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THERMAL EFFECTS OF SOLVATION PROCESSES ON ALKALI METAL ALCOXIDE FORMATION AND STABILITY

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Abstract

The formation of alkali metal alcoxides by an alcohol reacting on the elemental metal itself cannot be completed under stoichiometric conditions. As a consequence of solvation, the chemical activity of the reacting alcohol is drastically reduced. Thus, the reaction cannot undergo completion without a large excess of alcohol with respect to the alkali metal. Moreover, solvation processes can drop the reaction kinetics down to nearly zero. When an excess of alkali metal is reacted with alcohol, the heat accumulated by solvation can be suddenly released by an addition of pure alcohol. Extremely dangerous thermal runaways can be started this way.

Keywords: alcoholate, alcoxide, alkali metal, heat, thermal, runaway, solvation

Introduction

The formation of alkali metal alcoxides is interesting for two main applications: either for preparing metal-organic reagents or for destroying alkali metal wastes. However, the reaction of formation of such alcoxides led in the past to some severe accidents. The origins of these accidents can find their source in the high enthalpies of solvation of alcoxides by the initial alcohol employed for their preparation.

A goal of the present study is to show some aspects of the potentially dangerous thermal phenomena encountered when working with such compounds. Some specific dangers arise from the reaction of the metal itself, other ones are due to the high energies of solvation of alkali alcoxides by the alcohol from which they are prepared. Generally the enthalpy of a reaction as available from literature data is supposed to describe the overall energy balance between the formed and destroyed chemical bonds. In most of the cases, one considers that the concerned bonds are essentially the intramolecular ones, which are assumed to define the chemical species. The intermolecular contributions, which do not actually define the chemical species involved by the reaction, are generally assumed to be small when compared with the former ones. In fact, depending on the considered chemical system, such an assumption can

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be completely wrong. Some intermolecular bonds may be either nearly as strong or more numerous than the intramolecular ones, so that their total contribution to the apparent enthalpy may become the main factor defining the heat released by a reaction. Thus, the solvation phenomena can result in major contributions to the thermal behaviour. The corresponding heat generation may lead to an unexpected behaviour of the system if omitted. Since the solvation processes essentially depend on the concentration of the solvated and the solvating species, the operating conditions will become a main factor determining the apparent values of the thermal parameters such as entropy and enthalpy describing the reaction. The corresponding effects will result in thermodynamic as well as in kinetic changes of the chemical behaviour of the reacting species. On hand of several examples, the goal of this work is to specify the relative importance of the different contributions to the thermal magnitudes characterising the reaction of an alkali metal with an alcohol.

Theoretical aspects

When an alkali metal is brought into contact with an alcohol, a spontaneous reaction starts, leading to the formation of the corresponding alkali metal alcoxide and to the formation of free gaseous hydrogen (1).

$$\mathrm{ROH+M\rightarrow ROM+1/2H_2} \tag{1}$$

It is well known that this reaction works well for small alcohol molecules such as methanol or ethanol [1]. However, the obtained yields are always far below the values one could expect from the stoichiometry. Moreover, the reaction rates drop to very low values as soon as the molecular mass of the reacting alcohol increases [1]. The rate of the reaction with alcohols depends strongly on the presence in the molecule of other functions such as ethers or amines [2]. The presence within the molecule of such Lewis' basic functional groups enhances the ability of the molecule to stay adsorbed on the metal surface. The reaction mechanisms on the metal surface involve high order kinetics [3] the detailed discussion of which is not in the frame of this study. The longer the mean adsorption time of the reacting molecule on the metal surface, the higher the probability of high order reactions to take place. Such a mechanism can explain the reasons for which butoxyethanol reacts about twenty times faster than *n*-heptanol although both molecules exhibit nearly the same molecular volume (Fig. 1).

At very low alcohol concentrations (below 5 mol%) the formation of alcoxides is strongly inhibited. This fact can be explained by assuming high order reaction kinetics at the metal–solvent interface [3]. By increasing the concentration of alcohol in the *n*-octane which acts as a chemically nearly inert solvent, the reaction rates undergo a maximum for a molar ratio of initial alcohol to inert solvent close to 1/4 [5]. The reaction speeds for such a ratio (20 mol% butoxyethanol, 80 mol% *n*-octane) are shown by Fig. 2 as a function of the reaction rate. Figure 2 shows the corrected apparent values of the reaction speed for several alkali metals reacting with butoxyethanol. The plotted experimental values have been corrected from the decreasing free alcohol concentration resulting from the reaction with the alkali metal. This correction has been based on an idealised first or-

