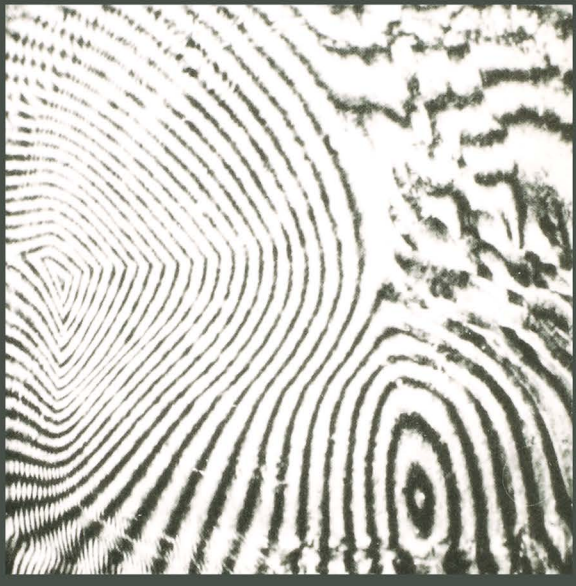
The Adam Hilger Series on Optics and Optoelectronics

KDP–FAMILY SINGLE CRYSTALS

L N RASHKOVICH



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KDP-family Single Crystals

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Translated from the Russian by Olga Shlakhova

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Series Editors' Preface

Optics has been a major field of pure and applied physics since the mid 1960s. Lasers have transformed the work of, for example, spectroscopists, metrologists, communication engineers and instrument designers in addition to leading to many detailed developments in the quantum theory of light. Computers have revolutionised the subject of optical design and at the same time new requirements such as laser scanners, very large telescopes and diffractive optical systems have stimulated developments in aberration theory. The increasing use of what were previously not very familiar regions of the spectrum, e.g. the thermal infrared band, has led to the development of new optical materials as well as new optical designs. New detectors have led to better methods of extracting the information from the available signals. These are only some of the reasons for having an *Adam Hilger Series on Optics and Optoelectronics.*

The name Adam Hilger, in fact, is that of one of the most famous precision optical instrument companies in the UK; the company existed as a separate entity until the mid 1940s. As an optical instrument firm Adam Hilger had always published books on optics, perhaps the most notable being Frank Twyman's *Prism and Lens Making.*

Since the purchase of the book publishing company by The Institute of Physics in 1976 their list has been expanded into all areas of physics and related subjects. Books on optics and quantum optics have continued to comprise a significant part of Adam Hilger's output, however, and the present series has some twenty titles in print or to be published shortly. These constitute an essential library for all who work in the optical field.

Preface

The book is intended for physicists, chemists and engineers who grow single crystals from solutions and employ them in physical research and devices.

Although the book is based on the author's research, it contains review material as well and can be used as a reference book. This is true especially as far as Chapter 1 is concerned. Chapter 1 contains nearly all the available data on the physico-chemical analysis of the systems discussed. Chapter 2 represents contemporary concepts on the crystal growth dislocation mechanism which is common for most crystals grown from low- and high-temperature solutions. The chapter on crystal growing is the shortest. The emphasis made is on the possibilities for the considerable speeding up of technological cycles without a deterioration of the crystal properties.

L N Rashkovich
June 1990

Introduction

About fifty years ago Busch discovered the second ferroelectric crystal, besides the already known rochellesalt, KH_2PO_4—otherwise known as KDP (Busch and Scherrer 1935). That was the beginning of large-scale investigations into the properties of KDP-family single crystals and their commercial applications. These fifty years of investigation are reviewed in two volumes of the journal *Ferroelectrics* (volumes 71 and 72). Let us recall the milestones in the history of these crystals. In 1938 Busch discovered the ferroelectric (and antiferroelectric) properties of KH_2AsO_4, $NH_4H_2PO_4$ and $NH_4H_2AsO_4$. In 1939 Ubbelohde discovered the ferroelectric phase transition in KD_2PO_4 (DKDP). In 1944 Zwicker and Sherrer found that KDP and DKDP possessed a significant electro-optic effect. The crystalline structure of KH_2PO_4 was described by West (1930) and then in 1953 Bacon and Pease determined the position of hydrogen atoms in this structure. The first theory of the ferroelectric phase transition in KDP was suggested by Slater in 1941.

