CHAPTER - III

RESULTS AND CALCULATIONS OF DERIVED PARAMETERS

3.1 Electrolytes in Water :

The sound velocity and density data at 25° C obtained in the present work represented in figures 14 to 18 and 7, for binary solutions were used to calculate adiabatic compressibilities (βad) at different concentrations of the solute by the following relation :

$$\beta ad = 1/u^2 d \qquad ---------- (7)$$

The variation of sound velocity (u) and adiabatic compressibility (βad) at 25° C with concentration (molality) for aqueous solutions of NaCl, KCl and Bu_4NBr are shown in figures 14 to 22. The probable error in βad can be calculated using expression :

$$\Delta\beta/\beta = 2\Delta u/u + \Delta d/d \qquad ---------- (8)$$

Where $\Delta\beta$, Δu and Δd represents uncertainty in determination of β, u and d respectively. The error in u and d are 0.5 $m.sec^{-1}$ and $\pm$ 0.1 x 10^{-5} $g.cm^{-3}$ respectively which makes the β values uncertain to $\pm$ 0.01 x 10^6 bar^{-1}. The table VII summarises the values of u, d and βad at $\simeq$ 0.2 and 0.8 m of electrolytes in water.

The apparent molal volume (ϕ_v) of the solute has been calculated by utilising the density data obtained in the present work by using the equation :

$$\phi_v = 1000\ (do - d)/mddo + M_2/d \qquad \text{---------}\ (9)$$

Where M_2, m, d and do represent the molecular weight of the solute, molality of the solution, density of the solution and density of water respectively.

The probable error in the ϕ_v values at the lowest concentration has been calculated by using the equation.

$$[\Delta\phi_v]^2 = [\delta\phi_v/\delta d].\ (\Delta d)^2 + (\delta\phi_v/\phi_m).(\Delta m)^2 \qquad \text{-----}\ (10)$$

The error at the lowest concentration is of the order of ± 0.5 $cm^3.mol^{-1}$.

The ϕ_v data for the salts is generally represented by equation :

$$\phi_v = \phi_v^o + S_v\ \sqrt{m} + B_v m \qquad \text{---------}\ (11)$$

Where S_v is Debye-Huckel limiting law slope for volume (=1.868 $cm^3.mol^{-3/2}$) and B_v is an adjustable parameter signifying deviation due to ion-ion interactions. The appropriate function $\phi_v - S_v\ \sqrt{m}$ are plotted against the molality of the salts in water (Fig.8). For the purpose of studying the reliability of the data, smooth extrapolations were made to arrive at ϕ_v^o values and which are compared with literature data in Table VIII.

The apparent molal adiabatic compressibility values for the salts (ϕ_k) were calculated by expression :

$$\phi_k = 1000 \; (\beta - \beta_o)/mdo + \beta\phi_v \qquad \text{---------} \; (12)$$

Where β and β_o represents adiabatic compressibility values of solution and pure solvent respectively.

The probable error in the calculation of apparent molal compressibility ($\Delta\phi_k$) value has been calculated by using the equation.

$$\Delta(\phi_k)^2 = (\delta\phi_k/\delta\beta).(\Delta\beta)^2 + (\delta\phi_k/\delta m)^2.(\Delta m)^2 + (\delta\phi_k/\delta\phi)^2 (\Delta d)^2 \qquad \text{---------} \; (13)$$

The error at the lowest concentration is of the order $\pm$ 2 x 10^4 cm^3 bar^{-1} mol^{-1}. The ϕ_k for the salts can be represented by the equation :

$$\phi_k = \phi_k^o + S_k\sqrt{m} + B_k m \qquad \text{----------} \; (14)$$

Where S_k is Debye-Huckel limiting law slope B_k also signifies the deviations due to solute-solute or ion-ion interactions. Figure 9 illustrates the ϕ_k, behaviour of

Table VII : **Density, Sound Velocity and Adiabatic compressibility Values of aqueous solution of salts at 25 °C.**

Salt	Molality (m)	Density (d) $g.cm^{-3}$	Sound velocty (u) $m.s^{-1}$	$\beta ad \times 10^{12}$ $dyn^{-1}.cm^{2}$
NaCl	0.1976	1.004723	1510.0	43.65
	0.7937	1.028646	1545.5	40.70
KCl	0.2006	1.005812	1507.5	43.75
	0.7974	1.032502	1534.5	41.13
Bu_4NBr	0.1949	1.001373	1542	42.00
	0.7968	1.014244	1642	36.57

Tablve VIII : **Apparent molal volumes and compressibilities of electrolytes at 25° C and nature of B_v parameters.**

Salt	ϕ^o_v cm^3 mol^{-1} Expt.	Lit.	B_v	ϕ^o_K x 10^4 cm^3 dyn^{-1} mol^{-1} Expt.	Lit.
NaCl	18.1	16.62	-ve	- 47.5	- 50.0
KCl	28.8	26.85	-ve	- 39.0	- 43.5
Bu_4NBr	301.4	300.4	-ve	- 22.0	- 20.0

salts in water. The values of ϕ_k^o obtained on the basis of smooth extrapolation to the infinite dilution for different salts in water along with literature values are collected in table VIII.

3.2 Non-Electrolytes in Water :

The variation of sound velocity (u) and adiabatic compressibility (βad) at 25^oC, with mole fraction (X_2) of DMF is shown in Figure 12.

Similarly the variation of ϕ_v and ϕ_k as a function of mole fraction (X_2) of DMF in the solution at 25^oC is shown in Fig. 13. Extrapolation to infinite dilution yields values of ϕ_v^o ($74.6\ cm^3.mol^{-1}$) and ϕ_k^o ($4.5 \times 10^4\ bar^{-1}\ cm^3.mol^{-1}$) Figure 13.

The experimental results are given in table IX. The densities of the mixtures are given relative to pure H_2O, (do = $0.997047\ g.cm^{-3}$). The relative values of βad, ϕ_v and ϕ_k are also listed in the same table. Here X_2 is the mole fraction of DMF.

3.3 Electrolytes in Mixed Aqueous Solvents :

The densities and sound velocities of the solutions of NaCl, KCl and Bu_4NBr in mixed aqueous solutions

Table IX : DMF - H_2O System, 25 °C

X_2	u $m.s^{-1}$	1000 $(d-d_o)$ $g.cm^{-3}$	$\beta ad \times 10^6$ bar^{-1}	ϕ_v $cm^3 mol^{-1}$	$\phi_k \times 10^4$ bar^{-1}
0.000	1497.96	0.000	44.69	-	-
0.021	1547.8	- 0.792	41.90	74.05	7.23
0.055	1603.6	- 0.693	39.03	73.58	11.18
0.099	1650.2	- 0.122	36.83	73.34	14.09
0.152	1681.0	+ 0.020	35.50	73.31	16.76
0.219	1689.0	- 1.489	35.21	73.52	19.77
0.318	1669.9	- 6.651	36.21	74.06	23.53
0.512	1601.0	- 18.801	39.88	75.05	29.10
0.700	1546.8	- 33.604	43.38	76.14	32.93
1.000	1459.3	- 52.470	49.71	77.38	38.46

of DMF have been determined at $25^{o}C$.

The adiabatic compressibilities (βad) of salts were calculated by using sound velocity (u) and density (d) data and putting these in the Laplace equation.

The apparent molal volume (ϕ_V) and the apparent molal compressibility (ϕ_k) of the salts in ternary solutions were calculated by using the equations.

$$\phi_V = \frac{1000\ (d_o - d)}{mdd_o} + \frac{M_2}{d} \quad \text{---------} \ (15)$$

Where M_2, m, d and d_o represent the molecular weight of the salt, molality of the solution, density of the solution and density of solvent respectively.

$$\phi_k = \frac{1000\ (\beta - \beta_o)}{md_o} + \beta\phi_v \quad \text{---------} \ (16)$$

Where β and β_o represent adiabatic compressibility values of solution and solvent respectively.

The variations of u and βad as a function of molality of salt are exhibitted in figures 14 to 22, and ϕ_v, ϕ_k as a function of square root of aquamolality for ternary systems are exhibitted in figures 23 to 31.

The values of ϕ_V^o obtained on the basis of smooth extrapolation in ternary solutions were used to

Table X : Apparent molal volumes and compressibilities of salts in mixed aqueous solutions, nature of B'_v and B'_k parameter, $\Delta\phi^o_v$ and $\Delta\phi^o_k$ for the electrolytes from water to mixed DMF-H_2O solvent systems at 25°C.

a) NaCl in DMF-H_2O.

X_2	ϕ^o_v $cm^3 mol^{-1}$	B'_v	$\phi^o_k \times 10^6$ $cm^3 bar^{-1} mol^{-1}$	B'_k	$\Delta\phi^o_v$	$\Delta\phi^o_k$
0.021	15.3	+ ve	- 123.0	+ ve	- 2.8	- 75.5
0.055	15.7	+ ve	- 40.0	+ ve	- 2.4	7.5
0.099	16.6	+ ve	- 30.2	+ ve	- 1.5	17.3
0.152	17.8	+ ve	- 26.1	+ ve	- 0.3	21.4
0.219	18.0	+ ve	- 20.9	+ ve	- 0.1	26.6
0.318	18.4	+ ve	- 16.3	+ ve	0.3	31.2

b) KCl in DMF-H_2O.

X_2	ϕ^o_v $cm^3 mol^{-1}$	B'_v	$\phi^o_k \times 10^6$ $cm^3 bar^{-1} mol^{-1}$	B'_v	$\Delta\phi^o_v$	$\Delta\phi^o_k$
0.021	26.5	+ ve	- 33.3	+ ve	- 2.3	5.7
0.055	27.0	+ ve	- 31.4	+ ve	- 1.8	7.6
0.099	28.7	+ ve	- 29.2	+ ve	- 0.1	9.8
0.152	31.0	- ve	- 23.1	+ ve	2.2	15.9
0.219	31.3	- ve	- 20.2	+ ve	2.5	18.8

c) Bu_4NBr in DMF-H_2O.

X_2	ϕ_v^o $cm^3 mol^{-1}$	B'_v	$\phi_k^o \times 10^4$ $cm^3 bar^{-1} mol^{-1}$	B'_k	$\Delta\phi_v^o$	$\Delta\phi_k^o$
0.0	301.4	- ve	- 22.0	+ ve	0.0	0.0
0.021	297.2	- ve	11.0	+ ve	- 4.2	33.0
0.055	294.0	zero	19.0	+ ve	- 7.4	41.0
0.099	293.2	+ ve	36.5	+ ve	- 8.2	58.5
0.152	294.0	+ ve	61.0	+ ve	- 7.4	83.0
0.219	298.3	+ ve	72.5	+ ve	- 3.1	94.5
0.318	300.0	+ ve	81.0	+ ve	- 1.4	103.0
0.512	312.6	- ve	73.5	+ ve	11.2	95.5
0.700	302.5	- ve	52.5	+ ve	1.1	74.5
1.0	294.4	+ ve	- 10.0	+ ve	- 7.0	12.0

calculate the transfer functions ($\Delta\phi_v^o$)$_t$, of salts from water to mixed aqueous solution at 25^{o}C by using the equation :

$$(\Delta\phi_v^o)_t = \phi_v^o(\text{mixed aqueous-electrolyte}) - \phi_v^o(\text{water-electrolyte}) \quad \text{----------} \ (17)$$

Similarly, the values of ϕ_k^o obtained by smooth extrapolation in ternary solutions were used for calculating the transfer functions ($\Delta\phi_k^o)_t$, of salts from water to mixed aqueous solutions at 25^{o}C by using the equation :

$$(\Delta\phi_k^\theta)_t = \phi_k^o(\text{mixed aqueous-electrolyte}) - \phi_k^o(\text{water-electrolyte}) \quad \text{----------} \ (18)$$

The variation of $\Delta\phi_v^o$ as a function of mole fraction (X_2) of DMF is shown in Figure 32.

Similarly, the variation of $\Delta\phi_k^o$ as a function of mole fraction (X_2) of DMF is shown in Figure 33.

