

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OKLAHOMA A. AND M. COLLEGE]

Extraction Studies on the Extent of Hydration of Salts in Non-aqueous Solvents¹

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An improved method of estimating the degree of hydration of salt in non-aqueous solution by extractions from aqueous solution is presented. The correction for the amount of non-hydrate water is applied to the total water extracted per mole of salt. Hydration numbers of LiCl, CaCl₂, ZnCl₂, Ni(ClO₄)₂ and Co(ClO₄)₂ in 2-octanol obtained using this method are given.

Considerable attention has recently been given to the extent of hydration of salts in non-aqueous solvents. The subject is of interest because of its bearing on the question of ionic hydration in aqueous solution and because of its importance in the solvent extraction of electrolytes.

A procedure for the determination of salt hydration in solvents immiscible with water was introduced by Katzin and Sullivan² who plotted the concentration of water in the non-aqueous phase as a function of the extracted salt concentration and equated the slope of this plot to the salt hydration number. Templeton and Daly³ have applied this procedure to the study of di- and trivalent metal nitrates in *n*-hexyl alcohol. From Fig. 2 of their article it can be seen that these plots are not linear and usually exhibit a minimum in dilute salt regions.

A procedure for the determination of salt hydration in solvents immiscible with water was introduced by Katzin and Sullivan² to the lowering by the salt of the water activity in the aqueous phase with a resultant decrease in the partition of "free" (*i.e.*, non-hydrate) water before a sufficient quantity of water associated with the hydrated salt is extracted to offset this effect. Although the importance of non-hydrate water and its relationship to water activities was thus recognized, no corrections for this variable were attempted. In the absence of such corrections, results obtained using the procedure of Katzin and Sullivan are somewhat questionable, as pointed out by Templeton and Daly.³

In conjunction with a study of the relative extraction of some divalent metal chlorides and perchlorates from aqueous solution into 2-octanol, the extent of hydration of these salts has been determined by a modification of Katzin and Sullivan's procedure in which an attempt is made to correct for the extraction of non-hydrate water. This correction is in some cases as much as 99% of the total water extracted and is never less than 5%.

A plot (Fig. 1) of the concentration of water extracted against the water activity of the aqueous salt solutions shows that, where salt extraction is negligible, the data for different salts lie on a common curve. This is to be expected since the only factors determining the extent of water extraction under these conditions are the magnitude of the distribution coefficient of water between the phases and the water activity.

In order to estimate the free water extracted in regions of measurable salt extraction it is assumed that (1) the presence of the extracted salt does not significantly alter the interaction between

the non-aqueous solvent and water, (2) the salt hydrate does not contribute appreciably to the water vapor pressure in the non-aqueous phase, and (3) in regions of low water activity, the free water in the non-aqueous phase follows Henry's law. Based on these assumptions, hydrate water is then defined as the difference between the analytically determined water content and the free water concentration necessary to give a water activity in the non-aqueous phase equal to that of the aqueous phase in equilibrium with it.

The assumption of the applicability of Henry's law is tested in Fig. 1b where the dotted line portion of the water extraction curve below point A is that predicted by Henry's law. The Henry's law constant was evaluated at point A. The agreement between the predicted water and that found to be extracted is good, and would be even better had the last few experimental points been corrected for the presence of a small amount of hydrate water. Salt extraction at these points is small but not negligible.

In applying the modified Katzin and Sullivan procedure, the curves of Fig. 1 were used to obtain the free water correction in cases where the water activity was relatively high. At water activities below 0.5, where all salts studied showed measurable extraction, the free water was calculated by Henry's law. The Henry's law constant was evaluated at the lowest value of water activity consistent with negligible salt extraction. This is necessary because of deviations from Henry's law in the higher water activity regions. In this calculation (as in Fig. 1), the water activity was taken as being equal to that in pure salt solutions of the same salt concentration as the equilibrated aqueous phases. This neglected the effect of the dissolved non-aqueous solvent on the water activity in the aqueous phase. Since the solubility of the non-aqueous solvent in the aqueous phase was very small, it is doubtful that this neglect introduced any serious error.

In cases where extracted salt concentrations were large, it can be expected that the first and second assumptions upon which the correction is based might not be justified. However, in these cases, the water activity was so low that free water extraction was relatively small. So even with a high percentage error in estimating the free water, the absolute error was not serious when compared to the large amount of hydrate water present.

Water activities at 25° for solutions of CoCl₂, CdCl₂ and ZnCl₂ were obtained from osmotic coefficients listed by Stokes⁴ and water activities of CaCl₂ at 30° were calculated from those at 25° using values obtained for the relative partial molal

(1) This work was made possible by a grant from the U. S. Atomic Energy Commission to the Research Foundation of Oklahoma A. and M. College, Contract No. AT(11-1)-71, Project 1.