In the 1930s to 1940s, crystals of $NH_4H_2PO_4$ (ADP), which is a crystallochemical analogue of KDP, found a fairly wide practical application. They were used as sound piezoelectric transducers in microphones, gramophones and other sound reproduction devices.

A new impetus was given to the production of the KDP-family crystals (especially KDP and DKDP) soon after the advent of lasers, when for the first time, the second harmonic of the fundamental radiation was produced at the KDP crystal using the effect of phase synchronism (Giordmaine 1962). At the present time, KDP-family crystals are the primary materials used in devices controlling laser radiation, its modulation, frequency conversion and scanning. They are manufactured in larger quantities than the sum total of all other crystals used in quantum electronics and all crystals grown from solutions in all their possible applications.

Hundreds of papers are devoted to investigation of the physical properties of the KDP-family crystals (with a general formula $(Me_1,Me_2)(H,D)_2(P,As)O_4$) and the number of such works does not diminish. The

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majority of the known data is represented in Landolt-Börnstein (1984) and in a number of reviews. For instance, Nelmes (1987) gave a summary of the structural studies, Eimerl (1987a) generalized the studies of electro-optical, linear and non-linear optical properties. The review by Courtens (1987) is devoted to mixed crystals of the spin-glass type. The theory and peculiarities of phase transitions in the KDP-family crystals are treated in more than a dozen monographs.

This book is devoted to the physical and physico-chemical problems related to growing the KDP-family crystals. Although these questions are dealt with in a great number of publications, the problem is still very important and requires further investigation because of the growing demands in optical perfection and sizes of crystals. The developing power optics need single-crystal elements with an aperture of ~ 100 cm—a fantastic size for artificial single crystals. Nevertheless, it is possible to grow such crystals. In power optics devices, powerful laser beams are being transmitted and even a slight absorption or scattering of light in a crystal may destroy the material or lead to an unacceptable distortion of the radiation characteristics. To preserve the high quality of large crystals is a more difficult task than that of increasing the sizes of crystals. But certain progress has been attained in solving this problem too. I hope the book will be useful for both industrial and research workers who study the problems of the growth and application of single crystals.

1 Phase Diagrams of the $Me_2O-P_2O_5(As_2O_5)-(H,D)_2O$ Systems in the Crystallization Region of Mono-substituted Salts

The study of phase diagrams of physico-chemical systems in which crystallization is taking place and the investigaton of phases coexisting in such systems provide the basis for improving the growth techniques and perfecting the optical properties of crystals. As far as the $Me_2O-P_2O_5(As_2O_5)-(H,D)_2O$ systems are concerned little research appears to have been done until now and there are still a considerable number of questions to be answered, particularly concerning heavy water systems.

There is in addition another important aspect of phase diagrams which deserves special attention. Substituting deuterium for hydrogen and altering an alkaline cation results in regular changes in the properties of solid and liquid phases. These problems are of some importance for both material science and solid state physics.

In the 1930s academician N S Kurnakov and his co-workers performed classical investigations of the $(NH_4)_2O-P_2O_5-H_2O$ system and particularly the $K_2O-P_2O_5-H_2O$ system. Thirty years later Barkova and Lepeshkov (1966, 1968) studied the $K_2O-P_2O_5-D_2O$ system, and Rashkovich *et al* (1967) examined the crystallization conditions and properties of $ND_4D_2PO_4$ solutions. Later the author studied similar systems with rubidium and caesium. The available material has been partially compiled by Eysseltova and Dirkse (1988).

In this chapter the systems in question are dealt with in turn. First, for each system the crystalline phases of mono-substituted salts followed by the

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dependence of the degree of deuteration of the solution on the temperature region of spontaneous crystallization are discussed. Then the data on solubility polytherms and isotherms and those on solution properties (density, conductivity, etc) are given. The last sections describe the characteristic properties of liquidus surfaces of the corresponding diagrams, general features of their topology, and the influence of kinds of cation and solvent on the topology of phase diagrams. Finally, isotopic exchange equilibrium in the liquid phase as well as between a crystal and solution is considered.