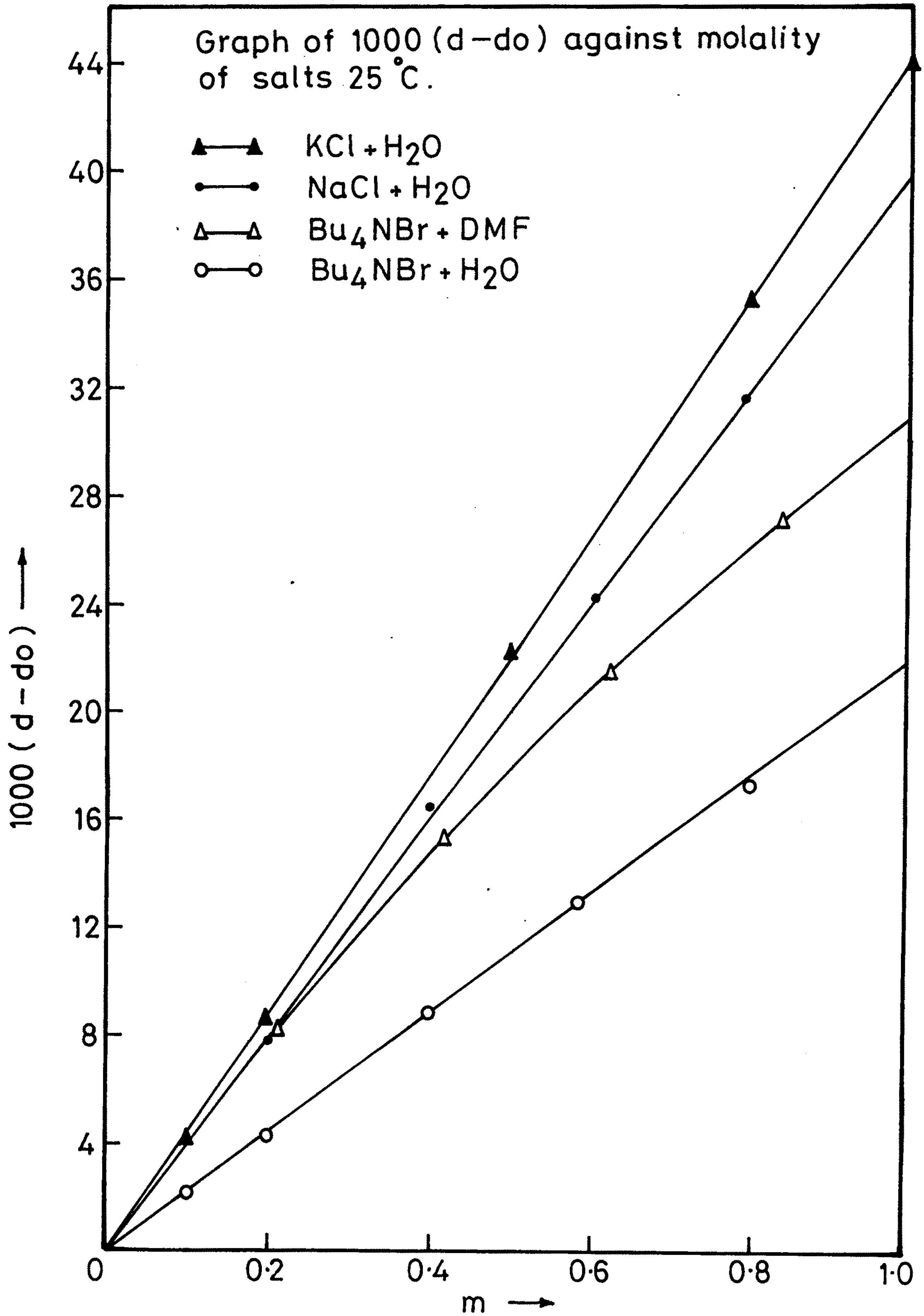

Graph of 1000 (d-do) against molality of salts 25 °C.
KCl + H2O
NaCl + H2O
Bu4NBr + DMF
Bu4NBr + H2O
1000 (d - do) ⟶
44
40
36
32
28
24
20
16
12
8
4
0
0·2
0·4
0·6
0·8
1·0
m ⟶

Fig. 7

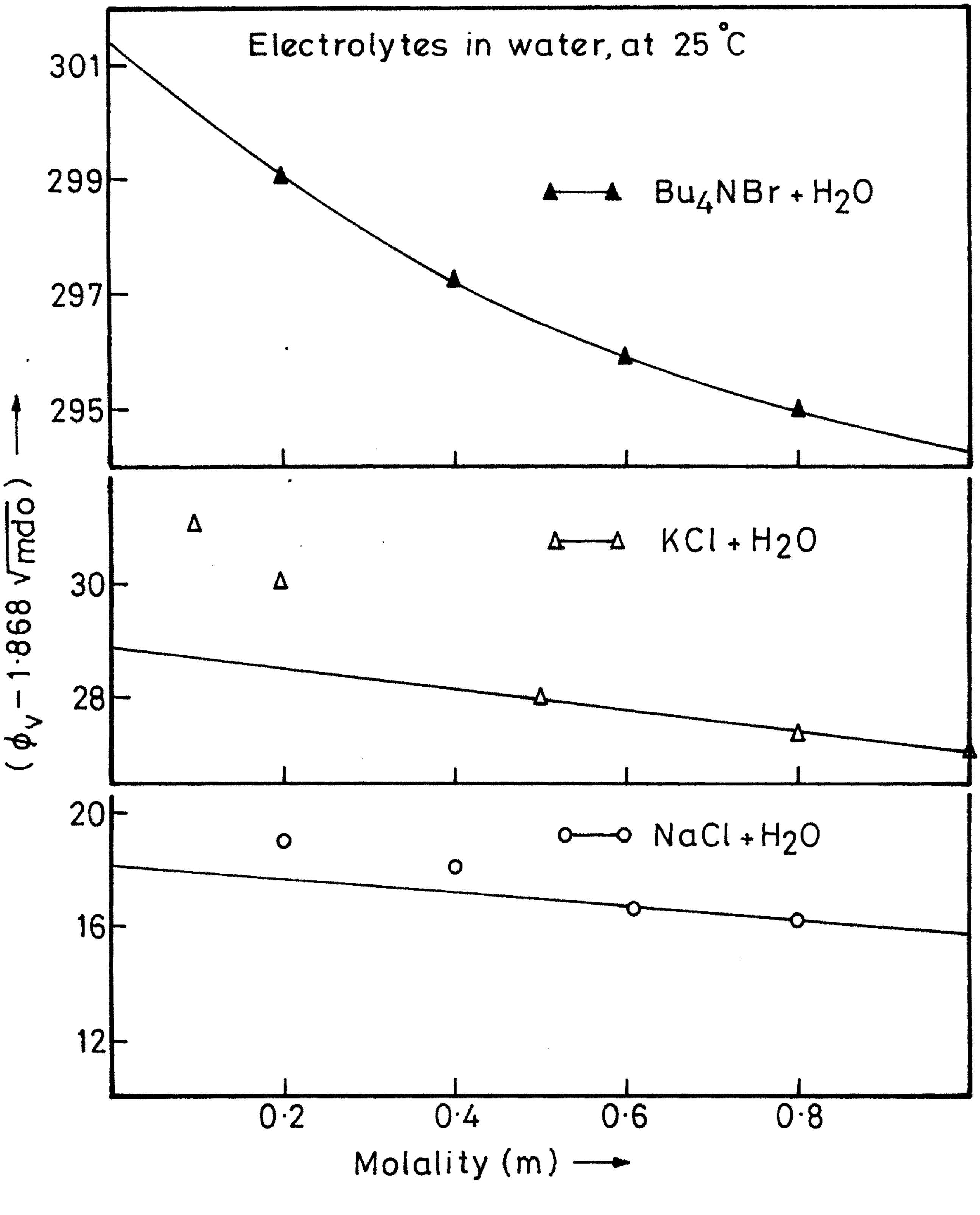

Electrolytes in water, at 25 °C
Bu4NBr + H2O
KCl + H2O
NaCl + H2O
301
299
297
295
30
28
20
16
12
(φv − 1·868 √mdo) →
0·2
0·4
0·6
0·8
Molality (m) →

Fig.8

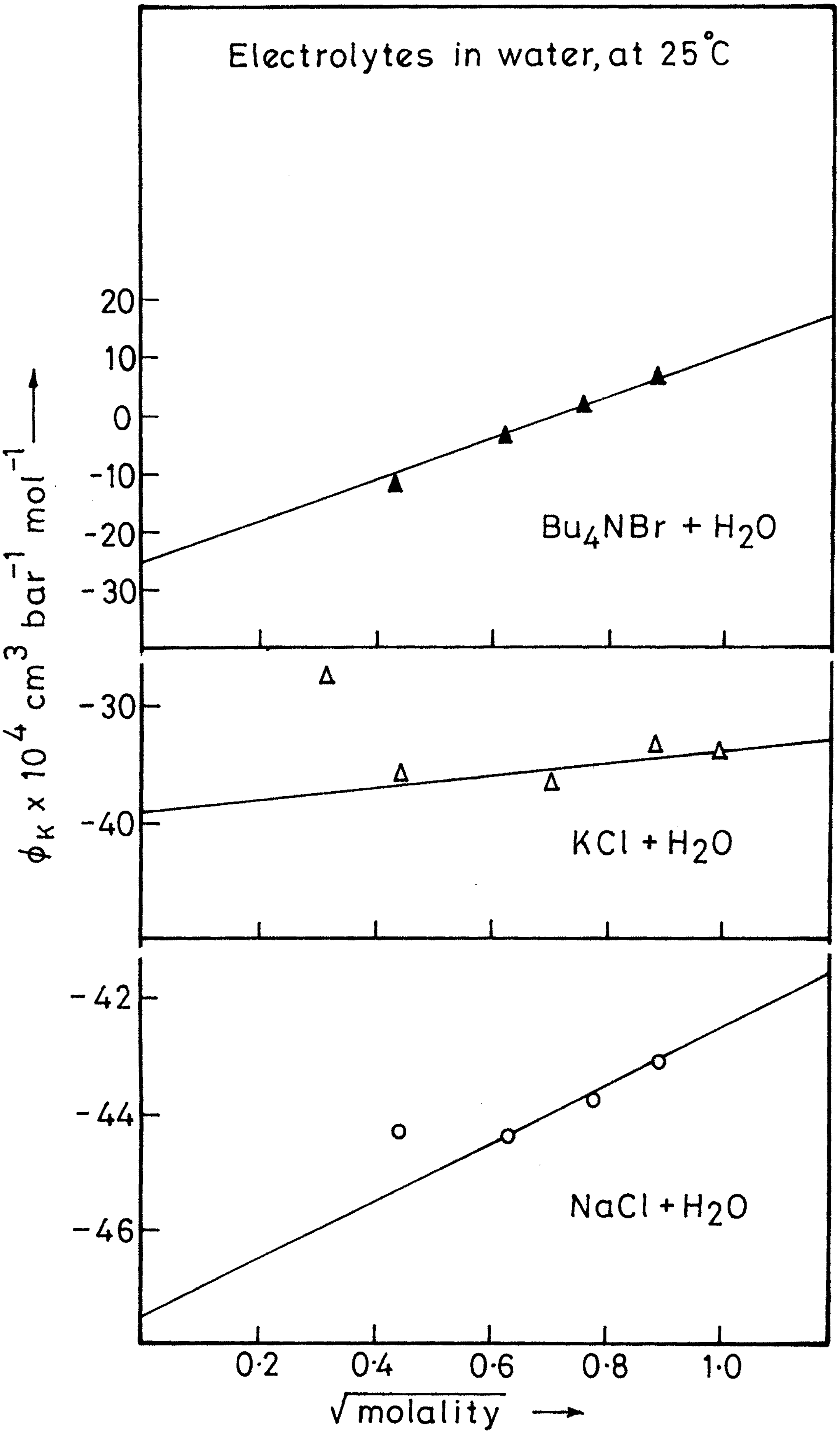

Electrolytes in water, at 25°C
20
10
0
-10
-20
-30
$Bu_4NBr + H_2O$
-30
-40
$KCl + H_2O$
-42
-44
-46
$NaCl + H_2O$
0·2
0·4
0·6
0·8
1·0
√molality →
$\phi_K \times 10^4$ cm^3 bar^{-1} mol^{-1} →

