$

where:

$$B_i^\phi = \beta_i^0 + \beta_i^1 \exp(-\alpha m^{1/2}) \quad i = \text{KCl, NaCl} \quad (3)$$

The parameters β_i^0 , β_i^1 and C_i^ϕ correspond to the pure salt solutions, while the parameters Θ_{NaK} and Ψ_{NaKCl} belong to the mixture solution. Related to these mixing parameters, the criteria assumed by Holmes et al. [6] in their study of this system at high temperatures have been adopted, where Θ_{NaK} was considered to be independent of molality and Ψ_{NaKCl} was taken as zero. A^ϕ is the Debye–Hückel constant for the osmotic coefficient, which was obtained from the work of Bradley and Pitzer [12] and is equal to 0.40575 at 45°C. Furthermore, b and α adopted the usual values of 1.2 and 2.0 kg^{1/2} mol^{-1/2}, respectively.

The values of the parameters corresponding to pure NaCl solution were evaluated by the expressions of Pitzer and Silvester [9], while those corresponding to pure KCl solution were obtained by least-squares fit of our experimental results of the system KCl–H₂O at the same temperature [8]. These values are shown in Table 3.

Table 2

Experimental values of the osmotic coefficients at different reduced molar fraction at 45°C

Exp. No.	y = 0.0000	y = 0.1699	y = 0.3367	y = 0.5012	y = 0.6672	y = 0.8333	y = 1.0000
2	1.1505	1.1192	1.0911	1.0662	1.0416	1.0231	1.0087
3	0.9925	0.9733	0.9617	0.9519	0.9403	0.9332	0.9251
4b	0.9453	0.9349	0.9265	0.9219	0.9138	0.9062	0.9041
5	1.0742	1.0505	1.0294	1.0101	0.9935	0.9775	0.9693
6	1.1162	1.0892	1.0653	1.0423	1.0248	1.0036	0.9917
7	1.0340	1.0152	0.9982	0.9817	0.9704	0.9580	0.9472

Table 3

Parameters of the Pitzer equation for the pure salt solutions at 45°C

Parameter	KCl ([8])	KCl ([13])	NaCl ([9])
β^0	0.05947	0.057542	0.088124
β^1	0.21226	0.243697	0.280839
C^ϕ	−0.00213	−0.0018076	−0.00056904

From the correlation of the experimental results given in Table 2, by the application of Eq. (2), a value of the mixing parameter Θ_{NaK} equal to $-0.0180919 \text{ kg mol}^{-1}$ has been obtained, with a root mean square deviation (RMSD) equal to 0.001497. It should be noticed that this value approaches that obtained by interpolation in the linear dependence of Θ_{NaK} on temperature found by Holmes et al. [6], which is equal to $-0.017241 \text{ kg mol}^{-1}$.

The dependence of ϕ with the total isopiestic molality, at different y values, is depicted in Fig. 1, which shows the experimental points as well as the correlation by the Pitzer equation.

The other approach used for the correlation of the experimental results was that proposed by Pan and Han [10] for the implementation of the method of McKay–Perring [11]. The corresponding dependence of the osmotic coefficient on the total isopiestic molality and the reduced molar fraction is:

$$\begin{aligned} \phi - 1 = & -A^\phi \{m^{1/2}/(1 + bm^{1/2})\} + A_1 m + A_2 m^2 + A_3 m(1 - y) + A_4 m^3 + A_5 m^2(1 - y) \\ & + A_6 m(1 - y)^2 + A_7 m^4 + A_8 m^3(1 - y) + A_9 m^2(1 - y)^2 + A_{10} m^5 + \dots \end{aligned} \quad (4)$$

The parameters A_i were determined from a least-squares fit of the experimental ϕ values, using

