CHAPTER 3

RESULTS

3.1 Experimental procedure

The effect of electrolytes on the temperature of sound velocity maximum (TSVM) in water was studied by measuring ultrasonic velocities in the aqueous electrolyte solutions in the temperature range 64-80°C. The accuracy in velocity measurement is ± 0.05 m s^{-1}. The details of the experimental method of determination of velocity together with the method of diffraction correction employed are described in Chapter 2. However, the following aspects, characteristic to measurements at high temperatures, need a special mention.

1. Solutions of desired concentration were prepared by weighing the samples using triple distilled degassed water to avoid formation of air bubbles at high temperatures which broaden the dip of the voltage variations across the quartz transducer observed in VTVM and hence limit the accuracy of velocity determination.
2. At each temperature usually six to eight measurements were made and the average value of velocity was recorded. The temperature gradients inside the experimental solution were minimised by stirring the contents of the interferometric cell periodically.
3. Solutions were maintained at each temperature for an hour and measurements were made after attainment of the thermal equilibrium
4. The temperature of the experimental solution was measured using a bead-type thermistor which forms one arm of a constant current Wheatstone bridge followed by Chopper-stabilized operational amplifier as null detector and VTVM as indicator.
5. To avoid any possible change of concentration of the solution, the interferometer was refilled with fresh solution for every three hours.

The symbols used in the tables that follow in Sections 3.2 and in Chapters 4 and 5 are explained in Table 3.1.1

Table 3.1.1. Explanation of symbols used and their units

Symbol	Significance	Units
u	Ultrasonic velocity	m s^{-1}
t	Temperature	°C
w	Weight fraction of solute	
m	Molality	mole kg^{-1}
u_2°	Ultrasonic velocity in the electrolyte at O°C	m s^{-1}
α	Temperature coefficient of ultrasonic velocity in the electrolyte	m s^{-1} $°C^{-1}$
$(T_s)_{id}$	TSVM in the solution for ideal mixing	°C
$(T_s)_{exp}$	Experimental TSVM in the solution	°C
ΔT_{str}	Structural contribution to the shift in TSVM in the solution	°C
ΔT_{obs}	The observed shift in TSVM in the solution	°C
w_1	Weight fraction of water	
w_2	Weight fraction of electrolyte 1	
w_3	Weight fraction of electrolyte 2	
α_1	Temperature coefficient of ultrasonic velocity in the electrolyte 1	m s^{-1} $°C^{-1}$
α_2	Temperature coefficient of ultrasonic velocity in the electrolyte 2	m s^{-1} $°C^{-1}$

3.2 Ultrasonic velocity versus temperature in dilute aqueous electrolytes

The electrolytes used in the present work are of A.R. grade quality. Double distilled degassed water was used to prepare solutions. Solutions of desired concentration were prepared by weighing the samples. The sulphates used are anhydrous. Anhydrous $LiSO_4$ was prepared by heating $Li_2SO_4H_2O$ at 700°C for several hours. Anhydrous Na_2SO_4 and K_2SO_4 were obtained by heating the salts for 24 hours at 200°C and 400°C respectively.

Ultrasonic velocity was measured as a function of temperature in the range 64 - 80°C at intervals of $\simeq$ 2°C in aqueous solutions of Li_2SO_4, Na_2SO_4, K_2SO_4, $MgSO_4$, $(NH_4)_2SO_4$, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$, NH_4Cl, NH_4Br and NH_4I. The data (diffraction corrected) are presented in Tables 3.2.2 to 3.2.13 and shown graphically in Figs. 3.2.2 to 3.2.13. In all cases the shape of the velocity - temperature curves are parabolic and similar to that for pure water. Hence a transparent template of the curve for water (shown graphically in Fig. 3.2.1 and the data presented in Table 3.2.1) was used to fix TSVM. The accuracy in fixing TSVM is ± 0.2°C.

Table 3.2.1 Ultrasonic velocity (u) versus temperature (t) for pure water

t	u
67.7	1554.34
69.1	1554.78
70.1	1555.20
72.1	1555.36
74.0	1555.44
76.1	1555.36
77.2	1555.24
78.4	1555.12
79.0	1554.99

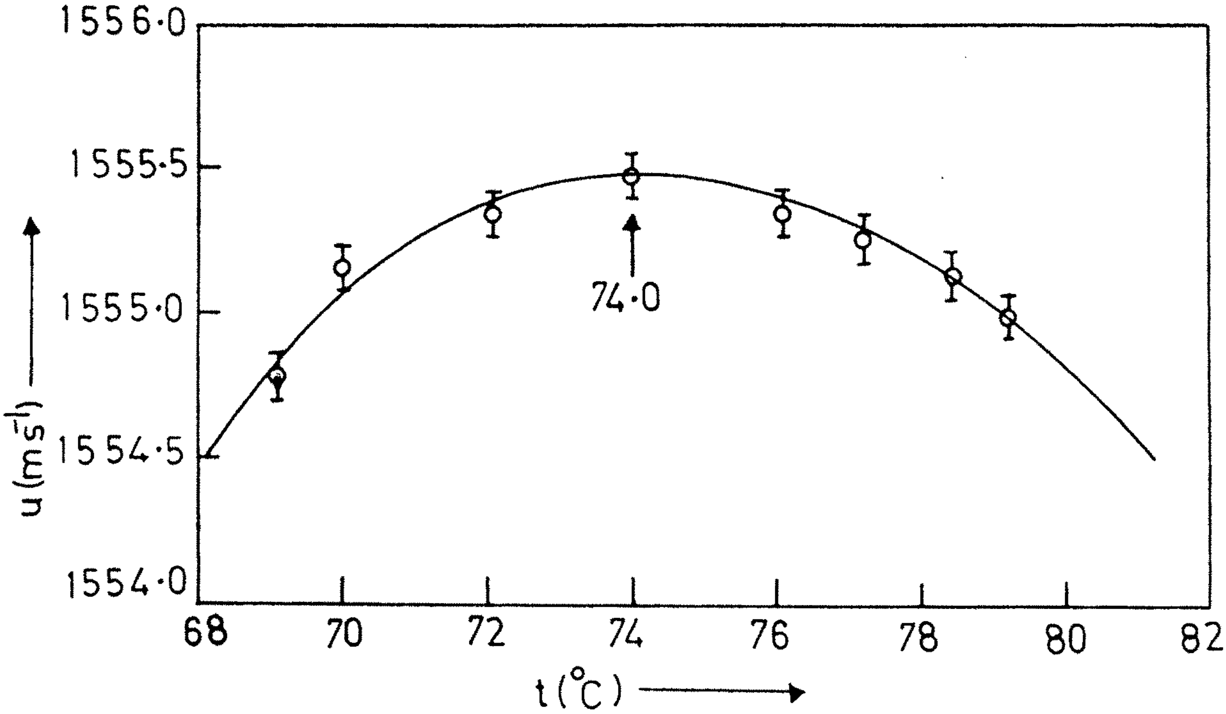

Fig. 3.2.1: Ultrasonic velocity (u) versus temperature (t) for pure water.

TABLE 3.2.2 Ultrasonic velocity (u) as a function of temperature (t) in aqueous solutions of lithium sulphate

t	u	t	u
w = 0.0061; m = 0.0558		w = 0.0424; m = 0.4073	
69.5	1558.75	68.9	1599.55
71.7	1559.02	71.0	1599.72
74.2	1559.50	72.7	1599.88
75.5	1559.40	74.7	1599.77
77.8	1559.15	76.6	1599.70
79.7	1558.85	78.2	1599.32
w = 0.0105; m = 0.1037		w = 0.0590; m = 0.5774	
70.2.	1563.75	67.9	1610.70
72.3	1564.00	69.8	1611.08
74.1	1564.16	71.9	1611.22
75.9	1564.10	73.9	1611.15
77.8	1563.97	75.8	1611.00
79.3	1563.62	77.5	1610.67
w = 0.0220; m = 0.2045		w = 0.0780; m = 0.7722	
70.1	1573.77	67.1	1618.52
71.8	1574.07	68.7	1618.80
73.5	1574.15	70.5	1618.92
75.3	1574.13	72.2	1618.92
77.1	1573.93	74.1	1618.65
79.1	1573.75	75.8	1618.50
		76.9	1618.46
w = 0.0328; m = 0.3086			
69.1	1584.37		
70.8	1584.80		
72.9	1584.95		
74.9	1584.95		
76.0	1584.72		
76.9	1584.68		