Note that in the first sections the deuteration degree, x, is taken to be the solution's deuteration degree (the ratio of heavy-water molar content to the total amount of water), unless stated otherwise.

1.1 The $[N(H,D)_4]_2O-P_2O_5-(H,D)_2O$ system

The first system to be considered is the $(NH_4)_2O-P_2O_5-H_2O$ system. This system was studied at 0, 25 and 50°C (Muromtsev and Nazarova 1938) and at 25°C (Flatt *et al* 1951). Earlier studies at 25°C are discussed by Volfkovich *et al* (1932). At 75°C the system was examined by Brosheer and Anderson (1946), and at 100°C by Wenyu (1985). Many works only described the temperature dependence of the $NH_4H_2PO_4$ solubility in water and in solutions of differing acidity. Apparently, data on the crystallization of $ND_4D_2PO_4$ were reported solely by Rashkovich *et al* (1967) and Vasilevskaya *et al* 1967.

1.1.1 Solid phase

In the whole existence region $N(H,D)_4(H,D)_2PO_4$ crystallizes only as tetragonal crystals, this habit being typical of a KH_2PO_4 crystal group. Changing the pH of the crystallization medium does not lead to the formation of new faces but affects the rate of face growth of prisms and dipyramids. Byteva (1962, 1965, 1966) showed that as pH increases from 3.5 to 6.3 this rate increases monotonically. Similar research was later carried out in more detail by Davey and Mullin (1976b). Impurities of trivalent metals combined with supersaturation, pH, temperature and stirring conditions may result in the so called tapering of crystals, i.e. non-parallel growth of prismatic faces, with the angle between them ranging from 0 to ≈ 30°C (Davey and Mullin 1974a, 1974b, 1976a, Loiacono *et al* 1982, Takubo *et al* 1984, Dam *et al* 1986). This phenomenon is also typical of other crystals of the KH_2PO_4 group. The nature of crystal morphology changes are not well understood. Thus, for instance, Aguilo and Woensdregt (1987) analysed variants of the possible equilibrium form of crystals and came to the conclusion that changing the ammonium content in solution cannot result in morphology changes, so the reason for this effect has to be sought elsewhere.

Napijala *et al* (1978) found the Curie temperature and other properties of $NH_4H_2PO_4$ crystals to depend on the pH of the solution they were grown from. They supposed that in an acid medium several NH_4^+ groups could be replaced by H_3O^+. Replacing hydrogen by deuterium is easier in an NH_4 group. This problem has not been studied in detail, however, but it is known that with the total deuteration degree $x > 0.9$ the replacement in an NH_4 group is complete, whereas in the anion the deuteration degree is less than the total one (Fukami *et al* 1986).

1.1.2 Solubility polytherms

The solubility of NH_4H_2PO in water was studied by Buchanan and Winner (1920), Volfkovich *et al* (1932), Bergman and Bochkarev (1938), Polosin (1946), Polosin and Treshchov (1953) and others. The results obtained are in good agreement and can be approximated quite well by linear relations if the values of the solubility c are taken in mass per cent. For example, Dauncey and Still (1952) gave the formula

$$c = 17.2 + 0.474\,t.$$

In 1967 Mullin and Amatavivadhana determined the solubility in the temperature range 20–40°C. For these results the author and co-workers obtained the following relation

$$c = (16.73 \pm 0.35) + (0.484 \pm 0.012)\,t \pm 0.18. \qquad (1.1)$$

The temperature dependence can be expressed by a more accurate though less convenient relation

$$\ln m = A + B/T + D \ln T$$

where m is the mole fraction of the salt and T is the absolute temperature. The following values are given (Broul *et al* 1979) for the coefficients

$$A = -11.9204 \qquad B = -1139.73\ \mathrm{K} \qquad D = 2.2684$$

or (Vogel *et al* 1983) for $t = 30$–60°C

$$A = 36.422 \qquad B = -3370.284\ \mathrm{K} \qquad D = -4.901.$$

All these relations differ at most by 0.2 wt %.

