

Isopiestic Determination of Osmotic Coefficients at 100°C by Means of a Simple Apparatus

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A new apparatus for isopiestic measurements at enhanced temperatures is described. It is simple in its construction and operation. Measurements were made in the binary systems NaCl–H₂O, LiCl–H₂O and LiNO₃–H₂O at $T = 100.3 \pm 0.05^\circ\text{C}$. The system CaCl₂–H₂O has been chosen as reference system. The reproducibility of the results is better than 0.1%. The isopiestic ratios of NaCl and LiCl agree with literature data to within 0.6 and 0.7%, respectively. From the experimental osmotic coefficients for the system LiNO₃–H₂O, vapour pressures were calculated and compared with the literature data up to concentrations of 16 mol per kg H₂O.

Dedicated to Professor Otto Bastiansen on his 70th birthday

Interest in the thermodynamic properties of water–salt systems is increasingly directed toward high concentrations^{1,2} and complex systems.^{3,4,5} The obvious lack of accurate experimental data for multicomponent electrolyte solutions hampers a well-founded discussion of the limitations and validity ranges of models describing quantitatively the thermodynamic properties within large concentration intervals. Most of the activity data for water–salt systems have been determined by isopiestic measurements. This method is generally applicable to solutions of non-volatile substances,⁶ and provides water activities for solutions of different compositions within one run. In addition, it is relatively insensitive to the presence of small amounts of gases other than water vapour.

At room temperature, the experimental set-up and procedure is quite simple⁶ and the method is therefore widely used. However, only a few attempts have been made to apply the method at temperatures above 50°C.^{7–11} The main difficulty is the necessity of closing the sample cups under equilibrium conditions and transferring them separately in a closed state to a balance. In order to

avoid this problem, the cups can be weighed directly inside the container by means of a built-in balance. Measurements were made up to 225°C in this way at Oak Ridge National Center.⁷ However, *in situ* weighing makes the system very complicated.

A lid-lowering mechanism was proposed to cover the sample cups within the desiccator.⁹ This technique was used for temperatures between 45 and 60°C.^{9–11} Since the lids rest on the cups only with their own weight, they do not close tightly enough at higher temperatures.

In this paper we describe an apparatus which allows the lids to be pressed down with gaskets against the upper edges of the sample cups. The apparatus has been tested at 100.3°C, but the principle can also be used at higher temperatures.

Experimental

Apparatus. A vertical section of the apparatus is presented in Fig. 1a. A cylindrical metal block (A), made of pure aluminium, was placed in a pressure-tight aluminium container (B). Block A is thermally insulated from the container's wall

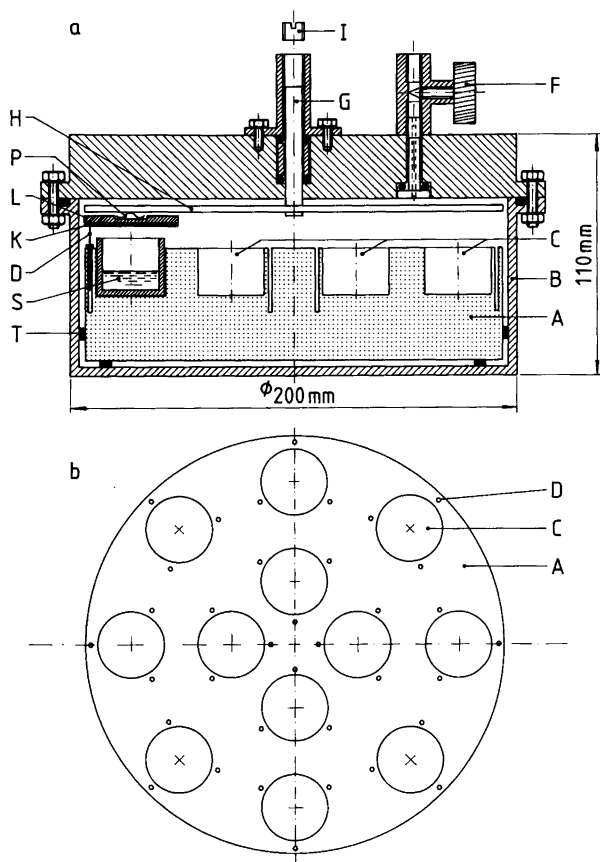


Fig. 1. (a) Vertical section of the apparatus for isopiestic measurements. (b) Top view of the aluminium block. A: aluminium block, B: aluminium container, C: holes for sample cups, D: piece of wire (\varnothing 1 mm), F: needle valve, G: steel bolt, H: stainless steel plate, I: screw, K: silicone gasket, L: lid, P: spring, S: sample cup, T: PTFE shim.

by small shims of PTFE (T). Fig. 1b shows a top view of block A. It contains 12 holes (C) for the sample cups which are distributed along two cir-

cles about the centre. Each hole C is surrounded by three small holes (diameter 2 mm). Into each of these 2 mm holes a piece of wire (D) (diameter

Table 1. Compositions of stock solutions (g salt per g solution) dependent on time.

