

*THE USE OF NON-AQUEOUS SOLVENTS IN THE STUDY OF
THE RARE EARTH GROUP*

BY B. S. HOPKINS AND L. L. QUILL

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS

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Aqueous solutions are almost invariably employed in the work which has as its object the separation of the members of the rare earth group. Differences in solubility between neighboring elements are very slight. As a result separations are slow, there are tremendous losses of expensive materials, and complete separations are almost or quite impossible. We have made a study of the solubilities of the chlorides and nitrates in various non-aqueous solvents in the hope that we might discover some solvent which has a distinctly selective action, thereby making possible more rapid, and more efficient separations. In our preliminary study we have confined our attention to anhydrous solvents and anhydrous salts. It is obvious that the greatest interest in such a study will center upon those cases in which the separations in aqueous solutions present the maximum difficulty.

Figure 1 shows the solubility of neodymium chloride in several alcohols, all of which are good solvents. The curves are regular, showing a fairly uniform increase in solubility with rising temperature. The ability to serve as a solvent increases quite regularly as we pass from the lower to the higher alcohols, methyl alcohol being an outstanding exception to this statement.

Figure 2 shows that iso-propyl alcohol is a very poor solvent for rare earth chlorides. It also shows that lanthanum chloride is slightly more soluble in both iso-propyl and propyl alcohol than is neodymium.

Figure 3 indicates that ethyl alcohol is a good solvent for lanthanum and neodymium chlorides, but in both cases the curves are not as smooth as those obtained when other alcohols are used as solvents. The behavior of ethyl chlorides indicates that complexes are easily formed. These may account for the sudden breaks in these curves. There may be some significance to the fact that at 30° both these curves drop somewhat, since similar breaks in other curves occur at about this temperature.

Ethylene glycol is a good solvent for the chlorides of neodymium and lanthanum as shown by figure 4. The curve for neodymium chloride shows a drop at 30°, but in the case of the lanthanum curve there is a marked decrease in solubility at 20°, which is followed by a surprisingly large increase at 30°. These anomalous points in the curve have been confirmed; they may be caused by the presence of a metastable state or to some other condition. It appears from these curves that the separation

of lanthanum and neodymium could be effected readily when their chlorides are extracted with ethylene glycol at 20°. This possibility is to be tested, but since these members of the group are easily separated by standard

