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A NEW EVALUATION OF THE RELATIVE APPARENT MOLAR ENTHALPIES OF KCl IN WATER AT 298.15 K

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ABSTRACT

The differential enthalpies of solution of KCl in water at 298.15 K were measured in the molality range 0.05–4.03 mol kg^{-1}. From the experimental results, the molality dependence of the relative apparent molar enthalpy $L_\phi(m)$ was obtained. The comparison with Parker values for L_ϕ showed discrepancies as great as 7% at $m = 4$ mol kg^{-1}. An extensive analysis of the literature data gave similar differences when the differential and integral enthalpies of solution were considered. From the enthalpies of dilution no definitive conclusions could be drawn because of the lack of precise data at higher molalities. Finally, from the analysis of the whole enthalpy data set for KCl (aq.) at 298.15 K a new molality dependence for L_ϕ is proposed.

INTRODUCTION

In previous work [1] we started a systematic study of the molality dependence of the enthalpy of several alkali halide solutions in water at 298.15 K. A calorimeter built in our laboratory for enthalpy-of-solution measurements at low molalities [2], was adapted to measure the differential enthalpy of solution [1]. From the measurements for NaCl solutions, the relative partial molar enthalpy $L_2(m)$ and the relative apparent molar enthalpy $L_\phi(m)$ were obtained and found to be in good agreement with Parker tabulations [3].

Whereas for NaCl aqueous solutions at 298.15 K, the enthalpy data and their thermodynamic analysis is complete [3–9], for KCl solutions there is a lack of data at higher molalities [3,4] and the thermodynamic treatment is not complete [3,5,7]. More recent measurements of the enthalpies of solution and dilution have not been used to obtain better values for $L_2(m)$ and $L_\phi(m)$. Even in the more recent analysis by Holmes and Messmer [7], the early high precision data obtained before the 1930s was not considered.

In this work we have measured the differential enthalpies of solution of KCl in water at 298.15 K in the molality range 0.05–4.0 mol kg^{-1}. After comparing the computed L_2 and L_ϕ values with those of Parker, an exhaustive analysis of the experimental values available in the literature was carried in order to obtain a new molality dependence of L_ϕ for aqueous KCl solutions at 298.15 K.

EXPERIMENTAL

The heat-flux calorimeter and the experimental procedure were the same as described previously [1,2]. For each measurement of the differential enthalpy of solution the temperature was determined within ± 0.02 K, an electrical calibration was carried out before and after each solution process and the initial mechanical effect was also considered [1]. The calorimetric resolution was 0.005 J.

The water used was doubly distilled and the solid potassium chloride was Merck Suprapur. It was heated for 5 h in a furnace at (774 ± 5) K. The molality values are better than 0.1%. All solute weighings are accurate to 0.003%.

RESULTS

In a real solution process the experimental differential enthalpy of solution $\Delta_{\text{sol}}H_2^{\text{exp}}$ is obtained by adding a small amount (Δn_2 mol) of solid salt to a solution of original molality m. If E is the energy absorbed and Δm is the change of molality, $\Delta_{\text{sol}}H_2^{\text{exp}}$ can be written as eqn. (1)

$$\Delta_{\text{sol}}H_2^{\text{exp}} = E/\Delta n_2 = \Delta_{\text{sol}}H_m^\infty + (1/\Delta m)\int_m^{m+\Delta m} L_2(m)\,\mathrm{d}m \qquad (1)$$

where $\Delta_{\text{sol}}H_m^\infty$ is the enthalpy of solution at infinite dilution. In Table 1, the experimental differential enthalpies of solution of KCl in water at temperature T_{mean} are shown. $\Delta_{\text{sol}}H_2^{\text{exp}}(298.15\text{ K})$ is the experimental differential enthalpy of solution adjusted to 298.15 K and after correcting for the error due to condensation of solvent vapour over the solution. ϵ is the estimated error [1].