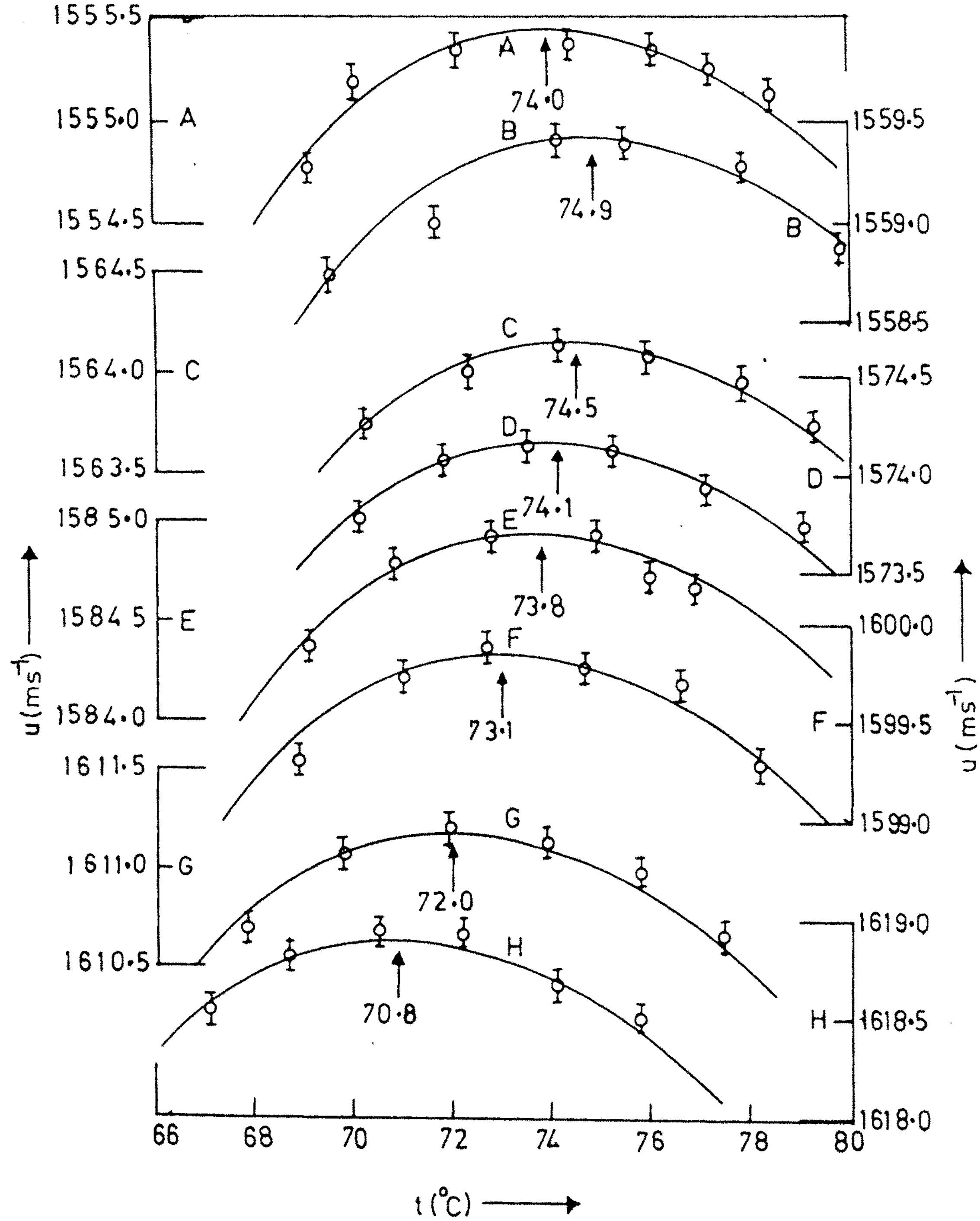

Fig. 3.2.2: Ultrasonic velocity (u) versus temperature (t) in aqueous lithium sulphate at different weight fractions.

A. Pure water; B. w = 0.0061; C. w = 0.0105; D. w = 0.0220; E. w = 0.0328; F. w = 0.0424; G. w = 0.0590; H. w = 0.0783.

TABLE 3.2.3 Ultrasonic velocity (u) as a function of temperature (t) in aqueous solutions of sodium sulphate

t	u	t	u
w = 0.0141; m = 0.1017		w = 0.0471; m = 0.3522	
69.1	1563.40	66.1	1589.55
71.3	1563.63	67.9	1589.80
72.9	1563.75	70.1	1589.80
74.8	1563.70	71.9	1589.71
76.5	1563.62	73.5	1589.38
78.1	1563.35	74.2	1589.20
w = 0.0250; m = 0.2018		w = 0.0563; m = 0.4329	
67.6	1575.65	65.2	1596.60
69.1	1576.00	66.8	1596.87
71.1	1576.10	68.3	1596.98
73.1	1576.10	70.0	1596.95
75.0	1576.04	71.8	1596.68
77.1	1575.65	73.5	1596.55
w = 0.0332; m = 0.2762		w = 0.0680; m = 0.5159	
67.1	1581.55	64.2	1606.87
69.0	1581.85	65.8	1607.10
71.0	1581.92	67.8	1607.23
72.5	1581.80	69.5	1607.05
74.2	1581.75	71.8	1606.92
76.2	1581.32	73.5	1606.55

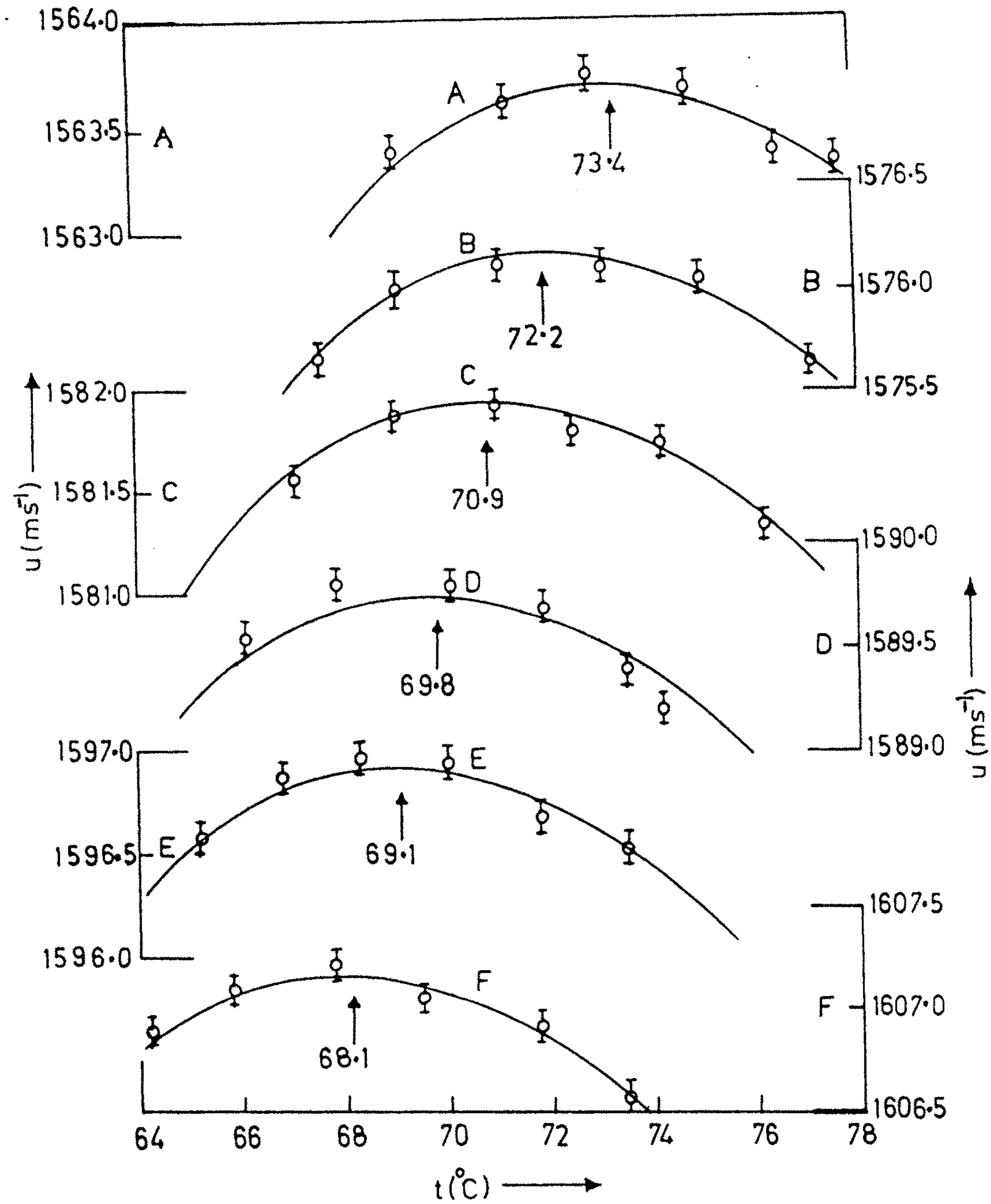

Fig. 3.2.3: Ultrasonic velocity (u) versus temperature (t) in aqueous sodium sulphate at different weight fractions.