Fig. 9

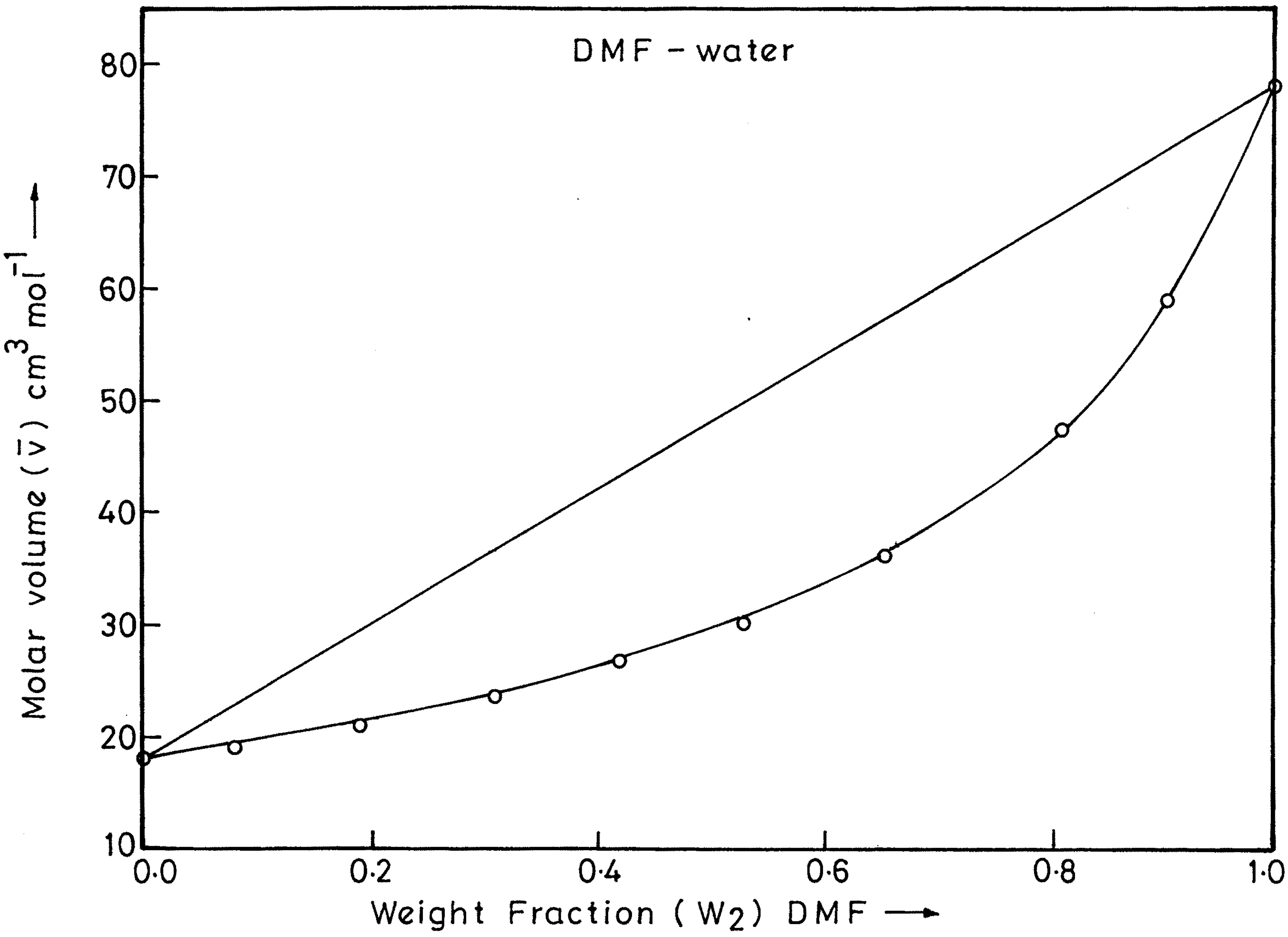
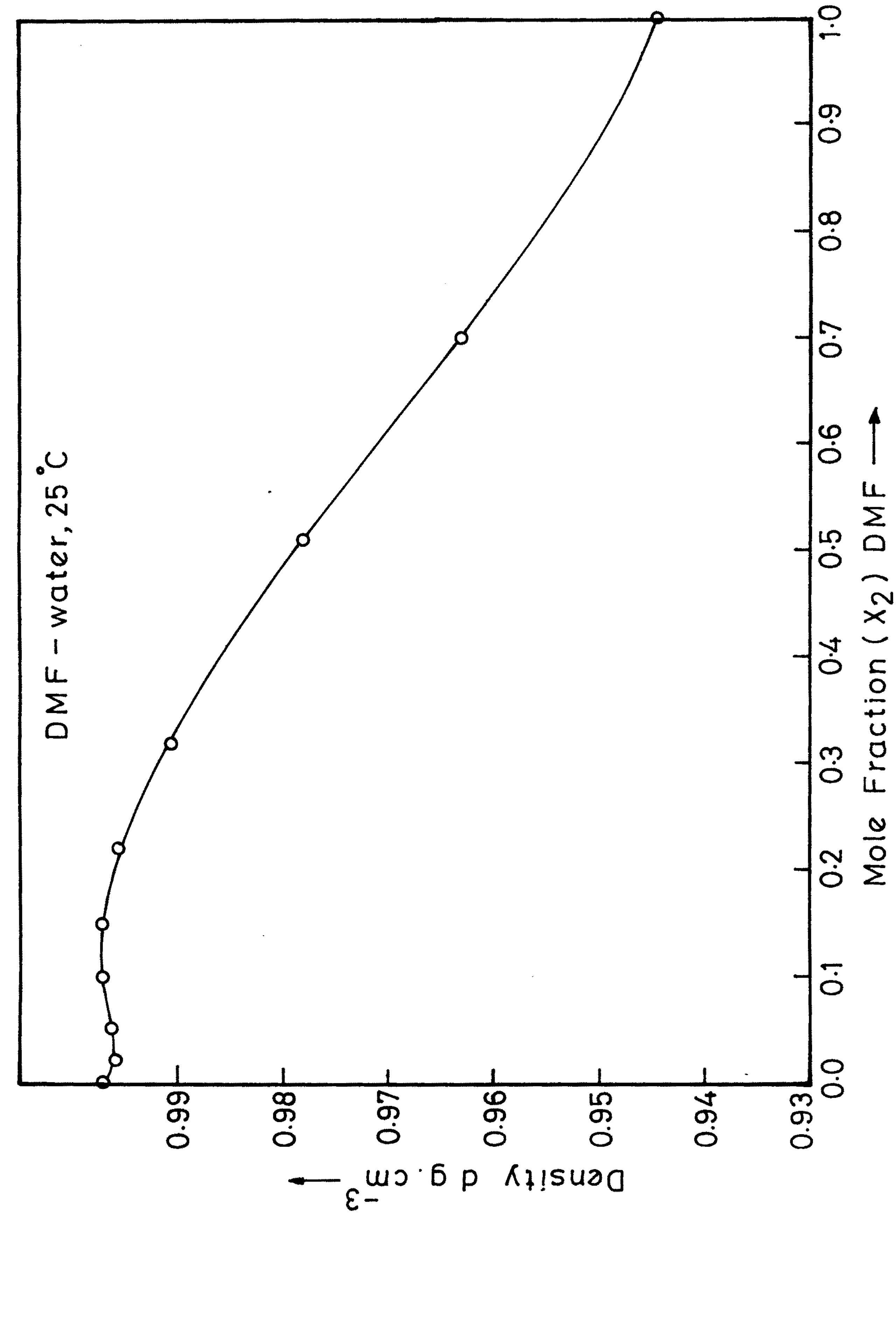

DMF - water
80
70
60
50
40
30
20
10
0·0
0·2
0·4
0·6
0·8
1·0
Molar volume ($\bar{v}$) $cm^3 mol^{-1}$
Weight Fraction (W_2) DMF

Fig. 10



DMF - water, 25 °C
0.99
0.98
0.97
0.96
0.95
0.94
0.93
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Mole Fraction (X_2) DMF →
Density d g.cm^{-3} →

Fig. 11

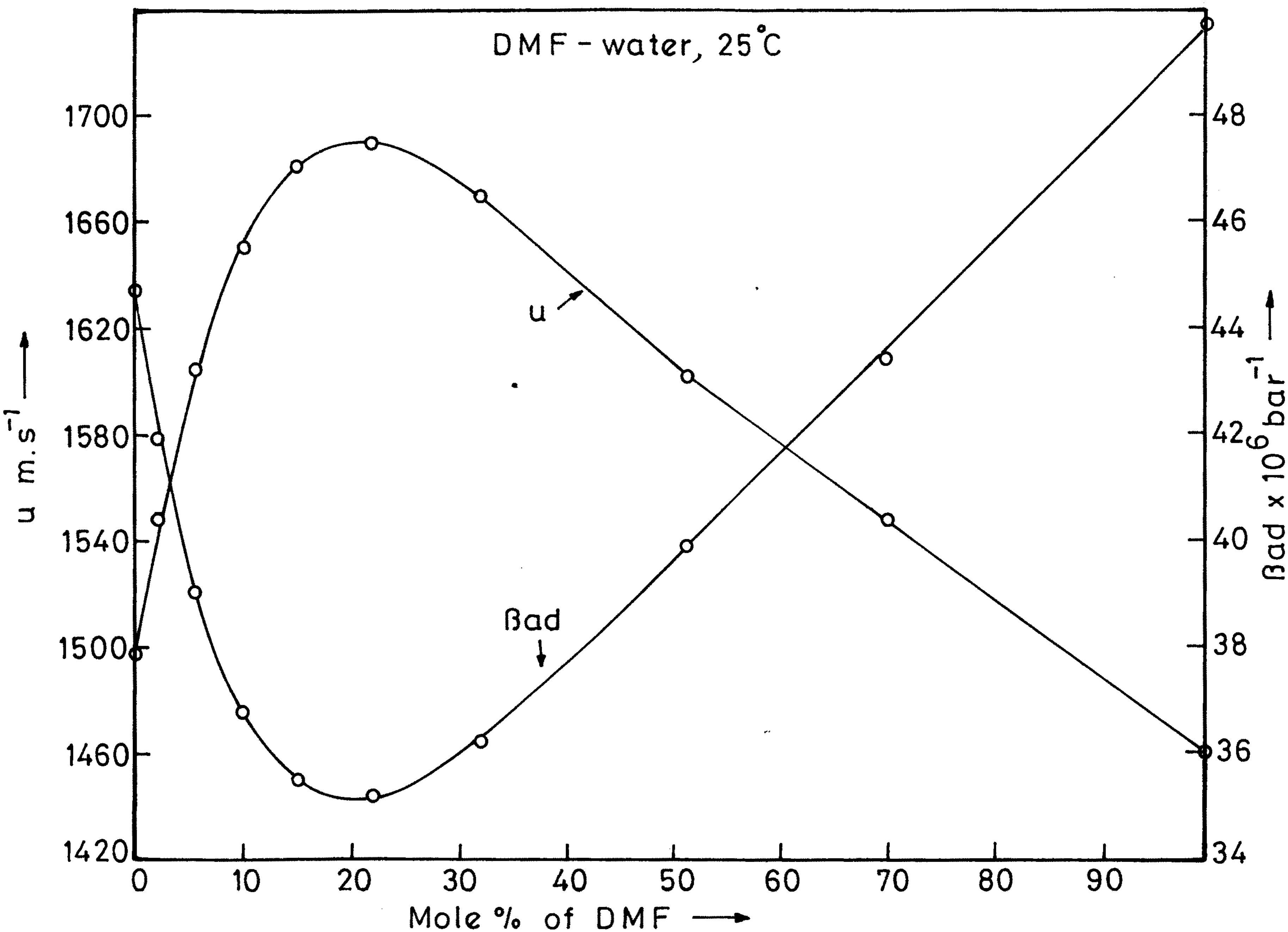

DMF - water, 25°C
u m.s⁻¹
1700
1660
1620
1580
1540
1500
1460
1420
βad x 10⁶ bar⁻¹
48
46
44
42
40
38
36
34
0
10
20
30
40
50
60
70
80
90
u
βad
Mole % of DMF

