



Figure 6. Volume changes on irradiation

Mixed resins provide greater protection against pollution of water by degradation products, although at some sacrifice in usable exchange capacity. Since reactor purification resins are commonly discarded rather than re-used because of radiation and regeneration problems, reduction of ion exchange capacity is costly. When H-OH mixed beds are used, pollution of water is minimal. When Li-OH mixed beds are used, nitrogenous material and lithium may be released.

NOMENCLATURE

R_A = residual anion exchange capacity

Total titratable alkalinity (to pH 4.0) eluted from a resin by a neutral salt solution. There are generally two well-defined inflection points in the titration curve, so that R_A is defined as the sum of (OH^-) and (HCO_3^-).

(OH^-), determined by titration to pH 7.2

(HCO_3^-), determined by titration from pH 7.2 to pH 4.0

Assignment of (OH^-) and (HCO_3^-) as ionic species was made for simplicity.

R_C = residual cation capacity

For H^+ resins, titratable acidity eluted from a resin by a neutral salt solution; for new resins R_C assumed to be same as T_C .

For Li^+ resins, lithium content of resin.

T_C = total cation exchange (salt-splitting) capacity. Titratable acidity eluted by a neutral salt solution from a resin after exhaustive regeneration with acid

T_A = total anion exchange (salt-splitting) capacity

Strong-base exchange groups on resin, determined by converting the resin to the desired anionic form by a salt solution, then eluting this anion from the resin by another salt solution, and determining the concentration of the eluted anion.

S = sulfate content of anion resin in mixed resin (Equation 4)

V = volatile base (NR_3) content of cation resin in mixed resin (Equation 3)

LITERATURE CITED

- (1) Baumann, E.W., *J. CHEM. ENG. DATA* 5, 376182 (1960).
- (2) Baumann, E.W., E.I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S.C., U. S. At. Energy Comm. Rept. DP-973 (1965).
- (3) *Ibid.*, Rept. DP-977 (1965).
- (4) Hall, G.R., Streat, M., *J. Chem. Soc.* 1963, 5205-11.
- (5) Keily, H.J., Rogers, L.R., *Anal. Chem.* 27, 759-64 (1955).
- (6) Marinsky, J.A., Giuffrida, A.J., Oak Ridge National Laboratory, Oak Ridge, Tenn., U. S. At. Energy Comm. Rept. ORNL-1978 (1957).
- (7) Smith, L.L., Groh, H.J., E.I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S.C., U. S. At. Energy Comm. Rept. DP-549 (1961).

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Solubility Measurements in Lithium-Potassium Nitrate Eutectic

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The solubilities of 10 simple alkali metal salts and seven transition metal salts have been measured in lithium-potassium nitrate eutectic at 160° C. These values were compared to the theoretical values calculated from the random mixture nearest neighbor approximation and ideal solution equations and to values in aqueous solutions. Hydrated transition metal salts, when dissolved in nitrate eutectic, were shown to be dehydrated under vacuum without hydrolysis. A new complex ion was obtained in a precipitate from nickel(II) and chloride solutions.

ALTHOUGH fused alkali metal nitrates are being used increasingly as solvent media for chemical reactions, data on solubility values are still very sparse, as the published values are almost confined to those of sparingly soluble halides of silver and thallium (7, 10). However, two correlations have been postulated from these values. Tien and Harrington (10) pointed out that the solubilities of silver chloride, bromide, and iodide in fused nitrates were almost equal to those in aqueous solution when extrapolated to the melt temperature, and Seward and Field (7) showed that experimental solubilities of silver chloride and thallous bromide could be calculated with a very good degree of agreement from an equation developed from the random mixture nearest neighbor approximation of ion environment.

A series of measurements at constant temperature has now been carried out on 17 solutes dissolved in lithium-potassium nitrate eutectic to extend the amount of data available and to test the general applicability of these two correlations. The temperature selected for measurement (160° C.) was kept near the melting point of the solvent (132° C.) to avoid any complication due to chemical reactions which occur with several of the solutes at temperatures above 200° C.

EXPERIMENTAL

Solvent. Analytical reagent grade potassium nitrate and reagent grade lithium nitrate were dried at 150° C. for 24 hours, mixed in the eutectic proportion (38 mole % LiNO_3), melted, and filtered under vacuum through a No. 3 sinter.