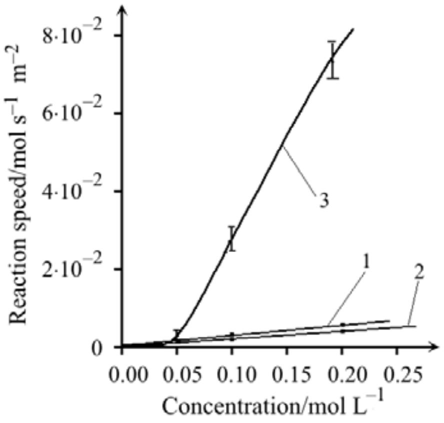

Fig. 1 Reaction speed of sodium *vs.* alcohol concentration at 293 K; 1–1-heptanol; 2–2-heptanol; 3–2-butoxy-ethanol

der reaction model [4]. Further, in order to compare the differences between the studied metals, the apparent values of the reaction speeds have also been corrected from the superficial atomic densities of the metals. Since these aspects are out of the frame of this study, we will not discuss them longer here. More details are available from [4]. The essential fact which must be pointed out here is that the reaction speed does not agree with a first order kinetic model the expected reaction speed of which is shown by the horizontal line EV (expected value) on Fig. 2.

Excepted for sodium, the reaction of alkali metals nearly stops long before completion is obtained (Fig. 2). For lithium, due to oxidation processes by traces of oxygen and nitrogen, the low reaction speed did not allow the measurements to be carried

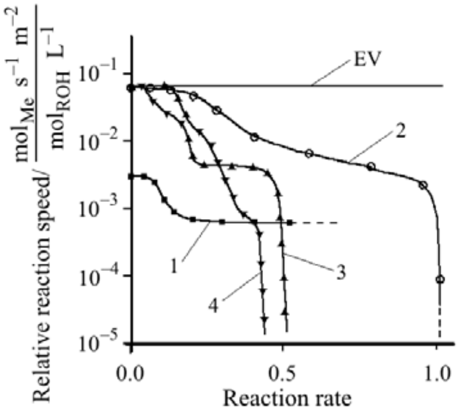

Fig. 2 Alkali metal alcoxide formation speed *vs*. reaction rate in an initial solution of 20 mol% butoxyethanol and 80 mol% *n*-octane. EV:expected value for a first order reaction; 1 – metallic lithium; 2 – metallic sodium; 3 – metallic potassium; 4 – metallic caesium

out with sufficient reliability beyond a rate of about 50%. The stepwise evolution of the reaction speed is a clear proof of the influence of solvation processes which result in stepwise changing properties for well defined molar ratii between the formed alcoxide and the remaining alcohol. Concerning the heat of solvation, we will no longer consider here other metals but sodium, since the determination of their corresponding solvation parameters are still in progress and are not yet available. However, Fig. 2 shows that for other alkali metals than sodium, solvation effects might even be stronger and lead to more important effects. Provided the reacting alcohol is diluted in an inert dry aliphatic solvent such as *n*-octane or ligroin, sodium is the only alkali metal which can undergo completion with respect to the alcohol [5], although the end step leading to completion goes on at a very slow speed. None of the other alkali metals achieves such a reactivity, not even caesium which could be expected to be much more reactive than sodium. When pure alcohol is used, even sodium cannot undergo completion. This observation shows how drastically solvation processes can modify the apparent behaviour of chemical species.

Figure 3 shows the effect of the dilution of several alcohols by *n*-octane on the reaction rate of the initial fast reaction step shown by Fig. 2, i.e. which corresponds to a reaction speed higher than about $5\cdot10^{-3}$ $\mathrm{mol_{Na}\ s^{-1}\ m^{-2}/mol_{ROH}\ L^{-1}}$ for all studied alcohols. The fast initial step of the reaction is nearly the same for all mentioned alcohols. One can thus compare different alcohols, the initial behaviour of which is comparable, although their final slow steps, lower by more than a factor by ten than the initial fast steps, may differ from each other by several orders of magnitude. Thus, the final behaviour of several alcohols after very long reaction times may be very different from each other, although their behaviours all along the fast initial reaction step can be very similar. Since diethyleneglycol monomethylether (methylcarbitol, point 4 Fig. 3) is not soluble in apolar solvents such as *n*-octane, only the rate for pure alcohol could be determined for this reagent. The very limit of the reaction rate after having completed the slow step by running reactions for up to 36 h are given in [5]. Beyond this limit, the poor stability of alcoxide solutions do not allow any further reliable conclusion.

