Portugaliae Electrochimica Acta 24 (2006) 295-303

PORTUGALIAE ELECTROCHIMICA ACTA

Activity Coefficients of Potassium Chloride in Aqueous Solutions of Potassium Chloride and Potassium Phthalate

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Received 22 November 2005; accepted in revised form 11 April 2006

Abstract

Mean activity coefficients of potassium chloride were determined in aqueous solutions of potassium chloride and potassium phthalate, in the temperature range 10-50 ºC and ionic strength range 0.05-4 mol kg^{-1}, from potentiometric measurements on a galvanic cell without liquid junction. By processing the results using the Pitzer model, interaction parameters for potassium phthalate were calculated as well as their temperature dependence.

Keywords: activity coefficients, potassium phthalate, Pitzer equations.

Introduction

Sodium and potassium phthalate salts have a large application in industry and in chemical analysis. Particularly potassium hydrogen phthalate has been used as a standard substance and a 0.05 mol kg^{-1} aqueous solution of this salt was selected as a primary standard for pH determination [1]. According to the methodology for assigning pH values to the standards, the chloride ion activity coefficient has to be calculated by means of the Debye-Hückel equation with the Bates-Guggenheim convention [1,2], valid for ionic strength not higher than 0.1 mol kg^{-1}. For more concentrated solutions this equation does not fit most experimental data and the Pitzer theory [3] appears to be more adequate to describe the non ideal behaviour of most electrolytes [4,5]. The Pitzer approach separates arbitrarily between electrostatic and specific short-range interactions, and enables these, expressed as virial coefficients, to be calculated for single electrolyte solutions and applied to the analysis of mixtures [5].

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In potassium hydrogenphthalate (KHPh) solutions, the three species, H_2Ph, HPh^- and Ph^{2-}, are at equilibrium and the interactions between Ph^{2-} and K^+ are also important for the evaluation of the deviations from ideal behaviour.
In this work potassium chloride activity coefficients were determined in mixed solutions of potassium chloride and potassium phthalate (indicated by K_2Ph, for simplicity) from potentiometric measurements, in the temperature range 10 to 50 ºC.
The Pitzer equation for the calculation of potassium chloride activity coefficient was then fitted to the experimental data and the interaction coefficients, relative to potassium and phthalate ions, could be evaluated, at each temperature, by multilinear regression analysis.

Experimental

Mean activity coefficients of potassium chloride in KCl + K_2Ph + H_2O systems were determined in the 10–50 ºC temperature range, from potential measurements in the following galvanic cell, without liquid junction,

$$\text{Ag, AgCl} \mid \text{KCl } (m_1), \text{K}_2\text{Ph } (m_2) \mid \text{K}^+ \text{ glass electrode}$$

where m_1 and m_2 are the molalities of potassium chloride and potassium phthalate, respectively. The ionic strength, I, varied from 0.05 to 4 mol kg^{-1}.
In cell (A), a commercial potassium responsive glass electrode, ABB Kent-Taylor, model 1057, and silver, silver chloride electrodes of the thermal electrolytic type [6], prepared in this laboratory, were used. The bias potentials of these electrodes were always lower than 0.1 mV. The cell response was tested by measuring the potential, on cell (A), E, at 25 ºC, with KCl solutions, and using the equation

$$E = E^0 + 2s \ln (m_{KCl} \gamma_{KCl}) \quad (1)$$

where E^0 is a constant and s is the nernstian slope. The activity coefficients, γ_{KCl}, were calculated by the Pitzer equation with the known interaction coefficients [3] and the slope was 2s = 52.11 mV (R^2=1, n=5), close to the theoretical value.
For the solution preparation, potassium chloride, Merck p.a., and potassium phthalate, Aldrich, 98%, were dried at 110 ºC for about 12 hours and cooled in a desiccator over blue gel. The solutions were prepared by weight, with buoyancy corrections, using deionized water with a specific conductivity of 0.1 μS cm^{-1}.
The H type cell vessels were immersed in a thermostated water bath (Grant, model LTD 20) and the temperature was controlled within ±0.05 ºC.
The potential differences of cell (A) were measured on a multimeter, Hewlett Packard, model HP 3458.