If in eqn. (1) we expand $L_2(m)$ in a Taylor series around the original molality m and keep terms up to the first order, we obtain

$$\Delta_{\text{sol}}H_2^{\text{exp}} = \Delta_{\text{sol}}H_m^\infty + L_2(m) + \left(\frac{\partial L_2(m)}{\partial m}\right)(\Delta m/2) \qquad (2)$$

Using the following molality dependence for $L_\phi(m)$

$$L_\phi(m) = Am^{1/2} + Bm + Cm^{3/2} + Dm^2 \qquad (3)$$

TABLE 1

Calorimetric differential enthalpies of solution of KCl in water at 298.15 K

m (mol kg^{-1})	Δm (mol kg^{-1})	E (J)	T_{mean} (K)	$\Delta_{\text{sol}}H_2^{\text{exp}}$(298.15 K) (cal [a] mol^{-1})	ϵ (cal mol^{-1})
0.05014	0.01804	10.937	298.148	4093	6
0.1017	0.01834	11.258	298.044	4221	10
0.1160	0.01577	9.513	298.354	4229	9
0.5002	0.01892	11.206	298.030	4145	12
0.9988	0.01690	9.292	298.405	3971	12
1.016	0.01908	10.455	298.305	3942	19
1.007	0.01831	10.298	298.001	3954	17
1.500	0.01647	8.761	298.090	3826	33
2.000	0.01711	8.816	297.972	3734	17
2.500	0.01958	9.423	298.325	3611	9
3.058	0.01622	7.589	297.912	3482	17
3.501	0.01778	7.997	298.148	3454	22
4.000	0.01961	8.572	298.016	3359	6
4.013	0.01956	8.646	298.071	3397	34
4.032	0.01775	7.874	298.081	3411	44

[a] 1 cal = 4.184 J throughout this paper.

where A is the limiting slope for $L_\phi(m)$ [10] and B, C, D are adjustable parameters, eqn. (2) can be written as [1]

$$\Delta_{\text{sol}}H_2^{\text{exp}} = \Delta_{\text{sol}}H_m^{\infty} + (3/2)A\{m^{1/2} + (1/4)m^{-1/2}\Delta m\} + B(2m + \Delta m) + (5/2)Cm^{1/2}\{m + (3/4)\Delta m\} + 3Dm(m + \Delta m) \tag{4}$$

As reported previously [1], the value of $\Delta_{\text{sol}}H_m^{\infty}$ was taken from the

TABLE 2

Calculated values of $L_\phi(m)$ at experimental molalities. $L_\phi(m)^{\text{P}}$ are taken from Parker [3]

m (mol kg^{-1})	$L_\phi(m)$ (mol kg^{-1})	$L_\phi(m)^{\text{P}}$ (mol kg^{-1})	$L_\phi(m)^{\text{P}} - L_\phi(m)$ (mol kg^{-1})
0.05014	71	72	1
0.1017	84	85	1
0.1160	85	87	2
0.5002	56	58	2
0.9988	−17	−18	1
1.016	−20	−20	0
1.007	−18	−19	−1
1.500	−88	−94	−6
2.000	−152	−164	−12
2.500	−211	−228	−17
3.058	−271	−293	−22
3.501	−316	−340	−24
4.000	−365	−391	−26
4.013	−366	−392	−26
4.032	−368	−394	−26

literature and B, C, D were obtained by fitting the experimental data. The calculated values of L_ϕ at the experimental molalities are shown in Table 2. The value 4112 cal mol^{-1} [2] was used for $\Delta_{\mathrm{sol}}H_m^\infty$. The comparison with the L_ϕ data from Parker [3] shows differences of about 5–7% for molalities greater than 1 mol kg^{-1}. The quantity $\{L_\phi(\mathrm{Parker}) - L_\phi(\mathrm{This\ work})\}$ grows systematically from 1 cal mol^{-1} at $m = 1$ mol kg^{-1} to 26 cal mol^{-1} at $m = 4$ mol kg^{-1}. These differences cannot be related to the experimental uncertainties (about 1%). It is evident that an extensive analysis of the literature enthalpy data for KCl is necessary, especially at molalities greater than 1 mol kg^{-1} and up to saturation.