Fig. 12

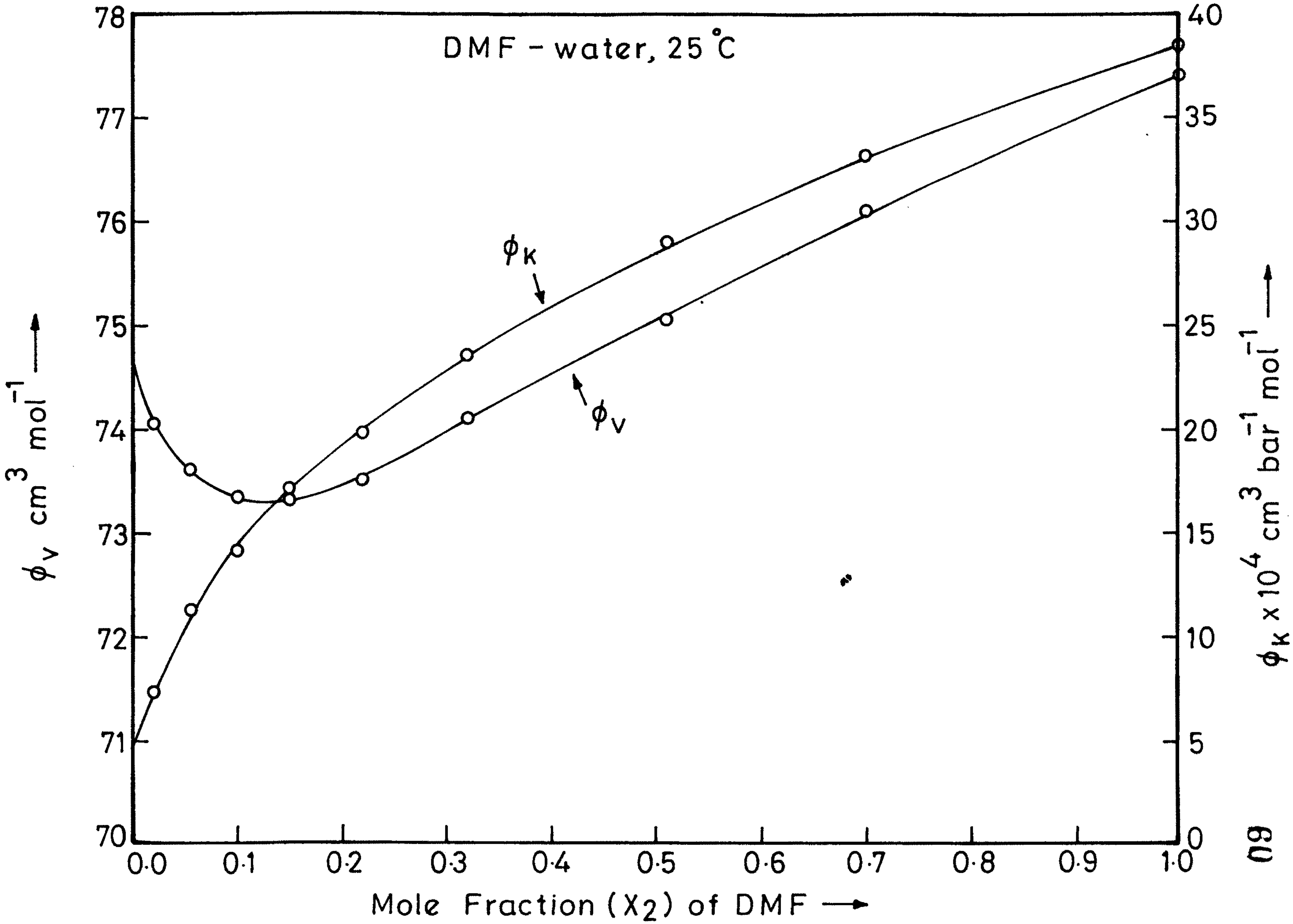

DMF - water, 25 °C
ϕ_K
ϕ_V
ϕ_V cm^3 mol^{-1} ⟶
$\phi_K \times 10^4$ cm^3 bar^{-1} mol^{-1} ⟶
Mole Fraction (X_2) of DMF ⟶
78
77
76
75
74
73
72
71
70
40
35
30
25
20
15
10
5
0
0·0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0

Fig. 13

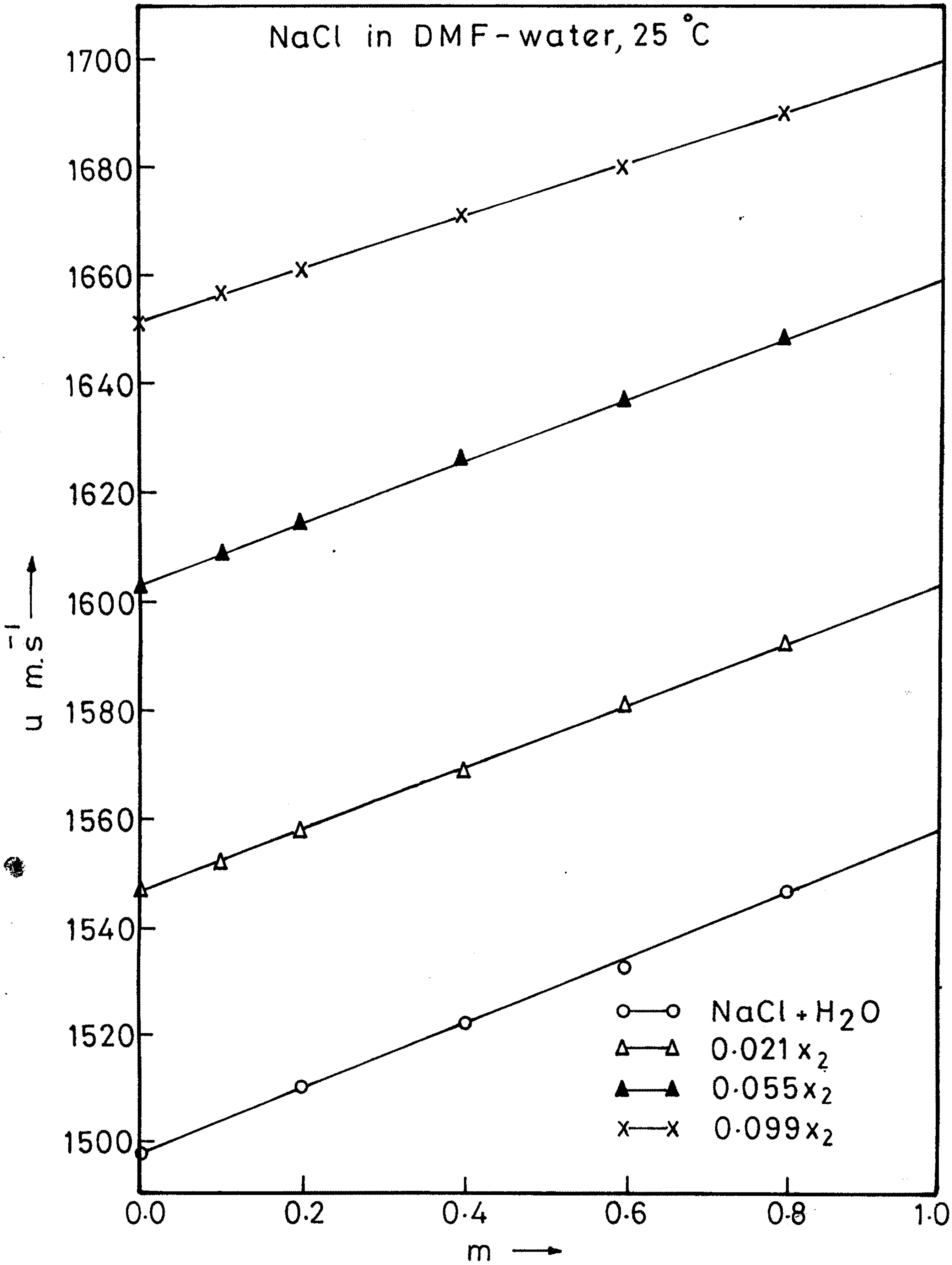

NaCl in DMF-water, 25 °C
1700
1680
1660
1640
1620
1600
1580
1560
1540
1520
1500
u m.s⁻¹
0.0
0.2
0.4
0.6
0.8
1.0
m
NaCl + H2O
0.021 x2
0.055 x2
0.099 x2

Fig. 14

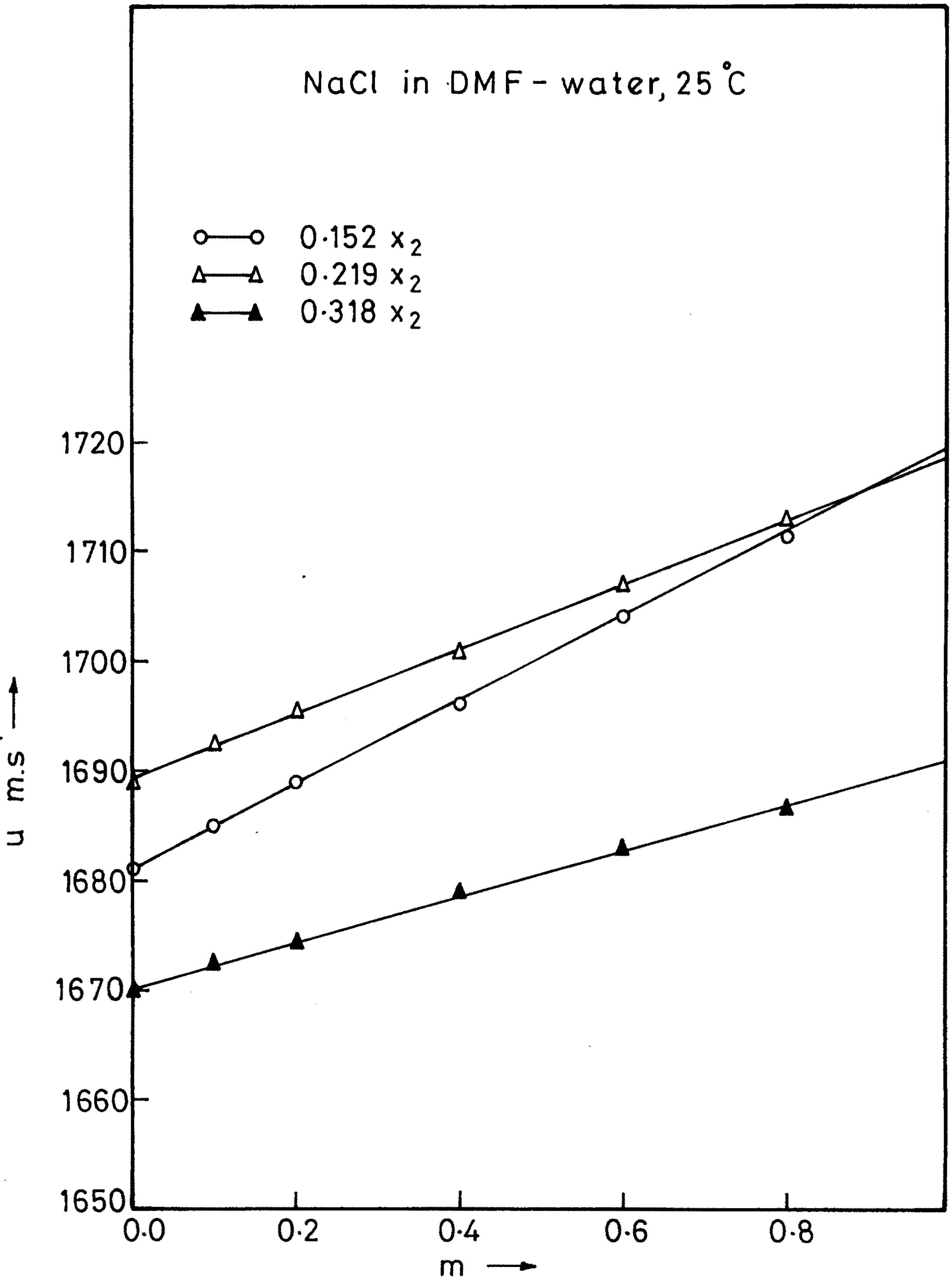

NaCl in DMF - water, 25 °C
0·152 x_2
0·219 x_2
0·318 x_2
1720
1710
1700
1690
1680
1670
1660
1650
u m.s⁻¹
0·0
0·2
0·4
0·6
0·8
m

Fig. 15

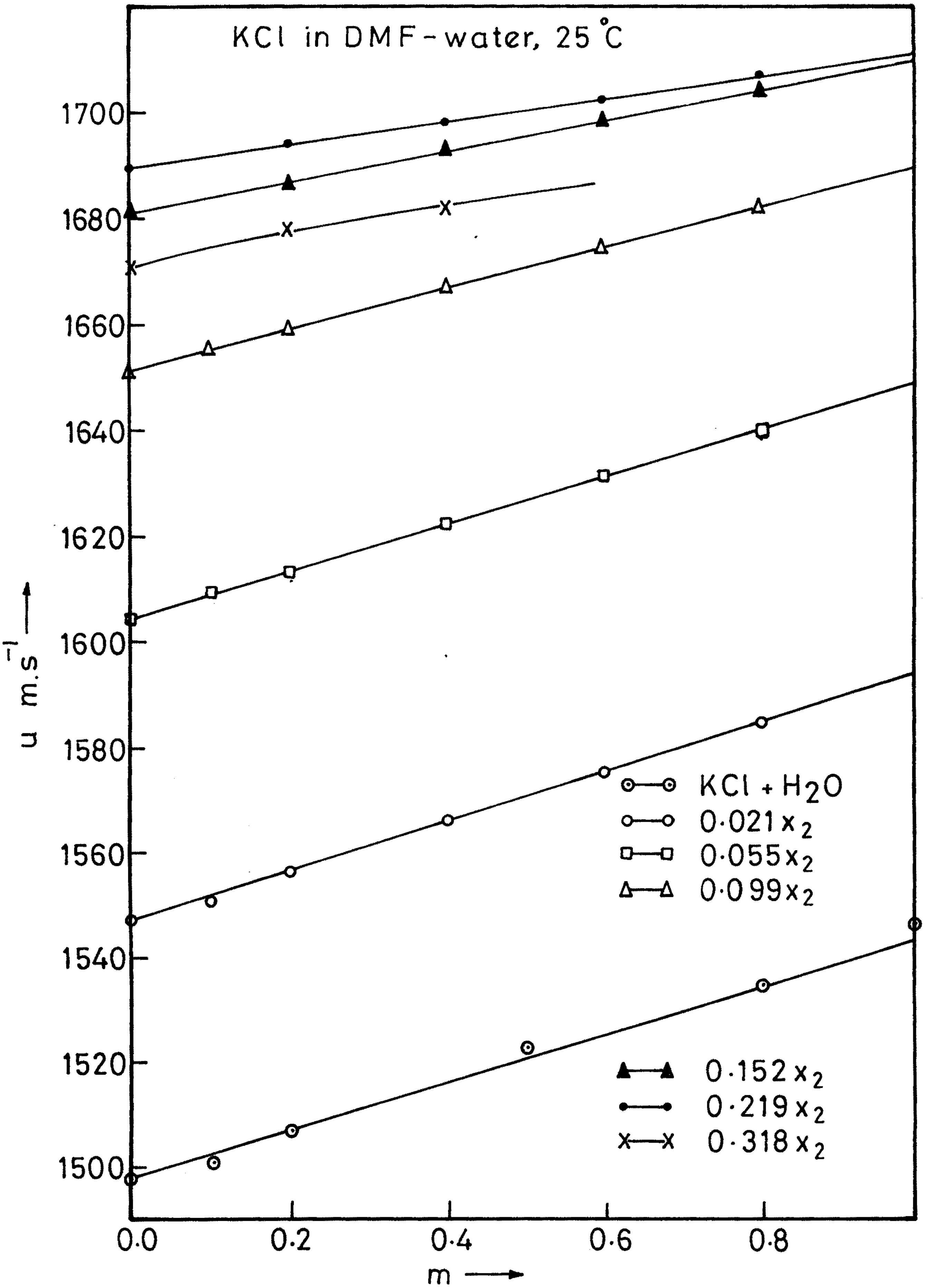

KCl in DMF-water, 25 °C
1700
1680
1660
1640
1620
1600
1580
1560
1540
1520
1500
u m.s⁻¹ →
0.0
0·2
0·4
0·6
0·8
m →
KCl + H2O
0·021 x2
0·055 x2
0·099 x2
0·152 x2
0·219 x2
0·318 x2