Table 1. Solutions composition, potential for cell A and experimental KCl activity coefficients at various temperatures.

m_{KCl}	m_{K2Ph}	10 ºC		20 ºC		25 ºC	
		E/mV	- ln γ_{KCl}	E/mV	- ln γ_{KCl}	E/mV	- ln γ_{KCl}
0.0496		15.70	0.20112	9.50	0.20330	7.58	0.20442
0.03993	0.00336	9.31	0.18578	2.18	0.20112	-0.41	0.20425
0.02499	0.00833	-5.03	0.18858	-12.52	0.19957	-15.56	0.21235
0.01997	0.00999	-11.34	0.18509	-19.22	0.19854	-22.57	0.21425
0.09993		48.55	0.26103	42.96	0.26326	40.38	0.26458
0.07987	0.00679	41.63	0.25731	35.58	0.26935	33.02	0.37920
0.05989	0.01359	32.20	0.27123	26.65	0.26589	23.57	0.38746
0.04991	0.01698	27.79	0.25180	20.89	0.26944	17.82	0.39280
0.03995	0.02039	21.70	0.24620	14.52	0.26450	11.03	0.26861
0.29956		97.54	0.37501	95.49	0.37609	91.9	0.37691
0.17976	0.04077	82.85	0.35240	78.67	0.38362	75.15	0.27314
0.14983	0.05096	77.19	0.35872	72.65	0.39249	69.09	0.27531
0.11983	0.06113	70.85	0.35738	65.57	0.40062	62.07	0.27707
0.49950		121.59	0.43332	118.75	0.43280	117.31	0.43289
0.39951	0.03398	114.92	0.42519	111.99	0.42109	110.01	0.43014
0.24960	0.08489	101.26	0.41563	96.62	0.43427	94.31	0.44620
0.19977	0.10193	94.52	0.42326	89.93	0.43552	87.37	0.45077
0.09986	0.13590	75.84	0.41809	70.11	0.43784	67.40	0.45144
0.99885		152.67	0.51168	151.01	0.50536	149.90	0.50512
0.49939	0.16986	133.94	0.46175	129.35	0.49812	127.36	0.51003
0.39959	0.20387	126.81	0.47708	122.44	0.50341	120.24	0.51718
0.19975	0.27180	107.83	0.47804	102.45	0.50906	100.25	0.51886
1.49824		169.56	0.55215	168.82	0.54357	168.04	0.53979
0.74907	0.25470	150.25	0.51411	147.37	0.53220	145.49	0.54489
0.59926	0.30576	142.30	0.54606	140.46	0.53731	138.57	0.54860
0.29958	0.41523	124.76	0.52433	120.78	0.54368	118.36	0.56074
1.99654		184.36	0.57483	185.05	0.56263	182.99	0.55706
1.59822	0.13590	177.99	0.56137	177.60	0.56533	175.58	0.55727
1.19828	0.27172	169.50	0.5558	167.83	0.57817	165.72	0.56961
0.99870	0.33970	164.03	0.55819	161.81	0.58701	159.91	0.57298
0.39954	0.54360	138.83	0.55598	135.19	0.59258	132.93	0.57942
2.99654		201.74	0.59133	201.39	0.57272	202.36	0.56402
1.79778	0.40766	187.80	0.55307	185.77	0.55638	185.36	0.57093
1.49799	0.50952	182.79	0.54579	179.67	0.56655	179.38	0.57736
1.19861	0.61156	176.19	0.55026	173.24	0.56238	172.42	0.58203
0.59917	0.81524	157.17	0.55201	153.18	0.56938	152.04	0.59064
3.99511		214.87	0.58526	217.02	0.56154	216.53	0.55033
2.39689	0.54353	199.97	0.56669	201.42	0.54482	200.97	0.52924
1.99729	0.67937	194.94	0.55987	195.71	0.54736	194.88	0.53786
1.59757	0.81508	188.76	0.55536	188.71	0.55405	187.65	0.54741
0.79868	1.08666	169.19	0.56848	168.41	0.56587	167.44	0.55280

