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Lead nitrate:
a thermal solubility study

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Abstract

Using a single-dewar isoperibol solution calorimeter, the integral enthalpy of solution at 25°C of lead nitrate was determined as 33.76 ± 0.13 kJ mol^{-1}. Using a method developed in this laboratory, known as the dynamic precipitation method, the differential enthalpy of solution was determined as 25.83 kJ mol^{-1}. Using a novel NMR spectroscopic technique based on the ion activity correction method, this non-ideal figure was corrected to give an enthalpy of solution of 34.48 kJ mol^{-1}.

Keywords: Activity coefficient; Lead nitrate; NMR; Solubility

1. Introduction

Careful consideration must always be taken on measuring an enthalpy of solution depending on how sparingly soluble the solute is. For another investigation [1] the enthalpy of solution of lead nitrate was required in a conjugated ionic system. The two methods used to give differential and integral enthalpies of solution were very different with respect to solubility. The commerical calorimeter used for the integral enthalpy measurement was felt to be only suitable for non-precipitation reactions mainly due to the efficiency of stirring within the reaction vessel. The dynamic precipitation method, whilst giving solubility enthalpies at higher ionic strength, was thought to give incorrect results as the concentrations departed further from ideality. As no experimental method exists for the determination of the activity coefficients of a single ionic species, an expression of the mean ionic activity coefficient has been determined based on the theoretical concept of Debye and Hückel [2]

$$\gamma_{\pm}^{\nu} = \gamma_{+}^{\nu+} \gamma_{-}^{\nu-} \qquad (1)$$

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where $\nu = \nu_+ + \nu_-$, is the total number of ions produced per molecule of electrolyte.

Substitutions in this equation give rise to the Debye–Hückel limiting law

$$-\ln \gamma_\pm = \alpha |Z_+ Z_-| I^{1/2} \tag{2}$$

where $\alpha = 0.5115$ for aqueous solution at 25°C, γ is the ionic activity coefficients [3], Z_+ and Z_- the numerical valencies, and I the ionic strength

$$I = \frac{1}{2} \sum m_\mathrm{i} Z_\mathrm{i}^2 \tag{3}$$

where m_i is the molality of ion i in solution.

Calculating an enthalpy of solution from a differential method can be seen as dependent on the calculation of a suitable set of values for the mean activity coefficient. The Debye–Hückel theory normally only applies to electrolytes in solution at very low concentrations ($m \leqslant 2 \times 10^{-3}$ mol kg^{-1}). Attempts to apply the theory to higher concentration solutions usually fail when applied to systems other than these they were originally postulated for. The possibility of extrapolation for values of γ from low to high concentrations is unsatisfactory because unpredictable deviations from the Debye–Hückel theory occur. The approach that was finally used in this work was based on some nuclear magnetic resonance (NMR) spectroscopy studies [4]. A method of electrolyte theory devised by Pitzer [5] was considered, but because reasonable results were obtained with the NMR spectroscopy derived activity coefficients at high concentration solutions when applied to Debye–Hückel theory, it was not pursued.

2. Experimental

2.1. *Enthalpy of solution of lead nitrate in water (Integral)*

The enthalpy of solution, $\Delta_\mathrm{sol}H^\ominus$, of lead nitrate (BDH, A.R., recrystallised from water) was measured using the LKB 8700-1 calorimetric system, the performance of which was checked using the enthalpy of neutralisation, $\Delta_\mathrm{n}H^\ominus$, of tris(hydroxymethyl)methylamine (THAM) in excess of HCl (0.1 mol dm^{-3}) and in NaOH (0.05 mol dm^{-3}) as test reactions. For THAM in 0.1 M HCl, $\Delta_\mathrm{n}H^\ominus = -29.88 \pm 0.014$ kJ mol^{-1} (literature value [6], $\Delta_\mathrm{n}H^\ominus = -29.790 \pm 0.031$ kJ mol^{-1}). For THAM in 0.05 M NaOH, $\Delta_\mathrm{n}H^\ominus = +17.185 \pm 0.005$ kJ mol^{-1} (literature value [7], $\Delta_\mathrm{n}H^\ominus = +17.189 \pm 0.005$ kJ mol^{-1}). The calorimetric results obtained are shown in Table 1.