Solutes. All are of analytical reagent grade. Alkali metal salts were dried at 150° C. for 12 hours. Sodium monoxide was prepared by heating sodium peroxide at 600° C. under vacuum until the pressure fell to 10⁻² mm. (4). Na₂O was 99.1% by titration with HCl. Anhydrous transition metal chlorides were prepared by refluxing the hydrates with thionyl chloride for 5 hours (1). Hydrated transition metal nitrates and sulfates were dehydrated in the solvent at 160° by evacuation of their solutions to 10⁻² mm. A slowly closed nitrogen leak was used to reduce the pressure gradually to prevent bumping in the early stages.

Solubility Determinations. Approximately 30 grams of eutectic were placed in a borosilicate glass tube fitted with a stirrer gland and a connection to the vacuum system. The tube fitted snugly into a well-lagged electric furnace, the temperature of which was maintained to ±2° C. by an Ether Transitrol controller, and measured with a Chromel-Alumel thermocouple. The melt was evacuated at 350° C. to 10⁻² mm. (about 8 hours), to remove residual traces of water. After cooling to 160° C., excess solute was added and stirring commenced under a current of nitrogen. Samples were taken with a preheated filter tube, moving inside the tubular stirrer. The filter consisted of a tightly packed glass wool plug ½ inch long. After solidification the solution above the plug was cut off and analyzed. Samples were taken after increasing periods of stirring to determine true equilibrium values. The length of the filter plug was increased to prove that lower solubilities were not obtained—i.e., that all solid solute particles were removed with a ½-inch plug.

Analysis. Samples from the solubility determinations were analyzed by conventional gravimetric and colorimetric methods. The nickel precipitate was analyzed gravimetrically, nickel as dimethylglyoxime, potassium as tetraphenylboron complexes, chloride as silver chloride, and nitrate as nitron nitrate.

Spectroscopic Measurements. These were carried out on a Unicam S.P. 700 spectrometer modified for use to 500° C. Thermogravimetric analysis was carried out using a Stanton TR-1 thermobalance.

X-ray powder photography used Ni filtered CuK α radiation with a 19-cm. power camera and a Joyce microdensitometer.

RESULTS

The solubility values determined at 160° are given in Table I.

Since the transition metal oxysalts were difficult to prepare as pure anhydrous solids, the dehydration by vacuum of hydrated salts dissolved in nitrate eutectic was studied at 160° C. When the pressure had fallen to 10⁻² mm. the theoretical amount of water had been evolved and the solidified solution showed no evidence of O-H bonds when examined as a fluorolube mull by infrared spectroscopy. The condensed water was only slightly acid—e.g., that from melt containing 10.3 mole % Co(NO₃)₂·6H₂O after pumping 3 days at 160°, had a pH of 1.5 and contained acid corresponding to 0.07% hydrolysis. Analysis of the slight black precipitate of cobalt oxide again indicated 0.07% hydrolysis. The identity of solutions prepared by vacuum dehydration with those prepared from anhydrous solutes was indicated by similar solubility values—e.g., 14.8 mole % at 160° C. using initially hydrated cobalt chloride as solute and 14.6% using anhydrous cobalt chloride—and by identical ultraviolet and visible spectra—e.g., of solutions of hydrated cobalt chloride after pumping, and of anhydrous cobalt chloride at the same cobalt concentration. A pronounced red shift of the visible maximum was found as the concentration was increased, together with an increased extinction coefficient, the values being 0.0023M, 554 m μ , ϵ_{\max} 73 ± 8; 0.0057M, 588 m μ , ϵ_{\max} 122 ± 5; and 0.187M, 617 m μ , ϵ_{\max} 146 ± 10, slight shoulder at 676 m μ .

Table I. Solubility of Various Solutes in Lithium-Potassium Nitrate Eutectic at 160° C.

