

## ENTHALPIES OF DILUTION FOR 1:3 AND 3:1 ELECTROLYTES AQUEOUS SOLUTIONS

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### Abstract

The enthalpies of dilution for aqueous solutions of  $[\text{Co}(\text{en})_3]\text{Cl}_3$ ,  $[\text{Co}(\text{pn})_3]\text{Cl}_3$  and  $[\text{Co}(\text{tn})_3]\text{Cl}_3$ , (where  $\text{en}$ =1,2-diaminoethane,  $\text{pn}$ =1,2-diaminopropane, and  $\text{tn}$ =1,3-diaminopropane) have been measured at 298.15 K, and up to  $1 \text{ mol kg}^{-1}$ , using a new large isoperibol calorimeter by the "long-jump" method. Relative apparent molar enthalpies,  $L_\phi$ , have been extracted as an empirical equation relating  $L_\phi$  and  $m$ . We have compared our complex salts with the 3:1 and 1:3 aqueous systems found in the literature. Theoretical predictions for 1:3 and 3:1 electrolytes in the Restricted Primitive Model are also shown.

**Keywords:** aqueous electrolyte, enthalpy of dilution, isoperibolic calorimetry

### Introduction

The enthalpy of dilution is an experimental thermal property of great interest in the study of the aqueous electrolyte solutions. The more easily measured enthalpy of solution is too sensitive to previous handle of the solid samples before the solution experiment; on the other hand, the heat capacities yield much less thermodynamic information.

We report in this contribution the experimental enthalpies of dilution at 298 K of some aqueous 3:1 cobaltamine-type salts. These compounds offer a great theoretical interest because the physical and chemical properties of the complex cations can be systematically changed by a suitable selection of the coordinated ligands and their aqueous solutions exhibit a pronounced stability. As the precise determination of enthalpies of dilution for dilute electrolyte aqueous solutions is a rather difficult problem and the direct investigation in the most dilute region ( $m < 10^{-4} \text{ mol kg}^{-1}$ ) is an almost unattainable task requiring calorimetric apparatus capable of measuring small temperatures changes to a millionth of a degree or better we have constructed instead an isoperibol calorimeter with a large vessel containing pure water and a relatively small cell for the initial solution samples. This calorimeter have been designed to study an alter-

native, indirect, and less ambitious approach to that dilute range of concentration, the so called "long-jump" calorimetric method (semiconcentrated initial aqueous solutions and diluted final ones).

Thermal properties of 3:1 and 1:3 electrolyte solutions have not been extensively studied and enthalpies of dilution for aqueous 3:1 cobaltaminytype salts remain unpublished. Experimental data found in literature for other 3:1 aqueous systems comprise rare earths salts [1, 2] and the compounds of the largely hydrolyzed cations  $Ga^{3+}$  and  $Cr^{3+}$  [3, 4]. Moreover, the only 1:3 published systems are the complex salts  $K_3[Fe(CN)_6]$  and  $Na_3[Fe(CN)_6]$  [5, 6].

The structure of the complex cations under study can be schematically represented as shown in Fig. 1. These coordination compounds of Cobalt(III) are very soluble in water and their aqueous solutions exhibit a pronounced stability. Our laboratory have previously investigated other thermodynamic properties (osmotic coefficients from cryoscopy and molar volumes) of their dilute aqueous solutions [7].

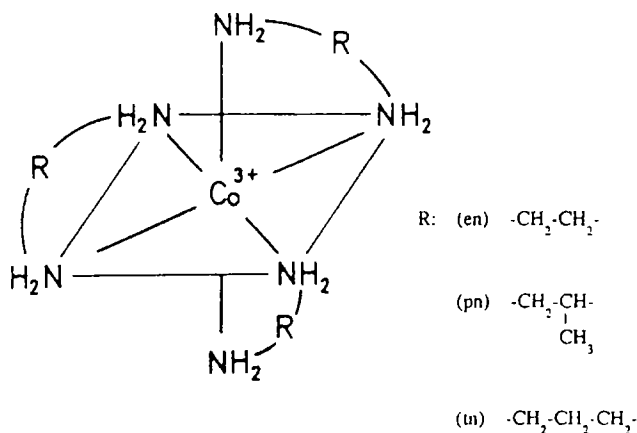


Fig. 1 Schematic view of the complex cations structure

## Experimental

Measurements were carried out with a constant-environment home-made calorimeter. The general features of the experimental arrangement and materials are described in detail elsewhere [7, 8]. The isoperibol calorimeter was designed to fulfill two requirements: very small heat leak modulus and high vessel-cell volume ratio.