(2) L. I. Katzin and J. C. Sullivan, *J. Phys. Colloid Chem.*, **55**, 346 (1951).

(3) C. C. Templeton and L. K. Daly, *This Journal*, **73**, 3989 (1951).

(4) R. H. Stokes, *Trans. Faraday Soc.*, **41**, 637 (1945); **44**, 295 (1948).

heat content of the solvent from heat of dilution data by Rossini.⁵ Water activities of LiCl solutions at 30° were taken from measurements by Johnson and Molstad.⁶ Calculated values of the water activities in mixtures of CaCl₂ and CoCl₂ were based on the assumption, tested by Robinson and Brown,⁷ that vapor pressure lowering effects of these salts were additive.

Water activities of solutions of Co(ClO₄)₂ and Ni(ClO₄)₂ are not available in the literature and were estimated on the assumption that they are similar to those of solutions of Zn(ClO₄)₂ at corresponding concentrations. This assumption seems reasonable in view of the striking similarity between the osmotic coefficients of solutions of zinc and magnesium perchlorates over the concentration range from 0.1–4.0 molal. Since solutions of the chlorides of these cations have markedly different osmotic coefficients even at fairly low concentrations, it would appear that the behavior in solutions of perchlorate salts containing cations of similar ionic charge and size is much less specific than that of salts having the same cations and other anions.

Water activities of Zn(ClO₄)₂ solutions were obtained from osmotic coefficients compiled by Stokes.⁴

Experimental

Materials.—All salts used in this study with the exception of cobalt and nickel perchlorates were C.P. grade. The perchlorates were prepared from the C.P. metal carbonates and reagent grade perchloric acid. The 2-octanol used was the pure anhydrous reagent obtained from the Matheson Chemical Company.

Analytical Methods.—Water was determined by the Karl Fischer technique using a dead-stop end-point. Both distilled water and sodium tartrate dihydrate were employed as primary standards. All flasks were oven-dried at 210° for two days prior to use and were pretitrated just before introduction of the sample.

Cobalt and nickel perchlorates were each determined colorimetrically in both phases by employing the natural color of the solutions as the basis of the method. Both salts were shown to follow Beer's law in both phases, and the color intensity in the octanol-rich phase was found to be insensitive to variations in the water content of this phase at water-to-salt mole ratios greater than six. The behavior at lower water ratios was not studied since they were never encountered under extraction conditions.

Absorption measurements were made with a Beckman DU spectrophotometer using corex cells of 1.00-cm. light path. The wave lengths used in the colorimetric procedures were 720 m μ for Ni(ClO₄)₂ in both water and octanol, and 510 m μ and 515 m μ for Co(ClO₄)₂ in water and octanol, respectively.

Solutions having concentrations lower than 10⁻² molal of Co(ClO₄)₂ and Ni(ClO₄)₂ in octanol were determined by back-extraction into water followed by polarographic determination of the metal in the extract.⁸

Lithium and calcium chlorides in the aqueous phase were determined by titration against aqueous silver nitrate using dichlorofluorescein as the indicator. A modified Volhard procedure employing alcoholic silver nitrate was used for the octanol phase. Very low concentrations (*i.e.*, 10⁻³ and lower) in the octanol phase were determined by evaporation of 50-g. samples of the phase, and titration of the salt residue dissolved in a minimum amount of water.

(5) F. R. Bichowsky and F. D. Rossini, "Thermochemistry of Chemical Substances," Reinhold Publ. Corp., New York, N. Y., 1936.

(6) E. F. Johnson and M. C. Molstad, *J. Phys. Colloid Chem.*, **55**, 257 (1951).

(7) R. A. Robinson and J. B. Brown, *Trans. Proc. Roy. Soc. New Zealand*, **77**, 1 (1948).

(8) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946.

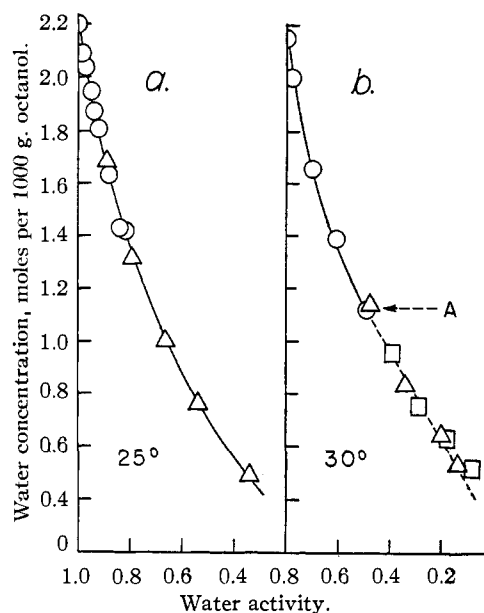


Fig. 1.—Water extraction from aqueous salt solutions in regions of negligible salt extraction; a, 25°, O, CdCl₂; Δ, CaCl₂; b, O, LiCl; Δ, CaCl₂; □, CaCl₂-CoCl₂ mixtures.