For sodium, the final obtainable reaction rate with respect to the alcohol decreases when increasing the initial alcohol concentration in *n*-octane beyond 50% by mole. Such an observation is also in good agreement with the assumption of solvation effects between the alcoxide and the organic solvents. Up to 50 mol% alcohol, a sufficient amount of *n*-octane will contribute to solvate the formed alcoxide, preventing the molecules of alcohol from chemical inactivation by solvation processes. At higher concentration levels of alcohol, the solvation processes can only be achieved by the molecules of the alcohol itself, which is this way partially disabled to react with the alkali metal. Thus, lower reaction rates are the consequence of solvation of the formed alcoxide by a part of the initial present alcohol. Anyway, the solvation effects are always strong enough to limit the reaction rate at values much lower than the theoretical stoichiometric 100% limit (expected value: 1 cf. Fig. 2) one could expect to reach by just considering the formal reaction (1) mentioned above. The final yields with respect to the initial amount of alcohol are about 50%.

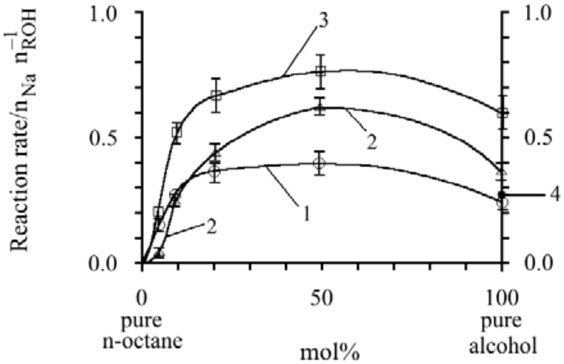

Fig. 3 Sodium reaction rate at end of fast step *vs*. alcohol molar concentration.
1 – 1-heptanol; 2 – 2-heptanol; 3 – 2-butoxy-1-ethanol;
4 – diethyleneglycol-monomethylether (methylcarbitol)

On the one hand of these results it becomes evident that solvation processes can result in important effects on both kinetic (Fig. 2) and thermodynamic (Fig. 3) parameters characterising a chemical reaction. A connected work [6] discusses the way the heat of reaction and the heat of solvation are related to each other and how the corresponding forms of energy can be released. It points out the importance of solvation phenomena on thermodynamics, kinetics and thermal measurements. For the system sodium alcoxide/alcohol the measurement of the corresponding heats of solvation showed their contributions to be nearly the half part of the total apparent enthalpy of the reaction. This system is a typical example for which the energy of solvation is at least as important as the heat of the reaction itself. In order to evaluate the actual importance of solvation phenomena in such systems, one had first to determine the experimental value of the enthalpy of solvation.

Experimental

In order to determine as precisely as possible the contributions of the solvation energies to the apparent heat of the formation of sodium alcoxides, the alcoxides must first be prepared at various levels of concentration by direct reaction of metallic sodium on several alcohols. In a second step, the formed alcoxides were mixed with a variable amount of pure alcohol in a Calvet-type Calorimeter.

Preparation of alkali alcoxides

The reaction is run by bringing into contact the metallic sodium with the alcohol. For the reaction, following reagents were used: *n*-hexanol: $C_6H_{13}OH$: Acros ref. 117890025>98%; butoxyethanol: $C_4H_9OC_2H_4OH$: Merck ref. 8.01554.2500>99%; methylcarbitol (diethyleneglycolmonomethylether): $CH_3OC_2H_4OC_2H_4OH$: Prolabo ref. 23832.294>99%; ethylcarbitol (diethyleneglycolmonoethylether): $C_2H_5OC_2H_4OC_2H_4OH$: Acros ref. 117 89 0025 >98%; metallic sodium: from Métaux Spéciaux (previously: Ugine Kuhlmann), nuclear grade.

The sodium sample has been first purified by a near melting point process as described by [7, 8], yielding samples with a total amount of impurity lower than 5 parts per million by mole The sodium samples were spherical (diameter: 5–15 mm), as obtained from the metal molten in an inert solvent (ligroin). Their mass has been determined by weighting, once the solvent had been wiped off. The precision of weighting was better than 0.5%.

n-Octane: C_8H_{18} Prolabo Rectapur ref. 26 025 238 >99%, (<0.9 ppm water); ligroin: mixture of saturated hydrocarbons, boiling point 120–150°C, <0.9 ppm water, obtained by rectifying technical grade petrol ether from Zundel & Kohler (boiling point 100–160°C).

The infrared and proton-NMR spectra did not show any signal indicating the presence of an impurity at a significant level of concentration in any organic reagent mentioned above.