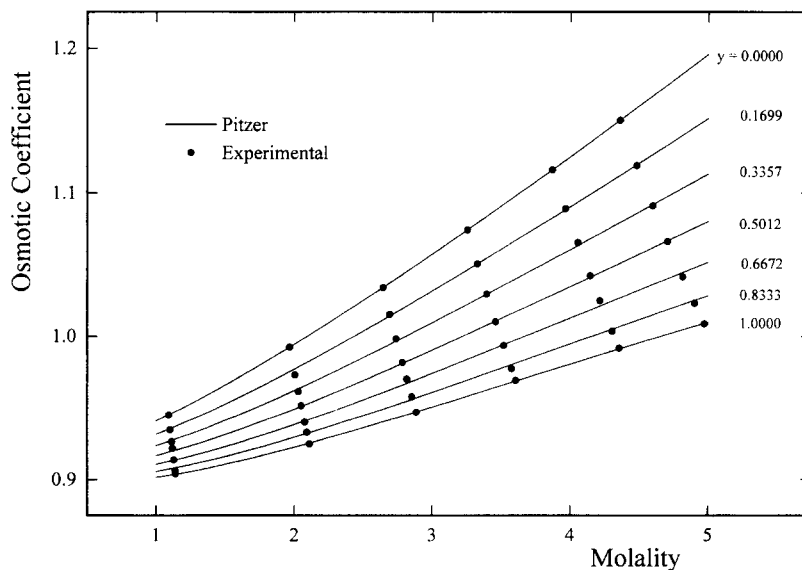


Fig. 1. Dependence of the osmotic coefficients of aqueous KCl–NaCl mixtures on concentration m at different y values at 45°C, correlated by Pitzer equation.

Table 4

Parameters of the Pan and Han equation obtained by correlation of the experimental osmotic coefficients at 45°C

A_1	0.130153
A_2	-0.062849
A_3	0.024704
A_4	0.02242
A_5	-0.003687
A_6	0.015049
A_7	-0.003844
A_8	0.000511
A_9	0.000727
A_{10}	0.000248

Eq. (4), and are shown in Table 4. The accuracy of the correlation can be appreciated by the value of the $\text{RMSD} = 0.0014768$, which is similar to that obtained from the least-squares fit of Eq. (2). The correlation of the osmotic coefficients can be observed in Fig. 2, where the experimental values were also included.

On the other hand, the experimental values of the osmotic coefficients were also compared with those evaluated with the Pitzer expression, using in this case the equations and corresponding constants recommended by Holmes and Mesmer [13] for the calculation of the parameters of the pure KCl solution. Meanwhile, the value of the mixing parameter Θ_{NaK} was that obtained by interpolation in its linear dependence on temperature [6], as it is indicated above. The calculated values of the KCl parameters are included in Table 3 and the Θ_{NaK} value was already given above. The calculated

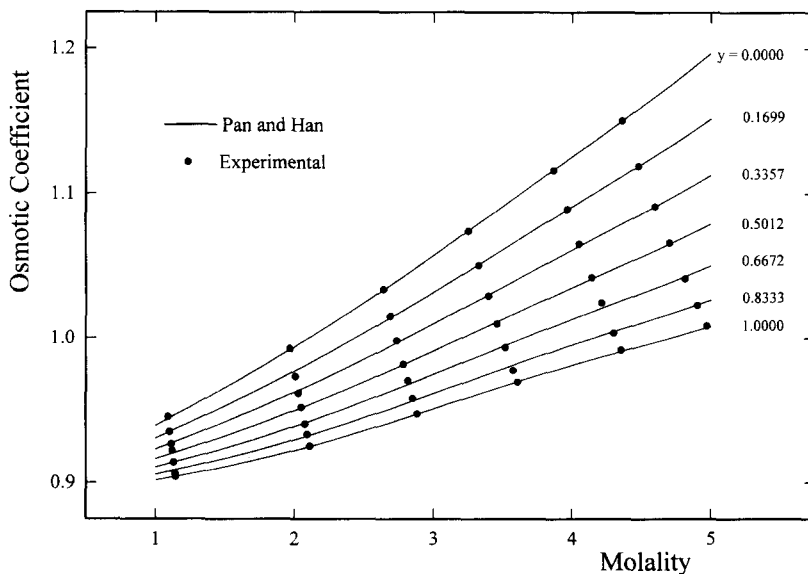


Fig. 2. Dependence of the osmotic coefficients of aqueous KCl–NaCl mixtures on concentration m at different y values at 45°C, correlated by Pan and Han equation.

