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ENTHALPIES OF SOLUTION OF SOME NITRATES IN AQUEOUS METHANOL SOLUTIONS AT 298.15 K

BARTŁOMIEJ PAŁECZ, JOLANTA BARCZYŃSKA
and STEFANIA TANIEWSKA-OSIŃSKA *

Department of Physical Chemistry, University of Łódź (Poland)

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ABSTRACT

Enthalpies of solution of $NaNO_3$, KNO_3, $Ca(NO_3)_2$ and $La(NO_3)_3$ in aqueous solutions of methanol were measured over the entire range of mixed solvent composition. The standard enthalpies of transfer of the electrolytes under study from water to the mixed solvent and the enthalpic pair interaction coefficients h_{NE} were calculated.

INTRODUCTION

Calorimetric investigations of electrolytic solutions in alcohol–water binary solvents have been described in a large number of scientific papers. However, very few data have been obtained for salts with bivalent and trivalent cations. In the earlier research performed in our laboratory, solutions of alkali and alkali earth cation halides in alcohol–water mixtures were studied [1–4]. The task was to observe the effect of the dissolved electrolyte on the properties and structure of the mixed solvents. We are now interested in carrying out measurements of the enthalpy of solution of some salts containing the common nitrate anion and cations of different valence in an alcohol–water mixture. In this paper we report the results of the measurement of the enthalpies of solution of $NaNO_3$, KNO_3, $Ca(NO_3)_2$ and $La(NO_3)_3$ in methanol–water mixtures at 298.15 K.

EXPERIMENTAL

$NaNO_3$ and KNO_3 (puriss, Polish Chemicals, Poland) were crystallized from water and dried under reduced pressure at 373 K. $Ca(NO_3)_2$ and $La(NO_3)_3$ (puriss, Fluka) were crystallized twice from ethanol and dried in

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* To whom correspondence should be addressed.

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vacuum at 373 K. Methanol (puriss, POCh, Poland) was purified by the standard method [5]. The water–alcohol mixtures were prepared by weight. The calorimetric system and the experimental procedure used are the same as presented in an earlier paper [6].

RESULTS AND DISCUSSION

The concentration of the dissolved electrolytes was varied from 0.001 to 0.05 mol kg^{-1} over the entire range of compositions of the methanol–water mixture. The data obtained allowed us to determine the standard enthalpies of solution of $NaNO_3$, KNO_3, $Ca(NO_3)_2$ and $La(NO_3)_3$ (Table 1) from water to the mixed solvent. The increase in the charge density of the cation (K^+, Na^+, Ca^{2+}, La^{3+}) causes an increase in the exothermic effect of solution. The standard enthalpies of solution $\Delta H_m^\ominus$ exhibit maxima for all salts investigated in the region of approximately 15 mol% of methanol. This region of composition has been attributed by several workers to the maximum ordering effect exerted by methanol on the water structure [7,8].

As can be seen the position of the maximum does not depend on the type of electrolyte within the limits of experimental error. Therefore, the position of the maximum is not related to the charge density of the cations. Beyond the maximum, a greater charge on the cation causes a sharper growth of the exothermic effect of the salt dissolution (Table 1); this is probably connected

TABLE 1

Standard enthalpies of solution $\Delta H_m^\ominus$ (kJ mol^{-1}) of $NaNO_3$, KNO_3, $Ca(NO_3)_2$ and $La(NO_3)_3$ in water–methanol mixtures at 298.15 K

$NaNO_3$		KNO_3		$Ca(NO_3)_2$		$La(NO_3)_3$	
X_2^a [a]	$\Delta H_m^\ominus$	X_2^a	$\Delta H_m^\ominus$	X_2^a	$-\Delta H_m^\ominus$	X_2^a	$-\Delta H_m^\ominus$
0	20.80	0	35.20	0	17.60	0	62.05
1	21.20	1	35.65	1	17.30	1	61.70
2	21.55	2	36.10	2	17.05	2	61.40
5	22.80	5	37.25	5	16.20	5	60.35
10	23.95	10	38.05	10	15.20	10	58.45
15	24.40	15	38.20	15	14.95	15	57.65
20	24.25	20	38.05	20	15.95	20	63.25
30	23.30	25	37.05	25	18.05	30	69.05
40	21.75	30	35.75	30	20.20	50	76.00
50	19.85	50	26.65	50	29.15	70	82.10
80	13.05	80	20.40	70	37.55	90	88.35
100	2.45	100	15.65	90	44.45	95	89.75
				95	45.75	100	89.20
				100	45.30		

[a] X_2^a is the concentration of methanol (mol%).

TABLE 2

Enthalpic pair interaction coefficients h_{NE} between methanol molecules and electrolytes ($NaNO_3$, KNO_3, $Ca(NO_3)_2$ and $La(NO_3)_3$) in water solutions at 298.15 K

Methanol–electrolyte	h_{NE} (J kg mol^{-2})
MeOH–$NaNO_3$	180
MeOH–KNO_3	200
MeOH–$Ca(NO_3)_2$	90
MeOH—$La(NO_3)_3$	75

with the different rate of change from water to methanol molecules in the solvation shells of the ions. In the alcohol-rich region a small minimum in $\Delta H_m^{\ominus}$ is observed for $Ca(NO_3)_2$ and $La(NO_3)_3$ which corresponds to about 95 mol% of methanol. A similar minimum has been observed previously in $CaCl_2$ solutions in methanol–water mixtures [2].

Using the data obtained we calculated [9] the interaction coefficients of the ion–alcohol molecule pair in water (Table 2). The positive values of the coefficients h_{NE} for all four electrolytes suggest that ions interact only weakly with methanol molecules and probably interact strongly with water molecules. The h_{NE} values for all the electrolytes decrease with an increase in the charge density of the cation, i.e. the increase in charge density is probably related to the increasing interaction between the electrolyte and alcohol molecules.

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