A. w = 0.0141; B. w = 0.0250; C. w = 0.0332; D. w = 0.0471; E. w = 0.0563; F. w = 0.0680.

TABLE 3.2.4 Ultrasonic velocity (u) as a function of temperature (t) in aqueous solutions of potassium sulphate.

t	u	t	u
w = 0.0123; m = 0.0713		w = 0.0425; m = 0.2750	
68.4	1559.54	65.2	1581.47
70.1	1560.05	66.9	1581.78
71.9	1560.12	69.0	1581.87
73.9	1560.15	70.8	1581.68
76.2	1560.10	72.9	1581.58
77.7	1559.75	74.5	1581.20
w = 0.0204; m = 0.1420		w = 0.0556; m = 0.3383	
67.9	1568.45	64.8	1585.98
69.8	1568.77	66.7	1586.21
71.2	1568.88	68.5	1586.25
73.1	1568.87	70.8	1586.13
75.0	1568.62	72.8	1585.92
76.8	1568.27	74.8	1585.60
w = 0.0319; m = 0.1882		w = 0.0631; m = 0.3912	
66.8	1572.82	64.2	1596.11
68.9	1573.11	65.9	1596.27
70.5	1573.13	67.9	1596.28
72.8	1572.90	69.8	1596.23
74.8	1572.75	71.4	1596.05
76.0	1572.56	72.9	1595.60

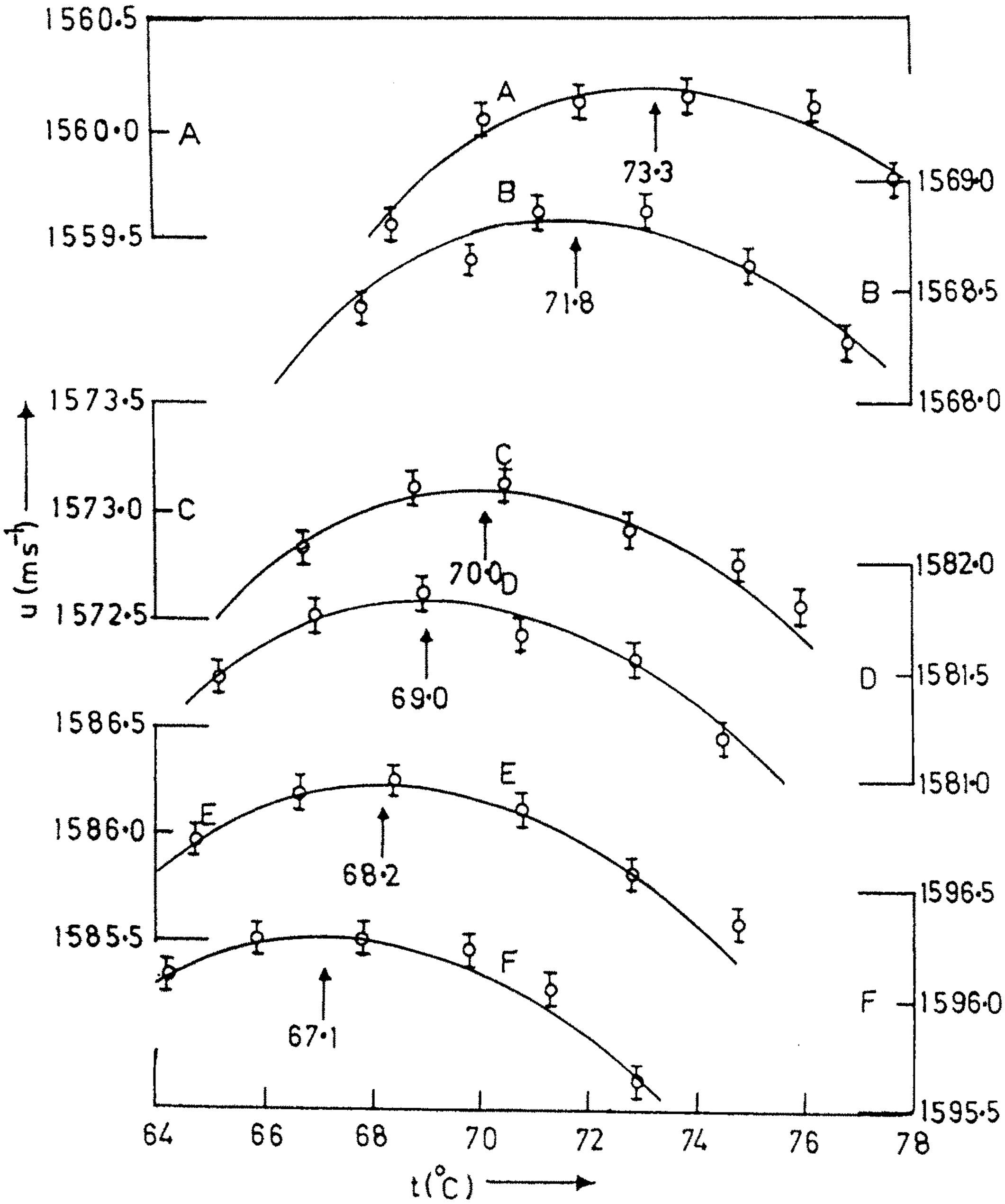

Fig. 3.2.4: Ultrasonic velocity (u) versus temperature (t) in aqueous potassium sulphate at different weight fractions.

A. w = 0.0123; B. w = 0.0201; C. w = 0.0319; D. w = 0.0425; E. w = 0.0556; F. w = 0.0631.

TABLE 3.2.5 Ultrasonic velocity (u) as a function of temperature (t) in aqueous solutions of magnesium sulphate

t	u	t	u
w = 0.0071; m = 0.0598		w = 0.0480; m = 0.4156	
69.7	1559.25	68.1	1576.37
71.3	1559.58	69.6	1576.78
73.1	1559.80	71.8	1576.87
74.9	1559.91	73.9	1576.80
76.9	1559.68	75.8	1576.52
78.7	1559.57	77.2	1576.14
w = 0.0144; m = 0.1209		w = 0.0601; m = 0.5392	
69.5	1563.20	67.9	1578.75
71.2	1563.43	69.8	1578.92
72.8	1563.77	71.8	1578.93
74.7	1563.78	73.8	1578.75
76.8	1563.65	75.7	1578.45
78.3	1563.45	77.0	1578.35
w = 0.0213; m = 0.1906		w = 0.0715; m = 0.6398	
68.8	1569.22	66.5	1579.77
70.8	1569.75	68.1	1580.12
72.7	1569.83	69.8	1580.33
74.8	1569.77	72.0	1580.22
77.0	1569.68	74.2	1580.03
78.7	1569.47	76.0	1579.55
w = 0.0372; m = 0.3240			
68.4	1574.67		
69.7	1574.95		
71.8	1575.18		
73.9	1575.13		
75.9	1575.01		
77.8	1574.88		

