NON-LINEAR OPTICAL CRYSTALS : GROWTH AND APPLICATIONS

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Lasers today have found a wide spectrum of applications in fields as diverse as scientific research, industry, defence, medicine and entertainment. Most of them required light of specific wavelength or frequency. However such needs are often a little difficult to satisfy because only limited number of frequencies - often only two or three - are available from any individual laser source. Though some tunable lasers are being developed now-a-days, their ranges of tuning are limited. To cover all the useful ranges of the electromagnetic spectrum, generation of a broad spectrum of frequencies ranging from ultra-violet (UV) to near infra-red is very essential.

Non-linear optical crystals such as Potassium dihydrogen phosphate (KDP), Ammonium dihydrogen phosphate (ADP), Potassium titanyl phosphate (KTP), L-Arginine phosphate (LAP), Lithium Niobate etc., play a major role in generating frequencies of a wide range of electromagnetic spectrum. Propagation of an electromagnetic wave in a nonlinear medium gives rise to vibrations at harmonics of fundamental frequency of the wave. Number of wavelengths available from a laser source is being increased in this way by a nonlinear crystal ; wavelengths both longer and shorter than the original can be produced.

Apart from their nonlinear optical applications, some of these crystals play a primary role in devices controlling and modulating laser radiation because of their inherent electro-optic response. Potassium dihydrogen phosphate (KDP) is one of the very few crystals used in electro-optic devices to modulate light waves in laser optic communications and other many applications. It has a wide transparency (0.7 to 1.8μm) in the useful range. Its non-linear optical co-efficient is 4.35×10^{-13} m/v and its electro-optic co-efficient (r_{63}) is 10.5×10^{-12} m/v and that of (r_{41}) is 8.3×10^{-12} m/v. Ammonium dihydrogen phosphate has a transparency range of 0.8 to 1.5 μm, non-linear optical co-efficient of 5.28×10^{-13} m/v and its electro-optic co-efficient (r_{63}) is 8.5×10^{-12} m/v and that of (r_{41}) is 24.5×10^{-12} m/v.

Growth of these crystals and fabrication of non-linear optical and electro-optical devices from them is one of the important areas of research in Science and Technology.

Potassium dihydrogen phosphate and Ammonium dihydrogen phosphate crystals are being crystallized by low temperature solution growth method. Saturated solution at higher temperature is prepared using recrystallized salts and triply distilled water. In order to improve the purity of the raw material or in other words to reduce the concentration of some specific impurities in the solution, say iron content, the raw material is synthesized in the laboratory itself, which results in high stability of the saturated solution compared to the one prepared by using commercially available salts. Determination of metastable zone width - a study of the stability of the saturated solution - is carried out, which reveals that the solution with laboratory synthesized salt gives higher zone width which enables faster cooling rates in a wide range of temperatures. Macro-impurities which are responsible for heterogeneous nucleation are separated out from the solution by filtering it with 0.2 micron nucleation filter.

Seed of required dimension is prepared from a good quality crystal by cutting it with wet-thread mechanism and then it is lapped and polished and mounted on a rotating platform. This set-up is kept inside a hermetically sealed crystallizer specially designed for better sealing and the solution is transferred. Constant temperature bath with a controlling accuracy of ±0.01°C is used to maintain the temperature and to adopt the pre-planed cooling rate. Temperature is reduced until the solution reached room temperature equilibrium state.

Grown crystal is harvested and then its quality and perfection are assessed by imaging the growth or any microscopic imperfections present in it by X-ray topography. Then it is sliced on a specific direction for device fabrication according to the application of the device. Sliced elements are lapped and beam-in and beam-out faces are polished for optical quality. Second, Third, Forth and Fifth Harmonic Generation elements are fabricated from the grown KDP and ADP crystals. Necessary device parameters like Walk-off length, Walk-off angle, etc., are being considered during fabrication. Energy conversion efficiency of the fabricated elements are studied with Q-switched Nd-YAG laser source of wavelength 1.06 μm.

Optical elements for electro-optic modulation cells are fabricated both for longitudinal and transverse modes of modulation, from the grown crystals. Suitable housing is made for the fabricated cells and their electro-optic response is studied using He-Ne laser source.