Table 1. Solutions composition, potential values for cell A and experimental KCl activity coefficients at various temperatures (cont.).

m_{KCl}	m_{K2Ph}	30 ºC		40 ºC		50 ºC	
		E/mV	- ln γ_{KCl}	E/mV	- ln γ_{KCl}	E/mV	- ln γ_{KCl}
0.0496		4.48	0.20582	-1.20	0.20874	-6.17	0.21199
0.03993	0.00336	-3.62	0.21453	-9.68	0.21954	-14.78	0.22027
0.02499	0.00833	-19.20	0.22171	-25.75	0.22628	-31.26	0.22516
0.01997	0.00999	-26.22	0.22312	-33.09	0.22932	-38.71	0.22597
0.09993		38.27	0.26595	32.97	0.26992	28.81	0.27288
0.07987	0.00679	30.27	0.27985	24.85	0.28042	20.32	0.28609
0.05989	0.01359	20.62	0.28524	14.83	0.28677	10.21	0.28832
0.04991	0.01698	14.60	0.29060	8.89	0.28697	4.15	0.28726
0.03995	0.02039	7.59	0.29439	1.63	0.29111	-3.27	0.29011
0.29956		90.87	0.37785	87.64	0.38046	84.71	0.38375
0.17976	0.04077	73.60	0.38473	69.44	0.39401	66.29	0.39082
0.14983	0.05096	67.31	0.39544	63.14	0.40106	59.99	0.39426
0.11983	0.06113	60.09	0.40235	55.95	0.40300	52.63	0.39514
0.49950		117.02	0.43311	114.56	0.43440	112.33	0.43654
0.39951	0.03398	108.91	0.44351	105.61	0.45542	103.36	0.45278
0.24960	0.08489	93.00	0.45856	89.72	0.46037	87.06	0.45598
0.19977	0.10193	85.96	0.46281	82.48	0.46403	79.86	0.45477
0.09986	0.13590	65.38	0.46875	61.55	0.46387	58.20	0.45572
0.99885		150.36	0.50342	149.10	0.50106	148.06	0.49977
0.49939	0.16986	126.01	0.53573	123.89	0.53442	122.69	0.52156
0.39959	0.20387	118.83	0.54238	116.71	0.53668	115.46	0.52059
0.19975	0.27180	98.56	0.54237	95.77	0.53670	94.09	0.51633
1.49824		169.44	0.53618	169.24	0.53021	168.96	0.52543
0.74907	0.25470	144.69	0.57615	143.68	0.57006	143.46	0.54955
0.59926	0.30576	137.77	0.57764	136.50	0.57214	136.14	0.55003
0.29958	0.41523	117.68	0.58100	115.67	0.57694	114.68	0.55419
1.99654		184.22	0.55168	185.20	0.54230	185.01	0.53421
1.59822	0.13590	175.78	0.56923	175.28	0.58211	175.78	0.55595
1.19828	0.27172	165.94	0.57802	165.20	0.58934	165.78	0.55596
0.99870	0.33970	160.21	0.57799	159.47	0.58580	159.99	0.55022
0.39954	0.54360	133.08	0.57845	131.13	0.59230	143.64	0.32516
2.99654		204.52	0.55551	206.90	0.54007	206.90	0.52608
1.79778	0.40766	185.48	0.59602	185.98	0.60377	187.70	0.54690
1.49799	0.50952	179.56	0.59938	179.82	0.60796	181.43	0.54954
1.19861	0.61156	172.66	0.60066	173.16	0.60058	174.38	0.54534
0.59917	0.81524	152.17	0.60483	151.71	0.61002	152.79	0.54499
3.99511		218.12	0.53928	221.33	0.51899	222.80	0.50026
2.39689	0.54353	201.00	0.54305	201.57	0.56122	203.47	0.52344
1.99729	0.67937	194.94	0.54914	195.56	0.56268	197.25	0.52523
1.59757	0.81508	187.61	0.55829	188.20	0.56790	189.83	0.52731
0.79868	1.08666	166.90	0.56676	166.72	0.57799	167.90	0.53316