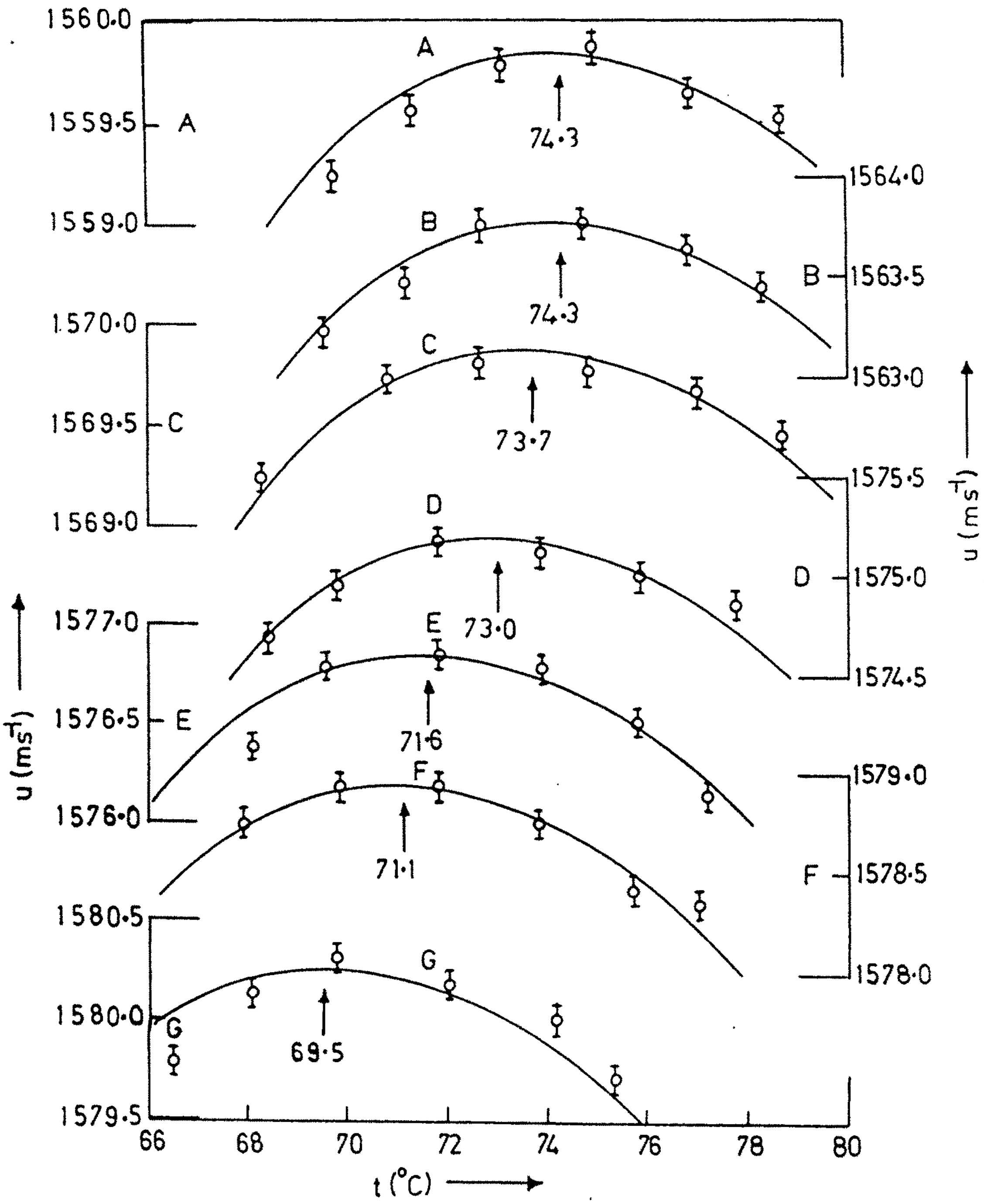

Fig. 3.2.5: Ultrasonic velocity (u) versus temperature (t) in aqueous magnesium sulphate at different weight fractions.

A. w = 0.0071; B. w = 0.0144; C. w = 0.0213; D. w = 0.0372; E. w = 0.0480; F. w = 0.0601; G. w = 0.0720.

TABLE 3.2.6 Ultrasonic velocity (u) as a function of temperature (t) in aqueous solutions of ammonium sulphate.

t	u	t	u
w = 0.0090; m = 0.0688		w = 0.0434; m = 0.3438	
68.5	1560.20	67.1	1587.68
69.5	1560.53	68.3	1587.92
71.2	1560.69	69.9	1588.10
72.4	1560.73	71.6	1588.11
73.4	1560.85	73.4	1587.92
75.5	1560.73	75.3	1587.80
77.9	1560.42		
w = 0.0213; m = 0.1653		w = 0.0511; m = 0.4079	
67.9	1569.41	65.8	1594.37
69.7	1569.68	67.2	1594.70
71.8	1569.90	69.1	1594.81
73.8	1569.90	70.8	1594.80
75.7	1569.71	72.5	1594.75
77.8	1569.52	74.2	1594.42
w = 0.0301; m = 0.2351		w = 0.0681; m = 0.5764	
67.9	1577.35	65.1	1602.20
69.4	1577.57	66.6	1602.46
70.9	1577.72	68.0	1602.60
72.9	1577.71	69.8	1602.58
74.4	1577.52	71.7	1602.35
76.4	1577.43	74.0	1602.17

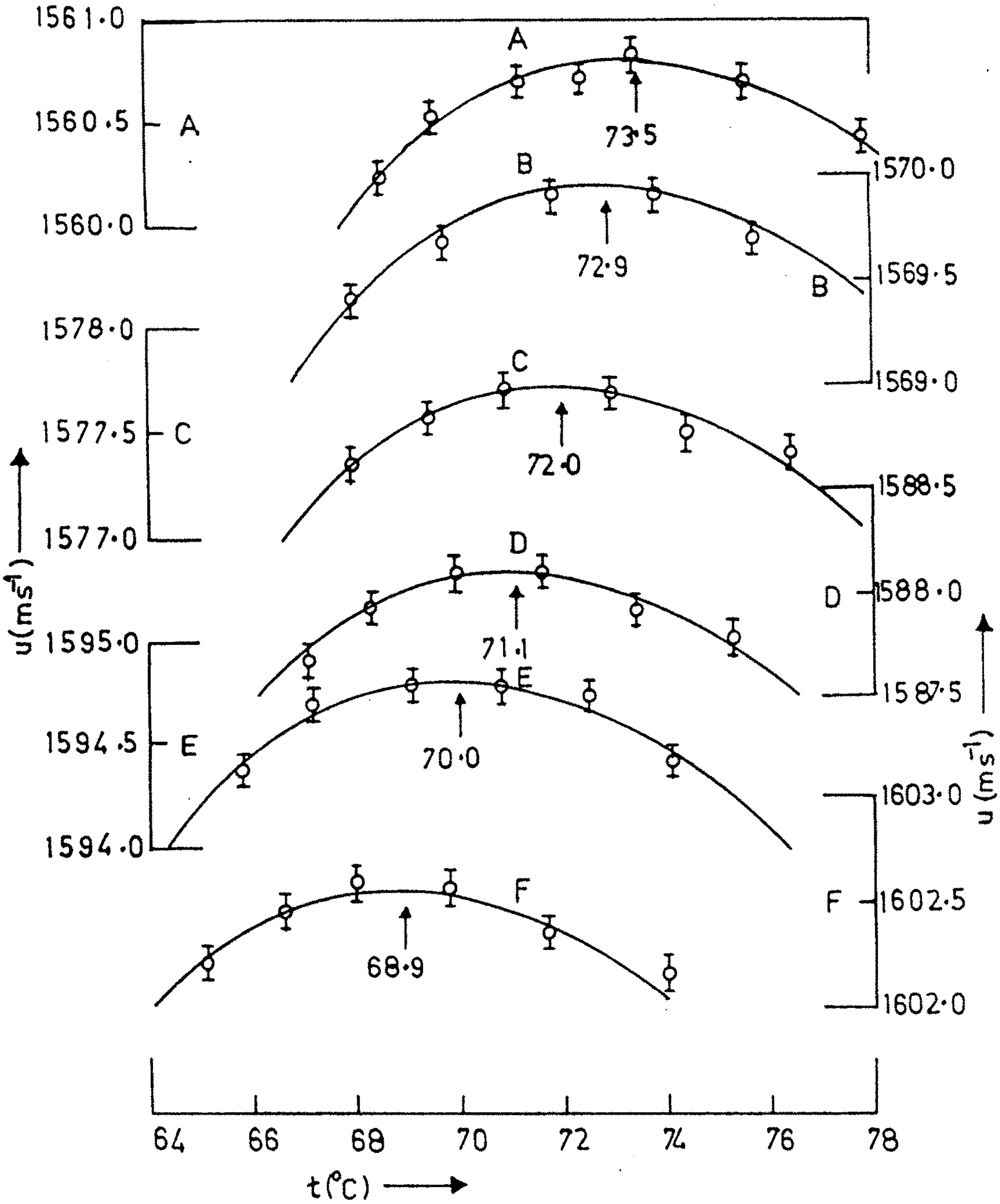

Fig. 3.2.6: Ultrasonic velocity (u) versus temperature (t) in aqueous ammonium sulphate at different weight fractions.

A. w = 0.0090; B. w = 0.0203; C. w = 0.0301; D. w = 0.0434; E. w = 0.0511; F. w = 0.0681.

TABLE 3.2.7 Ultrasonic velocity (u) as a function of temperature (t) in aqueous solutions of magnesium chloride

t	u	t	u
w = 0.0091; m = 0.1491		w = 0.0484; m = 0.8452	
69.8	1559.25	69.1	1570.25
71.3	1559.44	70.7	1570.72
72.9	1559.57	72.4	1570.83
74.8	1559.76	74.2	1570.92
76.9	1559.62	76.1	1570.73
78.5	1559.31	77.9	1570.63
w = 0.0142; m = 0.2432		w = 0.0542; m = 0.8946	
69.2	1562.80	68.8	1571.61
71.2	1563.51	70.4	1571.93
73.0	1563.37	72.1	1572.22
75.1	1563.38	74.2	1572.23
77.1	1563.12	76.0	1572.03
78.8	1562.48	77.9	1571.90
w = 0.0281; m = 0.4831		w = 0.661; m = 1.1974	
69.7	1565.23	68.8	1573.30
71.1	1565.62	70.6	1573.72
73.2	1565.70	72.4	1573.91
75.2	1565.64	74.2	1573.77
77.2	1565.57	76.0	1573.77
78.8	1565.25	77.9	1573.60
w = 0.0342; m = 0.5638			
69.2	1568.45		
71.1	1568.73		
72.7	1568.92		
74.7	1568.87		
76.4	1568.80		
78.2	1568.71		