KDP and ADP are isomorphus crystals belonging to the same tetragonal class with point group of -42m and form solid solutions with full range of compositions. But morphology of the mixed crystals changes with compositions and only crystals with habitual morphology can be obtained from the two end regions of the mixed composition series. Growth imperfections present in the mixed crystals grown with different compositions are studied by X-ray Topography. Variation in lattice parameters with composition is studied by powder as well as single crystal X-ray structural refinement method. Basically, KDP is a ferroelectric material, shows a transition from its paraelectric state at 123 K whereas ADP shows an antiferroelectric transition at 148 K. Due to the interaction between the ferroelectric and antiferroelectric components, spin-glass state is existing in the middle range compositions.

Growth parameters optimization, imperfection studies and quality assessment, device fabrication and their performance studies etc., will be presented in this paper.

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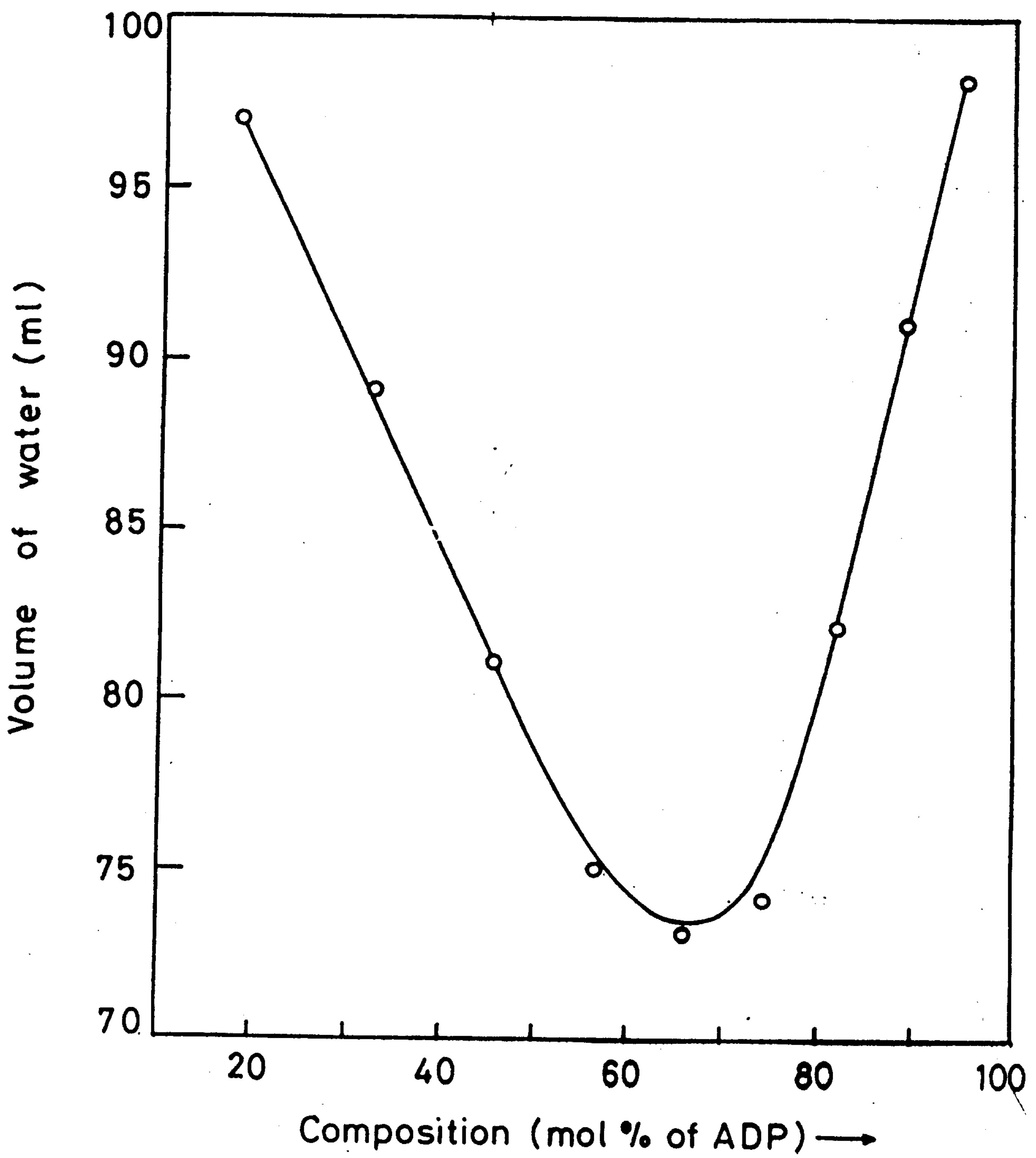
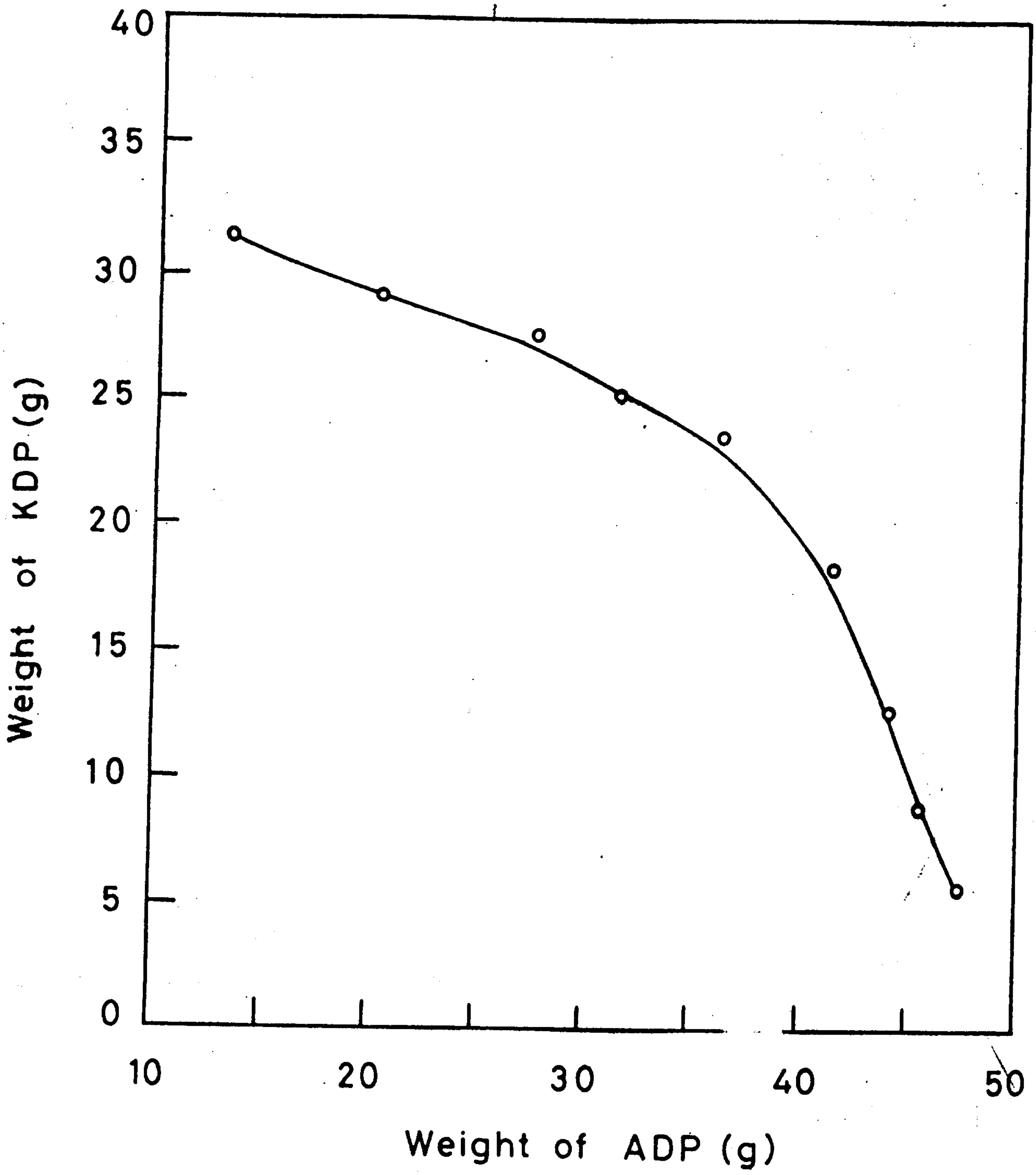
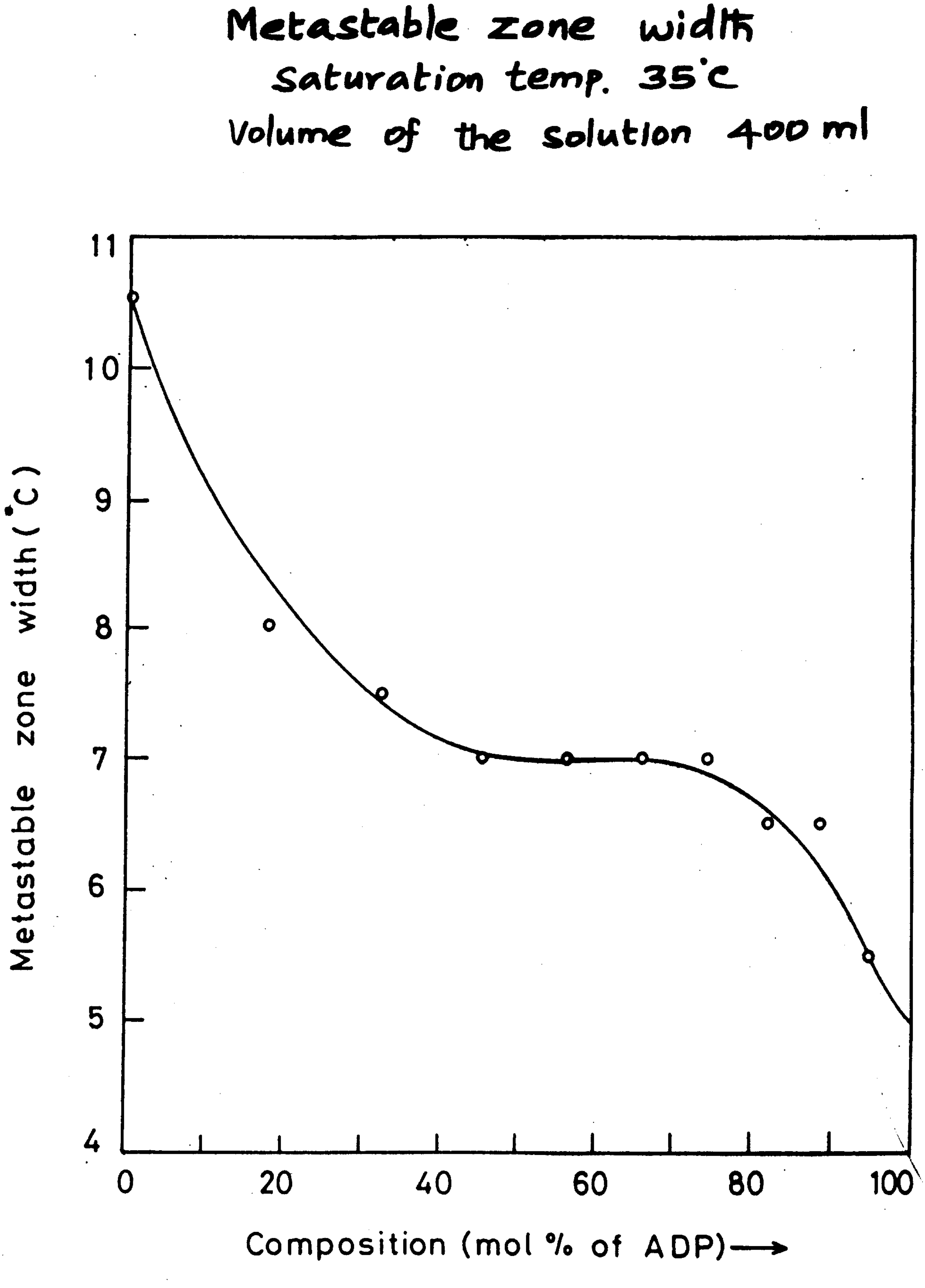
Level of Undersaturation