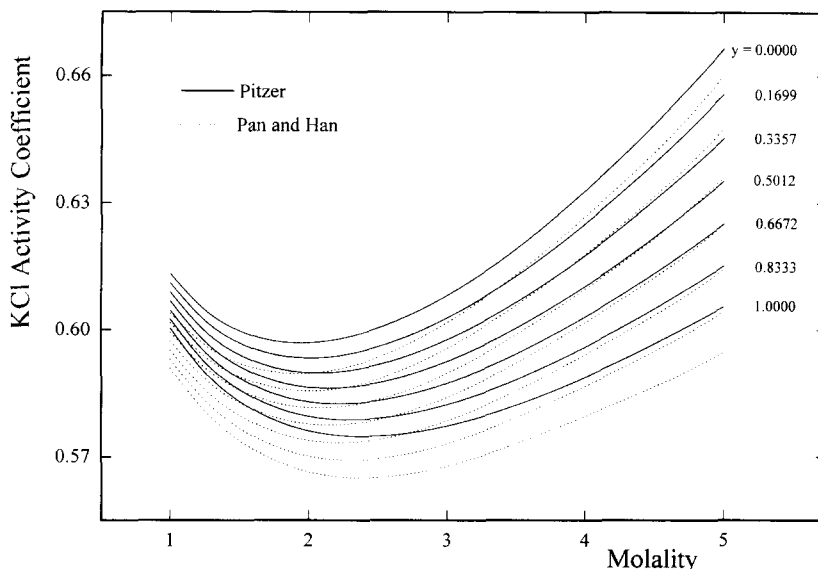


Fig. 3. Dependence of the activity coefficients of KCl in aqueous KCl–NaCl mixtures on concentration m at different y values at 45°C.

osmotic coefficients show a good agreement with the experimental ones, as can be appreciated by the $\text{RMSD} = 0.001764$ value.

The activity coefficients of solutes KCl and NaCl can be calculated by the following Pitzer formulation:

$$\ln \gamma_{\text{KCl}} = -A^\phi \left\{ m^{1/2} / (1 + bm^{1/2}) + 2 \ln(1 + bm^{1/2}) / b \right\} + m \left\{ B_{\text{KCl}}^\phi + y(B_{\text{NaCl}}^\phi - B_{\text{KCl}}^\phi + \Theta_{\text{NaK}}) \right\} \\ + m^2 \left\{ 3C_{\text{KCl}}^\phi / 2 + y(C_{\text{NaCl}}^\phi - C_{\text{KCl}}^\phi + \Psi_{\text{NaKCl}} / 2) + y(1 - y)\Psi_{\text{NaKCl}} / 2 \right\} \quad (5)$$

$$\ln \gamma_{\text{NaCl}} = -A^\phi \left\{ m^{1/2} / (1 + bm^{1/2}) + 2 \ln(1 + bm^{1/2}) / b \right\} \\ + m \left\{ B_{\text{NaCl}}^\phi + (1 - y)(B_{\text{KCl}}^\phi - B_{\text{NaCl}}^\phi + \Theta_{\text{NaK}}) \right\} \\ + m^2 \left\{ 3C_{\text{NaCl}}^\phi / 2 + (1 - y)(C_{\text{KCl}}^\phi - C_{\text{NaCl}}^\phi + \Psi_{\text{NaKCl}} / 2) + y(1 - y)\Psi_{\text{NaKCl}} / 2 \right\} \quad (6)$$

where:

$$B_i^\gamma = 2\beta_i^0 + \frac{2\beta_i^1}{\alpha^2 m} \left\{ 1 - \exp(-\alpha m^{1/2})(1 + \alpha m^{1/2} - \alpha^2 m / 2) \right\}, \quad i = \text{KCl, NaCl} \quad (7)$$

and the other symbols are the same as in Eq. (2).

The activity coefficients of both electrolytes in the mixture were calculated with Eqs. (5) and (6) and the results obtained are shown in Fig. 3 (KCl) and Fig. 4 (NaCl), as continuous lines.

Furthermore, the activity coefficients of KCl and NaCl in the ternary solution were also evaluated