Fig. 16

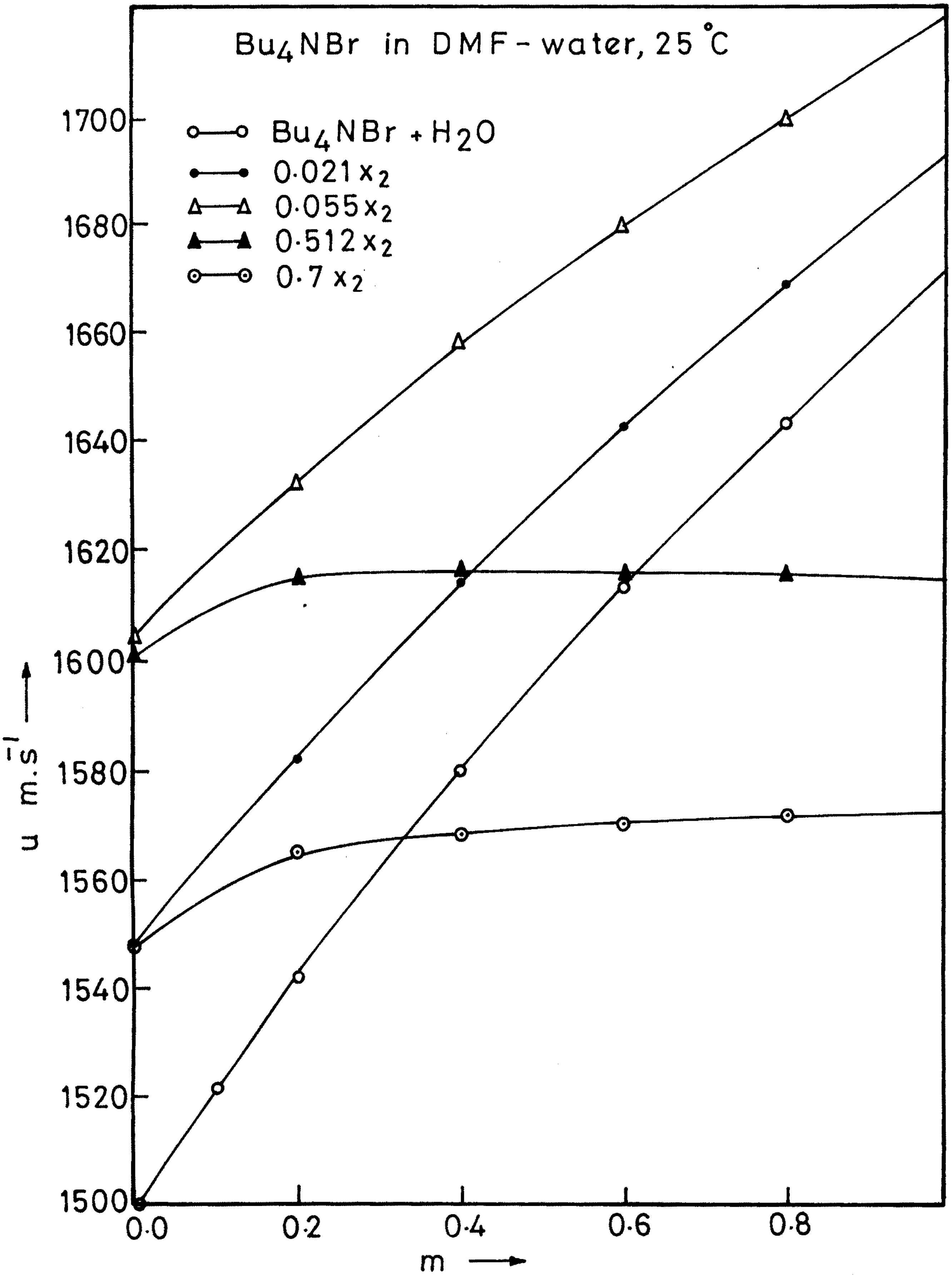
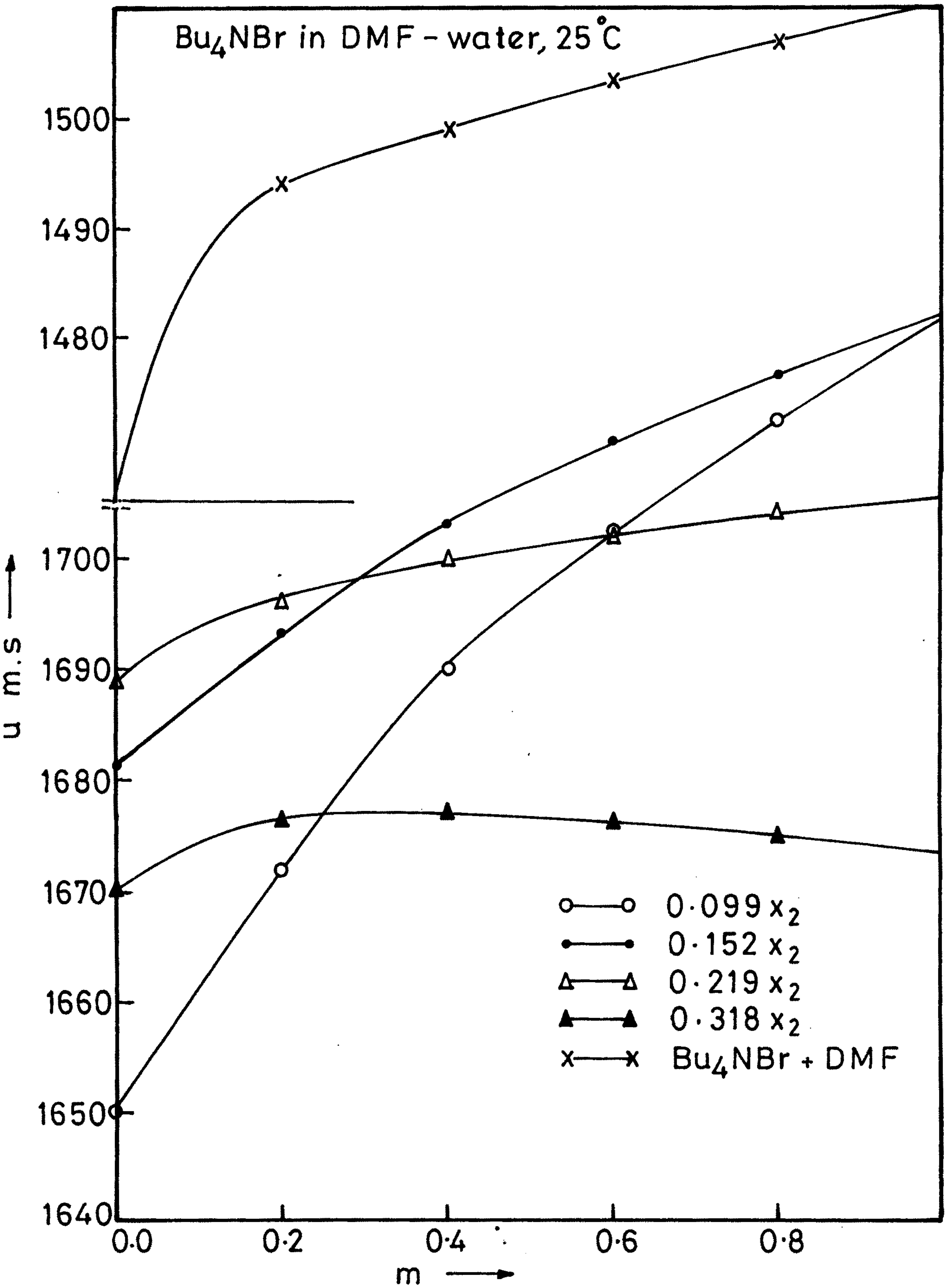

Bu4NBr in DMF-water, 25 °C
Bu4NBr + H2O
0·021 x2
0·055 x2
0·512 x2
0·7 x2
1700
1680
1660
1640
1620
1600
1580
1560
1540
1520
1500
u m.s⁻¹ →
0·0
0·2
0·4
0·6
0·8
m →

Fig. 17



Bu4NBr in DMF - water, 25°C
1500
1490
1480
1700
1690
1680
1670
1660
1650
1640
u m.s⁻¹
0.0
0·2
0·4
0·6
0·8
m
0·099 x2
0·152 x2
0·219 x2
0·318 x2
Bu4NBr + DMF