THERMODYNAMIC ANALYSIS OF THE KCl ENTHALPY DATA AT 298.15 K

The experimental enthalpy data for aqueous KCl solutions at 298.15 K has been reviewed by Parker [3] and more recently by Smith-Magovan and Goldberg [4]. In this work we have considered only the original data points when available. In Table 3 the references considered are summarized jointly with the molality range covered and the number of experimental points, N_{exp}.

For the study of L_ϕ molality dependence, the differential heats of solution, $\Delta_{\mathrm{sol}}H_2$, the (integral) heats of solution, $\Delta_{\mathrm{sol}}H_m$ and the (integral) heats of dilution, $\Delta_{\mathrm{dil}}H_m$, have been analysed separately. Only experimental results at 298.15 K were considered. The use of corrected enthalpies to 298.15 K by using the apparent molar heat capacities, as was done by Parker, could introduce errors which are in general difficult to evaluate, specially with the oldest literature.

In the enthalpy of solution database set, some of the references reviewed in ref. 1 which only cover molalities closer to zero were excluded because we are interested in the behaviour of L_ϕ at higher molalities. The information about the behaviour of $\Delta_{\mathrm{sol}}H_m$ at low molalities is covered adequately by the references shown in Table 3. Also, for completeness in this table are included several references in which only an analytic expression for L_ϕ is given. These expressions will be used later for comparison with the results obtained in this work after the analysis of the literature data.

The three data set ($\Delta_{\mathrm{sol}}H_2$, $\Delta_{\mathrm{sol}}H_m$, $\Delta_{\mathrm{dil}}H_m$) were fitted by means of the least squares method using eqn. (1) for $L_\phi(m)$ with the following thermodynamic relationships

$$\Delta_{\mathrm{sol}}H_2 = \Delta_{\mathrm{sol}}H_m^\infty + L_2(m) \qquad (5)$$

$$\Delta_{\mathrm{sol}}H_m = \Delta_{\mathrm{sol}}H_m^\infty + L_\phi(m) \qquad (6)$$

$$\Delta_{\mathrm{dil}}H_m = L_\phi(m_{\mathrm{f}}) - L_\phi(m_{\mathrm{i}}) \qquad (7)$$

TABLE 3

Enthalpy data base for KCl(aq) at 298.15 K

Property	Ref.	Molality range (mol kg^{-1})	N_{exp}
$\Delta_{sol}H_2$	[a]	0.05–4.00	15
	11	0.18–4.68	15
	12	0.0004–0.50	18
	13 [b]	0.0004–0.50	18
	14	0.15–4.64	15
$\Delta_{sol}H_m$	2	0.01–0.06	19
	11	0.37–4.54	15
	12	0.0004–0.50	18
	13 [b]	0.0004–0.50	18
	14	0.31–4.46	15
	15	0.03–1.11	6
	16	0.05–4.18	11
	17	0.104	1
$\Delta_{dil}H_m$	17	0.15–3.41	1
	18	0.06–4.49	12
	19	0.186–3.16	23
	20, 21	0.111–2.26	9
	22	0.00138–0.01	3
	23 [c]	0.00138–0.01	3
	24	0.000326–0.5	22
	25	0.06–0.30	2
	26	0.12–3.0	7
L_{ϕ}^{d}	5	0–4.5	–
	7	0–3.4	–
	27	8.0×10^{-4}–0.015	81 [e]
	28 [f]	0–1.0	–

[a] This work. [b] Corrected data from ref. 12. [c] Same data as in ref. 22. [d] Only an analytic function is given for L_{ϕ}. [e] 81 is the number of experiments quoted in that paper. [f] These data were used for comparison after correcting them to 25 ° C.

where

$$L_2 = \left(\frac{\partial (mL_{\phi})}{\partial m} \right)_{T,p} \tag{8}$$

In eqn. (7), m_i and m_f represent the initial and final molalities in a heat of dilution experiment.