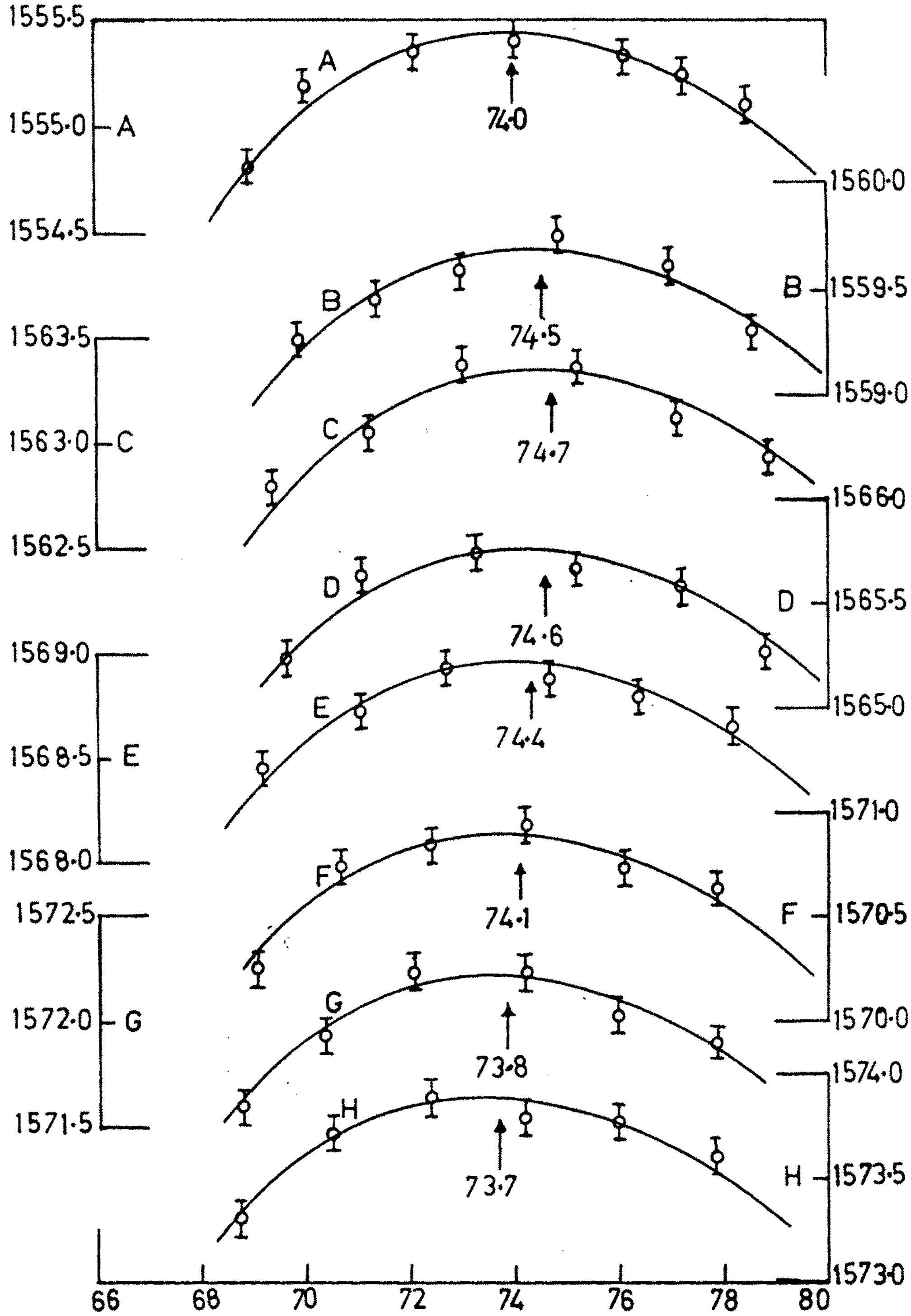

Fig. 3.2.7: Ultrasonic velocity (u) versus temperature (t) in aqueous magnesium chloride at different weight fractions.

A. Pure water B. w = 0.0091; C. w = 0.0142; D. w = 0.0283; E. w = 0.0342; F. w = 0.0484; G: w = 0.0540; H. w = 0.0661.

TABLE 3.2.8 Ultrasonic velocity (u) as a function of temperature (t) in aqueous solutions of calcium chloride

t	u	t	u
w = 0.0142; m = 0.1911		w = 0.0440; m = 0.6082	
68.5	1558.07	68.3	1563.57
70.1	1558.54	70.1	1564.00
72.0	1558.70	72.3	1564.15
74.3	1558.83	75.0	1564.07
76.7	1558.73	76.8	1564.95
78.8	1558.42	77.8	1563.74
w = 0.0257; m = 0.3488		w = 0.0536; m = 0.7516	
68.2	1560.21	68.2	1566.91
70.1	1560.60	70.1	1567.28
71.8	1560.82	72.1	1567.40
74.2	1560.97	74.0	1567.47
76.1	1560.80	75.9	1567.23
78.1	1560.71	77.5	1566.98
w = 0.0351; m = 0.4865		w = 0.0646; m = 0.9144	
68.3	1561.75	67.6	1568.90
70.1	1562.14	69.4	1569.17
72.2	1562.28	71.1	1569.45
74.5	1562.55	74.0	1569.42
76.3	1562.20	75.2	1569.25
78.0	1562.01	77.2	1568.92

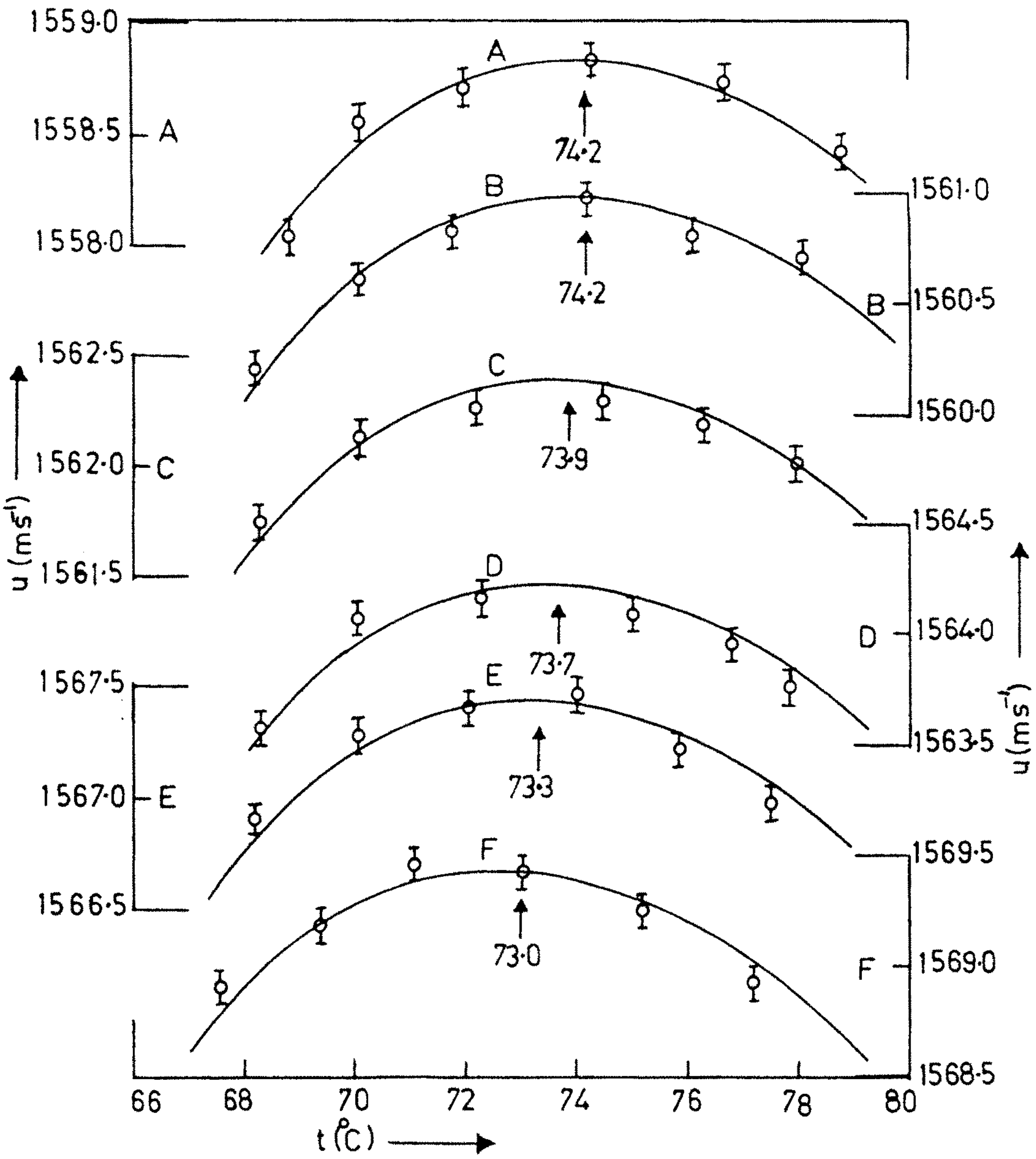

Fig. 3.2.8: Ultrasonic velocity (u) versus temperature (t) in aqueous calcium chloride at different weight fractions.