Heating $NH_4H_2PO_4$ in air results in the decomposition of the salt. This process begins at $t < 130$°C (after one hour at 130°C, less than 5 wt % of the salt has been transformed into pyrophosphate $(NH_4)_2H_2P_2O_7$; at 170°C, the transformation into pyrophosphate is complete (Rilo and Kulikov 1981)). The maximum rate of mass loss in a non-deuterated crystal is observed at ≈ 225°C, and with $x = 95\%$ at 235°C. Upon decomposition of ADP, the NH_3 group is released at a slightly lower temperature than H_2O.

If the heating is being performed in a closed container, these transformations are reversible; thus Pastor (1985), for example, melted $NH_4H_2PO_4$ at 215°C

(with a pressure < 200 atm) in a closed quartz ampoule and upon cooling no transformations of the phase composition were observed. This fact led Pastor to suggest a technique of growing crystals from the melt.

The solubility of $ND_4D_2PO_4$ in D_2O (with the deuteration degree of solution being $\approx 98\%$) was measured by the author using the concentration flow technique (Mullin 1972, p 42). The following data were obtained

Salt concentration (wt %)	35	40	44.4	50	55
Saturation temperature (°C)	20	30.4	41.1	52.9	64.8.

These results can also be approximated by a linear dependence

$$c = (26.2 \pm 0.3) + (0.446 \pm 0.006)t \pm 0.2. \tag{1.2}$$

1.1.3 Solubility isotherms

The solubility isotherms of $NH_4H_2PO_4$ in the $(NH_4)_2O$–P_2O_5–H_2O system at 25°C and 50°C are given in figure 1.1(*a*), according to the data of Muromtsev and Nazarova (1938) and of Flatt *et al* (1951). At 25°C both branches are, in fact, linear; the solubility minimum is singular and corresponds to a stoichiometric solution. The linear dependence constant of the isotherm branches are given in table 1.16. The acid branches of the isotherms intersect the straight line corresponding to the molar ratio of the solution $(NH_4)_2O/P_2O_5 = 1/2$, consequently, the ultraacid salt $NH_4H_5(PO_4)_2$ dissolves in water incongruently. At 75°C and 100°C the isotherms have the same shape.

The correlation between the concentration of solutions saturated at 30°C and their pH was studied by Byteva (1968).

The ice crystallization field in this system was examined by Kurnakov *et al* (1938). Figure 1.1(*b*) shows that in this region there is a distinct kink corresponding to solutions with molar ratio $(NH_4)_2O/P_2O_5 = 1$.

1.1.4 Properties of solutions

(a) *Density*

The concentrational dependence of the density of $NH_4H_2PO_4$ solutions with stoichiometric composition at 23°C was investigated by Chomjakow *et al* (1933). The analysis of their data yields the following dependence

$$d = 0.9965 + 0.0058c \pm 0.0005 \text{ (g cm}^{-3}\text{)}. \tag{1.3}$$

Mullin and Amatavivadhana (1967) determined solution densities at three temperatures. Their data can be generalized by the following relations:

$$\begin{aligned} &20°\text{C: } d = (0.9982 \pm 0.0008) + (0.00580 \pm 0.00005)c \pm 0.0009 \\ &30°\text{C: } d = (0.9962 \pm 0.0011) + (0.00579 \pm 0.00006)c \pm 0.0011 \\ &40°\text{C: } d = (0.9921 \pm 0.0010) + (0.00586 \pm 0.00006)c \pm 0.0010. \end{aligned} \tag{1.3a}$$