The water content of all organic products has been determined by a coulometric Karl Fischer's technique with a typical accuracy of about 3% and a detection limit below 0.9 ppm.

The amount of alcohol was chosen so that the total amount of sodium could be dissolved in by forming the corresponding alcoxide. The reaction has been carried out in a borosilicate (Pyrex) glass vessel inerted by argon as a cover gas.

Such a procedure led to conversion yields with respect to the initial alcohol not higher than about 50% mol. The sodium content of the liquid alcoxide containing phase was determined both by the mass of the dissolved sodium and by spectroscopic determination of sodium in the sample by direct atomic absorption spectrometry on the organic sample [9] (Varian AA-6 Spectrometer, at 330.3 nm, accuracy: 2%)

In order to produce higher concentrations of alcoxides, following procedure must be applied: the raw alcoxides solutions as formed by the direct reaction of sodium with the alcohol must be vacuum (2 Torr) evaporated under gentle heating conditions (up to 80°C) in a Rotavapor rotating evaporator. The highest sodium concentrations obtained this way were about 110 g L^{-1} Na corresponding to equivalent yields of about 70% with respect to the initial alcohol. Higher concentrations would have required higher evaporating temperatures or too long evaporating times, leading to partial thermal decomposition of the sample [10].

Measuring the enthalpies of solvation

In order to determine the enthalpies of solvation, a given amount of a sodium alcoxide solution has been mixed with a known amount of pure alcohol at constant temperature. This mixing step has been performed in a Setaram C-80 Calvet calorimeter fitted with its turn-over mixing cell (Fig. 4). The determination of the heat flow generated by the dilution process led to the value of the enthalpy of mixing by integration. For this purpose, one used up to 3 mL of pure alcohol placed in the central part of the cell and up to 3 mL of sodium alcoxide solution placed in the surrounding peripheral sample holder (Fig. 4). The system was then allowed to settle until reaching its equilibrium temperature. The calorimetric measurement was started by regularly turning the whole calorimeter upside down all along the experiment in order to manage mixing and continuous stirring of the sample.

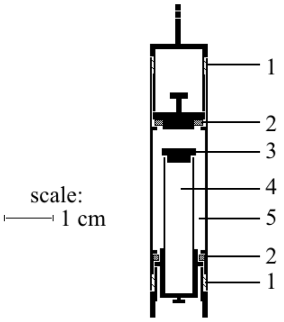

Fig. 4 Calorimetric mixing cell; 1 – screw gasket; 2 – gasket; 3 – stirrer; 4 – inner container; 5 – peripheral container

The heat of mixing of a solution of sodium alcoxide in alcohol with a well defined amount of the same pure alcohol depends on the corresponding dilution factor. The dilution factor is defined in this work by the volumic ratio V_a/V_{tot} of the initial alcoxide solution to the final solution containing both the initial alcoxide and the alcohol which has been added for the dilution. The obtained values are related to the initial sodium concentration of the sample. The different initial concentration levels of sodium in the alcoxide solution were ranging from 10 to 110 g L^{-1} Na. The heats of mixing have been determined for a dilution factor ranging from 1 to 30. For concentration levels lower than 10 g Na L^{-1}, the signal to noise ratio became very important (full black circular marks distributed over a large area along the line for 10 g L^{-1} in Fig. 5) . On the other hand, although concentration levels higher than 110 g L^{-1} can be obtained in practice, the working temperature required to reach such high concentration starts decomposition processes [10] so that above this concentration, the values obtained by extrapolation from results up to 110 g L^{-1} seem to be more reliable than values obtainable from chemicals the purity of which would be bad.

Results and discussion

Figure 5 shows for different initial sodium concentrations the measured heats of mixing which are plotted *vs.* the dilution factor. Since the mass by volume is nearly the same for all present species (about 1000 g dm^{-3}) the ratii by volume are very close to the ratii by mass. Further, since the molar masses and densities of all studied alcohols are very similar to each other, the sodium content by mass of the alcoxides is a parameter allowing a good direct comparison between the different studied systems.