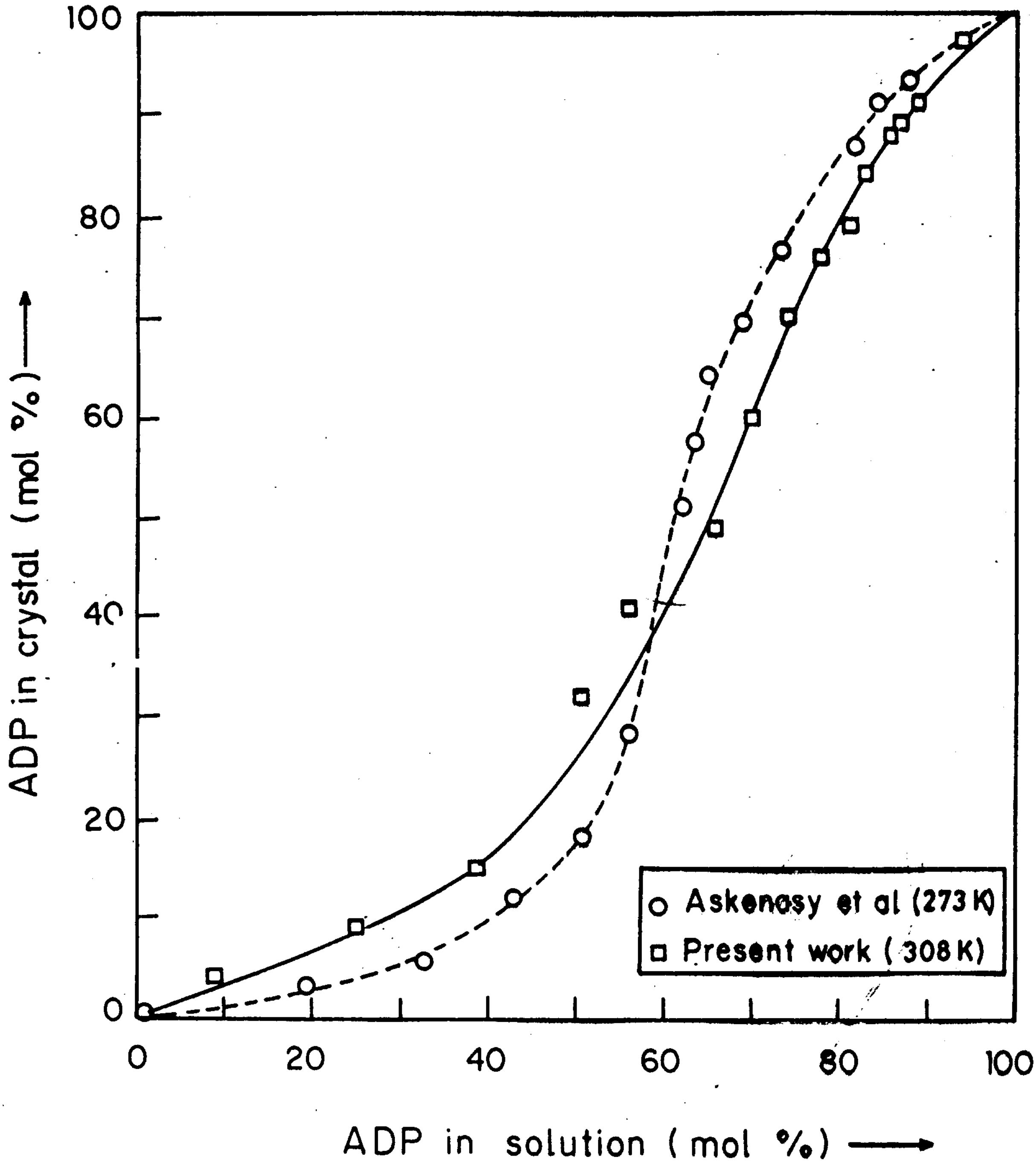