Zinc and cadmium chlorides were determined in the aqueous phase by titration against silver nitrate and in the octanol phase by back-extraction and polarographic analysis.⁸

Mixtures of CoCl₂ and CaCl₂ were analyzed by first carrying out a total chloride determination on both phases using methods previously described; cobalt was then determined by an amperometric titration employing α -nitroso- β -naphthol,⁸ and the calcium obtained by difference.

Experimental Conditions.—All solutions were equilibrated in ground-glass-stoppered flasks for 24 hours on a mechanical shaker at room temperature. They were then placed in a constant temperature bath at either 25 or 30° for six hours prior to phase separation and analysis.

Results and Discussion

Figures 2 through 4 are plots of the difference between the analytical water concentration in the octanol-rich phase and the free-water concentration (estimated by methods previously described in this paper) against salt concentration in the octanol-rich phase for the five salts studied in this investigation. Points plotted in these figures were taken from concentration regions where salt extraction was appreciable.

For the purpose of affording a comparison between results obtained from the procedure used in this investigation and that of Katzin and Sullivan, uncorrected plots (dashed lines) are shown in the figures for LiCl, Co(ClO₄)₂ and CaCl₂.

As shown by the figures, all salts studied showed satisfactory linear relationships between salt extracted and hydrate water, whereas a plot against total water gives a physically meaningless negative slope for CaCl₂ and an "S" shaped curve for LiCl from which any arbitrary slope between 0 and 1 could be assigned. Even in the case of Co(ClO₄)₂, which gives a reasonably linear plot against total water, the slope so obtained is in error by approximately 12%. Since this was the most favorable case for a procedure ignoring changes in free water extraction (because of the relatively large fraction of the total water which was due to hydration), it is clear that the procedure of Katzin and Sullivan can

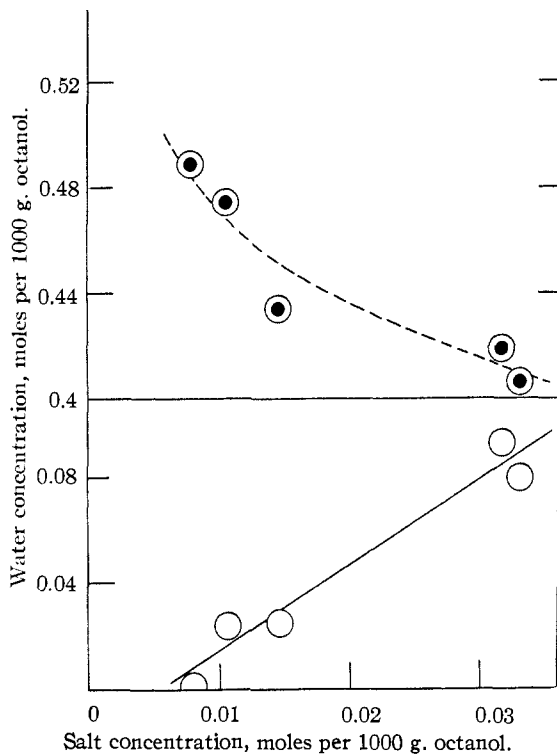


Fig. 2.—Water extracted from aqueous CaCl_2 solutions in regions of measurable salt extraction: \circ , hydrate water; \odot , total water.