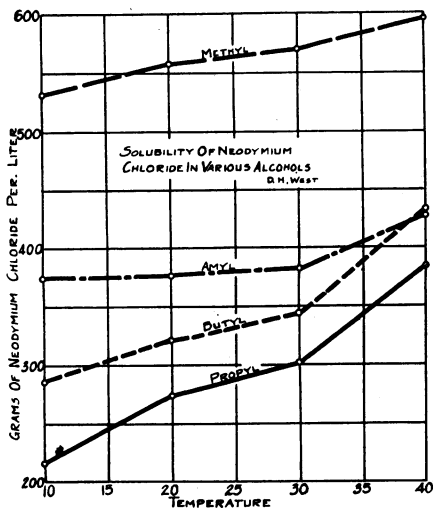


FIGURE 1

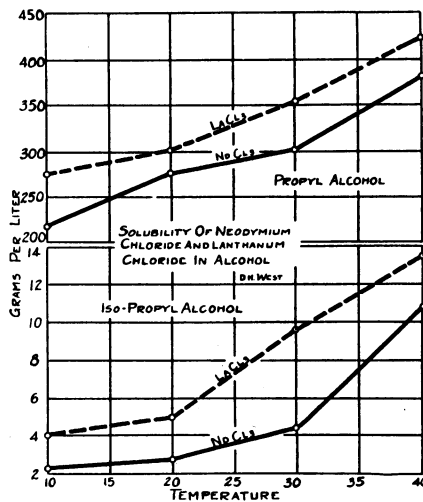


FIGURE 2

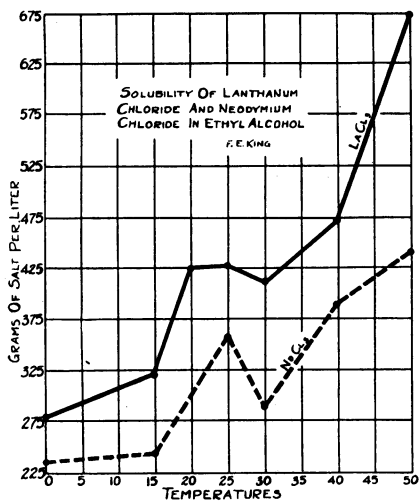


FIGURE 3

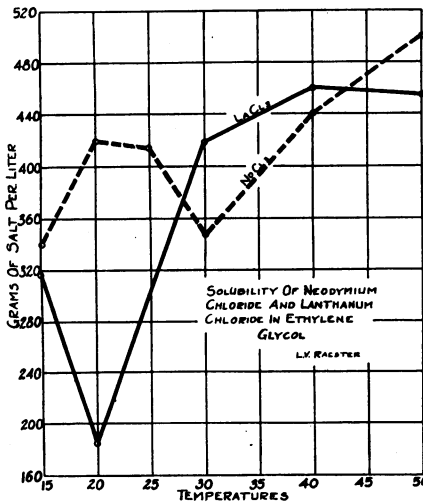


FIGURE 4

methods of procedure, there appears to be little need for such a method of separation.

In figure 5 we find a remarkable similarity in the solubilities of lanthanum and neodymium chlorides when glycerol is used as a solvent. A remarkably large dip in both curves occurs at 30°.

Turning now to the solubility of the anhydrous nitrates we find in figure 6 the atomic numbers plotted as abscissa and the solubilities at 25° as ordinates, for both dioxan and ethyl ether. It is to be observed

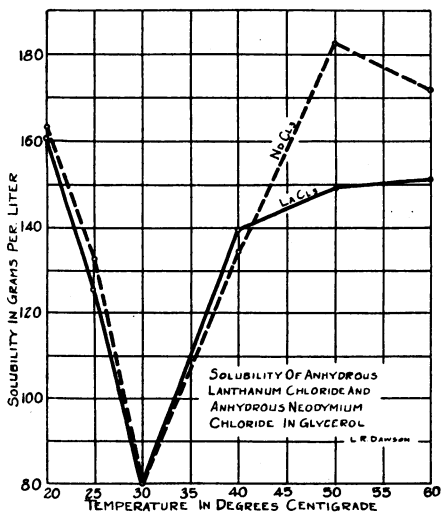


FIGURE 5

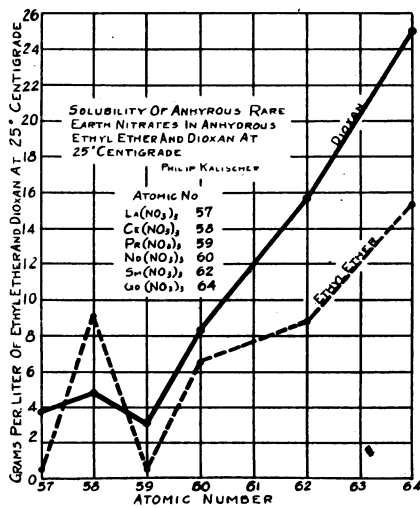


FIGURE 6

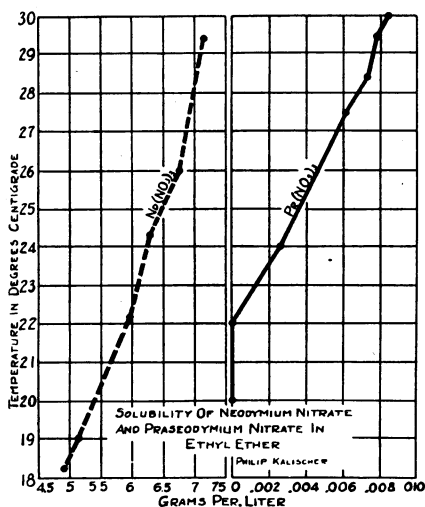


FIGURE 7

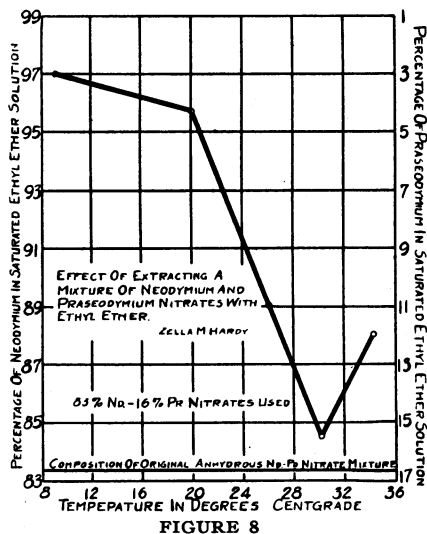
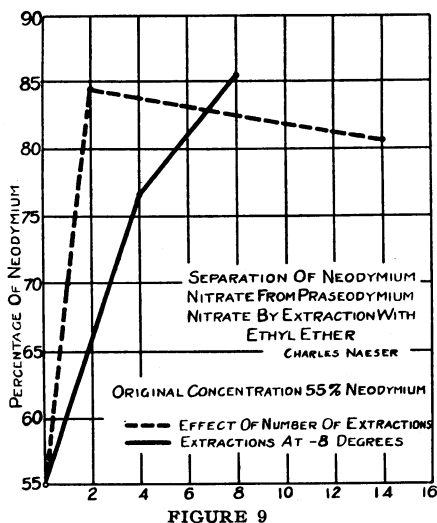