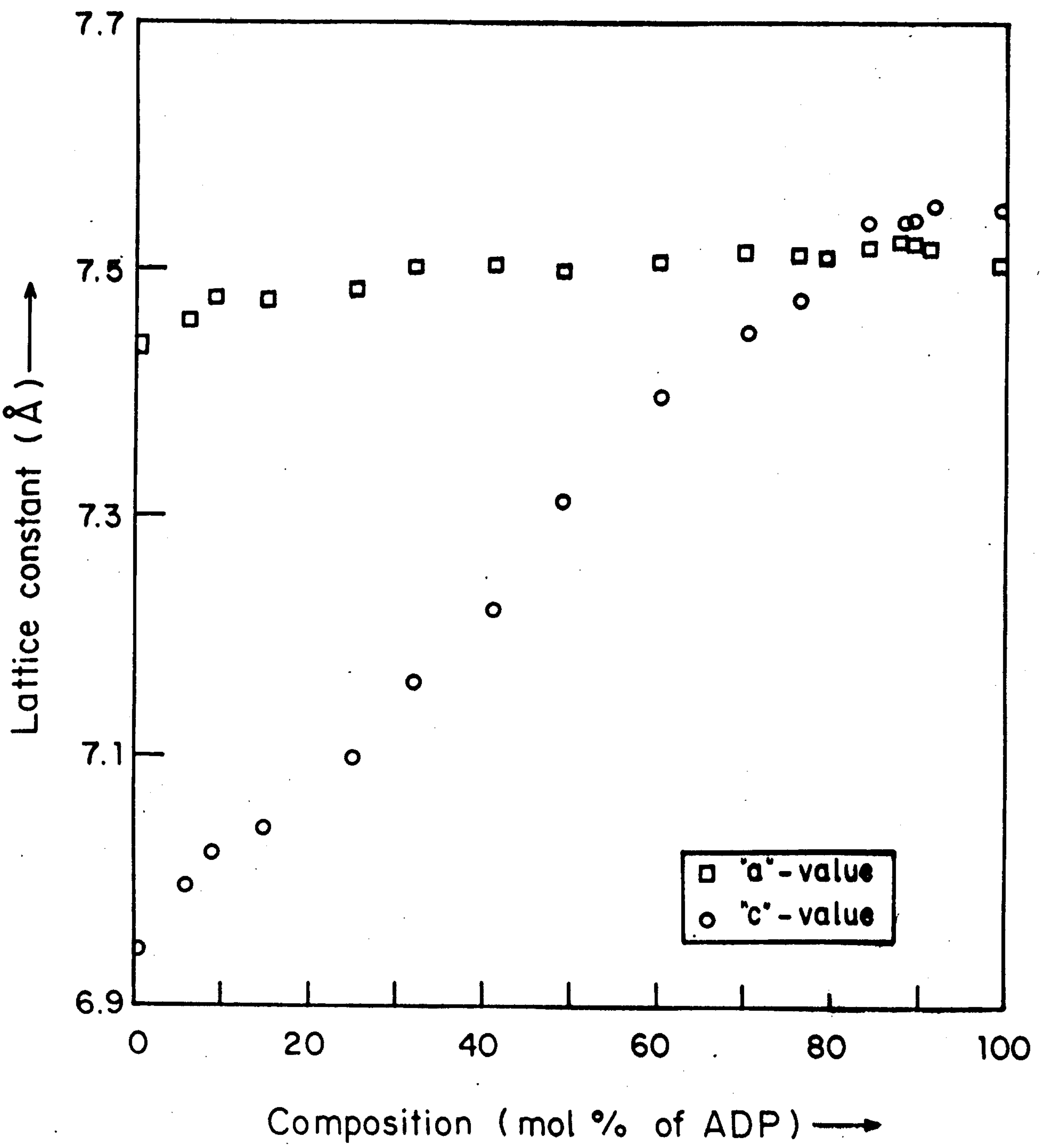
Mutual Solubility at 35°C
(in 100 ml)