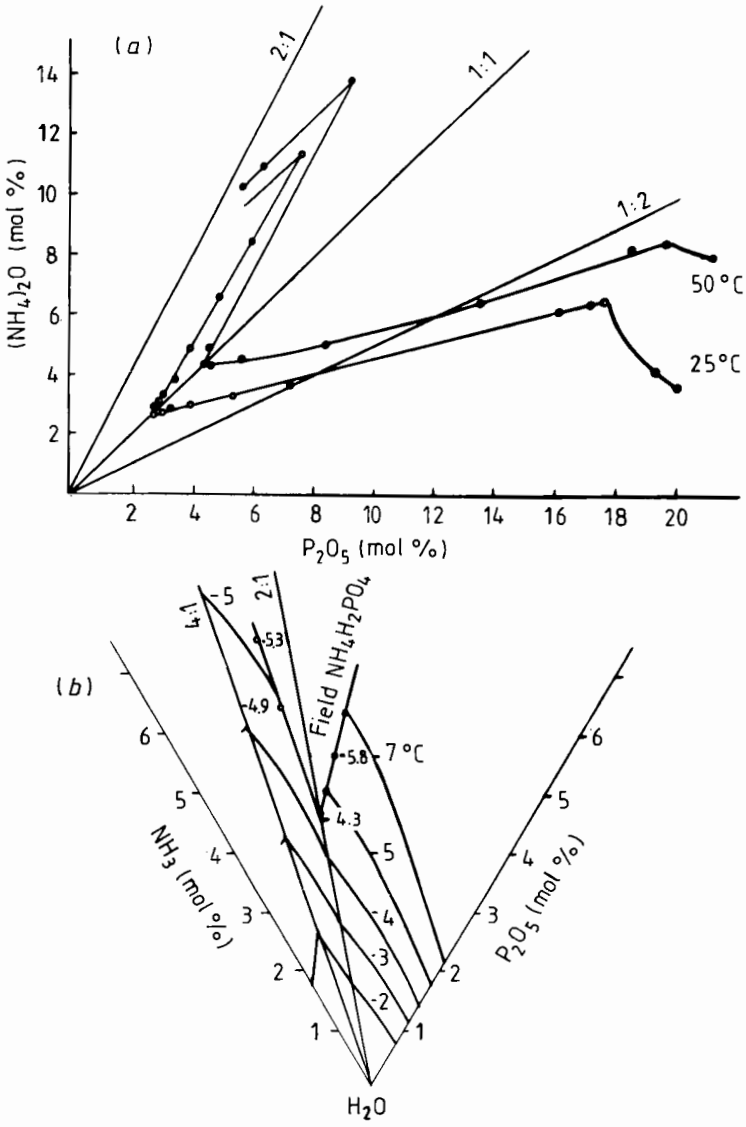

Figure 1.1 (*a*) The solubility isotherms of $NH_4H_2PO_4$: ●, Muromtsev and Nazarova (1938); ○, Flatt *et al* (1951); and (*b*) the crystallization isotherms of ice (Kurnakov *et al* 1938).

From these data and equation (1.1), we determine the saturated solution density to be

$$d_{sat} = 1.093 + 0.00282t \pm 0.003. \tag{1.4}$$

We measured the density of solutions with the salt concentration varying from 9 to 50 wt %. The experiments were carried out at different temperatures (25–75°C). In solutions with high concentrations, a temperature about 5°C above the saturation temperature was maintained. Regardless of varying temperature, the data obtained (figure 1.2) are described by equation (1.3).

If concentration is expressed in volume fractions, $c^* = cd$, then the solution density can be expressed in terms of the partial density of water d_w and that of the salt d_s

$$d = d_w + (1 - d_w/d_s)c^*. \tag{1.5}$$

Fedotova and Tsekhanskaja (1984) calculated the partial densities using, unfortunately, very old data on concentration dependencies of solution densities. They concluded that, with increasing concentration, d_s decreases and d_w increases. With rising temperature, d_s and d_w decrease (table 1.1). The result would be different if equation (1.3*a*) were used; these relations can be approximated by equation (1.5) practically with the same standard deviation and d_s and d_w prove to be independent of concentration. These results are also given in table 1.1.