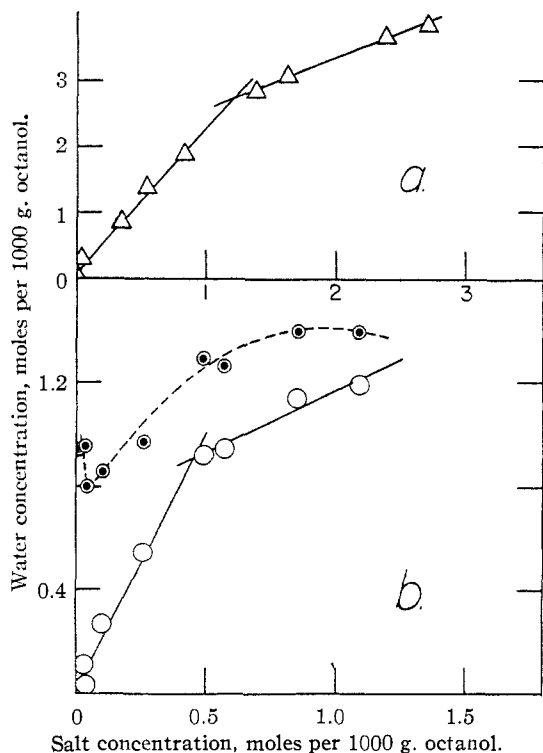


Fig. 3.—Water extracted from aqueous salt solutions in regions of measurable salt extraction: \circ , hydrate water with LiCl ; \odot , total water with LiCl ; Δ , hydrate water with ZnCl_2 .

in no case give more than the correct order of magnitude of the extent of salt hydration, and this

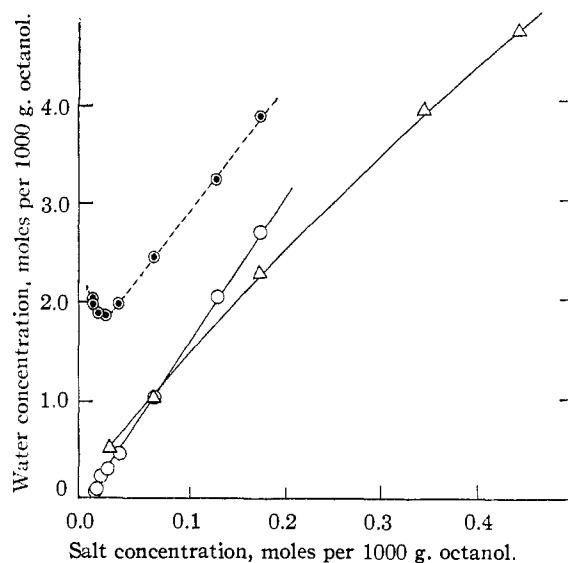


Fig. 4.—Water extracted from aqueous salt solutions in regions of measurable salt extraction: \circ , hydrate water with $\text{Co}(\text{ClO}_4)_2$; \odot , total water with $\text{Co}(\text{ClO}_4)_2$; Δ , hydrate water with $\text{Ni}(\text{ClO}_4)_2$.

only in those cases where salt extraction and salt hydration are large.

Slopes obtained from the corrected plots are listed in Table I along with the aqueous phase concentration regions to which they apply.

TABLE I

Salt	Aqueous phase salt concn., m	Slope	Temp., $^{\circ}\text{C}$.
ZnCl_2	0.01–7.0	2.2	25
	7.0–19.6	0.8	25
LiCl	7.3–13.9	2.2	30
	13.9–18.6	0.6	30
CaCl_2	4.7–8.5	2.9	25
$\text{Co}(\text{ClO}_4)_2$	0.5–2.4	14.7	30
$\text{Ni}(\text{ClO}_4)_2$	1.3–3.8	10.0	30

The decrease in hydration indicated for ZnCl_2 and LiCl by the appearance of a second linear portion in the corrected plots seems reasonable in solutions of as high a salt content as these. Similar changes occur in the extent of hydration of solid hydrates precipitated from very concentrated solutions. The smaller slopes found for both salts after the transition point might be attributed either to a replacement of water by octanol (made possible by the lowered water activity) or to the adoption of some less highly solvated structure. Extensive polymerization or a chain structure with bridging through the chloride ions might lead to this result.

The slightly erratic behavior of CaCl_2 is probably due to the relatively low extraction of this salt. As a consequence, hydrate water associated with the salt is only slightly in excess of the probable experimental error in the water analysis. For this reason, this hydration number is somewhat less certain than the others listed.

The extremely high hydration of the perchlorates is notable when compared with the low values shown by the two chlorides of the same valence

type which were studied. A possible explanation might be the inability of the perchlorate ion to function as a coordinating anion or even to approach the cation closely in forming an electrostatic ion pair. The cation would then be left free to exert a maximum influence in orienting solvent molecules.

This explanation is in accord with the fact that

very high activity coefficients are encountered in concentrated aqueous solutions of perchlorate salts. Since the cation would be effectively masked by solvent from specific interactions with the anion, this might also explain the lack of individualistic behavior of perchlorates in comparison with the corresponding chlorides.