2.2. *Solubility and enthalpy of solution of lead nitrate*

The method of dynamic precipitation [9] was used to determine the solubility of lead nitrate in water and in aqueous solutions of varying ionic strength. Temperature readings repeatable within ± 0.2°C were obtained, using a calibrated 0.1°C thermometer. The results obtained are illustrated in Table 2. Using the data and an application

Table 1
Enthalpy of solution of lead nitrate in water

m/g	Dilution/n[a]	$\Delta_{sol}H^{\ominus}$/(kJ mol^{-1})[b]
0.10019	18181.5	33.73
0.11734	15523.5	34.00
0.12049	15118.3	34.00
0.20125	9051.2	33.69
0.24062	7570.3	33.71
0.18893	9641.4	33.64
0.13422	13571.7	33.64
0.24188	7531.0	33.67
	$\Delta_{sol}H^{\ominus}$(mean) =	33.76 ± 0.13 kJ mol^{-1}

[a] n is the molar ratio of lead nitrate to water.
[b] Literature [8] $\Delta_{sol}H^{\ominus} = 33.47 \pm 0.7$ kJ mol^{-1} [10000 H_2O].

Table 2
Solubilities (C) at different temperatures for lead(II) nitrate in water, in 0.5 mol dm^{-3} aqueous sodium perchlorate and in 1.0 mol dm^{-3} aqueous sodium perchlorate

Temperature/°C	C/(mol dm^{-3})	Temperature/°C	C/(mol dm^{-3})
Water		0.5 mol dm^{-3} $NaClO_4$	
59.2	2.82	50.4	2.37
50.8	2.57	45.4	2.07
42.7	2.40	39.1	2.21
38.6	2.40	31.8	1.95
31.8	2.12	28.1	1.84
26.5	1.99	24.0	1.74
33.6	2.26	19.7	1.66
48.4	2.53	1.0 mol dm^{-3} $NaClO_4$	
58.0	2.79	55.8	2.36
64.7	2.97	45.3	2.15
60.2	2.82	39.4	1.97
67.9	3.09	31.7	1.82
49.6	2.57	25.4	1.69
43.0	2.38	21.8	1.62
38.7	2.27		
34.2	2.18		
30.1	2.09		
26.5	2.01		
23.5	1.93		
20.5	1.88		

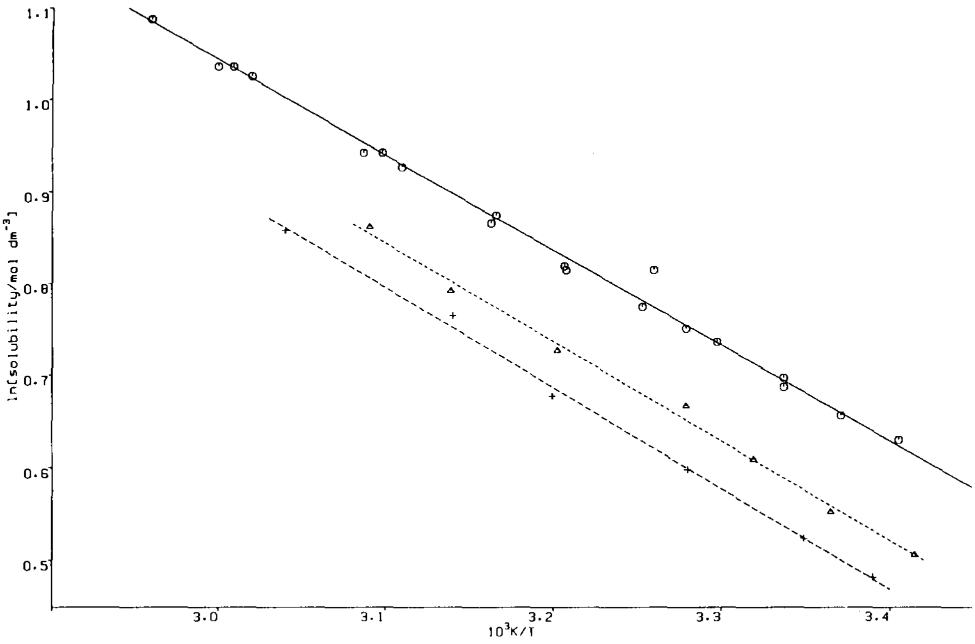

Fig. 1. Graph of log solubility vs. inverse temperature for lead(II) nitrate in water (○), in 0.5 mol dm^{-3} aqueous sodium perchlorate (Δ), and in 1.0 mol dm^{-3} aqueous sodium perchlorate (+).