The cylindrical calorimeter vessel was constructed of thin-walled brass and holds a volume of about  $825 \text{ cm}^3$ . Two sample cells were used during the present investigation; a brass combination stirrer-sample cell ( $\approx 35 \text{ cm}^3$ ) with inner

spiral propeller for the systems KCl and  $[\text{Co}(\text{en})_3]\text{Cl}_3$  at 298 K and thin-walled glass ampoules of smaller volume ( $\cong 10 \text{ cm}^3$ ) for the rest. Both class of cells were screwed to a steel rod and drove at a constant speed of approximately 250 rpm by a synchronous motor. The shaft was mounted in three ball bearings and could be moved up and down during a run.

## Results and discussion

The corrected temperature rise,  $\Delta T_{\text{corr}}$ , was obtained following the treatment developed by Brunetti, Prosen and Goldberg [9]. Equation (1) was fitted to the time-quartz thermometer data ( $t, \theta$ ) during the initial and final rating periods

$$\theta = \theta_{\infty} - (\theta_{\infty} - \theta_0)\exp[-k(t - t_0)] \quad (1)$$

where  $\theta_{\infty}$  is the convergence temperature,  $k$  is the calorimeter heat leak modulus or cooling constant ( $\cong 6 \times 10^{-3} \text{ s}^{-1}$ ) and  $\theta_0$  is the temperature at the time  $t_0$ , any selected time in the rating period used. The parameters  $k$  and  $\theta_{\infty}$  were obtained from simultaneous resolution of Eq. (1) both for the initial and the final rating periods by using a non-linear least squares procedure. Finally, the measured quartz thermometer temperature rise,  $\Delta\theta$ , was related to the actual observed temperature rise,  $\Delta T$ .

The molar enthalpy of dilution, at the mean dilution temperature, was calculated from

$$\Delta_{\text{dil}}H = -\bar{\epsilon}\Delta T_{\text{corr}}/N \quad (2)$$

where  $\bar{\epsilon}$  is the average of the initial and final electrical energy equivalents and  $N$  is the number of solute moles. All the experiments were carried out within  $\pm 0.05 \text{ K}$  of the assigned dilution temperature, 298.15 K.

The experimental results for  $\Delta_{\text{dil}}H$  were fitted, using a least squares technique, to the equation

$$\Delta_{\text{dil}}H(m_i \rightarrow m_f) = L_{\phi}(M_f) - L_{\phi}(m_i) \quad (3)$$

where the relative apparent molar enthalpy,  $L_{\phi}(m)$ , is given by a polynomial.

The enthalpy of dilution of KCl in water at 298.15 K was used to verify the precision and accuracy of the instrument. Table 1 gives our experimental molar enthalpies of dilution for this system and those obtained from Parker [10]. The agreement between the last two columns of Table 1 is excellent within the margin of error.