Results and discussion

Solutions composition is given in table 1 along with the potential difference of cell (A), E, and mean activity coefficients of potassium chloride. For each series of measurements, the ionic strength was kept constant. Mean activity coefficients for KCl in the system KCl + K_2Ph + H_2O, γ_{KCl}, were calculated from emf data, using the rearranged form of the Nernst equation

$$\ln(\gamma_{KCl}) = \Delta E/2s - 1/2 \ln[(m_1+2m_2)\, m_1] + \ln(m^0_{KCl}) + \ln(\gamma^0_{KCl}) \quad (2)$$

where ΔE is the difference between two measurements on cell (A), with and without K_2Ph, m_1 and m_2 are the molalities of KCl and K_2Ph, respectively, m^0_{KCl} is the molality of KCl in the solutions without K_2Ph and γ^0_{KCl} is the activity coefficient of KCl calculated by the Pitzer equation with the ionic interaction coefficients given in Table 2. These values were obtained from data at 25 ºC and the respective temperature derivative [5]. The cell potentials, without K_2Ph, were also used to evaluate the s value, in equation (1), at each temperature, which is compared with the theoretical value [7] in Table 3.

Table 2. Pitzer parameters for potassium chloride [5].

t / ºC	$\beta^{(0)}$ / kg mol^{-1}	$\beta^{(1)}$ / kg mol^{-1}	C / kg^2 mol^{-2}
10	0.03966	0.19614	-0.00004
20	0.04545	0.20685	-0.00029
25	0.04835	0.21220	-0.00042
30	0.05125	0.21756	-0.00055
40	0.05704	0.22827	-0.00080
50	0.06284	0.23898	-0.00106

Due to the low hydrolysis constants for phthalate ion, the hydrogen phthalate ion and hydroxide ion molalities are very small, compared to that of phthalate ion, and they were neglected in the following calculations.

Table 3. Slope values for cell A (equation 1).

t / ºC	s / mV	s_{th} [a] / mV
10	25.05	24.40
20	25.84	25.26
25	26.06	25.70
30	26.64	26.12
40	27.60	26.98
50	28.20	27.85

[a] s_{th} Theoretical values [7].

According to the Pitzer formalism [3], mean activity coefficients of KCl in the $KCl + K_2Ph + H_2O$ system are given by

$$\begin{aligned}\ln\gamma_{KCl} = {} & F_1 + (m_K + m_{Cl})\left(\beta^{(0)}_{K,Cl} + \beta^{(1)}_{K,Cl}F_2 + m_K C_{K,Cl}\right) + \\ & + m_{Ph}\theta_{ClPh} + (m_K m_{Cl})\left(\beta^{(1)}_{K,Cl}F_3 + C_{K,Cl}\right) + \\ & + 1/2(m_K m_{Ph} + m_{Cl} m_{Ph})\psi_{K,Cl,Ph} + \\ & + m_{Ph}\left(\beta^{(0)}_{K,Ph} + \beta^{(1)}_{K,Ph}F_2 + m_K C_{k,Ph}\right) + \\ & + (m_K m_{Ph})\left(\beta^{(1)}_{K,Ph}F_3 + C_{K,Ph}\right) \\ & + m_{Cl} m_{Ph}\theta'_{Cl,Ph} \qquad (3)\end{aligned}$$

where F_1, F_2 and F_3 are functions of the ionic strength, I,

$$F_1 = -A_\phi \left[\frac{\sqrt{I}}{1+1.2\sqrt{I}} + \frac{2}{1.2} \ln\left(1+1.2\sqrt{I}\right) \right] \quad (4)$$

$$F_2 = \frac{1}{2I}\left[1-\left(1+2\sqrt{I}\right)\exp\left(-2\sqrt{I}\right)\right] \quad (5)$$

$$F_3 = \frac{1}{2I^2}\left[-1+\left(1+2\sqrt{I}+2I\right)\exp\left(-2\sqrt{I}\right)\right] \quad (6)$$

m is the molality of the species indicated in subscript, $\beta^{(0)}$,$\beta^{(1)}$ and C are interaction coefficients of the indicated salts, θ and ψ are the second and third virial coefficients, respectively, for the mixed electrolyte, and θ' is the θ derivative with respect to ionic strength [5].