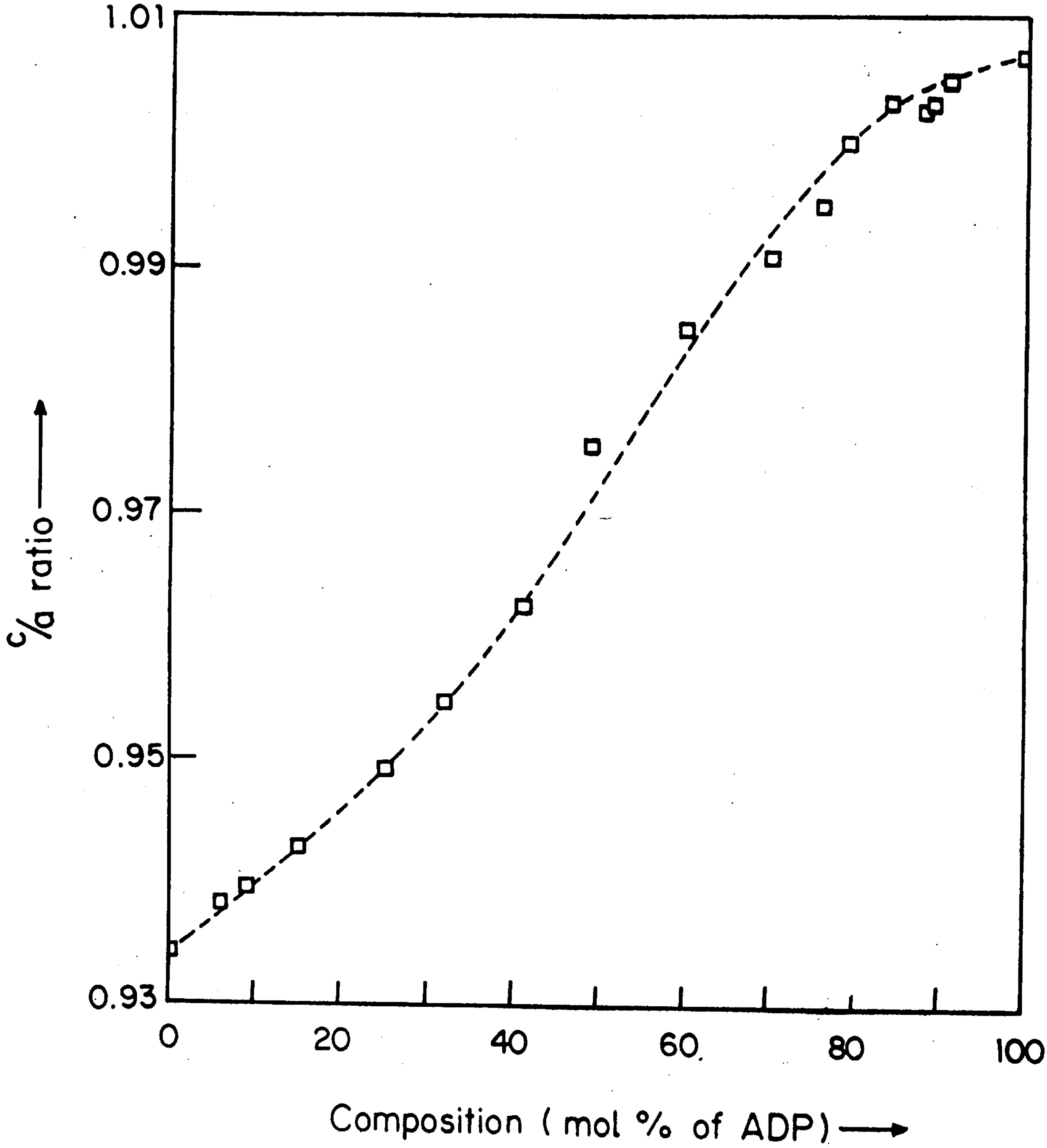


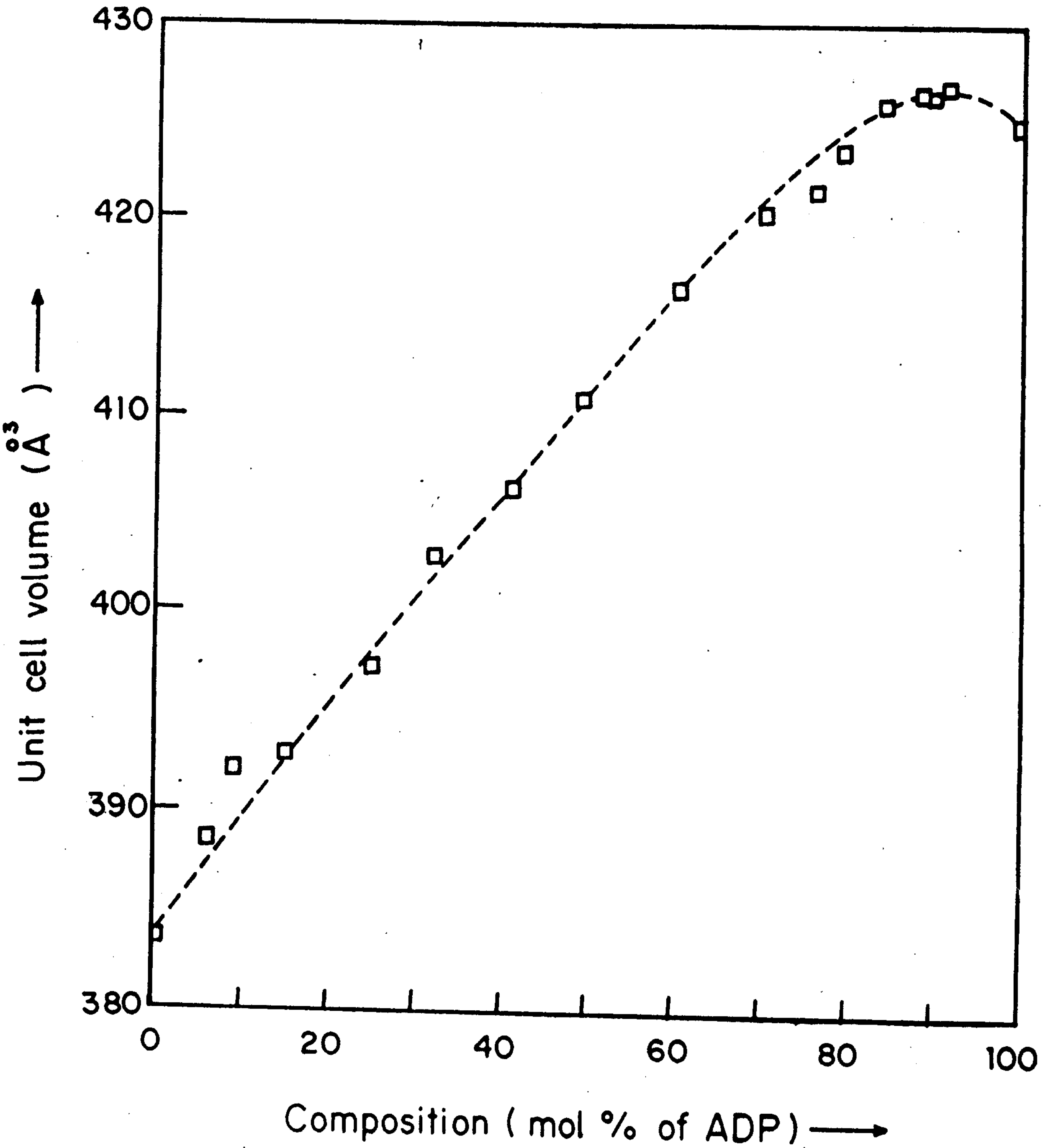
Metastable zone width
Saturation temp. 35°C
Volume of the solution 400 ml
11
10
9
8
7
6
5
4
Metastable zone width (°C)
0
20
40
60
80
100
Composition (mol % of ADP)⟶


ADP in crystal (mol %)
ADP in solution (mol %)
Askenasy et al (273 K)
Present work (308 K)
0
20
40
60
80
100
0
20
40
60
80
100



7.7
7.5
7.3
7.1
6.9
Lattice constant (Å) ⟶
0
20
40
60
80
100
Composition (mol % of ADP) ⟶
"a"-value
"c"-value


1.01
0.99
0.97
0.95
0.93
c/a ratio
0
20
40
60
80
100
Composition (mol % of ADP)



Unit cell volume (Å^3)
430
420
410
400
390
380
0
20
40
60
80
100
Composition (mol % of ADP)