The general procedure was as follows: first, the experimental data from each reference were analysed in order to evaluate their quality and molality behaviour; next, the whole set was fitted and the general behaviour of L_{ϕ} was obtained. The results obtained are discussed separately and at the end of the paper a comparative discussion is given.

The experimental determination of $\Delta_{sol}H_2$ for electrolyte solutions was made principally by Lange and coworkers [11–13], Partington and Soper [14] and more recently by Craft and Van Hook [17] and the present authors [1]. In spite of the fact that the number of experimental measurements is low the data cover the whole molality range up to 4.5 mol kg^{-1} adequately. The agreement among different authors is good (within experimental uncertainty) giving the same behaviour as m increases. In Fig. 1 the experimental results are plotted against m jointly with the fitted expression and the $\Delta_{sol}H_2$ values calculated from Parker's data [3]. In Table 4 the results of the fit are given with the standard deviation of the fit, $\sigma = 16.8$ cal mol^{-1}. The discrepancies from the values of Parker are found again (about 10% at $m = 4.5$ mol kg^{-1}) and are reflected in the differences on the adjustable parameters in eqn. (1).

TABLE 4

Results of $\Delta_{sol}H_2$, $\Delta_{sol}H_m$, $\Delta_{dil}H_m$ and L_ϕ data treatment using eqn. (3)

Property	N [a]	m_{min} (mol kg^{-1})	m_{max} (mol kg^{-1})	$\Delta_{sol}H_m$ (cal mol^{-1})	B(cal kg mol^{-2})	C(cal kg$^{3/2}$ mol$^{-5/2}$)	D(cal kg^2 mol^{-3})	σ(cal mol^{-1})
$\Delta_{sol}H_2$	59	3.3×10^{-4}	4.5	4115	−670.716	234.605	−30.445	16.8
$\Delta_{sol}H_m$	81	3.9×10^{-4}	4.54	4115	−696.261	280.706	−47.378	16.1
$\Delta_{dil}H_m$	32	3.3×10^{-4}	3.41	–	−711.659	232.462	−19.271	7.0
L_ϕ^P	42	0.000111	4.6225	–	−721.347	271.348	−38.615	–
L_ϕ^b	84	0.000111	4.6225	–	−683.6	257.787	−38.949	–

[a] Number of points used in each fit. [b] Proposed molality dependence for L_ϕ.

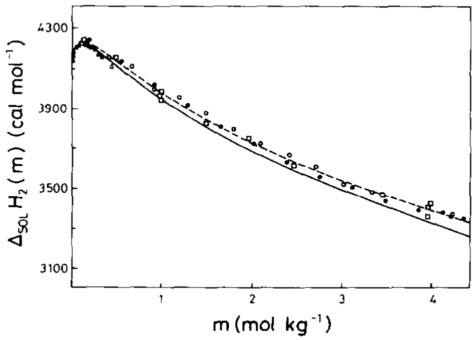

Fig. 1. Plot of the differential heats of solution vs. molality. Experimental values from (●) ref. 11; (▲) ref. 12; (○) ref. 14 and (□) the present work. (— — —) Fit of the experimental data; (———) $\Delta_{sol}H_2$ from Parker.

HEATS OF SOLUTION

After the review of Parker [3], several experimental determinations of $\Delta_{sol}H_m$ were made at high concentrations [15,16]. As a result, the whole data cover the existence domain of the KCl solution well. With the exception of the oldest data reported by Wüst and Lange [11] and Partington and Soper [14] at molalities lower than 1 mol kg^{-1}, the trend is the same for different authors. This can be seen in Fig. 2 where the result of the fit and the Parker tabulation are shown also. Again the difference between the curve of Parker and the fitted line (about 6% at $m = 4.5$ mol kg^{-1}) is evident. The behaviour of $\Delta_{sol}H_m$ is very similar to that of $\Delta_{sol}H_2$ as can be seen in Table 4 where the results of the fit are summarized. If we take into account the differences in the two kinds of experimental measurements, we can conclude that the agreement is good.