Solute	Solubility, Mole %	Solute	Solubility, Mole %
KCl	8.11 ± 0.06	Na ₂ CO ₃	0.001 ± 0.001
KBr	3.13 ± 0.01	CuCl ₂	3.16 ± 0.01
KI	0.91 ± 0.03	Cu(NO ₃) ₂	9.4 ± 0.2
KSCN	88.9 ± 0.1	NiCl ₂	1.47 ± 0.02
KCN	22.3 ± 0.1	Ni(NO ₃) ₂	34.6 ± 0.1
KOH	5.7 ± 0.2	CoCl ₂	14.6 ± 0.02
NaOH	3.76 ± 0.05	Co(NO ₃) ₂	7.8 ± 0.2
Na ₂ O	1.33 ± 0.04	CoSO ₄	4.69 ± 0.05
Na ₂ O ₂	0.07 ± 0.02		

When anhydrous nickel chloride (yellow) was used as solute, a golden-brown precipitate formed. A similar precipitate resulted from adding saturated potassium chloride solution to a nickel nitrate solution. Besides adhering melt, the precipitate contained small amounts of excess nickel chloride or nitrate, the latter as a solution in the melt, according to the method of preparation. The analytical results, therefore, did not lend themselves to detailed interpretation, a typical precipitate analyzing as 13.9% Ni, 18.8% Cl, 41.7% NO₃, and 21.7% K. However, the results indicated an average Cl⁻:Ni⁺² ratio of 2.3 and a slightly higher NO₃⁻:Ni⁺² ratio. X-ray powder photography gave lines corresponding to the nitrate melt and also some new lines not attributable to NiCl₂, Ni(NO₃)₂, KCl, or LiCl. The *d* values in Angstroms and relative intensities, (in parentheses) of the lines due to the new compound were 6.61 (8), 6.26 (8), 5.06 (7), 4.16 (10), 3.19 (8), 2.54 (4), and 2.48 (10). Thermogravimetric analysis showed the precipitates to decompose at 350° to 600° C., maximum rate at 500° C., with a weight loss corresponding to 2.3 NO₃⁻ groups per nickel, whereas nickel nitrate dissolved in melt decomposed at 300° to 480° C., maximum rate 440° C.; anhydrous nickel chloride at 600° to 910° C., maximum rate 880° C.; and nitrate eutectic at 600° to 1000° C., maximum rate 970° C.

DISCUSSION

As the solubilities of a wider range of solutes were now available, the applicability of the two previous attempts (7, 10) to calculate fused nitrate solubilities was examined. Using the random mixture nearest neighbor approximation (7) equations were derived for uni-univalent solutes in lithium-potassium nitrate eutectic as solvent. However, as the values calculated were found to be in error by 1 to 4 orders of magnitude, the equations were not developed to include bivalent ions. Comparing the nitrate eutectic solubilities with the aqueous solubilities extrapolated to the melt temperature (10) showed that the calculated values were larger by a factor varying from 1.1 to 7000, though less than 5 in a majority of cases. A slightly closer correlation was obtained using the ideal solution equation. Although, with certain solutes, particularly of the alkali metals—e.g., NaOH, KOH (5), and Na₂O, Na₂O₂ (6)—compound formation may have altered the composition of the equilibrium solid phase and reduced the accuracy of solubilities calculated for uncombined solutes, it was evident that at present little useful information could be obtained by calculation.

Transition metal salts were generally readily soluble, probably because of stabilization of particular nearest neighbor anion configurations by ligand field forces. In the case of cobalt(II), where the chloride was considerably more soluble than the nitrate and potassium chloride itself, the suggestion of coordination was supported by the progressive shift of the 556-m μ maximum to larger wavelengths and

higher extinction coefficients. An identical shift had been found (3, 9) in very dilute cobalt chloride where the chloride-cobalt ratio reached high values—e.g., 38 to 1—and interpreted by Gruen (2) as the gradual replacement of bidentate nitrate ligands by chloride ions. It would seem that the higher cobalt chloride concentrations used here counterbalanced the lower chloride-cobalt ratios. The unusually low nickel chloride solubility was almost certainly due to the relatively insoluble nature of the complex formed. X-ray powder data and thermogravimetric analysis showed this to be a new compound and not merely nickel chloride with adhering melt. Quantitative analysis indicating chloride-nickel and nitrate-nickel ratios of between 2 and 2.5 suggested that it might be a complex ion of the type $(\text{LiK})_2\text{NiCl}_2(\text{NO}_3)_2$.

Measurements on the dehydrated solutions of initially hydrated transition metal salts showed that complete dehydration occurred without appreciable hydrolysis. The small amount of acid formed from the dehydration of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ could be accounted for by the slow reaction $\text{Co}(\text{II}) + \text{NO}_3^- \rightarrow \text{Co}_3\text{O}_4 + \text{NO}_2$ (8). The kinetic data, determined at 350° to 400° C. in sodium-potassium nitrate,

extrapolated and applied to lithium-potassium nitrate, indicated the correct order of magnitude.