The interaction of like charged ions, $\theta_{Cl,Ph}$, includes the effect of short range forces, ${}^{s}\theta_{Cl,Ph}$, and electrostatic effects of higher order, ${}^{E}\theta_{Cl,Ph}$, and cannot always be neglected for unsymmetrical electrolyte mixtures. They are given by

$$\theta_{Cl,\,Ph} = {}^{s}\theta_{Cl,\,Ph} + {}^{E}\theta_{Cl,\,Ph} \quad (7)$$

and

$$\theta'_{Cl,Ph} = {}^{E}\theta'_{Cl,Ph} \quad (8)$$

For this work, ${}^{E}\theta_{Cl,Ph}$ and ${}^{E}\theta'_{Cl,Ph}$ were calculated, at each temperature, following the procedure described by Pitzer [5]. The K_2Ph interaction parameters could be obtained from multilinear regression on the equation

$$Y = m_{Ph}(\beta^{(0)}_{K,Ph}+{}^{s}\theta_{Cl,Ph})+m_{Ph}(F_2+m_K F_3)\beta^{(1)}_{K,Ph}+2(m_K+m_{Ph})C_{K,Ph} \quad (9)$$

where Y includes the experimental $\ln\gamma_{KCl}$, the items that correspond to specific interactions relative to KCl and ${}^{E}\theta_{Cl,Ph}$ and ${}^{E}\theta'_{Cl,Ph}$, according to equation (3). For most electrolytes, the mixing parameter, ψ, is close to zero [5] and was discarded in the present calculation. As shown by equation (9) it is not possible to determine $\beta^{(0)}_{K,Ph}$ and ${}^{s}\theta_{Cl,Ph}$ separately. Nevertheless ${}^{s}\theta_{Cl,Ph}$ is expected to be much smaller than $\beta^{(0)}_{K,Ph}$, from comparison to other electrolytes of the same kind; so we believe this is a good approximation for $\beta^{(0)}_{K,Ph}$. The results are presented in Table 4. Their temperature dependence can be expressed by

$$\beta^{(0)}_{K,Ph}+{}^{s}\theta_{Cl,Ph} = 1.59\text{E-}01 + 6\text{E-}04(T-T_r) + 2.02\text{E-}04(T-T_r)^2 \quad (10)$$

$$\beta^{(1)}_{K,Ph} = 1.46 - 4.8\text{E-}02(T-T_r) + 1.39\text{E-}03(T-T_r)^2 \quad (11)$$

$$C_{K,Ph} = 8.2\text{E-}03 - 2\text{E-}05(T-T_r) - 3.0\text{E-}05(T-T_r)^2 \quad (12)$$

where T is the absolute temperature and T_r = 298.15 K is the reference temperature.

Table 4. Pitzer interaction parameters for K_2Ph including higher order electrostatic interactions.

t / ºC	$\beta^{(0)} + {}^{s}\theta$ / kg mol^{-1}	$\beta^{(1)}$ / kg mol^{-1}	C / kg^2 mol^{-2}	σ [a]
10	0.181 (0.059)	2.54 (0.32)	0.0024 (0.0081)	0.0132
20	0.181 (0.047)	1.68 (0.26)	0.0056 (0.0064)	0.0106
25	0.161 (0.022)	1.48 (0.12)	0.0098 (0.0031)	0.0050
30	0.189 (0.048)	1.00 (0.26)	0.0052 (0.0065)	0.0107
40	0.162 (0.060)	1.39 (0.33)	0.0039 (0.0082)	0.0136
50	0.323 (0.035)	0.99 (0.19)	-0.0123 (0.0048)	0.0079

[a] Residual standard deviation of regression. Standard errors are shown in brackets.