Salt	Date of analysis				
	15.10.86	26.01.87	15.03.87	05.05.87	01.07.87
CaCl ₂	0.45987 ^a 0.45964 ^d	0.46137 ^b —	0.46219 ^c 0.46219 ^d	0.46137 ^b —	0.46150 ^b —
LiCl	0.32166 ^a 0.32273 ^d	0.32313 ^b —	0.32338 ^d —	— —	0.32318 ^b —
LiNO ₃	—	0.42420 ^b	0.42423 ^e	—	0.42568 ^b
NaCl	—	—	0.25423 ^f	0.25458 ^b	0.25458 ^b

^aGravimetric determination of Cl⁻ as AgCl. ^bDetermination of water content by drying of about 2 g of solution. ^cComplexometric titration of Ca²⁺ with EDTA. ^dArgentometric titration of Cl⁻. ^eDetermination of water content using "Karl Fischer" method. ^fCalculated from solution preparation from anhydrous salt.

Table 2. Experimental isopiestic molalities m (mol salt per kg H₂O) and isopiestic ratios $R = (m_{\text{salt}}/m_{\text{CaCl}_2})$ at 100.3 °C.

m_{CaCl_2}	m_{NaCl}	R_{NaCl}	m_{LiCl}	R_{LiCl}	m_{LiNO_3}	R_{LiNO_3}
7.0724	—	—	—	—	15.2838	2.1610
5.9548	—	—	—	—	12.6058	2.1169
5.7977	—	—	—	—	12.2120	2.1064
5.7857	—	—	—	—	12.1877	2.1065
5.6361	—	—	—	—	11.8149	2.0963
5.4359	—	—	—	—	11.3010	2.0790
5.0929	—	—	—	—	10.4404	2.0500
4.4156	—	—	—	—	8.7103	1.9726
4.1283	—	—	—	—	7.9872	1.9347
3.8659	—	—	6.3015	1.6300	—	—
3.7247	—	—	—	—	6.9873	1.8759
3.6724	—	—	—	—	6.8590	1.8677
3.3754	6.5979	1.9547	—	—	6.1484	1.8215
3.0016	—	—	—	—	5.2850	1.7607
2.9726	5.6023	1.8846	—	—	5.2171	1.7551
2.9112	—	—	4.6410	1.5942	—	—
2.7005	—	—	—	—	4.6166	1.7095
2.6421	4.8306	1.8283	—	—	4.4974	1.7022
2.6343	—	—	—	—	4.4738	1.6983
2.5444	—	—	3.9982	1.5714	—	—
2.3316	—	—	—	—	3.8412	1.6475
2.2055	3.8554	1.7481	—	—	3.5858	1.6258
2.0454	3.5134	1.7177	3.1379	1.5341	—	—
2.0414	—	—	3.1278	1.5322	—	—
1.9955	3.4122	1.7099	—	—	3.1723	1.5897
1.9058	—	—	—	—	3.0001	1.5742
1.5526	—	—	—	—	2.3592	1.5195
1.4993	—	—	—	—	2.2589	1.5066
1.4486	2.3190	1.6009	—	—	2.1708	1.4986
1.4037	—	—	2.0617	1.4688	—	—
1.2259	—	—	—	—	1.7937	1.4632
1.2019	1.8603	1.5478	—	—	1.7558	1.4609
1.0676	—	—	1.5274	1.4307	—	—
0.89309	1.3230	1.4814	1.2587	1.4094	1.2593	1.4100
0.84469	1.2439	1.4726	—	—	—	—
0.79296	1.1575	1.4597	1.1069	1.3959	1.1048	1.3933
0.74465	1.0793	1.4494	—	—	—	—
0.59079	0.83747	1.4175	0.81037	1.3717	0.80618	1.3646
0.52157	—	—	—	—	0.70828	1.3580
0.45616	0.63528	1.3927	0.62144	1.3623	0.61403	1.3461
0.35081	0.48129	1.3719	0.47501	1.3540	0.46945	1.3382