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The Thermal Decomposition of Nitrous Oxide¹

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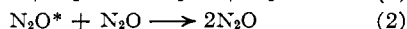
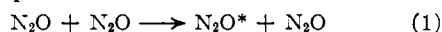
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A study of the isotopic composition of the nitrogen from the thermal decomposition of a sample of N₂O enriched in N¹⁵N¹⁴O shows that no equilibration of the nitrogen atoms takes place during the decomposition reaction. It is shown that NO neither exchanges with N₂O nor catalyzes the equilibration of nitrogen during the decomposition of N₂O. These results support the unimolecular decomposition mechanism and add restrictions to the chain mechanism.

Introduction

The homogeneous decomposition of nitrous oxide is classical in gas kinetics. No completely satisfactory description of the order of the reaction was available until Pease² proposed a 3/2 order reaction instead of the second order rate law of Hinshelwood and Burk³ and the combinations of unimolecular reactions suggested by Volmer,⁴ Musgrave and Hinshelwood,^{5a} and Hunter.^{5b} Pease's rate law is in good agreement with the experimental data over the wide ranges of temperature and pressure investigated. Another feature of the 3/2 power rate law is that it leads to an activation energy independent of pressure, whereas the first order rate constants lead to activation energies which rise by about 30% in the pressure interval 0-40 atmospheres. Pease proposed a mechanism consistent with the 3/2 order rate law involving chains which include nitrogen atoms and nitric oxide.

Subsequent to the completion of the work described in this paper, Johnston⁶ reported the results of an analysis of all the published data on the rates of the decomposition. His analysis is consistent with the assumption that the decomposition may in part be heterogeneous. After one corrects for the heterogeneous portion of the reaction, the kinetics follow those expected for a unimolecular reaction. The second order rate constants for activation in the Rice-Ramsperger-Kassel theories now lead to a single activation energy. The reaction mechanism can be pictured as



(1) Research carried out under the auspices of the Atomic Energy Commission. Presented at the 118th meeting of the American Chemical Society, September 3-8, 1950, Chicago, Ill.

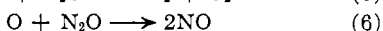
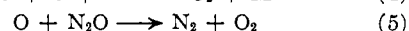
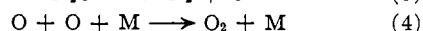
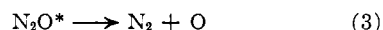
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(4) M. Volmer and H. Kummerow, *Z. physik. Chem.*, **B9**, 141 (1930); M. Volmer and N. Nagasako, *ibid.*, **B10**, 414 (1930).

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(6) H. S. Johnston, *J. Chem. Phys.*, **19**, 663 (1951).



We have carried out some experiments on the decomposition of mixtures of N¹⁵N¹⁴O and N¹⁴N¹⁴O and looked for possible equilibration of N¹⁴ and N¹⁵ in the nitrogen product. It is known that the homogeneous equilibration of nitrogen gas is slow at 750°. Some additional experiments were carried out to look for exchange between N¹⁴O and each of the isomers N¹⁵N¹⁴O and N¹⁴N¹⁵O. The results of these studies are in agreement with predictions from the unimolecular decomposition mechanism. The nitrogen atom-nitric oxide chain mechanism of Pease is ruled out.

Experimental

Samples of N₂O enriched in either N¹⁵N¹⁴O or N¹⁴N¹⁵O were prepared by methods described previously^{8,9} from the thermal decomposition of N¹⁵H₄N¹⁴O₃ and N¹⁴H₄N¹⁵O₃, respectively. Enriched N¹⁵H₄NO₃ and HN¹⁵O₃ were obtained from Eastman Kodak Co.

The N₂O decomposition reactions were carried out in sealed cylindrical quartz vessels 3 × 20 cm. filled to a pressure of about 80 mm. at room temperature. The decomposition and exchange reaction temperatures were about 750°.

The exchange experiments between N₂O and N¹⁴O were similarly carried out in quartz reactors. Matheson tank NO was used without further purification. Semi-quantitative tests on the purity of the tank NO indicate possible errors from this source of the order of 1% in the 29/28 and 31/30 ratios in the exchange experiments. NO₂ was observed as a reaction product after the vessel was cooled to room temperature for analysis. It was separated from the N₂, NO and O₂ by passing the mixture through a trap cooled to -80°.

All samples were analyzed mass spectrometrically after the reaction mixture cooled to room temperature. In all cases the decomposition of N₂O was complete.

Results and Discussion

The results of a typical mass spectrometric analysis of the N₂ and NO formed from the thermal

(7) G. C. Joris and H. S. Taylor, *ibid.*, **7**, 893 (1939).

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(9) J. Bigeleisen and L. Friedman, *ibid.*, **18**, 1656 (1950).