Fig. 18

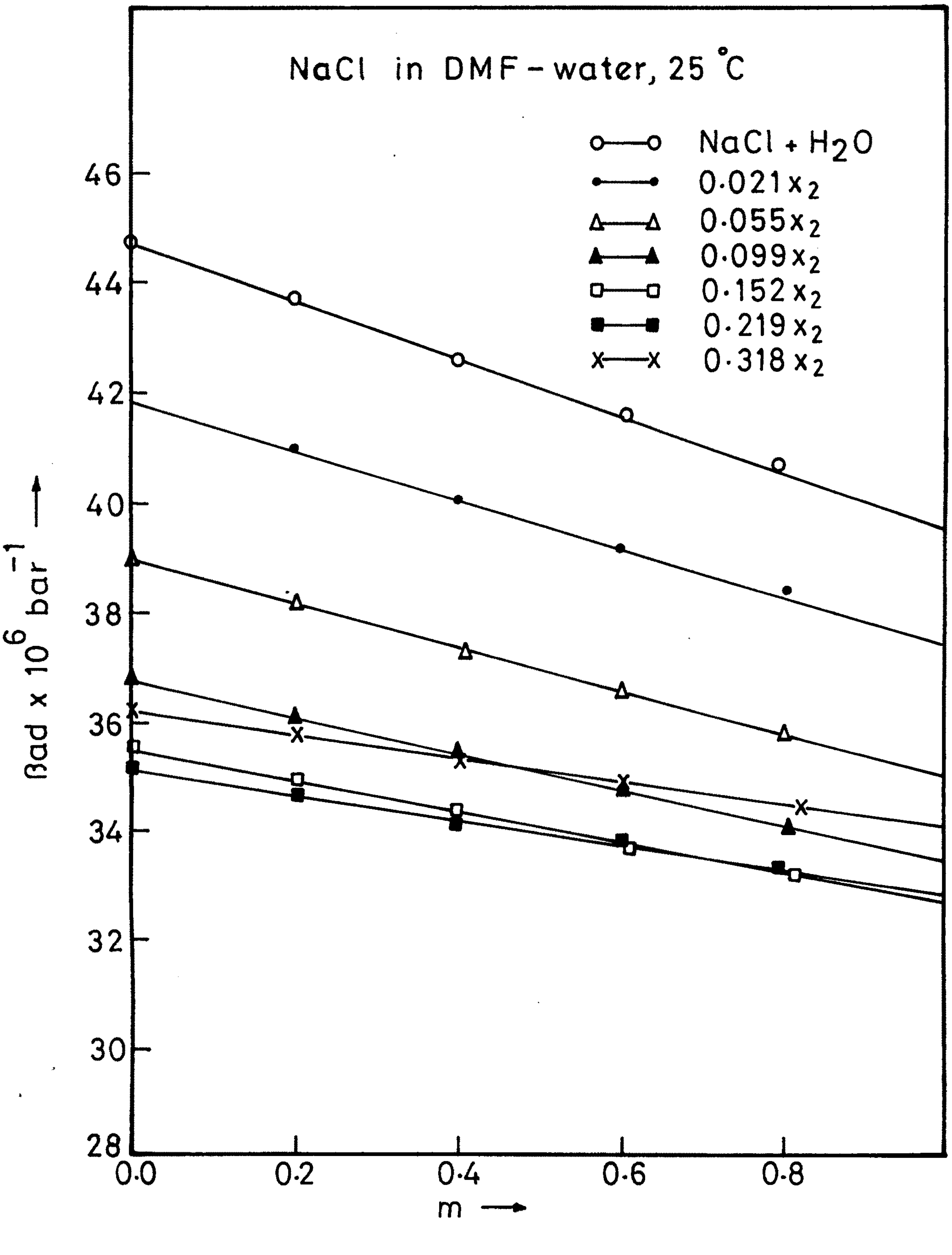
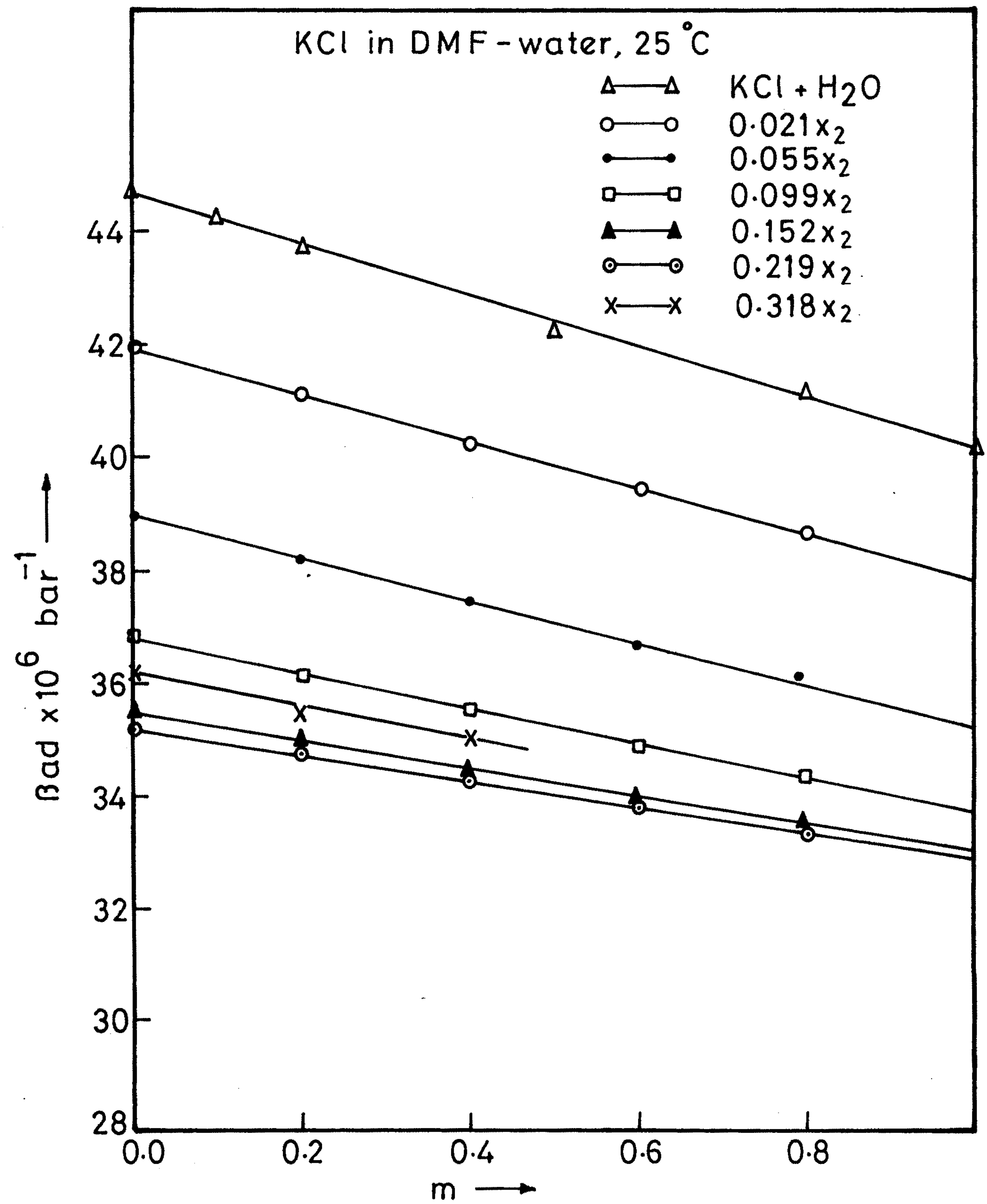

NaCl in DMF-water, 25 °C
NaCl + H2O
0·021 x2
0·055 x2
0·099 x2
0·152 x2
0·219 x2
0·318 x2
46
44
42
40
38
36
34
32
30
28
βad x 10^6 bar^-1
0·0
0·2
0·4
0·6
0·8
m

Fig. 19



KCl in DMF - water, 25 °C
KCl + H2O
0·021x2
0·055x2
0·099x2
0·152x2
0·219x2
0·318x2
ßad x10^6 bar^-1
44
42
40
38
36
34
32
30
28
0.0
0·2
0·4
0·6
0·8
m

Fig. 20

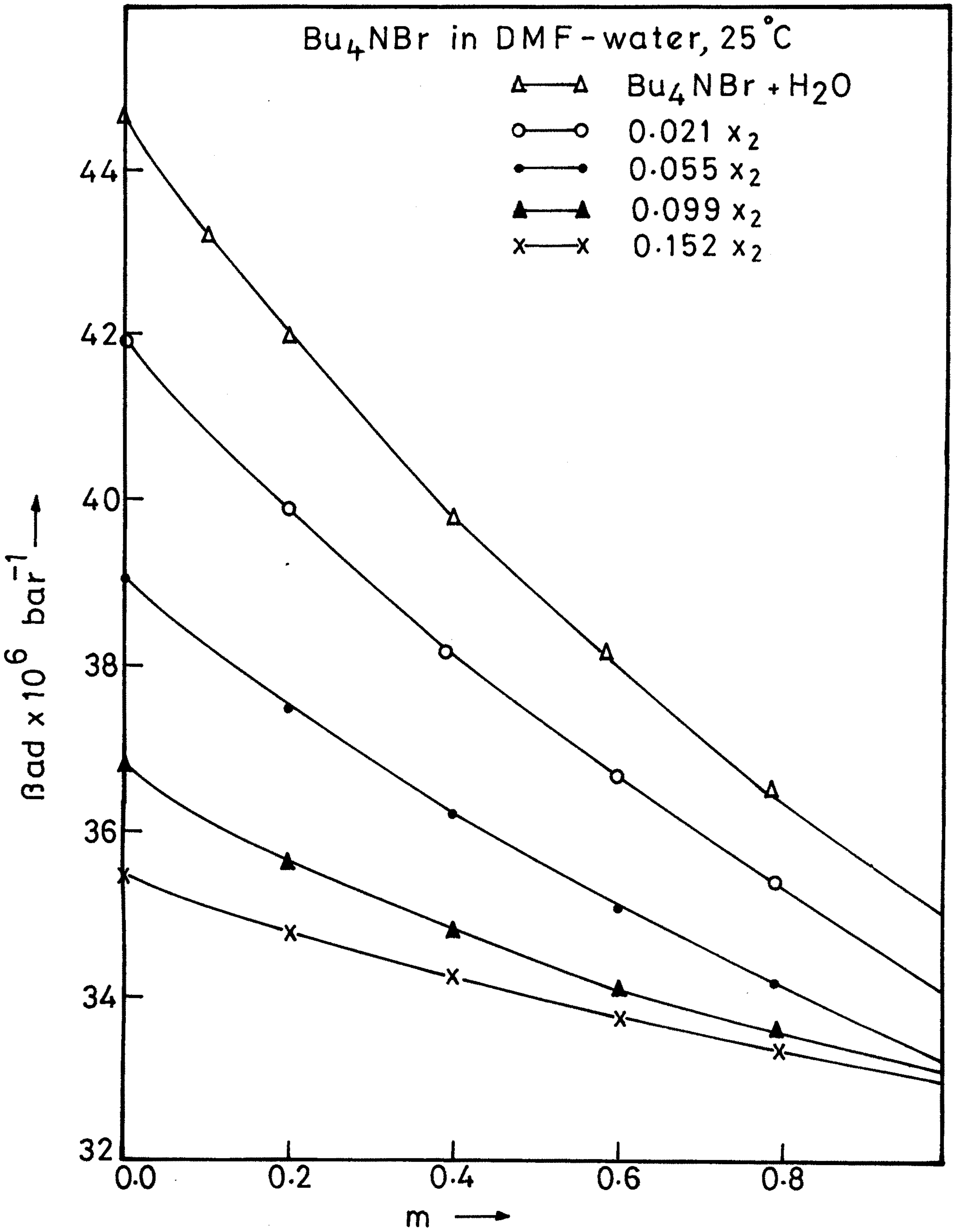

Bu₄NBr in DMF-water, 25 °C
Bu₄NBr + H₂O
0.021 x₂
0.055 x₂
0.099 x₂
0.152 x₂
ßad x 10⁶ bar⁻¹
44
42
40
38
36
34
32
0.0
0.2
0.4
0.6
0.8
m

Fig. 21

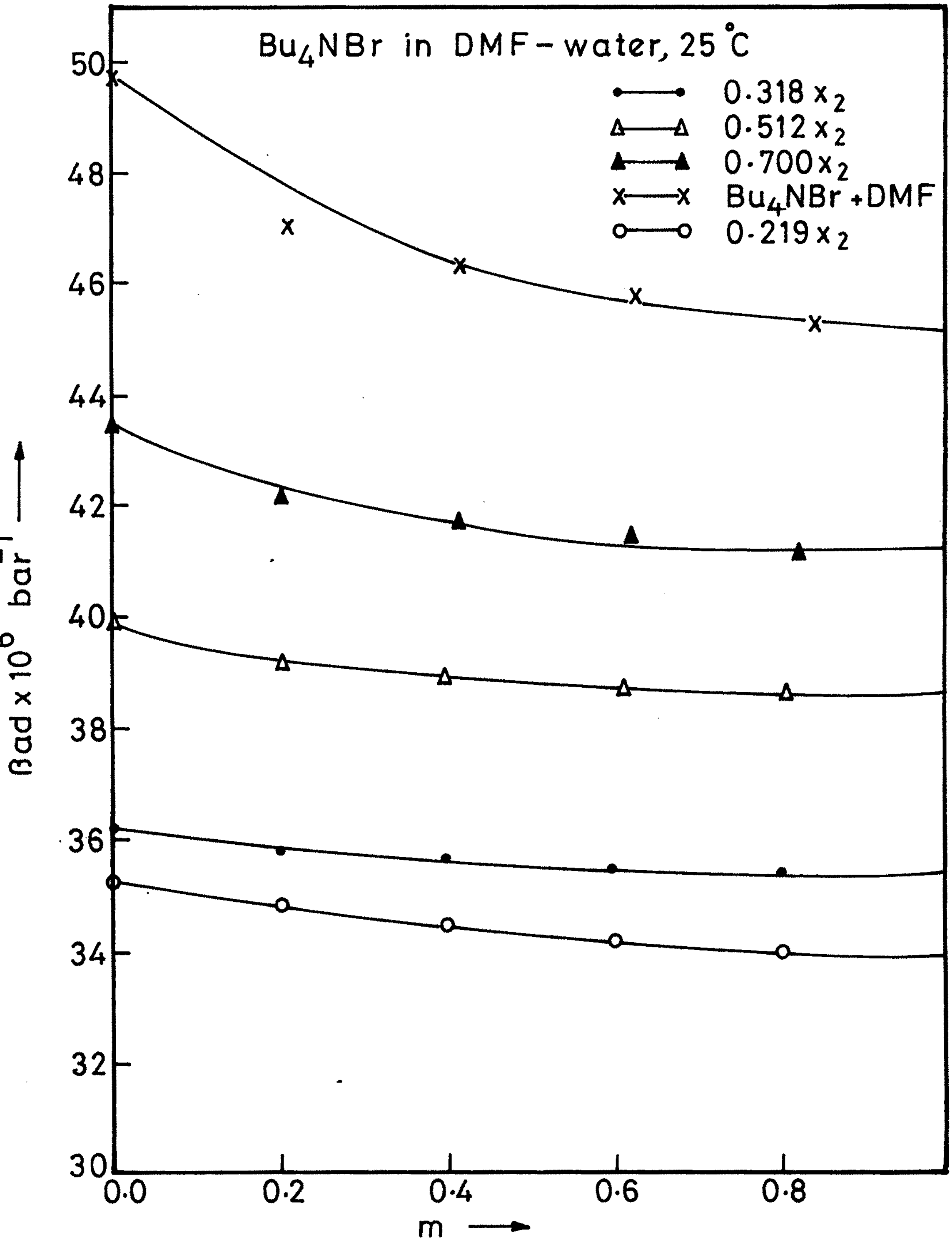

Bu4NBr in DMF-water, 25 °C
0·318 x2
0·512 x2
0·700 x2
Bu4NBr + DMF
0·219 x2
ßad x 10^6 bar^-1
m
30
32
34
36
38
40
42
44
46
48
50
0·0
0·2
0·4
0·6
0·8