Table 3
Aqueous solubility data

	H_2O	0.5 M $NaClO_4$	1.0 M $NaClO_4$
Solubility of lead nitrate at 25°C/mol dm^{-3}	1.97	1.77	1.68
$\Delta_{sol}H^\ominus/(\mathrm{kJ\ mol^{-1}})$	25.83	26.74	27.29
n	20	7	6
m	−1.036	−1.072	−1.606
c	4.152	4.168	4.188
r	0.997	0.997	0.998
$\Delta_{sol}S^\ominus/(\mathrm{J\ mol^{-1}K^{-1}})$	34.52	34.65	34.82

Key: n, no. of readings; m, slope ($\Delta_{sol}H^\ominus/R$); c, intercept with $\ln S$ axis ($\Delta_{sol}S^\ominus/R$); r, correlation coefficient.

[10] of the van't Hoff isochore, differential enthalpies of solution have been estimated (see Table 3)

$$\ln S = -(\Delta_{sol}H^\ominus/nRT) + (\Delta_{sol}S^\ominus/R) \qquad (4)$$

where S is the solubility of completely ionised system.

A plot of $\ln S$ versus $1/T$ gave a straight line of gradient $\Delta_{sol}H^{\ominus}/nR$, and a Y-axis intercept of $\Delta_{sol}S^{\ominus}/R$ (see Fig. 1).

3. Results and discussion

Comparison of the $\Delta_{sol}H^{\ominus}$ values from the dynamic precipitation and the calorimetric method showed a difference of approximately 8 kJ. This difference was far greater than any experimental error; it was thus necessary to consider the nature of the experiment for an explanation. As the solute in the differential enthalpy method is an electrolyte, the activities of the individual ionic species in solution need to be considered. The heat of solution if determined at infinite dilution would allow an activity coefficient of unity to be used. Because a finite value for the activity coefficient has been determined experimentally at equivalent ion concentrations to that of the enthalpy of solution determinations, it is not necessary to determine any heat of dilution.

4. Activity correction

In some recent work [4], the study of aqueous lead nitrate solutions was undertaken using NMR spectroscopy. In this work, a postulation of a $PbNO_3^+$(aqueous) ion existing in acidic solutions was made. A single ^{207}Pb resonance signal was observed for each solution of lead nitrate, and was thought to be due to the rapid exchange between Pb^{2+}(aqueous) and $PbNO_3^+$(aqueous). From shifts in the position of the signal with acidity, the equilibrium constant for

$$Pb^{2+}(aq) + NO_3^-(aq) \rightleftharpoons PbNO_3^+(aq)$$

was calculated. Applying the Debye–Hückel approximation in the form

$$\ln \gamma_{\pm} = -4A[I^{1/2}/(1 + I^{1/2})] + CI \qquad (5)$$

where $A = 0.5115$ for water, and combining Eqs. (3) and (5), a range of C values were produced at given temperatures. Using statistical analysis, the value for C at 298.15 K was obtained. This value was then substituted into Eq. (5) and the mean activity coefficients calculated over the range of concentrations used experimentally. Once the values of $-\ln \gamma_{\pm}$ had been calculated, they could then be used in conjunction with the experimental data from the dynamic precipitation method to determine $(\mathrm{d}\ln \gamma_{\pm}/\mathrm{d}m)_{sat}$. This was then substituted into the Williamson [11] equation, Eq. (6), with other ancillary data, to produce an activity-corrected enthalpy of solution

$$\Delta_{sol}H^{\ominus} = nRT^2(\mathrm{d}\underline{m}/\mathrm{d}T)_{sat}((\partial \ln \gamma/\partial \underline{m})_T + (1/\underline{m})_{sat}) \qquad (6)$$

where n is the stoichiometric number of ions produced per mole of electrolyte, and $\underline{m}$ is the molality of the saturated solution.

From the statistical analysis mentioned above, a linear regression equation of the form $y = mx + c'$ was calculated, with $y = 3.5 \times 10^{-3}x - 0.861$; the correlation coefficient was $r^2 = 0.88$, giving $C = 0.1938$ at 298.15 K. Using this C value, the values of

$-\ln\gamma_{\pm}$ were calculated, see Table 4. From the data, the following were calculated: $(\mathrm{d}\ln\gamma/\mathrm{d}m)_{\mathrm{sat}} = -0.3948$; and $(\mathrm{d}m/\mathrm{d}T)_{\mathrm{sat}} = 0.02513$.

Substituting with ancillary data into Eq. (6), an enthalpy of solution was calculated. It can be seen (Table 5) that this method of correction has proved most successful. The enthalpy of solution was calculated with the assumption of there only being three moles of ions produced in solution, Pb^{2+} and $2NO_3^-$ in neutral pH solutions.