For diluted alcoxides, since the solvation processes are not fast, the low corresponding thermal power leads to noisy signals. Figure 5 shows the experimental results as obtained from the calorimeter by mixing sodium ethylcarbitolate with ethylcarbitol containing less than 300 mg L^{-1} of water. Pure ethylcarbitolate corresponds to a sodium concentra-

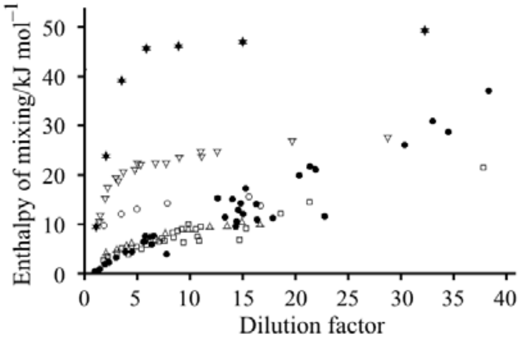

Fig. 5 Enthalpy of mixing of sodium ethylcarbitolate *vs*. dilution factor V_a/V_{tot}:
✱ – Na: 105.8 g L^{-1}; ▽ – Na: 51.7 g L^{-1}; ○ – Na: 35.5 g L^{-1}; △ – Na: 20.8 g L^{-1};
□ – Na: 20.5 g L^{-1}; ● – Na: 10.6 g L^{-1}

tion of about 7 mol L^{-1} (equivalent to about 170 g L^{-1} Na). The enthalpy of solvation of sodium alcoxide would be the enthalpy of mixing measured at infinite dilution factor for a pure alcoxide. Since one cannot obtain a sufficiently pure alcoxide by direct preparation for the reasons mentioned above, the determination of the heat of solvation was carried out by extrapolating the values of heats of mixing obtained for increasing sodium concentrations.

An important conclusion arising from Fig. 5 is that more than 90% of the heat of solvation is already released when the dilution factor is higher than 5 for alcoxide solutions the sodium concentration of which is at least about 30 g L^{-1}. That means that determinations for dilution factors up to 30 will result in experimental values very close to the ideal theoretical value corresponding to an infinite dilution factor. They can therefore be considered as to provide an excellent approximation of the enthalpy of solvation.

In order to verify the reversibility of the solvation process, half part of the samples have been prepared directly by reacting sodium for a time long enough to reach the expected alcoxide concentration. The other half part of the samples have been prepared by reacting sodium with alcohol for a shorter time, and consecutive vacuum evaporation of the excess of alcohol until the same alcoxide concentration was reached. The observable thermal behaviour was found to be completely independent on the way the final alcoxide concentration was obtained. That means the solvation process is completely reversible. This conclusion is in good agreement with the sodium NMR spectra which show complete identity for a given alcoxide concentration, independently on the way that concentration has been reached [4].

In order to fit the experimental results to a convenient model one must first discuss the experimental behaviour of the alcoxides.

From Fig. 5, one observes that for sodium concentrations higher than about 50 g L^{-1} Na (i.e. about 2 mol L^{-1}), the heat of mixing for dilutions factors higher than 5 lead to experimental values which are nearly proportional to the alcoxide concentration. In other words, that means that each time the dilution factor is increased by a constant factor, the system releases the same proportion of the heat of mixing left to be released by the already performed solvation process. This corresponds an exponential contribution to the observable heat of mixing as a function of the dilution factor V_a/V_{tot}.

Further, with increasing the initial dilution of the alcoxide, when the exponential contribution becomes negligible, a linear process appears to be superimposed on the exponential one. This process results in significant effects only for diluted solutions of alcoxide, typically below 20 g L^{-1} (about 1 mol L^{-1}) Na. Presently, it could not be determined whether this heat flow must be considered as to be an effective contribution to the heat of solvation or to be an artefact resulting from the low reaction speeds and correspondingly low measurable thermal power. Anyway, since the linear contribution is small in comparison with the exponential one, especially at high concentrations (beyond 50 g L^{-1} Na), where the effects of solvation become very important, we will not discuss it further in this work. However, for modelling purposes of the experimental results, we will take into account that linear part of the heat of solvation to develop the equations describing the heat of solvation as a function of the dilution ratio at various initial alcoxide concentrations.

Thus, the relation relating the enthalpy of solvation to the dilution factor $f=V_a/V_{tot}$ can be given by following function (2) which takes into account both exponential and linear contributions mentioned above :

$$\Delta H_{dil}=A[1-\exp(-B\{f-1\})]+K(f-1) \tag{2}$$

Table 1 Numerical values for the parameters *A*, *B* and *K* fitting best to the experiment

Concentration/g L^{-1} Na	*A*	*B*	*K*
10.6	10	2.00	5.61
20.5	25	1.30	3.06
35.5	78	1.55	1.61
51.7	139	1.13	1.60
105.8	295	0.71	0.91