A. w = 0.0142; B. w = 0.0257; C. w = 0.0351; D. w = 0.0440; E. w = 0.0536; F. w = 0.0646.

TABLE 3.2.9 Ultrasonic velocity (u) as a function of temperature (t) in aqueous solutions of strontium chloride

t	u	t	u
w = 0.0105; m = 0.0826		w = 0.0417;m = 0.2747	
68.4	1556.77	68.3	1563.71
70.1	1557.05	70.1	1564.20
71.9	1557.32	72.3	1564.25
73.6	1557.35	74.1	1564.28
76.0	1557.35	76.0	1564.10
78.2	1556.96	77.8	1563.95
w = 0.0258; m = 0.1680		w = 0.0531; m = 0.3580	
68.9	1559.71	68.6	1567.10
70.6	1560.07	70.1	1567.25
72.3	1560.33	72.0	1567.37
74.1	1560.25	73.7	1567.42
76.0	1560.22	75.7	1567.15
77.8	1559.88	77.6	1567.02
w = 0.0335; m = 0.2305		w = 0.0649; m = 0.4097	
68.7	1562.27	68.1	1568.11
70.7	1562.62	70.3	1568.27
72.8	1562.67	72.1	1568.45
74.5	1562.60	74.0	1568.30
76.1	1562.50	75.8	1568.22
78.0	1562.32	77.8	1567.78

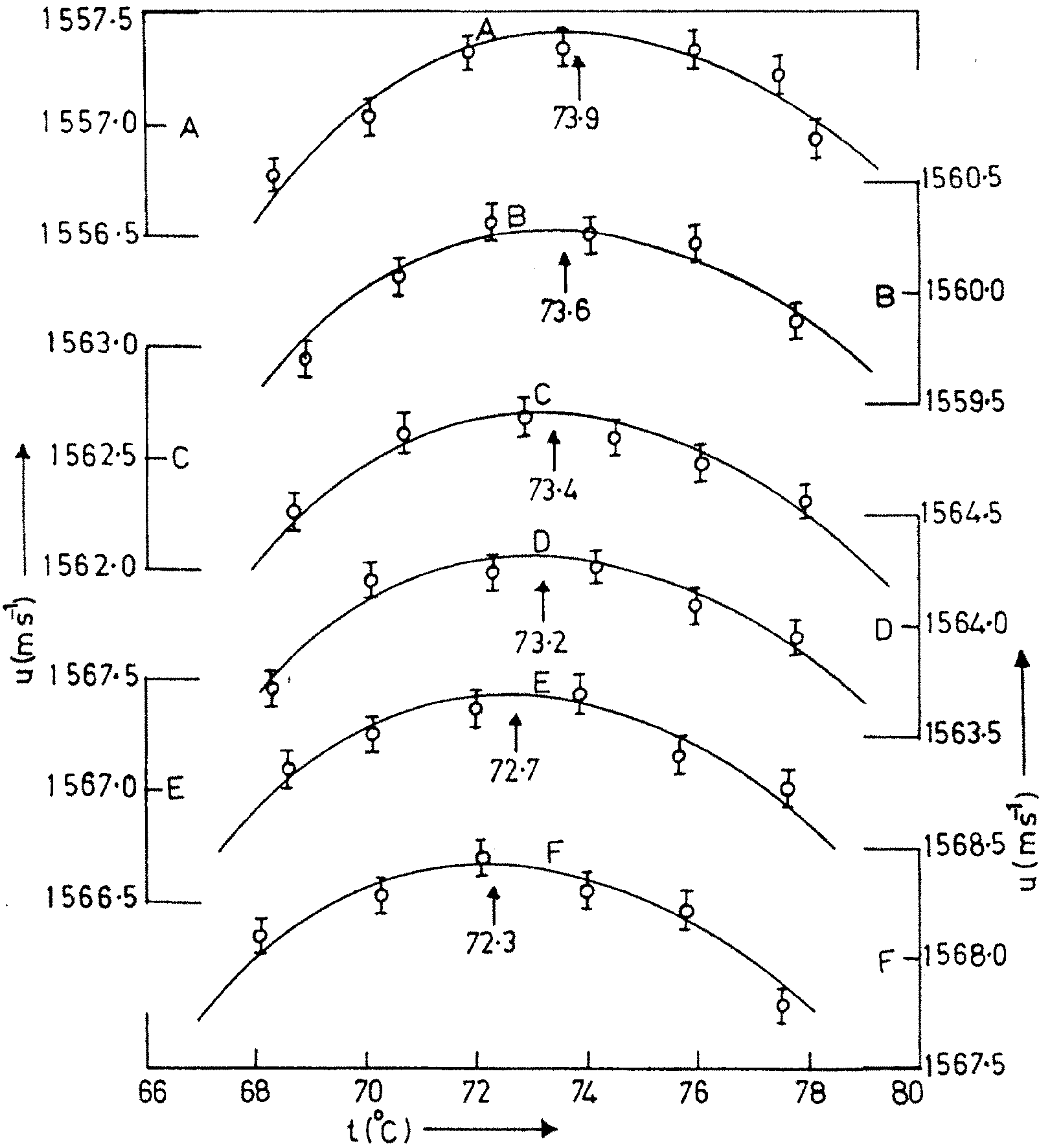

Fig. 3.2.9: Ultrasonic velocity (u) versus temperature (t) in aqueous strontium chloride at different weight fractions.

A. w = 0.0105; B. w = 0.0258; C. w = 0.0335; D. w = 0.0417; E. w = 0.0531; F. w = 0.0649.

TABLE 3.2.10 Ultrasonic velocity (u) as a function of temperature (t) in aqueous solutions of barium chloride.

t	u	t	u
w = 0.0151; m = 0.0777		w = 0.0415; m = 0.2004	
68.6	1555.80	68.8	1559.48
70.2	1556.13	70.8	1559.77
71.5	1556.37	72.5	1559.93
73.0	1556.38	74.3	1559.73
75.1	1556.22	76.3	1559.67
77.2	1556.10	77.6	1559.32
w = 0.0243; m = 0.1214		w = 0.0553; m = 0.2749	
68.8	1556.91	68.3	1560.70
70.9	1557.15	70.2	1560.91
73.0	1557.37	72.2	1560.85
75.3	1557.18	74.2	1560.70
77.2	1557.07	76.0	1560.62
78.3	1556.72	77.6	1560.32
w = 0.0309; m = 0.1495		w = 0.0690; m = 0.3419	
68.2	1558.85	67.3	1563.25
70.1	1559.13	69.1	1563.42
71.9	1559.15	70.9	1563.48
74.0	1559.16	73.1	1563.37
75.5	1559.08	74.9	1563.21
77.5	1558.71	76.6	1562.80