From a statistical point of view, C is zero at most temperatures studied. Even so, its values show a regular variation with temperature. The difference between ln γ_{KCl}(exp), calculated by equation (2), and ln γ_{KCl}(calc), obtained by equation (3), with the parameters presented in Table 4, was calculated for each solution. Fig. 1 shows these differences for these ionic strengths and temperatures.

The calculations were repeated without the higher order electrostatic terms and the results are given in Table 5. Both equations fit the experimental data identically and both sets of parameters are of the same order of magnitude. So, in these ionic strength and temperature ranges, the inclusion of the higher order electrostatic effects does not seem to improve the fit significantly. The K_2Ph parameters were also redetermined including the mixing parameter, $\psi_{K,Cl,Ph}$, with ${}^{E}\theta_{Cl,Ph}$ and ${}^{E}\theta'_{Cl,Ph}$ in equation (3) and no better fit was found.

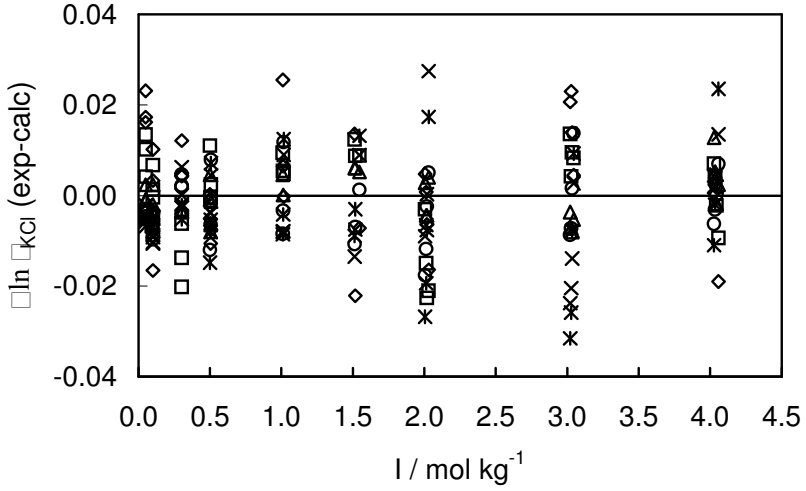

Figure 1. Difference between experimental (equation 2) and calculated (equation 3) ln γ_{KCl} in aqueous KCl + K_2Ph solutions: ◊ 10 ºC; □ 20 ºC; Δ 25 ºC; × 30 ºC; ⁎ 40 ºC; o 50 ºC.

Table 5. Pitzer interaction parameters for K_2Ph without higher order electrostatic interactions.

t / ºC	$\beta^{(0)} + \theta$ / kg mol^{-1}	$\beta^{(1)}$ / kg mol^{-1}	C / kg^2 mol^{-2}	σ [a]
10	0.120 (0.062)	2.16 (0.34)	0.0053 (0.0084)	0.0139
20	0.119 (0.048)	1.30 (0.26)	0.0085 (0.0066)	0.0109
25	0.099 (0.025)	1.09 (0.14)	0.0128 (0.0034)	0.0056
30	0.127 (0.044)	0.61 (0.24)	0.0082 (0.0060)	0.0099
40	0.099 (0.054)	1.00 (0.29)	0.0067 (0.0073)	0.0121
50	0.265 (0.030)	0.56 (0.16)	-0.0103 (0.0042)	0.0068

[a] Residual standard deviation of regression. Standard errors are shown in brackets.