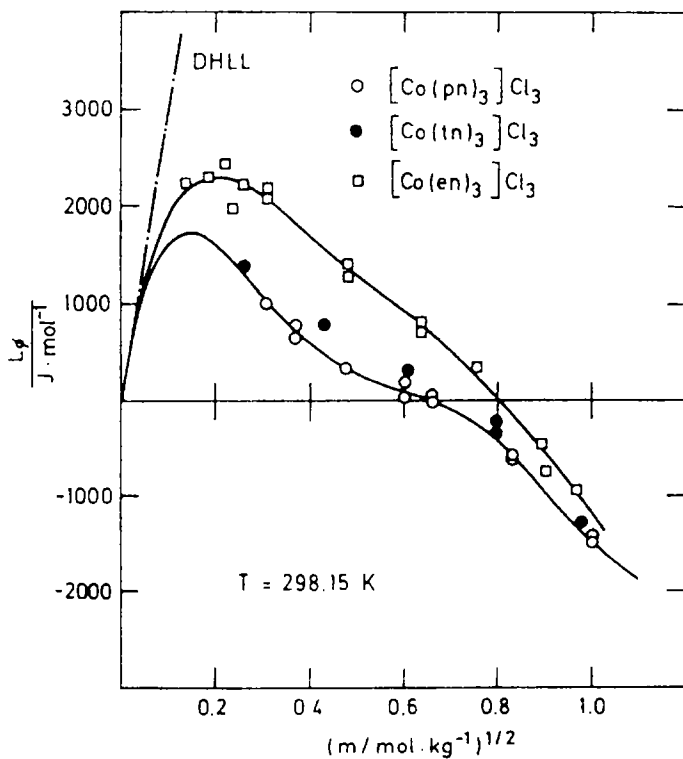
Dilution experiments for aqueous solutions of  $[\text{Co}(\text{en})_3]\text{Cl}_3$ ,  $[\text{Co}(\text{pn})_3]\text{Cl}_3$  and  $[\text{Co}(\text{tn})_3]\text{Cl}_3$ , at 298.15 K, are shown in Fig. 2 where plots of the  $L_{\phi}(m)$  curves of fitting are drawn against  $m^{1/2}$ . Also shown are the experimental values

for the initial molalities. The vertical distance from the geometrical symbols to the  $L_{\varphi}(m)$  curves is obtained from the full deviation between  $\Delta_{\text{dil}}H(\text{experimental})$  and  $\Delta_{\text{dil}}H(\text{calculated})$ .

**Table 1** Enthalpies of dilution of aqueous KCl at 298.15 K<sup>a</sup>

$m_i$	$10^2 m_f$	$10^2 N$	$\Delta_{\text{dil}}H(m_i \rightarrow m_f)$	
			Experimental	Literature <sup>b</sup>
0.174	0.782	0.619	-184±28	-209±5
0.239	1.057	0.841	-198±21	-182±5
0.657	2.956	2.357	111±8	98±5
0.957	4.119	3.281	318±6	309±5
1.031	4.250	3.385	355±5	358±5
1.131	4.723	3.757	423±5	429±5
1.601	6.745	5.360	738±4	747±5

<sup>a</sup>Units:  $m$ , mol kg<sup>-1</sup>;  $N$ , mol;  $\Delta_{\text{dil}}H$ , J mol<sup>-1</sup>. <sup>b</sup>Ref. 10



**Fig. 2** Experimental enthalpies of dilution for the three complex cations chlorides, at 298 K, plotted as  $L_{\varphi}(m)$  against  $m^{1/2}$

Our aqueous compounds are the first reported 3:1 electrolytes systems which exhibit a pronounced maximum when  $L_{\phi}(m)$  is plotted against  $m^{1/2}$ . The general behavior of the 3:1 electrolytes found in the literature shows a steadily rise of  $L_{\phi}(m)$ , more noticeable above  $1 \text{ mol kg}^{-1}$ , characteristic of the strongly hydrated cations [1-4].