The density of an $ND_4D_2PO_4$ solution with a concentration of 40 wt % measured at 35°C is 1.334 g cm^{-3}. The density of D_2O at the same

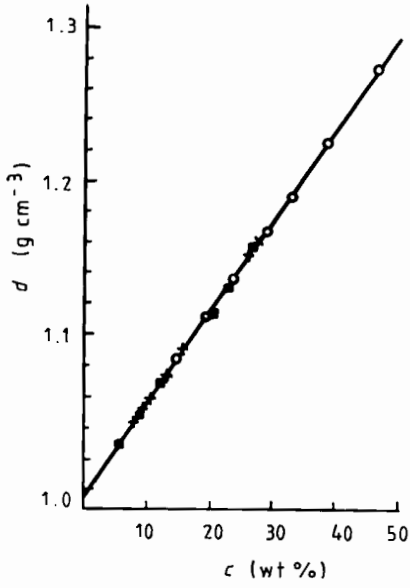

Figure 1.2 The solution density of $NH_4H_2PO_4$: +, Chomjakow *et al* (1933); □, Mullin and Amatavivadhana (1967) at 30°C; ○, Rashkovich *et al* (1967).

Table 1.1 Partial density of water and $NH_4H_2PO_4$ in solution in g cm^{-3} (crystal density 1.792 g cm^{-3}).

(*a*) From Fedotova and Tsekhanskaja (1984)

		25°C		60°C	
m	*c* (wt %)	d_s	d_w	d_s	d_w
0	0	0.998	2.15	0.981	2.12
0.02	11.5	1.000	2.04	0.982	2.01
0.04	21.0	1.005	1.94	0.987	1.92
0.06	29.0	1.013	1.85	0.995	1.83
0.08	35.0	—	—	1.007	1.75

(*b*) From Mullin and Amatavivadhana (1967) using equation (1.3*a*)

t (°C)	d_w	d_s	$B = 1 - d_w/d_s$
20	1.005 ± 0.007	1.94 ± 0.02	0.484 ± 0.001
30	1.003 ± 0.006	1.95 ± 0.02	0.486 ± 0.001
40	0.999 ± 0.005	1.97 ± 0.01	0.493 ± 0.001

temperature is 1.100 g cm^{-3}. Assuming the concentration dependence of the density to be linear we obtain

$$d = 1.100 + 0.00585c. \tag{1.6}$$

(b) *Refraction indices*

The refraction indices of solutions were measured at 40°C under a sodium lamp. The experimental data are described by linear dependences (Rashkovich *et al* 1967)

$$n_{NH_4H_2PO_4} = (1.3311 \pm 0.0002) + (0.001371 \pm 0.000009)c \pm 0.0003$$
$$n_{ND_4D_2PO_4} = (1.3276 \pm 0.0006) + (0.00140 \pm 0.00003)c \pm 0.0008. \tag{1.7}$$

When the temperature of solutions with constant concentration was changed by 10°C, the refraction index changed by 0.0015 for H_2O solutions and by 0.0010 for D_2O solutions (Rashkovich *et al* 1967). According to Takubo and Makita (1989), at 40°C $n_{NH_4H_2PO_4} = 1.3305 + 0.0013761c$. These authors obtained similar relations at 20°C and 60°C and give the temperature dependence for saturated solutions (at 0–70°C) as

$$n_{NH_4H_2PO_4} = 1.3608 + 0.00048731t.$$

(c) *Conductivity*

Watkins and Jones (1915) measured the conductivity and dissociation degree of $NH_4H_2PO_4$ in aqueous solutions with concentrations less than 2.8 wt % at 0–35°C. In such solutions the dissociation degree did not actually depend on temperature and amounted to 66% at maximum concentration. The specific conductivity of solutions with constant concentration depended linearly on temperature.

Rashkovich *et al* (1967) made measurements at a frequency of 1 kHz with an accuracy of $\pm$ 0.2%. The accuracy of the temperature measurements was ± 0.05°C, that of the concentration ± 0.1 wt%. Some of these experimental data are shown in figure 1.3. One can see that the conductivity (χ) of solutions with constant concentration increases linearly with rising temperature. Constants of the corresponding equations are given in table 1.2.