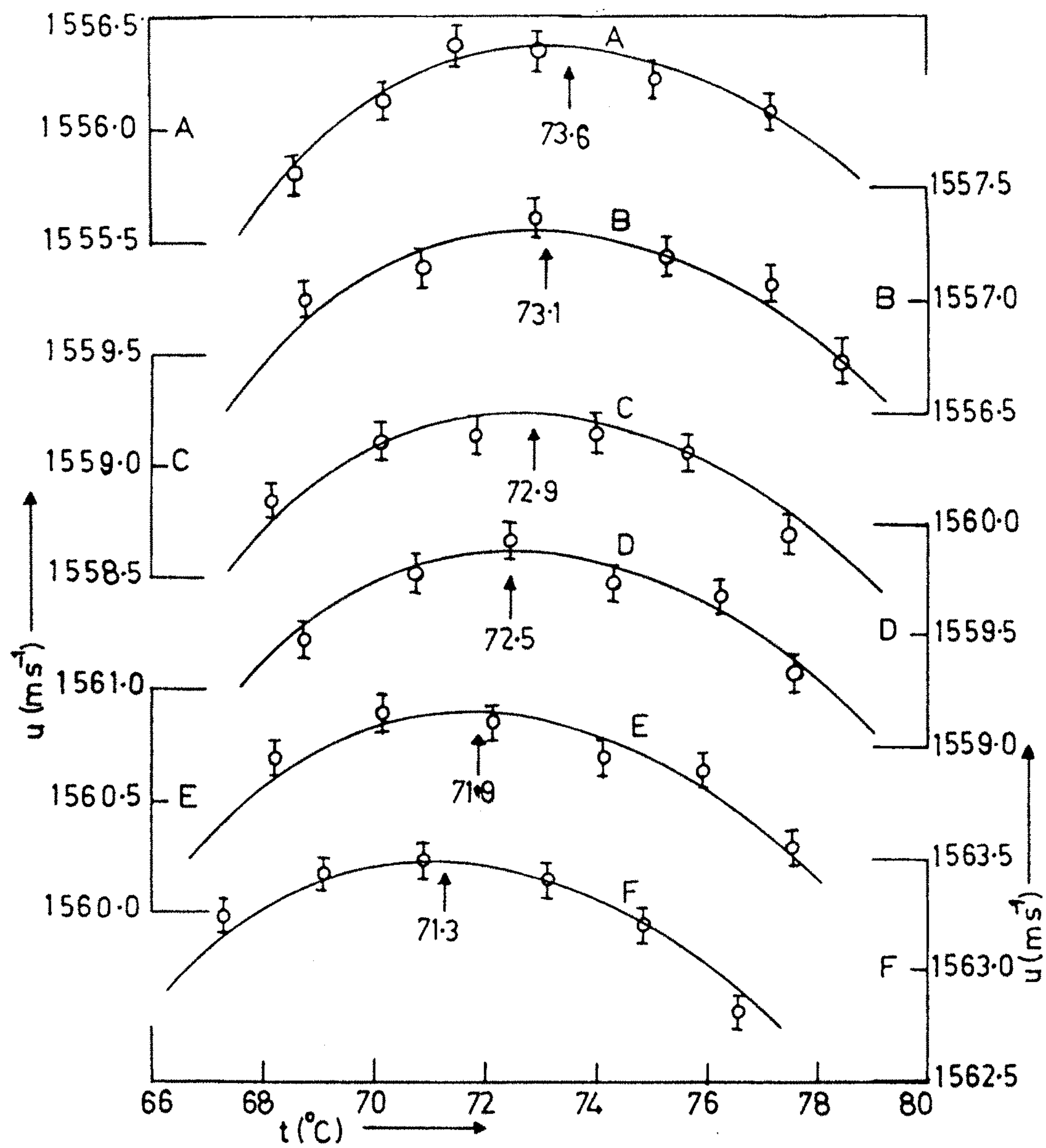

Fig. 3.2.10: Ultrasonic velocity (u) versus temperature (t) in aqueous barium chloride at different weight fractions.

A. w = 0.0151; B. w = 0.0243; C. w = 0.0309; D. w = 0.0415; E. w = 0.0553; F. w = 0.0690.

TABLE 3.2.11 Ultrasonic velocity (u) as a function of temperature (t) in aqueous solutions of ammonium chloride.

t	u	t	u
w = 0.0092; m = 0.1732		w = 0.0371; m = 0.7259	
69.6	1560.04	68.4	1572.15
70.3	1560.23	69.7	1572.40
72.2	1560.52	71.2	1572.60
73.9	1560.53	73.4	1572.87
75.8	1560.45	75.9	1572.78
77.8	1560.20	77.7	1572.40
w = 0.0150; m = 0.2834		w = 0.0482; m = 0.9372	
69.3	1563.83	68.6	1574.60
71.2	1564.12	70.3	1575.06
73.5	1564.37	72.1	1575.15
75.5	1564.28	74.1	1575.30
77.4	1564.17	75.9	1575.08
78.8	1564.10	77.5	1574.62
w = 0.0232; m = 0.4442		w = 0.0658; m = 1.3165	
68.8	1569.68	68.8	1576.45
70.7	1569.98	70.7	1576.83
73.0	1570.41	72.9	1576.87
75.1	1570.25	75.0	1576.75
77.3	1570.15	76.7	1576.65
78.7	1569.96	78.1	1576.40

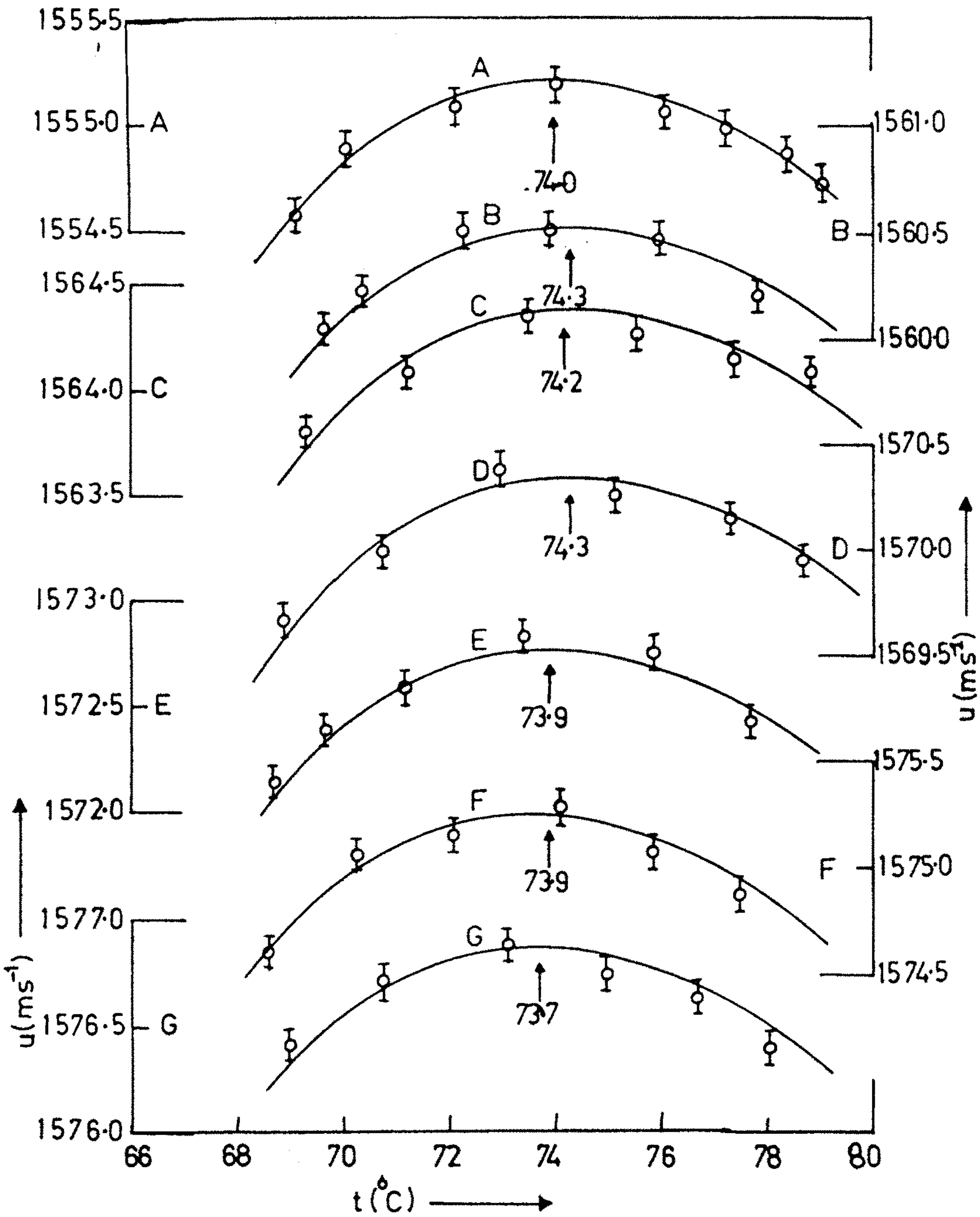

Fig. 3.2.11: Ultrasonic velocity (u) versus temperature (t) in aqueous ammonium chloride at different weight fractions.