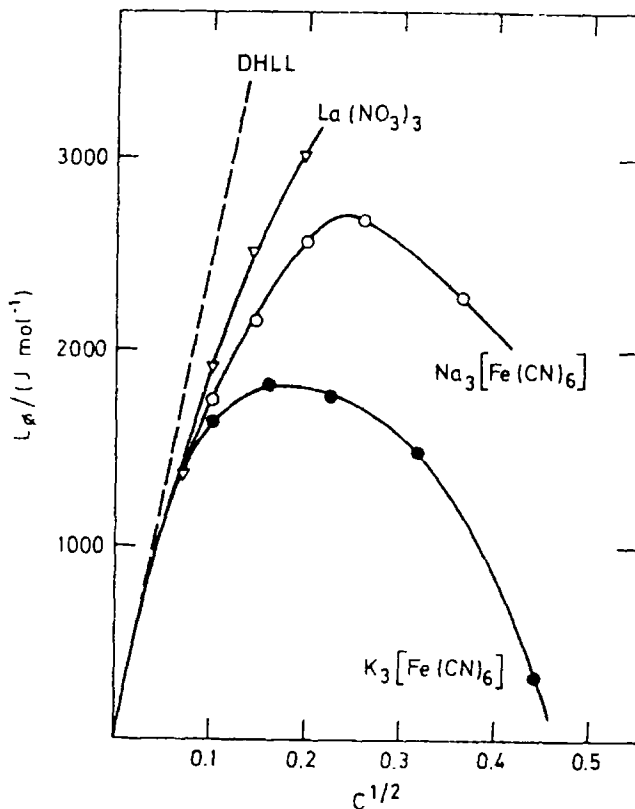


Fig. 3 Variation of the relative apparent molar enthalpy with the square root of molarity, at 298.15 K, for the 1:3 systems  $\text{K}_3[\text{Fe}(\text{CN})_6]$  and  $\text{Na}_3[\text{Fe}(\text{CN})_6]$ ; also shown is the 3:1 salt  $\text{La}(\text{NO}_3)_3$ . DHLL is the Debye-Hückel limiting slope

We also show the relative apparent molar enthalpies of the 1:3 electrolytes  $\text{K}_3[\text{Fe}(\text{CN})_6]$  and  $\text{Na}_3[\text{Fe}(\text{CN})_6]$  at 298 K [5, 6]. As seen in Fig. 3, there exists a good agreement, both in shape and numerical, between these systems and the cobaltamine-type chlorides. Conversely,  $\text{La}(\text{NO}_3)_3$  shows a steadily increasing slope. Thus, the well-established hydrophobic character of ferricyanides in aqueous solution can be also attributed to our complex cations in the increasing order  $[\text{Co}(\text{en})_3]^{3+} < [\text{Co}(\text{tn})_3]^{3+} < [\text{Co}(\text{pn})_3]^{3+}$ ; conversely, the previously reported 3:1 electrolytes suffer a pronounced hydration and show an opposite trend.

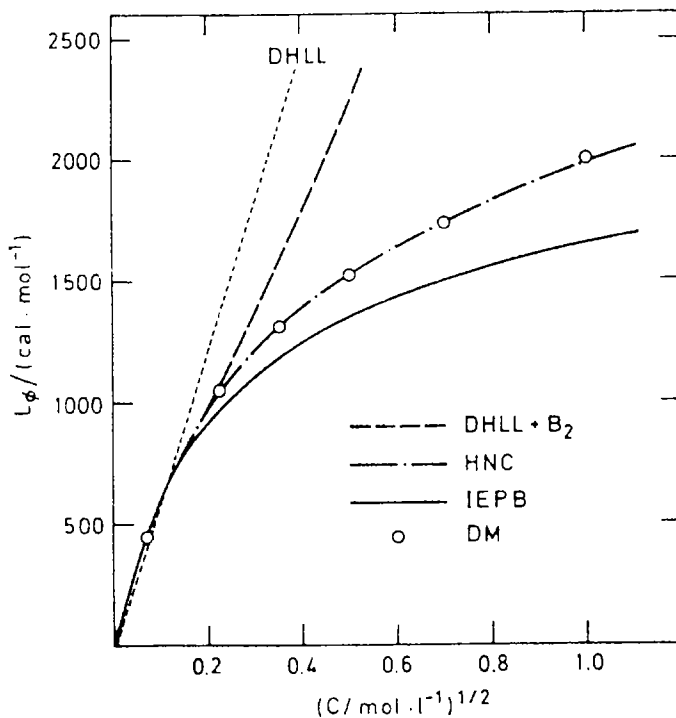


Fig. 4 Predictions for the Restricted Primitive Model (aqueous 3:1 system, at 298 K, with  $r = 2.1 \text{ \AA}$ ) within several approximations

Finally, in Fig. 4 we show the predictions of the Restricted Primitive Model (RPM) for aqueous 3:1 or 1:3 systems within several approximations at 298 K and with the ionic radius  $r = 2.1 \text{ \AA}$ . DHLL +  $B_2$  is the second approximation to the Mayer's theory, IEPB is the numerical integration of the Poisson-Boltzmann equation, HNC is the hypernetted chain theory, and DM is Molecular Dynamics simulation [11–13]. As can be seen in Fig. 4 (where DHLL is the Debye-Hückel limiting law) the RPM results only exhibit an upward trend.

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This work was supported in part by CICYT (M.E.C., Spain) under Research Project No.: PB92-0553.

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