HEATS OF DILUTION

It seems, from Table 3, that adequate experimental values for $\Delta_{dil}H_m$ for aqueous KCl solutions at 298.15 K and up to 4.5 mol kg^{-1} exist. However, careful analysis of the data shows that for $\Delta_{dil}H_m$ the distribution of experimental points within the molality range and their quality is too sparse to be adequate for a precise determination of $L_\phi(m)$.

The data of Bishop [18], Stearn and Smith [19] and Pratt [20] are the oldest and cover the area up to 4.5 mol kg^{-1}. The individual analysis of these three data sets shows remarkably different behaviour if they are compared with the values of Parker. The L_ϕ values obtained from Bishop and from Stearn and Smith are shown in Fig. 3. The discrepancies with respect to Parker's data are as great as 100 cal mol^{-1}. These data were

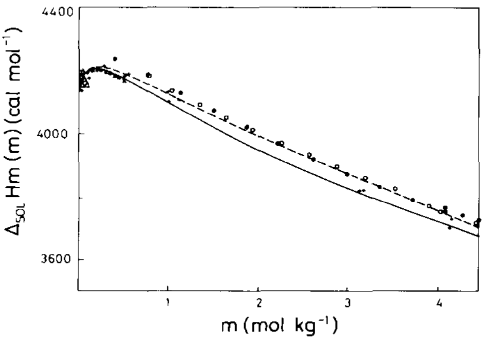

Fig. 2. Plot of the heats of solution vs. molality. Experimental values from (△) ref. 2; (●) ref. 11; (*) ref. 13; (○) ref. 14; (+) refs. 15–17. (— — —) Fit of the experimental data; (———) $\Delta_{sol}H_m$ from Parker.

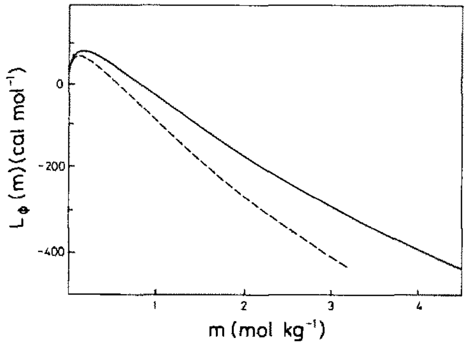

Fig. 3. Plots of the relative apparent molar enthalpy vs. molality from (······) ref. 18, (— — —) ref. 19 and from (———) Parker.

deleted from the final fit even though when they were fitted jointly the agreement with the values of Parker was good due to a compensation effect.

The data of Pratt give reasonable behaviour but only cover up to 2.3 mol kg^{-1}. Moreover, a study of the temperature dependence of the enthalpy of KCl aqueous solutions by means of the Bahe Lattice Model [29], showed that Pratt's data are not in agreement with other data at temperatures below 298.15 K. However, due to the general lack of precise data at these temperatures no definitive conclusions could be drawn and Pratt's data were used in the final fit.

The high precision data of Lange and coworkers [22–25] unfortunately only cover the high dilution range (Table 3) as in the case of Vichutinskii and Golikov [27]. The more recent data of Wood et al. [26] only cover two dilution ranges: 3.0 to 0.33 mol kg^{-1} (two measurements) and 1.0 to about 0.12 mol kg^{-1} (five measurements). In the paper of Craft and Van Hook [17] only one experimental measurement is reported.