Fig. 22

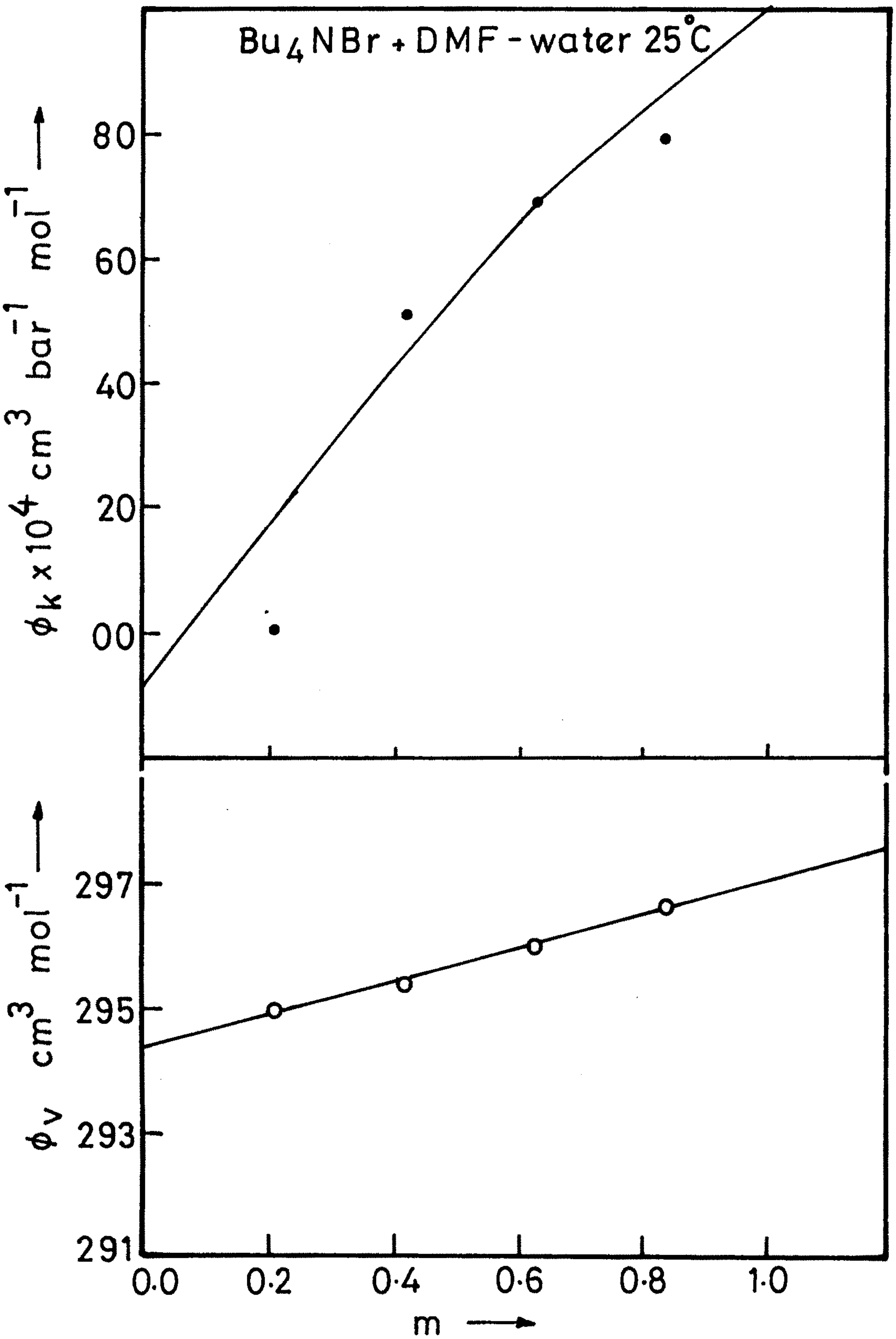

Bu4NBr + DMF - water 25°C
φk x 10^4 cm^3 bar^-1 mol^-1
80
60
40
20
00
φv cm^3 mol^-1
297
295
293
291
0.0
0·2
0·4
0·6
0·8
1·0
m

Fig. 22 (a)

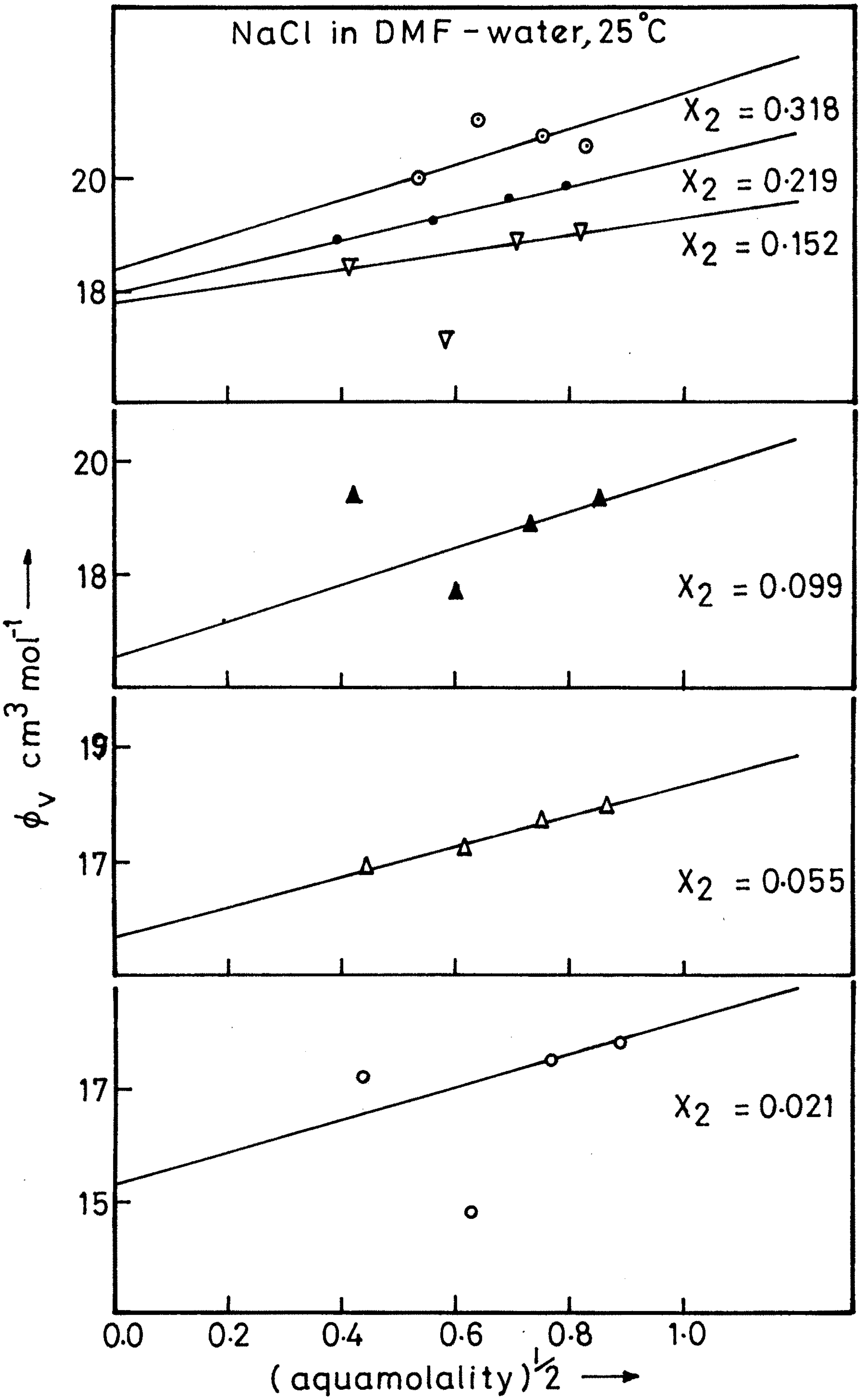

NaCl in DMF - water, 25°C
X_2 = 0·318
X_2 = 0·219
X_2 = 0·152
X_2 = 0·099
X_2 = 0·055
X_2 = 0·021
20
18
20
18
19
17
17
15
ϕ_v cm³ mol⁻¹ ⟶
0.0
0·2
0·4
0·6
0·8
1·0
(aquamolality)$^{1/2}$ ⟶

Fig. 23

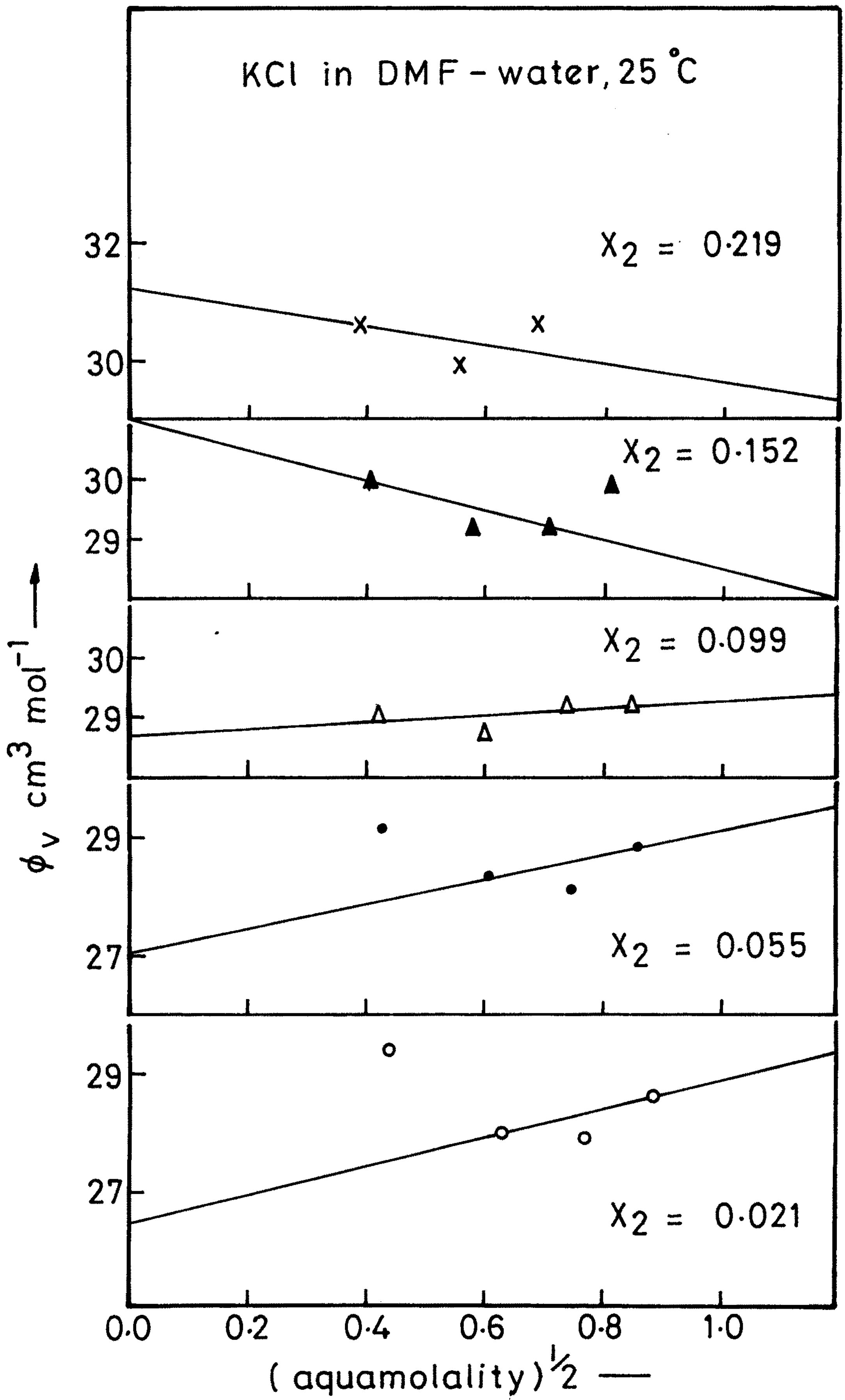

KCl in DMF - water, 25 °C
X2 = 0·219
X2 = 0·152
X2 = 0·099
X2 = 0·055
X2 = 0·021
32
30
30
29
30
29
29
27
29
27
φv cm3 mol-1
0·0
0·2
0·4
0·6
0·8
1·0
(aquamolality)½