Empirical dependences of the conductivity are found to be in good agreement with the data for the constants a and b given in table 1.2. These dependences are:

for H_2O solutions,

$$a/c = 0.3961 - 0.04415\sqrt{c} \qquad b/c = 0.01432 - 0.001487\sqrt{c} \qquad (1.8)$$

for D_2O solutions,

$$a/c = 0.2485 - 0.0251\sqrt{c} \qquad b/c = 0.009495 - 0.0008011\sqrt{c}. \qquad (1.9)$$

Extrapolation of the author's data over the range of low concentrations agrees with the results obtained by Watkins and Jones (1915). These authors

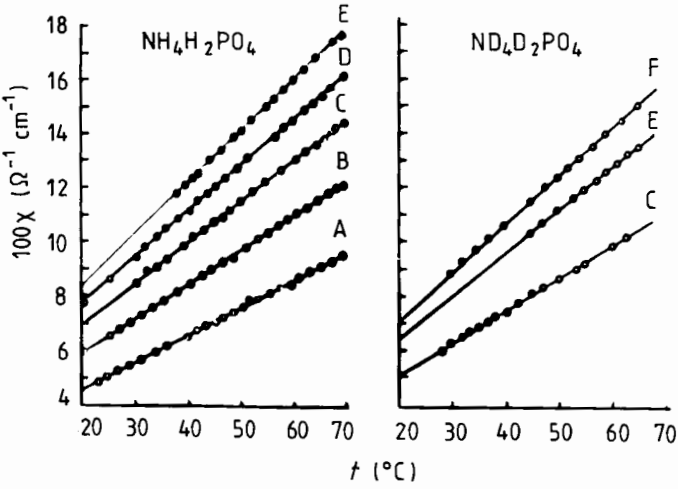

Figure 1.3 Conductivity of $N(H,D)_4(H,D)_2PO_4$ solutions of different concentration, c (wt %): A, 10; B, 15; C, 20; D, 25; E, 30; F, 39.

Table 1.2 Constants of the equation $100\chi = a + bt$. The temperature range is 25–70°C, χ is in Ω^{-1} cm^{-1}, t is in °C.

c (wt %)	a	b
(*a*) H_2O solutions		
8.6	2.31	0.0853
10	2.56	0.0991
15	3.34	0.1260
20	3.94	0.1500
25	4.43	0.1685
30	4.67	0.1890
35	4.75	0.1950
40	4.62	0.1990
(*b*) D_2O solutions		
20	2.72	0.1183
30	3.36	0.1533
39	3.55	0.1750

calculated the value of the molar conductivity as $\lambda = 66.66\,\Omega^{-1}\,\text{cm}^2$ at 25°C for solutions of 0.25 molar concentration ($c = 2.83$ wt %). Calculation by empirical formulae (equations (1.8) and (1.9)) yields $\lambda = 66.70\,\Omega^{-1}\,\text{cm}^2$.

Increasing the solution concentration at constant temperature leads first to an increase in χ and then, as a result of decreasing ion mobility and dissociation degree, χ diminishes. The concentration corresponding to maximum conductivity can easily be found by differentiating the equation for χ with respect to concentration. For H_2O solutions this concentration c_{max} is 38.1 wt % at 25°C and 39.3 wt % at 60°C. For D_2O solutions at the same temperature the maximum values of χ are 51.6 and 55.8 wt % of $ND_4D_2PO_4$, respectively. The fact that these values are higher than in the case of $NH_4H_2PO_4$ indicates a stronger interaction of dissolved particles in H_2O. The weak temperature effect on the concentration value corresponding to maximum conductivty indicates (in agreement with the results obtained by Watkins and Jones (1915)) the weak temperature effect on the dissociation degree.

Due to a lower mobility of D^+ ions as composed to H^+ ions, the specific conductivity of $ND_4D_2PO_4$ is less than that of $NH_4H_2PO_4$ solutions (c and t being equal). Therefore, regardless of the higher solubility of $ND_4D_2PO_4$, the conductivity of saturated solutions of this salt is less than in the case of $NH_4H_2PO_4$ (figure 1.4). Molar conductivity of 0.25 mol $ND_4D_2PO_4$ at 25°C is $48.04\,\Omega^{-1}\,\text{cm}^2$ as compared to $69.70\,\Omega^{-1}\,\text{cm}^2$ for