A. Pure water; B. w = 0.0092; C. w = 0.0150; D. w = 0.0232; E. w = 0.0371; F. w = 0.0482; G: w = 0.0658.

Table 3.2.12 Ultrasonic velocity (u) as a function of temperature (t) in aqueous solutions of ammonium bromide.

t	u	t	u
w = 0.0115; m = 0.1189		w = 0.0449; m = 0.4795	
69.1	1553.25	68.2	1554.17
71.1	1553.76	69.9	1554.42
72.9	1553.78	71.8	1554.51
74.5	1553.83	74.4	1554.65
76.2	1553.70	75.8	1554.62
77.9	1553.61	77.1	1554.30
w = 0.0208; m = 0.2165		w = 0.0553; m = 0.5971	
68.8	1553.87	68.1	1554.35
70.3	1554.05	69.8	1554.80
72.2	1554.17	72.0	1554.92
74.1	1554.17	74.2	1554.91
75.5	1554.18	75.7	1554.83
77.1	1553.95	77.1	1554.70
w = 0.0290; m = 0.3053		w = 0.0636; m = 0.6930	
68.3	1553.78	67.8	1554.85
70.1	1554.20	69.5	1555.26
72.0	1554.98	71.7	1555.37
74.2	1554.37	73.7	1555.30
76.0	1554.25	75.5	1555.30
77.4	1554.21	77.2	1554.88

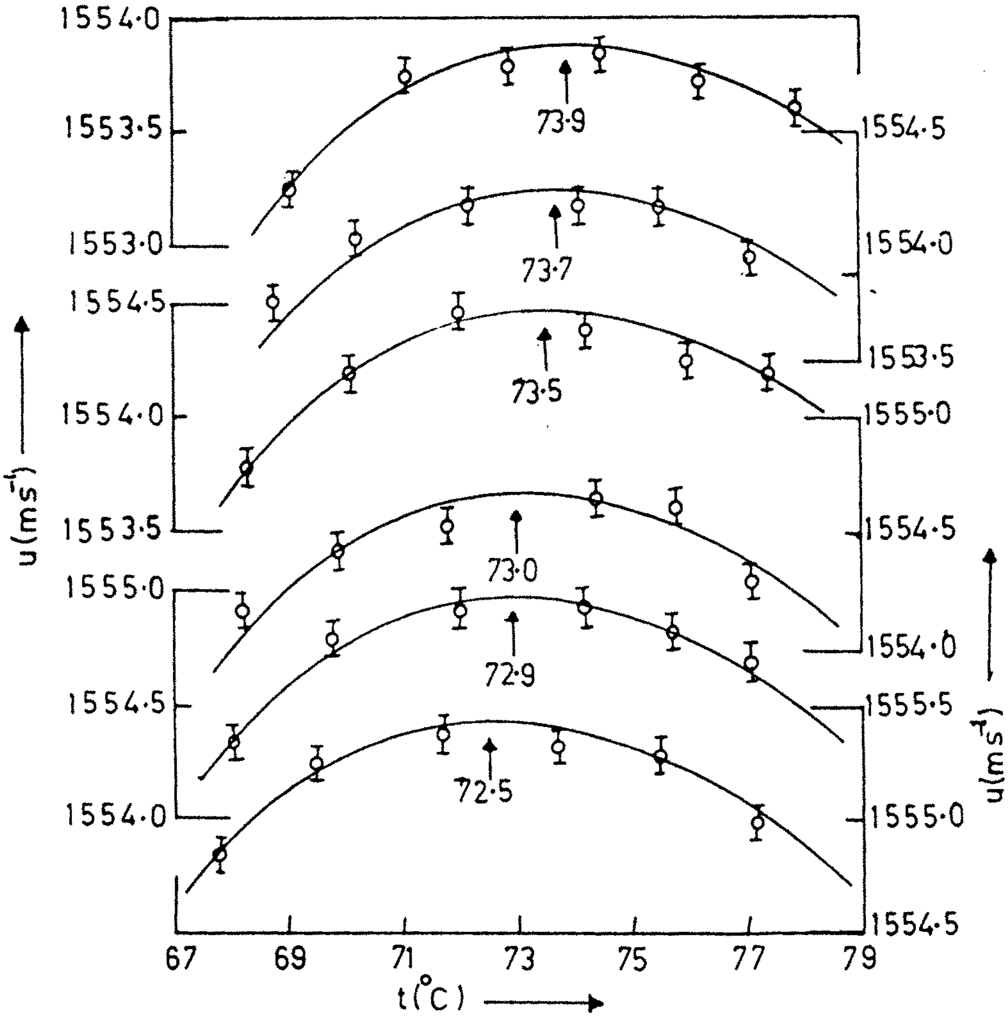

Fig. 3.2.12: Ultrasonic velocity (u) versus temperature (t) in aqueous ammonium bromide at different weight fractions.

A. w = 0.0015; B. w = 0.0208; C. w = 0.0293; D. w = 0.0449; E. w = 0.0553; F. w = 0.0636.

TABLE 3.2.13 Ultrasonic velocity (u) as a function of temperature (t) in aqueous solutions of ammonium iodide.

t	u	t	u
w = 0.0056; m = 0.0390		w = 0.0220; m = 0.1556	
68.8	1551.63	68.1	1549.85
70.2	1552.50	70.0	1550.10
72.0	1552.12	71.8	1550.21
73.8	1552.23	73.7	1550.30
76.1	1552.22	75.7	1550.02
77.8	1551.81	77.2	1549.88
w = 0.0120; m = 0.0841		w = 0.0322; m = 0.2295	
68.5	1551.30	67.8	1549.20
69.9	1551.41	68.6	1549.59
71.1	1551.60	72.1	1549.62
72.9	1551.80	74.0	1549.60
74.8	1551.63	76.0	1549.53
76.5	1551.62	77.3	1549.12
w = 0.0179; m = 0.1259			
68.1	1550.21		
69.9	1550.52		
71.1	1550.83		
72.9	1550.83		
75.1	1550.70		
77.3	1550.58		

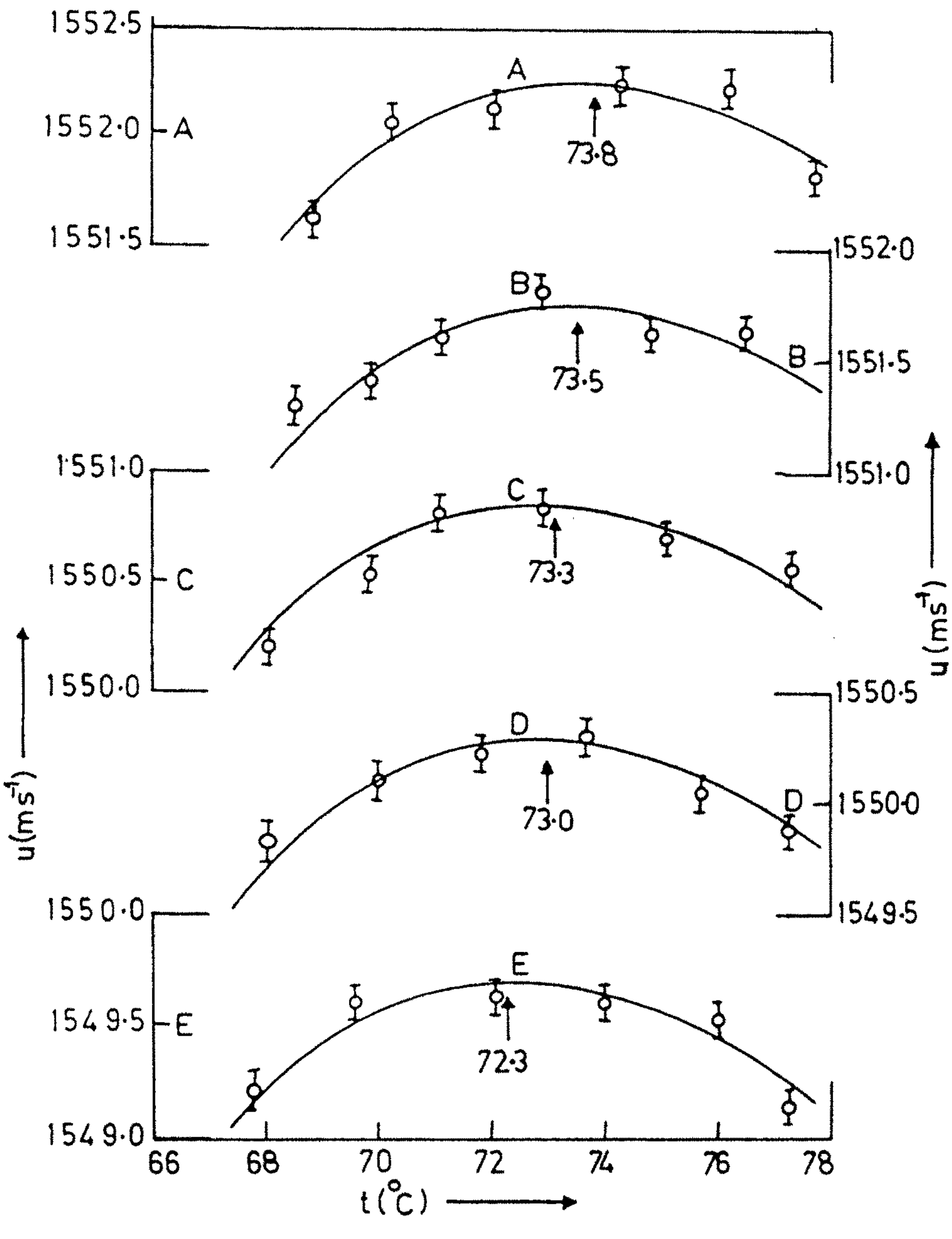

Fig. 3.2.13: Ultrasonic velocity (u) versus temperature (t) in aqueous ammonium iodide at different weight fractions.

A. w = 0.0056; B. w = 0.0120; C. w = 0.0179; D. w = 0.0220; E. w = 0.0322.