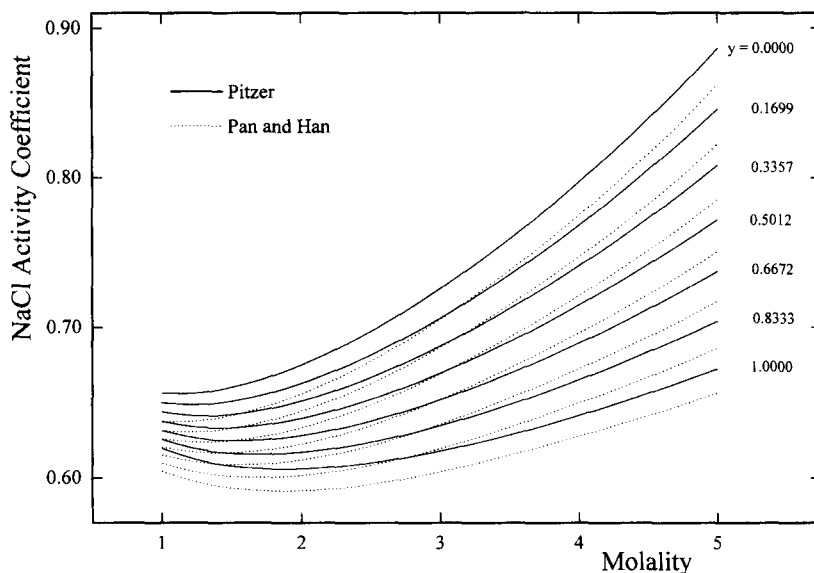


Fig. 4. Dependence of the activity coefficients of NaCl in aqueous KCl–NaCl mixtures on concentration m at different y values at 45°C.

with the equations developed by Pan and Han [10] for the application of the McKay–Perring method [11]. For the present case, they can be written as:

$$\ln \gamma_{\text{KCl}} = (\phi - 1) + \int_0^m (\phi - 1) d \ln m + (1 - y) \int_0^m \frac{\partial \phi}{\partial y} d \ln m \quad (8)$$

$$\ln \gamma_{\text{NaCl}} = (\phi - 1) + \int_0^m (\phi - 1) d \ln m - y \int_0^m \frac{\partial \phi}{\partial y} d \ln m \quad (9)$$

The integrals in Eqs. (8) and (9) can be obtained from Eq. (4):

$$\begin{aligned} \int_0^m (\phi - 1) d \ln m = & -\frac{2 A^\phi}{b} \ln(1 + b m^{1/2}) + A_1 m + (A_2/2) m^2 + A_3 m(1 - y) + (A_4/3) m^3 \\ & + (A_5/2) m^2(1 - y) + A_6 m(1 - y)^2 + (A_7/4) m^4 + (A_8/3) m^3(1 - y) \\ & + (A_9/2) m^2(1 - y)^2 + (A_{10}/5) m^5 + \dots \end{aligned} \quad (10)$$

$$\int_0^m \frac{\partial \phi}{\partial y} d \ln m = A_3 m + (A_5/2) m^2 + 2 A_6 m(1 - y) + (A_8/3) m^3 + A_9 m^2(1 - y) + \dots \quad (11)$$

Therefore, substituting Eqs. (7), (10) and (11) into Eqs. (8) and (9) respectively, the activity coefficients of KCl and NaCl in the mixture were evaluated. The results obtained are shown in Fig. 3 (KCl) and Fig. 4 (NaCl), as dashed curves.

It should be noticed that the activity coefficients evaluated through the method proposed by Pan and Han are less than those obtained through the equation of Pitzer. The difference is approximately constant and equal to 0.010 for KCl and 0.015 for NaCl. Taking into account that when the expression of Pitzer for the osmotic coefficient (Eq. (2)) is used in the equations derived by Pan and Han (Eqs. (8) and (9)), the corresponding equations for the activity coefficients (Eqs. (5) and (6)) are obtained and that both methods give almost the same correlation of the experimental osmotic coefficients in the concentration range analyzed, the difference in the activity coefficients should be due to a disagreement in the extrapolated dependence of the osmotic coefficients corresponding to the low concentration range ($m < 1$). This fact can be clearly appreciated in Eqs. (8) and (9) because, as the lower limit of the integrals is zero, they are involving a concentration range where the experimental determinations were not carried out. In this sense, it should be taken into account that six of the constants of the Pitzer equation correspond to the binary mixtures, which are usually obtained in a concentration range wider than the usual domain of the isopiestic measurements. Therefore, it can be concluded that in the present case, the activity coefficients calculated by the Pitzer equations should be more accurate than those obtained by the method of Pan and Han.

4. Conclusions

The isopiestic method was applied to obtain experimental values of the osmotic coefficients for the NaCl–KCl–H₂O mixture at 45°C, which lies in a temperature range where there is not experimental data reported in the literature. The value of the mixing parameter Θ_{NaK} of the Pitzer equation calculated from the experimental results is in agreement with that obtained from the linear dependence on temperature proposed by Holmes et al. [6].

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