1 mm) is inserted to about 2/3 of its depth, as shown on the left-hand side of Fig. 1a. Small silicone rubber slivers hold the sticks in position. The sticks support the lids (L) on their gaskets (K), which are positioned about 10 mm above the sample cups (S). The cups are made of aluminium. Their inner wall is protected against corro-

sion by a thin coating of silicone laquer. In some experiments, vitreous carbon cups of the same dimensions were used. The cups are closed by turning the screw (I). Thereby the bolt (G) and the connected steel plate (H) are pushed down. After making contact with the lids, they also move down together with their supporting sticks.

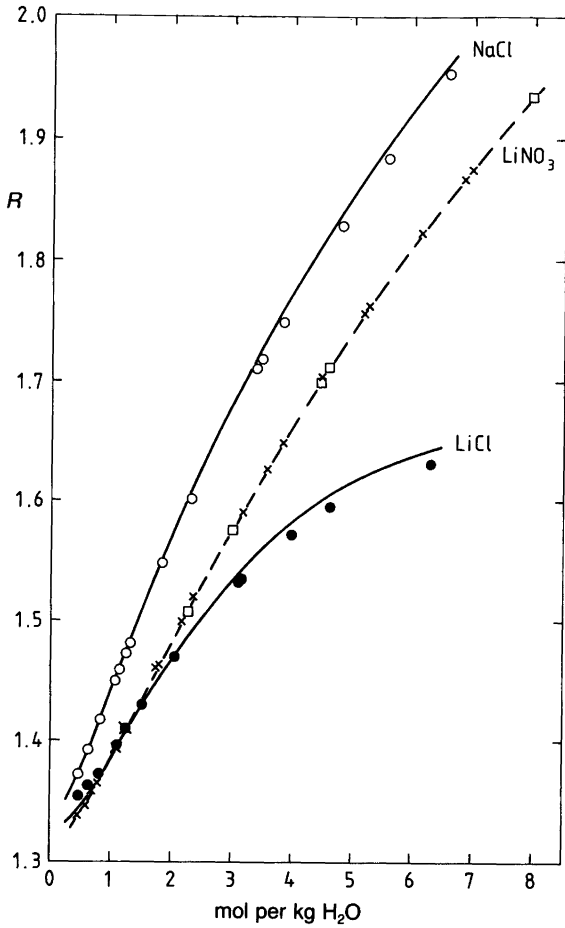


Fig. 2. Comparison of isopiestic ratios $R = m_x / m_{CaCl_2}$ from various sources at 100.3°C. NaCl: (—) calc. from Φ_{NaCl}^{14} and $\Phi_{CaCl_2}^{12}$, ○ this work; LiCl: (—) from Φ_{LiCl}^{13} and $\Phi_{CaCl_2}^{12}$, ● this work; LiNO₃: (---) interpolation curve of exp. values from this work; (×) aluminium cups; (□) vitreous carbon cups.

Finally, the lids are pressed onto the cups. Small differences in the height of the cups and an occasional slant of the plate H are compensated by springs (P), which are located on the lids.

The equilibration was performed in a thermo-

stat (E3-Haake Mess-Technik GmbH & Co, Karlsruhe, F.R.G.) filled with glycerol/water mixture. To minimize temperature gradients in the bath, an additional stirrer was positioned at the corner opposite to the temperature control

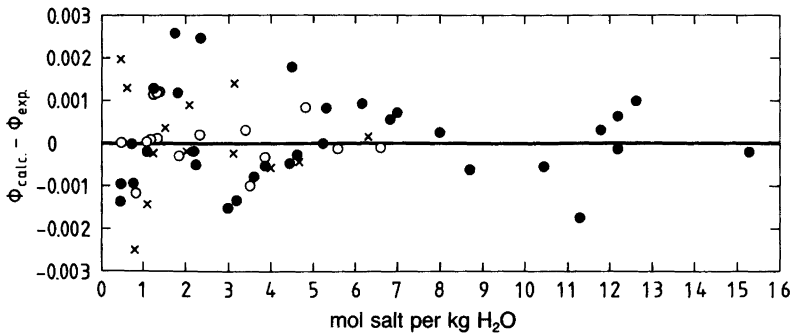


Fig. 3. Deviation plot for the exp. osmotic coefficients from eqn. (1) using the parameters in Table 2. ○ NaCl-H₂O, ● LiCl-H₂O, × LiNO₃-H₂O.

unit. The temperature was measured by means of a mercury thermometer having a scale of 1/10 K graduation. This thermometer was compared with a platinum resistance thermometer (Thermohm, Leeds & Northrup Co., Philadelphia, USA) which had been calibrated by the U.S. National Bureau of Standards.