FIGURE 8

that the curves are quite similar, each one showing an abnormal value for cerium nitrate. This is not surprising since cerium has many properties in which it differs rather sharply from other members of the rare earth group. The elements of higher atomic number are more soluble in these solvents than are those of lower atomic number.

Because of the difficulty of separating the neodymium and praseodymium there is unusual interest in finding a preferential solvent for one in the presence of the other. Figure 7 shows that neither is extensively soluble in ethyl ether, but that at temperatures below 22° , neodymium nitrate is slightly soluble, while praseodymium nitrate is essentially insoluble. The first attempt to utilize this difference in solubility for the separation of these elements was accomplished by using a mixture containing 83 per cent neodymium nitrate and 16 per cent praseodymium nitrate. The material was shaken for several hours with ether at various temperatures. At 30° there was only a slight enrichment in the neodymium content of the extract as is shown in figure 8. At 10° the ether soluble material contained 97 per cent neodymium, an increase of 14 per cent in one extraction.

By modifying a Soxhlet extractor in such a manner as to permit carrying out the extraction in the vicinity of 10°C ., it was found to be possible to produce a rapid increase in the neodymium content of the extract. The dotted curve shown in figure 9 shows the rate at which this separation takes place in terms of the number of times the Soxhlet apparatus is permitted to siphon off. Starting with material containing 55 per cent neodymium, after one ex-



traction the percentage has increased to 70 per cent while two extractions yield a solution containing nearly 85 per cent neodymium. If, however, the siphon is allowed to drain for fourteen times, the proportion of neodymium in the extract is noticeably less. This is apparently due to the fact that after the ether has dissolved essentially all of the neodymium nitrate in the thimble, there is some tendency to dissolve praseodymium nitrate even at the low temperature used.

The solid curve in figure 9 shows the result of a method of fractionation by the use of our modified Soxhlet apparatus. Starting again with material containing 55 per cent neodymium an extract containing 77 per cent of this element was obtained. The solvent was then removed from the extract and the residue again extracted with ether. This second extract was found to contain about 86 per cent neodymium nitrate. By this time the fraction had become so small that a continuation of the proc-

ess was impracticable but it appeared to be possible to extract a small quantity of neodymium which was present in praseodymium. Accordingly, we selected a mixture which was composed of 94 per cent praseodymium and 6 per cent neodymium and extracted the latter with ether. The residue contained such a small quantity of neodymium that it could not be detected by spectroscopic means and we believe that this method of separation may also be applied in other cases.

*THE DETERMINATION OF THE STRUCTURES OF THE HEXAFLUORIDES OF SULFUR, SELENIUM AND TELLURIUM BY THE ELECTRON DIFFRACTION METHOD**

BY L. O. BROCKWAY AND LINUS PAULING

GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY

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The application of electron diffraction methods in the study of gas molecules was first made by Mark and Wierl,¹ who investigated the structure of a large number of molecules in this way. Using methods closely similar to theirs, and briefly discussed in the following paragraphs, we have determined the atomic configuration and interatomic distances in SF₆, SeF₆ and TeF₆.

The Debye formula² for the relative intensity as a function of the scattering angle θ for x-radiation diffracted by widely separated gas molecules with random orientation is

$$I = k \sum_i \sum_j f_i f_j \frac{\sin x_{ij}}{x_{ij}}, \quad (1)$$

in which

$$x_{ij} = 4\pi l_{ij} \frac{\sin \theta/2}{\lambda} \quad (1a)$$

with l_{ij} the distance between the i th and the j th atoms, λ the wave-length of the incident radiation, and k a constant for given experimental conditions. The summations extend over all the atoms in one molecule. For electron diffraction the x-ray-scattering factors f_i and f_j for the atoms are replaced by electron-scattering factors ψ_i and ψ_j , which were shown by Mott³ to be given by the expression

$$\psi_i = \frac{Z_i - f_i}{\left(\frac{\sin \theta/2}{\lambda}\right)^2}, \quad (2)$$