The values $\beta^{(0)}_{K,Ph}$ = 0.12 mol^{-1} kg and $\beta^{(1)}_{K,Ph}$ = 0.7 mol^{-1} kg, reported by Chan and collaborators [8], were obtained, at 25 ºC, from measurements on a Harned cell, where the electrolytes were potassium hydrogen phthalate and potassium chloride, with ionic strength ranging from 0.02 to 2 mol kg^{-1}. Partanen and Minkkinen [9] used extensive Harned cell data of Hamer, Pinching and Acree [10] and Hamer and Acree [11] to determine the same parameters, $\beta^{(0)}_{K,Ph}$ = 0.31 mol^{-1} kg and $\beta^{(1)}_{K,Ph}$ = 0.70 mol^{-1} kg. The ionic strength of those solutions was lower than 0.5 mol kg^{-1}, as they were prepared for the determination of the ionization constants of phthalic acid by extrapolation to zero ionic strength.

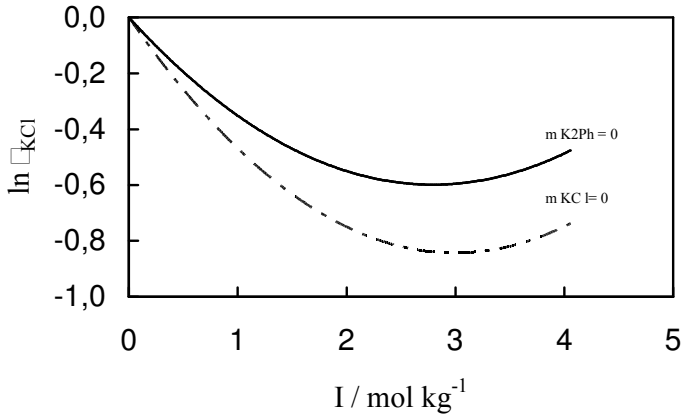

Figure 2. Calculated potassium chloride activity coefficient by equation (3): — single KCl (m_{K2Ph} = 0) --- single K_2Ph (m_{KCl} = 0).

Mendonça and Jussola also determined activity coefficients of KCl in aqueous solutions of KCl and K_2Ph using potentiometric data from a cell like the one indicated in the present work. Their Pitzer parameters, at 25 ºC, are $\beta^{(0)}_{K,Ph} + {}^{s}\theta_{Cl,Ph}$ = 0.25 ± 0.01 mol^{-1} kg, $\beta^{(1)}_{K,Ph}$ = 0.86 ± 0.08 mol^{-1} kg, $C_{K,Ph}$ = -0.10 ± 0.002 mol^{-2} kg^{-2} and $\psi_{K,Cl,Ph}$ = 0.014 ±0.005 mol^{-2} kg^{-2} [12], with ionic strength varying from 0.6 to 4.5 mol kg^{-1}. The values determined in the present work, given in Table 4, refer to a wider ionic strength range and show a regular variation with temperature.

The variation of ln γ_{KCl} with ionic strength is illustrated in Fig. 2 for the mixed electrolyte. The activity coefficient was calculated by equation (3), with the parameters given in Table 4, at 25 ºC. The two lines represent the limit situations where only KCl ($m_{K2Ph} = 0$) is present or only K_2Ph ($m_{KCl} = 0$).

Conclusions

Mean activity coefficients of KCl were determinated in the system KCl + K_2Ph + H_2O, in the temperature range 10-50 ºC, from potentiometric measurements in a galvanic cell without liquid junction. The ionic strength varied between 0.05 and 4 mol kg^{-1}. The results were processed using the Pitzer theory. The interaction parameters obtained for potassium phthalate enable the calculation of mean activity coefficients of this salt in water or in aqueous solutions of potassium chloride, in those ionic strength and temperature ranges.

The results indicate that the inclusion of the higher order electrostatic terms in the Pitzer equation improves only slightly its fit to the experimental data. On another hand, if they are included, the new parameters are closer to those of other organic electrolytes of the same type [5]. As there is no phthalate ion selective electrode available, the potentiometric data were obtained from mixtures of two electrolytes with a common ion, K^+. However, the Pitzer formalism enabled the use of the known parameters of one electrolyte in order to evaluate those relative to the other.

References

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