One could expect the terms *A* and *B* which characterise the exponential part of the experimentally observable behaviour to be independent on the concentration. The fact that the best fitting requires both terms *A* and *B* to vary the opposite way suggests that the mechanism of solvation undergoes a progressive evolution when changing from concentrated alcoxides to more and more diluted ones. That means that the energy of solvation of the solvating molecules which are very close to the sodium atom differ significantly from the energy of solvation of the farther ones. Figure 6 shows the experimentally fitted heats of mixing for sodium methylcarbitolate with methylcarbitol. The enthalpy of solvation is obtained from the limit the heat of dilution reaches when the dilution factor is increased up to 30. Since for sodium concentrations up to 100 g L^{-1}, the reversibility of the adsorption phenomena could be experimentally verified, it is assumable to extrapolate the behaviour of pure alcoxide from the values observable for concentrated solutions. The extrapolated line for a sodium concentration of 170 g L^{-1} (Fig. 6) leads to an experimental value of the solvation enthalpy for sodium methylcarbitolate of about 70 kJ mol^{-1}. This value can be considered as a good estimate of the enthalpy of solvation of pure sodium ethylcarbitolate by dry sodium ethylcarbitol.

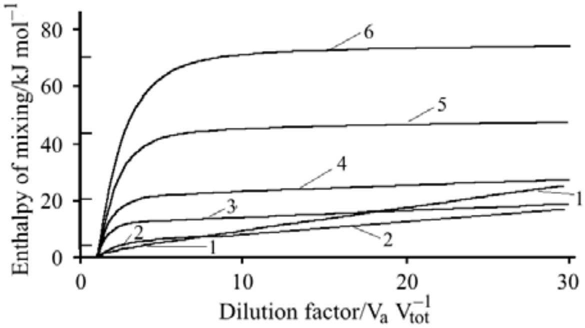

Fig. 6 Fitted enthalpy of mixing of sodium ethylcarbitolate *vs*. dilution factor V_a/V_{tot}; 1 – Na: 10.6 g L^{-1}; 2 – Na: 20.5 g L^{-1}; 3 – Na: 35.5 g L^{-1}; 4 – Na: 51.7 g L^{-1}; 5 – Na: 105.5 g L^{-1}; 6 – Na: 170 g L^{-1} (extrapolated). For reasons of readibility, the experimental points of Fig. 5 have not been shown on this figure. The fit of the lines 3 to 6 is better for all points than the size of the marks used in Fig. 5. Just for lines 1 and 2, corresponding to low concentrations and thus weak thermal effects, the experimental points are distributed at random along the fitted lines due to the lower accuracy of the corresponding thermal measurements

Figure 7 shows the enthalpy of solvation as it could be observed from alcoxide solutions at various concentrations. The measured values of the enthalpy of mixing ΔH_{dil} are generally expected to be proportional to the initial concentration of the alcoxide before dilution, so that the enthalpy of solvation one can deduce from these values should remain constant, independently on the initial concentration of the sample. Figure 7 shows that for sodium ethylcarbitolate this is only the case above 50 g L^{-1} (~2 mol L^{-1}). That means that the values of the enthalpy of dilution ΔH_{dil} cannot be tabulated without referring to the concentration. Further, since above 50 g L^{-1} Na, the function describing the enthalpy of solvation leads to a constant value (Fig. 7), the extrapolation at high sodium

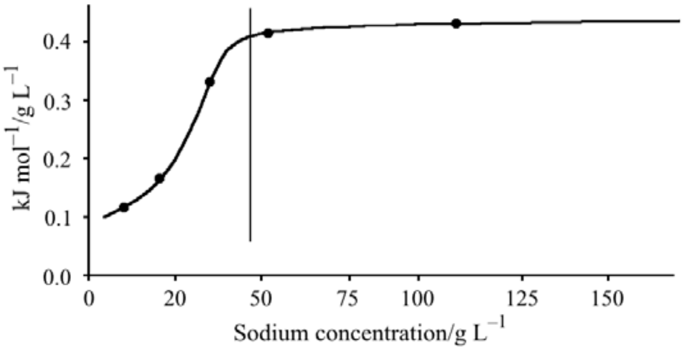

Fig. 7 Relative enthalpy of solvation at infinite dilution as a function of initial sodium concentration

concentrations carried out in order to estimate the enthalpy of solvation for pure sodium ethylcarbitolate (nearly 170 g L^{-1} Na) seems to be valid.