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LITERATURE CITED

- (1) Freeman, J.H., Smith, M.L., *J. Inorg. Nucl. Chem.* 7, 224 (1958).
- (2) Gruen, D.M., "Fused Salts," B.R. Sundheim, ed., pp. 324-5, McGraw-Hill, New York, 1964.
- (3) Gruen, D.M., *J. Inorg. Nucl. Chem.* 4, 74 (1957).
- (4) Horsley, G.W., At. Energy Res. Estab. (Gt. Brit.), Rept. M/R 1441 (1954).
- (5) Jänecke, E., *Z. Anorg. Chem.* 188, 72 (1930).
- (6) Kohlmüller, R., *Ann. Chim.* 4, 1183 (1959).
- (7) Seward, R.P., Field, P.E., *J. Phys. Chem.* 68, 210 (1964).
- (8) Sláma, I., *Collection Czech. Chem. Commun.* 28, 1069 (1963).
- (9) Tananaev, I.V., Dzhurinskii, B.F., *Dokl. Akad. Nauk. SSSR* 134, 1374 (1960).
- (10) Tien, H.T., Harrington, G.W., *Inorg. Chem.* 2, 369 (1963).

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Densities of Molten AlCl_3 and NaCl-AlCl_3 Mixtures

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The "float" method was used to measure liquid densities of AlCl_3 and NaCl-AlCl_3 mixtures containing 52.0, 61.8, and 73.0 mole % AlCl_3 . All melts were studied over a range of temperatures and the data fitted to equations of the form $\rho = \alpha - \beta t$ by a least-squares analysis. Molar volumes showed negative deviations from additivity as large as 22%.

SALT mixtures containing AlCl_3 are useful solvents for various molten salt studies largely because of their highly acidic character. This feature has been used to advantage by Corbett (4) in the stabilization of lower oxidation states such as Bi(I), Cd(I), and Ga(I). These solvents are also optically transparent over a very wide wavelength region. This combination of high acidity and transparency makes them particularly attractive for spectrophotometric studies of lower oxidation state systems. An example of such systems, which is under study in this laboratory (1), is the lower oxidation state(s) of bismuth dissolved in NaCl-AlCl_3 mixtures. The purpose of the present work was to determine densities of these mixtures which are required for the calculation of optical extinction coefficients.

Previous density measurements on the NaCl-AlCl_3 system were done by pycnometric methods. Kryagova (6) measured the densities of several compositions between 50.2 and 67.4 mole % AlCl_3 and at temperatures from 190° to 280° C. Yamaguti (11) measured the densities of a 50 mole % AlCl_3 mixture at several temperatures between 182° and 350° C. Both of these authors reported density values larger than those reported here—e.g., for a 50 mole % AlCl_3 mixture at 250° C. values of 1.690, 1.674, and 1.639 grams per cc. were obtained by Yamaguti, Kryagova, and this work, respectively. Loss of AlCl_3 either by vaporization to a cold zone or by reaction with ambient moisture is one of the most serious sources of error in working with these systems and may explain the higher density values obtained in previous work.

EXPERIMENTAL

Density Determination. The float method for measuring density consists of measuring the temperature at which quartz floats of known density neither fall nor rise in the liquid under study. This method is capable of high accuracy and is particularly well suited to measurements on the volatile AlCl_3 -containing melts.

The floats were made by blowing a small bubble of quartz and leaving a solid quartz "tail" which could be ground off until the desired density was obtained. The float densities were determined by weighing first in air and then submerging in water using the buoyancy apparatus described by Smith and Petersen (9). The floats had a "teardrop" shape and were approximately 8 mm. in diameter and 20 mm. long.

Melts were held in 12-mm. i.d. \times 15-mm. o.d. quartz tubes which were loaded in a dry box with weighed amounts (15 to 20 grams, total) of the purified salts. Three or four floats of known density were placed in the tubes in order of decreasing density. Since the floats could not pass each other, they remained in this order and each float dropped in succession as the temperature was raised. This eliminated the problem of float identification during a run. The loaded tubes were removed from the dry box and sealed off under vacuum to a length of about 15 cm. This sealed tube was then attached to a 20-cm. length of 6-mm. quartz rod which served as a handle during the density measurements.