From the discussion above, it is evident that the $L_\phi(m)$ behaviour that can be obtained from $\Delta_{\text{dil}}H_m$ data cannot be considered as definitive. The results of the fit are shown in Fig. 4 and in Table 4. Surprisingly, the behaviour of L_ϕ agrees well with Parker's study even though that part of the data used in this work was not considered. However, at $m = 3.2$ mol kg^{-1} the L_ϕ curve obtained from $\Delta_{\text{dil}}H_m$ rises showing important deviations with respect to the Parker curve as molality increases up to 4.5 mol kg^{-1}. For example, at $m = 3.5$ mol kg^{-1} the difference is 26 cal mol^{-1} which corresponds to an error of 8.5% comparable to those obtained from $\Delta_{\text{sol}}H_2$ and $\Delta_{\text{sol}}H_m$ data.

DISCUSSION AND CONCLUSIONS

In Fig. 4 the three L_ϕ curves obtained in this work are plotted jointly with that obtained by Parker. A clear separation exists between the L_ϕ values

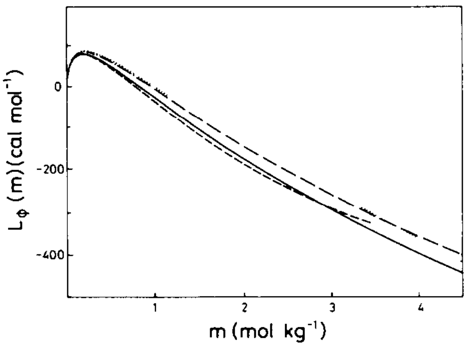

Fig. 4. Plot of the molality dependence of L_ϕ obtained from (······) $\Delta_{sol}H_m$; (·–·–·) $\Delta_{sol}H_2$; (— — —) $\Delta_{sol}H_{dil}$ and (———) Parker.

obtained from $\Delta_{sol}H_2$ and $\Delta_{sol}H_m$ measurements with respect to L_ϕ values from $\Delta_{dil}H_m$. This behaviour appears in the literature [5,7] but was unnoticed. In Fig. 5, the $L_\phi(m)$ values obtained by Silvester and Pitzer [5] and by Holmes and Mesmer [7] are ploted and compared with those of Parker. The similarities between Figs. 4 and 5 are evident. These are reasonable if we take into account that Silvester and Pitzer used the heat of solution data of Wüst and Lange at high concentrations [11], whereas Holmes and Mesmer only considered the heat of dilution data of Wood et al. [26] and of Craft and Van Hook [17]. In Fig. 5, the L_ϕ values obtained for KCl aqueous solutions at 303.15 K by Leung and Millero [28] up to 1 mol kg^{-1} are plotted for comparison after correcting to 298.15 K using the heat capacity data of Desnoyers et al. [30]. These results agree well with Holmes and Mesmer but this behaviour is reasonable if we remenber that Leung and Millero's data were used in the general fit by Holmes and Mesmer [7].

From the analysis presented in this work, we propose a new set of L_ϕ values for KCl aqueous solutions at 298.15 K based on $\Delta_{sol}H_2$ and $\Delta_{sol}H_m$

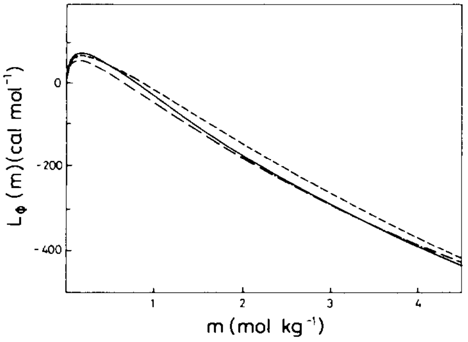

Fig. 5. Plot of the molality dependence of L_ϕ obtained from (— — —) ref. 5; (·–·–·) ref. 7; (······) ref. 28 and (———) Parker.

data. The dependence of L_ϕ on m was obtained by fitting the L_ϕ values computed by means of eqn. (3) using the two sets of parameters given in Table 4 corresponding to the differential and integral heats of solution fits. The new set of adjustable parameters, given in Table 4, can be used to compute $L_\phi(m)$ at round molalities. At present the differences with respect to the L_ϕ values obtained from heat of dilution data remain to be explained. Due to the lack of extensive data a careful study of $\Delta_{\mathrm{dil}}H_m$ at 298.15 K covering the whole molality range would be of interest. It must be noted that in the case of NaCl aqueous solutions at 298.15 K, these differences were not found as was discussed earlier [1].