Within the thermostat bath a rocking mechanism was installed; this lifts one side of the isopiestic apparatus by about 15 mm, 20 times per hour.

Procedure. A total amount of 0.8–1.5 g of either concentrated stock solution or anhydrous salt and water was weighed into every sample cup. The isopiestic apparatus was then closed, slowly evacuated and smoothly heated to the desired temperature. For all the experiments the equilibration temperature was kept at 100.3 ± 0.05 °C. Depending on the concentration and the amount of solution, equilibrium was attained within 20 to 72 h. The screw I (Fig. 1a) was then turned to close the sample cups inside the apparatus. After this, the apparatus was removed from the thermostat bath, cooled down and the valve (Fig. 1) opened. Since the vapour pressure of the cold solution was low compared with atmospheric pressure, the lids were pressed even more tightly against the cups. The container could be opened and the closed cups safely transferred to a balance. Not until just before the determination of the final weight were the lids carefully lifted and air let into the cups.

Because of the considerable vapour pressures at 100 °C, the final weighings were corrected according to the amount of water in the vapour phase at equilibrium temperature and pressure. For this purpose a computer sub-routine has been written; this uses an iterative procedure to calculate the vapour pressure. It starts with the calculation of the fugacity of water for the uncorrected final concentration of the reference solution from the known concentration dependence of the osmotic coefficient. The second virial coefficient is taken into account to convert fugacity into vapour pressure and then to calculate the amount of water in the vapour space of the cups. This amount of water is subtracted from the final weight and gives an improved concentration of the reference solution, which itself serves as a new input value in the vapour pressure calculation. Once the vapour pressure is known from

reference solutions, this value is used to correct the amount of water in the vapour space of the sample cups.

Usually the same samples were used for two or three experiments at differing water activities. Addition or evaporation of water in the apparatus yielded the desired water content variation.

Substances. Stock solutions were prepared from the following reagents: CaCl_2 (Calciumchloride dihydrate, *pro analysi*; Merck, Darmstadt, F.R.G.), LiCl (Lithiumchlorid, Erg. B6; Merck, Darmstadt, F.R.G.), LiNO_3 (Lithium nitrate, "Baker Analyzed" reagent; Noury-Baker N.V., Deventer, Holland) and NaCl (Natriumchlorid, *pro analysi*; Merck, Darmstadt, F.R.G.).

Sodium chloride was dried for 48 h at 170 °C before dissolving the required amounts of de-ionized water. The lithium salts as well as calcium chloride were also dissolved in de-ionized water, and if necessary the solutions were filtered through quartz filters. Final compositions were determined analytically by means of various methods and checked over periods of two months (Table 1). All stock solutions were stored in plastic bottles placed inside a large glass container.

Results and discussion

$\text{CaCl}_2\text{-H}_2\text{O}$ has been chosen as reference system. For this system reliable activity data are available at enhanced temperatures over an extensive concentration range.¹² In each run, three cups of reference solution and nine cups containing test solution were equilibrated. Proof of the reproducibility of our method and procedure is

Table 3. Regression coefficients of eqn. (1) and standard deviations σ_ϕ .

Parameter	System		
	$\text{NaCl-H}_2\text{O}$	$\text{LiCl-H}_2\text{O}$	$\text{LiNO}_3\text{-H}_2\text{O}$
$\beta^{(0)}$	0.09997	0.14866	0.15204
$\beta^{(1)}$	0.33692	0.26228	0.33293
$C \cdot 10^3$	-1.8967	-2.1725	-10.262
$D \cdot 10^4$	-1.9619	1.7390	1.7666
$E \cdot 10^5$	—	—	2.0736
$F \cdot 10^7$	—	—	-9.5995
$\sigma_\phi \cdot 10^3$	0.7	1.4	1.1

provided by comparing the final concentrations of the triplicated reference solutions. The cumulative portion of runs with maximum deviations of 0.03, 0.05, 0.07, and 0.1 % were 48, 69, 82 and 100 %. Runs with deviations exceeding 0.1 % were excluded.