The last point to discuss is the validity of these measurements in a general case. Often, industrially used alcohols may contain a variable amount of water as a low level impurity. Water is more or less soluble in all the studied alcohols. Therefore, we paid special attention to its influence on the apparent heat of solvation of the alcoxides. Figure 8 shows the results obtained for various alcohols at various water contents. Since the maximum concentration of sodium used for Fig. 8 is about 60 g L^{-1} Na, one expects the maximum heat of mixing not to be higher than about 25 kJ mol^{-1}, as it could be determined from Fig. 6. From that Fig. 8, it becomes evident that small amounts of water (lower than 4000 ppm i.e. less than 0.25 mol L^{-1}) result in a huge increase of the dilution enthalpy by more than 50 kJ mol^{-1}, which cannot be explained by the formation and solvation of sodium hydroxide, the enthalpy of solvation of which is about 40 kJ mol^{-1}. Heats of mixing more than seven times higher than expected from the results mentioned by Fig. 6 can be obtained when the water content of the alcohol is even as low as 0.4% by mass.

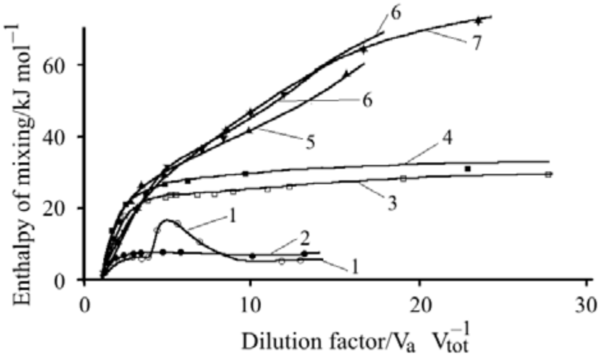

Fig. 8 Heat of mixing for various alcohols with their sodium alcoxide at various water contents; 1 – *n*-hexanol, 42.7 g L^{-1} Na, 275 mg L^{-1} H_2O; 2 – *n*-hexanol, 29.9 g L^{-1} Na, 275 mg L^{-1} H_2O; 3 – ethylcarbitol, 51.6 g L^{-1} Na, 950 mg L^{-1} H_2O; 4 – butoxyethanol, 47.5 g L^{-1} Na, 600 mg L^{-1} H_2O; 5 – methylcarbitol, 61.0 g L^{-1} Na, 4000 mg L^{-1} H_2O; 6 – methylcarbitol, 47.4 g L^{-1} Na, 4000 mg L^{-1} H_2O; 7 – methylcarbitol, 32.0 g L^{-1} Na, 4000 mg L^{-1} H_2O

The results of Fig. 8 appear as to be divided into three groups corresponding to increasing water contents, regardless on the type of the alcohol. The highest values of the enthalpy of solvation are observed for water contents up to 4000 ppm by mass. Solvation enthalpies up to 70 kJ mol^{-1} have been observed for sodium concentrations lower than 60 g L^{-1}. By taking into account the results of Fig. 6, that means that the actual solvation enthalpy of the pure alcoxide could be as high as 200 kJ mol^{-1}. This enthalpy is the same as the value generally assumed to be the enthalpy of the reaction of sodium with an alcohol [11]. Such a high enthalpy of solvation can completely stop the reaction in its early steps. This is in good agreement with the poor reactivity of medium size alcohol molecules as studied in this work, mentioned by [1].

The anomalous behaviour of *n*-hexanolate, leading to a maximum for a dilution factor close to 5 is observed for all experiments. However, operating temperature seems to play an essential role in the onset point of this phenomenon, which appears for a dilution factor between 3 and 10. We suggest to attribute it to the existence of a structured solution reducing drastically its entropy for a specific composition. A dilution factor close to five suggests the existence of octahedral species made of one molecule of alcoxide and five molecules of alcohol. However, variable delay in the generation of the heat of dilution after mixing for a same sample concentration suggest the existence if complex kinetic mechanisms ruling this phenomenon. The discussion of these aspects is not in the frame of this contribution, since further work is still required in order to define precisely the origins and the mechanisms of the specific behaviour of sodium hexanolate.

Conclusions

The reaction of sodium with an alcohol is a heterogeneous reaction. The simple mechanism of the formal reaction (1) cannot explain the differences observed between some very similar alcohols. Solvation effects play an essential role. The consequences are on thermodynamics by modifying the activities of the reacting species, and on kinetics by modifying the adsorption equilibria [1].

The strong solvation phenomena taking place in systems as described in this work can result in drastic effects on the reaction rate. Although this work does not discuss this aspect, the described solvation phenomena are strongly temperature dependent [4], so that changes in temperature can lead to severe changes in entropy. The subsequently rising temperature will auto-accelerate this process. As discussed in [6], this can result in important spontaneous exothermic phenomena. As a consequence, sodium alcoxide may become dangerous, starting easily fast thermal runaway processes [5, 10].