REFERENCES

1 A. Sanahuja and J.L. Gómez-Estévez, J. Chem. Thermodyn., in press.
2 A. Sanahuja and E. Cesari, J. Chem. Thermodynam., 16 (1984) 1195.
3 V.B. Parker, Thermal Properties of Aqueous Uni-univalent Electrolytes, NSRDS NBS 2, U.S. Government Printing Office, Washington, DC, 1965.
4 D. Smith-Magovan and R.N. Goldberg, A Bibliography of Sources of Experimental Data Leading to Thermal Properties of Binary Aqueous Electrolyte Solutions, NBS Special Publication 537, U.S. Government Printing Office, Washington, DC, 1979.
5 L.F. Silvester and K.S. Pitzer, J. Solution Chem., 7 (1978) 327.
6 L.E.S. Smith, J.T. Cone and W.A. Van Hook, J. Solution Chem., 9 (1980) 81.
7 H.F. Holmes and R.E. Mesmer, J. Phys. Chem., 87 (1983) 1242.
8 K.S. Pitzer, J.C. Pelper and R.H. Busey, J. Phys. Chem. Ref. Data, 13 (1984) 1.
9 E.C.W. Clarke and D.N. Glew, J. Phys. Chem. Ref. Data, 14 (1985) 489.
10 E.C.W. Clarke and D.N. Glew, J. Chem. Soc., Faraday Trans. 1, 76 (1980) 1911.
11 J. Wüst and E. Lange, Z. Phys. Chem., 116 (1925) 161.
12 E. Lange and J. Monheim, Z. Electrochem., 35 (1929) 29.
13 E. Lange and J. Monheim, Z. Phys. Chem., Abt. A, 150 (1930) 349.
14 J.R. Partington and W.E. Soper, Phil. Mag., S7, 7 (1929) 209.
15 I.V. Bazlova, M.S. Stakhanova, M.Kh. Karapet'yants and K.K. Vlasenko, Russ. J. Phys. Chem., 39 (1965) 658.
16 V.K. Abrosimov, A.V. Ionov and G.A. Krestov, Radiokhimiya, 19 (1977) 862.
17 Q.D. Craft and W.A. Van Hook, J. Solution Chem., 4 (1971) 901.
18 F.L. Bishop, Phys. Rev. 1, 26 (1908) 169.
19 A.E. Stearn and G.McP. Smith, J. Am. Chem. Soc., 42 (1920) 18.
20 F.R. Pratt, J. Franklin Inst., 185 (1918) 663.
21 F.R. Pratt, in E.W. Washbrum (Ed.), International Critical Tables, Vol. V, 1929, p. 161.
22 E. Lange and G. Messner, Z. Electrochem., 33 (1927) 431.
23 E. Lange and G. Messner, Naturwissenschaften, 15 (1927) 521.
24 E. Lange and P.G. Leighton, Z. Electrochem., 34 (1928) 566.
25 J. Monheim and H. Streeck, unpublished measurements. Quoted in E. Lange and J. Meixner, Physik Z., 30 (1929) 670.
26 R.H. Wood, R.A. Rooney and J.N. Braddock, J. Phys. Chem., 73 (1969) 1673.
27 A.A. Vichutinskii and A.G. Golikov, DAN SSSR, 238 (1978) 9.
28 W.H. Leung and F.J. Millero, J. Chem. Thermodynamics, 7 (1975) 1067.
29 J.L. Gómez-Estévez, Ph.D. Thesis, Universidad de Barcelona, Barcelona, 1983.
30 J.E. Desnoyers, C. de Visser, G. Perron and P. Picker, J. Solution Chem., 5 (1976) 605.