The method of dynamic precipitation [9] is a comparatively cheap and simple method for obtaining solubility data, although as originally produced it is only

Table 4
Results of Debye–Hückel approximation

$\underline{m}$/(mol kg^{-1})	T/K	I/(mol kg^{-1})	CI	$-4A\left[\frac{I^{1/2}}{1+I^{1/2}}\right]$	$-\ln\gamma_{\pm}$
2.826	332.35	7.065	1.3692	1.4867	0.1175
2.581	323.95	6.453	1.2506	1.4681	0.2175
2.406	315.85	6.015	1.1657	1.4534	0.2877
2.266	311.75	5.665	1.0978	1.4407	0.3429
2.126	304.95	5.315	1.0300	1.4270	0.3970
1.992	299.65	4.980	0.9651	1.4128	0.4477
2.267	306.75	5.667	1.0983	1.4408	0.3425
2.541	321.54	6.353	1.2312	1.5255	0.2943
2.796	331.13	6.990	1.3547	1.4845	0.1298
2.982	337.84	7.455	1.4448	1.4975	0.0527
2.832	333.33	7.08	1.3721	1.4871	0.1150
3.098	341.05	7.74	1.5000	1.5050	0.0050
2.582	322.75	6.455	1.2509	1.4681	0.2172
2.383	316.15	5.957	1.1545	1.4513	0.2968
2.278	311.85	5.695	1.1037	1.4418	0.3381
2.181	307.35	5.453	1.0568	1.4325	0.3757
2.093	303.25	5.232	1.0139	1.4236	0.4097
2.012	299.65	5.03	0.9748	1.4150	0.4402
1.937	296.65	4.84	0.9379	1.4066	0.4687
1.889	293.65	4.722	0.9151	1.4012	0.4861

Key: I, ionic strength; $A = 0.5115$, universal constant for water; $C = 0.1938$ at 298.15 K.

Table 5
Enthalpy of solution in kJ mol^{-1} of lead nitrate and method of measurement

		n[a]
Calorimetric value $\Delta_{\mathrm{sol}}H^{\ominus}$ (measured)	33.76 ± 0.13	–
Dynamic pptn. $\Delta_{\mathrm{sol}}H^{\ominus}$ (uncorrected)	25.83	3
Dynamic pptn. $\Delta_{\mathrm{sol}}H^{\ominus}$ (activity corrected)	34.48	3
Literature value [12] $\Delta_{\mathrm{sol}}H^{\ominus}$ [10000 H_2O]	33.47 ± 0.7	–

[a] Stoichiometric number of ions produced per mole of electrolyte.

comparable to other data similarly obtained. This study indicates that if given a suitable set of experimentally derived activity coefficients, the data can be corrected to be comparable with that obtained by more expensive and complicated calorimeter systems.

Ancillary data

$(1/\underline{m})_{\mathrm{sat}} = 0.224\ \mathrm{mol}^{-1}\ 1000\ \mathrm{g}\ H_2O$ [13].

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References

[1] J. R. Payne, Ph.D. Thesis, University of London, February 1986.
[2] P. Debye and E. Hückel, Phys. Z., 24 (1923) 185; 25 (1924) 97.
[3] G.N. Lewis and M. Randall, Thermodynamics, 2nd edn., McGraw-Hill, London, 1961, p. 242.
[4] K.J. Mordecai, Ph.D. Thesis, University of London, November 1982.
[5] K.S. Pitzer, Acc. Chem. Res., 10 (1977) 371.
[6] E.J. Prosen and M.V. Kilday, J. Res. Natl. Bur. Stand., 77A (1973) 581.
[7] J.O. Hill, G. Öjelund and I. Wadsö, J. Chem. Thermodyn., 1 (1969) 111.
[8] D.D. Wagman, W.H. Evans, V.B. Parker, R.M. Schumm, I. Marlow, S.M. Bakey, K.L. Churney and R.L. Nuttall, J. Phys. Chem. Ref. Data, Natl. Bur. Stands., 11 (1982) 2.
[9] A.N. Smith, Ph.D Thesis, University of London, January 1983.
[10] D.J.G. Ives, Chemical Thermodynamics, MacDonald, London, 1971 p. 129.
[11] A.T. Williamson, Trans. Faraday Soc., 40 (1944) 421.
[12] D.D. Wagman, W.H. Evans, I. Halow, V.B. Parker, S.M. Bailey and R.H. Schumm, Selected Values of Chemical Thermodynamic Properties, Natl. Bur. Stands. Tech. Note 270–2, U.S. Government Printing Office, Washington DC, 1966.
[13] H. Stephen and T. Stephen, Solubility of Inorganic and Organic Compounds, Pergamon Press, Oxford, 1963, p. 321.