Since solvation processes modify the energies characterising both initial and final states of the reacting species, they will also modify the activation energy of the reaction. These changes must be taken into account each time one tries to carry out thermokinetic measurements. These aspects have been pointed out by [12]. The dependency of the activation energy on the reaction rate is an important aspect which has been often mentioned and the effects of which have been discussed by [13–15]. The present work shows some possible origins of the temperature and reaction rate dependency of the activation energy of condensed phase reactions.

Another main consequence of these solvation processes is that the heat released by the reaction depends on the residual alcohol concentration. At the very end of the reaction, when the formed alcoxide concentrations become high, the exothermic solvation process does no longer take place. As a result, large amounts of potential heat are stored in the system. The addition of fresh alcohol in order to re-start a reaction which has become weak will locally release by solvation this potential heat stored in the system. Due to all the described factors of instability, the system may become very dangerous and result in runaway situations without any possibility of control by usual parameters such as temperature, pressure or concentration, as discussed in [5] and [16]. Moreover, the heat which has not been released by solvation in highly concentrated solutions of alcoxides will become free during their thermal decomposition. That means that concentrated solutions are much more dangerous than it could be expected by just considering properties depending linearly on the concentration.

This study shows how complex an apparently simple reaction can be. The solvation process, especially when traces of water are present in the solvent, may give rise to more than 50% of the total heat amount generated by the reaction. Since other forms of released energy are small in comparison with the thermal effects, this will result in a complete blocking of the reaction as soon as the reaction rate is near 50%. However, since the stability of the formed solvates is strongly temperature dependent, any change in the temperature of the reagents will generate drastic changes in the behaviour of the system. One must therefore be extremely careful when trying to predict the reaction speed or the reaction rate from calorimetric data which do not specify the respective contributions of the solvation effects to the apparent enthalpy of the reaction, which includes both the heat of solvation and the heat of reaction. On the other hand, one must always keep in mind the importance of minor species on the solvation processes. The example of water given in this work shows how important it may be to characterise not only the main species, but also the eventually present impurities of a system.

The reaction of sodium with alcohols is a typical case for which solvation effects bring an important contribution to the total enthalpy of the reaction. For apparent reaction enthalpies of about 180 kJ mol^{-1}, one generally has a typical reaction enthalpy of about 100 kJ mol^{-1} and a solvation enthalpy of about 80 kJ mol^{-1} depending on the working conditions required by the calorimetric device used for the measurement.

Further, this study shows how difficult to carry out the accurate measurement of the enthalpy of an apparently simple reaction can be. Solvation effects can lead to important variations of the entropy of the system. The resulting changes in the free enthalpy of the reaction modify strongly the final equilibrium state of the system, which depends mainly on the initial stoichiometry of the reagents. The same way, the activation energies undergo changes while the reaction undergoes completion [14], since this process induces changes in the concentration levels of the solvating species. Reaction speeds can thus become very small, rendering difficult an accurate heat flow detection and thus reaction enthalpy measurements. To overcome such problems, a large excess of the solvating species must be used, and therefore, all authors who determined the enthalpy of reaction of sodium with alcohols reacted the metal with a more or less large excess of alcohol, so that their values for the reaction enthalpy include a more or less important part of the heat of solvation. Thus, one must carry out numerous experiments under various stoichiometric conditions in order to distinguish the variable solvation contribution from the constant reaction contribution to the total observable enthalpy.

Another important aspect is for chemical safety: when solvation effects stop a reaction by entropic effects, the yielded products may store high amounts of potential thermal energy due to poor solvation. Addition of fresh reagent to restart the reaction will lead locally to concentration gradients generating hot spots by solvation effects. The adiabatic temperature increase can reach values up to 100 K [18, 6]. When taking into account the poor thermal stability of some alcoxides [2, 16, 17], such a hot spot formation can lead to extremely dangerous situations, able to generate violent explosions and heavy accidents.

Therefore sodium alcoxides are a good example of a class of products for which solvation effects generate major dangers. They become particularly dangerous compounds when pure alcohol is added once they are heated up close to their decomposition temperature by an initial reaction of alcohol on an excess of metallic sodium. The danger is increased drastically by the presence of traces of water in the alcohol, and no reaction of this type should be run without a careful previous determination of the water content of the reagents. The opposite reaction of sodium added into an excess of alcohol is harmless, since the solvation effects taking place immediately after the formation of the alcoxide evacuate continuously the potential heat of solvation. That means that in order to be safe, one must always add sodium to the liquid alcool phase, but never add an alcohol to an excess of metallic sodium.

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