Measurements were made with the binary systems NaCl–H₂O, LiCl–H₂O and LiNO₃–H₂O. The experimental results are summarized in Table 2. Isopiestic molalities, *m*, as well as isopiestic ratios, *R*, are presented. On the basis of recommended equations for osmotic coefficients given in the literature for CaCl₂–H₂O,¹² LiCl–H₂O¹³ and NaCl–H₂O,¹⁴ isopiestic ratios $R = (m_{\text{LiCl}}/m_{\text{CaCl}_2})$ and $R = (m_{\text{NaCl}}/m_{\text{CaCl}_2})$ were calculated at 100.3 °C and compared with our own results (Fig. 2). As can be seen for NaCl, the agreement is excellent at low concentrations; however, a significant shift reaching 0.6 % occurs at higher concentrations. For LiCl, the maximum deviations between our experimental and the calculated values are 0.7 %. Fig. 2 also shows the experimental results for the system LiNO₃–H₂O with an interpolation curve. The results obtained with vitreous carbon cups are in full agreement with the results with the aluminium cups. This can be taken as an indication that at higher vapour pressures, the heat transference through the gas phase is more important than through the crucible materials.

An extension of the ion-interaction formalism as in Ref. 12 was applied to describe the data in Table 2. For 1:1 electrolytes the equations have the following form:

$$\Phi - 1 = f + m \cdot B + m^2 \cdot C + m^3 \cdot D + m^4 \cdot E + m^5 \cdot F \quad (1)$$

where

$$f = -A \cdot M / (1 + b \cdot M) \quad (1a)$$

$$B = \beta^{(0)} + \beta^{(1)} \cdot \exp(-x) \quad (1b)$$

$$M = m^{1/2}, x = \alpha \cdot M, b = 1.2, \alpha = 2.0 \quad (1c)$$

with *A* as the Debye-Hückel parameter for the osmotic coefficient Φ taken from Ananthaswamy,¹⁵ and *m* the molality of the salt. $\beta^{(0)}$, $\beta^{(1)}$, *C*, *D*, *E* and *F* represent adjustable parameters, which were estimated by non-linear regression. Their numerical values are listed in Table 3. It

Table 4. Vapour pressure data of the system LiNO₃–H₂O at 100.3 °C from various sources.^a

<i>m</i> /mol per kg H ₂ O	<i>p</i> /kPa		
	Ref. 8	Ref. 16	This work
5.505	78.5	80.4	78.8
7.051	71.7	73.8	71.9
8.207	66.8	69.1	66.9
9.983	60.1	62.2	59.7
11.732	53.9	56.1	53.2
13.912	46.9	49.4	46.2
16.245	40.9	43.2	40.7 ^b

^aData in columns 2 and 3 are taken from Table 3 in Ref. 16. ^bConcentration above the fitted range of eqn. (1).

was necessary to use the complete set of 6 parameters of eqn. (1) only for the system LiNO₃–H₂O, where concentrations of up to 15 mol per kg H₂O had to be fitted. The quality of the fit is demonstrated in the deviation plot of Fig. 3. Generally, the experimental osmotic coefficients are described to within ± 0.002 . Only a few values exceed this limit. For the majority of points, the scattering around the zero line is less than ± 0.001 . This can be considered as a measure of the reproducibility in our experiments. In most cases, the differences plotted in Fig. 3 correspond to the reproducibility found for the final concentration of the reference solutions. The larger deviations occur especially at lower concentrations. The standard deviations, σ_{Φ} , given in Table 3, agree with the typical error limits for isopiestic measurements.

Recently, Sacchetto *et al.*¹⁶ determined the vapour pressure of the system LiNO₃–H₂O over a wide range of concentrations at several temperatures, using a dew point method. They compared their results with vapour pressures which were calculated from the isopiestic ratios $R = (m_{\text{LiNO}_3}/m_{\text{LiCl}})$ at 100.3 °C as reported by Braunstein and Braunstein.⁸ Table 4 shows this comparison, extended using our own values derived from the osmotic coefficients for LiNO₃ according to the parameter set in Table 3. For the conversion of vapour fugacities to pressures, the same value of the second virial coefficient ($B = -450 \text{ cm}^3 \text{ mol}^{-1}$) was used as in Ref. 16. Our data agree with those of the isopiestic measurements of

Braunstein,⁸ although it must be borne in mind that different reference solutions were applied.

Summarizing, our findings demonstrate successful operation of the apparatus described above. The results allow one to begin measurements on mixed solutions at enhanced temperatures, and we plan to carry this out in the near future.

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