Fig. 24

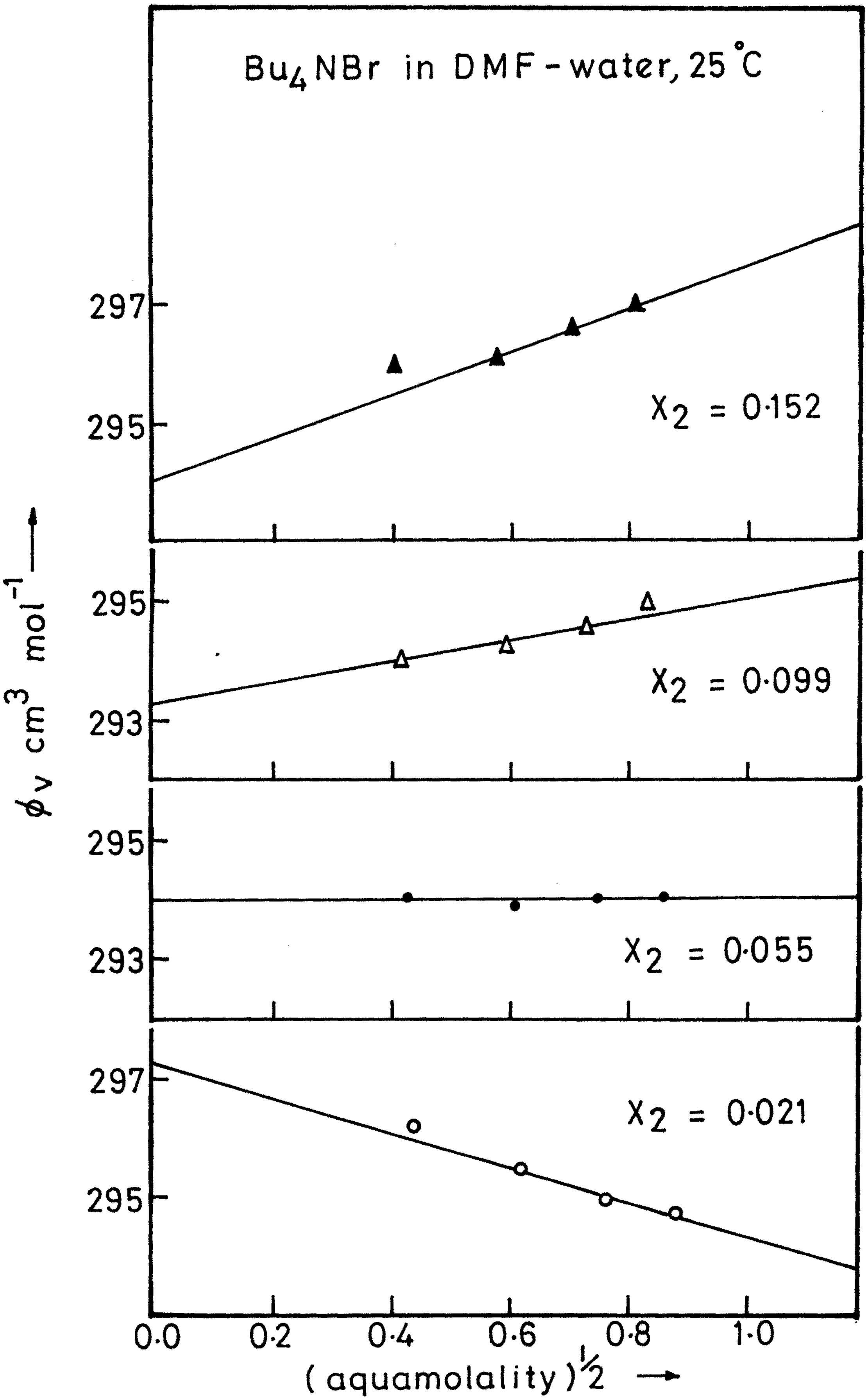

Bu4NBr in DMF-water, 25°C
X2 = 0·152
X2 = 0·099
X2 = 0·055
X2 = 0·021
297
295
295
293
295
293
297
295
ϕv cm3 mol-1
0·0
0·2
0·4
0·6
0·8
1·0
(aquamolality)½

Fig. 25

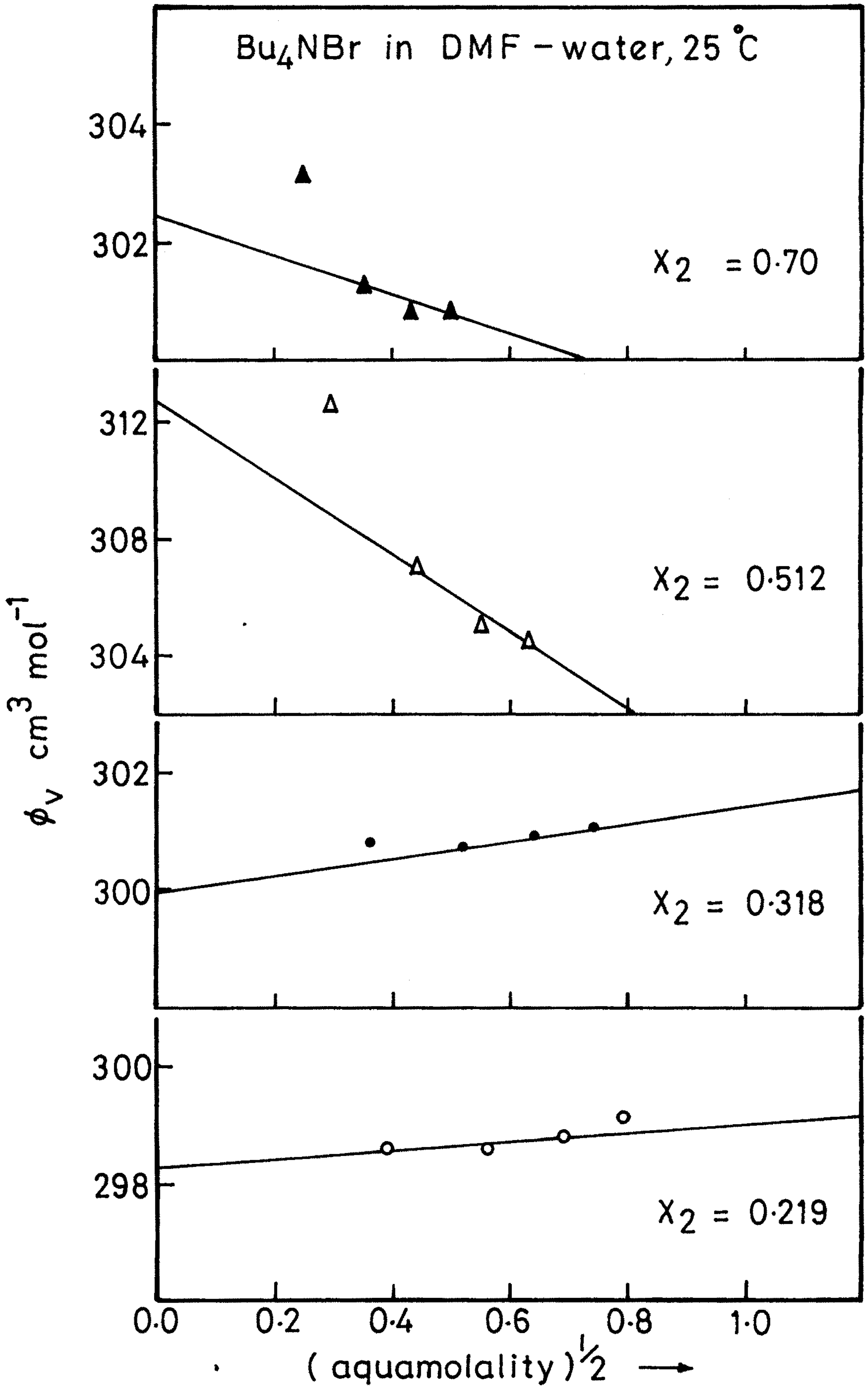

Bu4NBr in DMF - water, 25 °C
304
302
X2 = 0·70
312
308
304
X2 = 0·512
302
300
X2 = 0·318
300
298
X2 = 0·219
φv cm3 mol-1
0·0
0·2
0·4
0·6
0·8
1·0
(aquamolality)½ →

Fig. 26

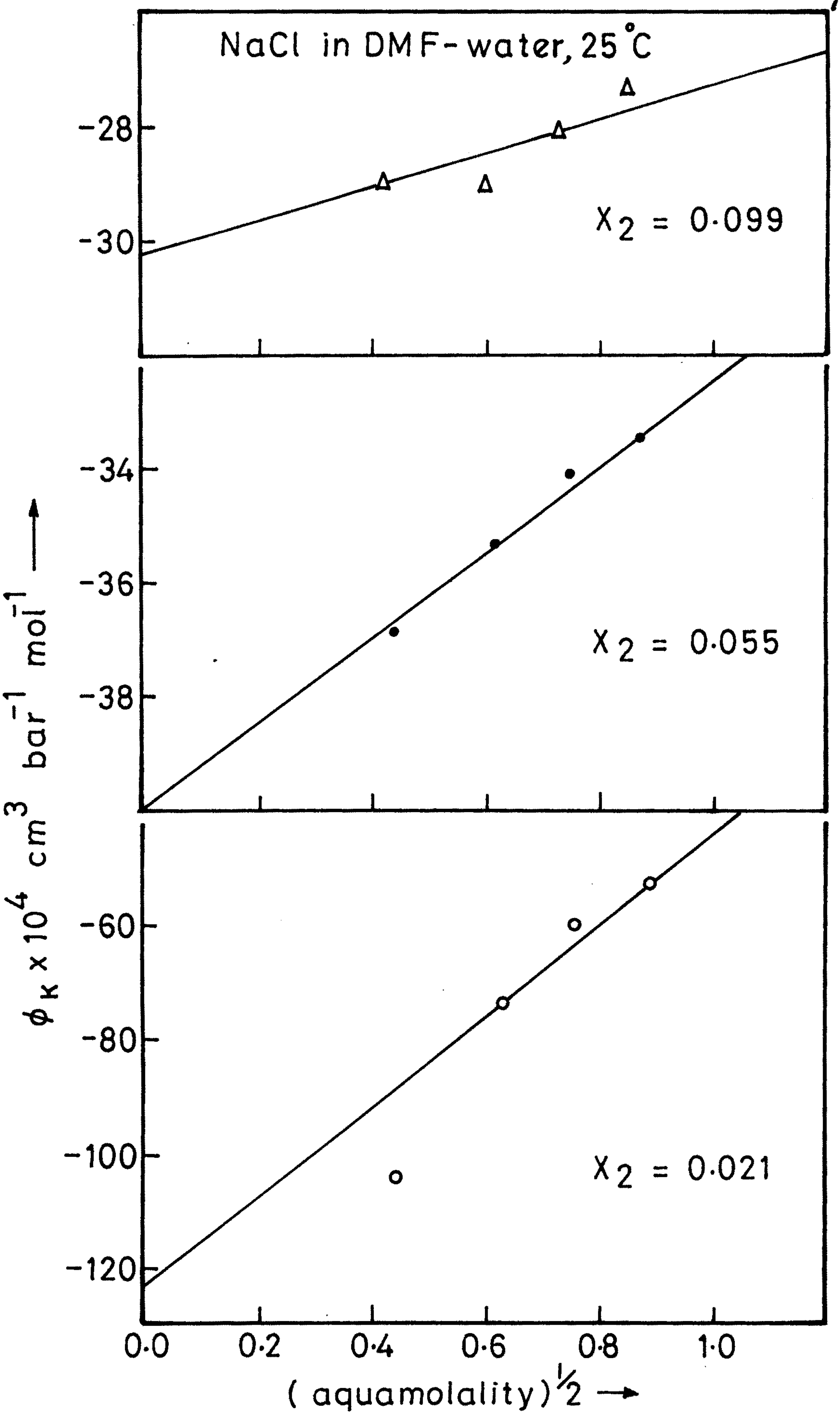

NaCl in DMF-water, 25°C
-28
-30
X2 = 0·099
-34
-36
-38
X2 = 0·055
-60
-80
-100
-120
X2 = 0·021
ϕκ x 10^4 cm^3 bar^-1 mol^-1
0·0
0·2
0·4
0·6
0·8
1·0
(aquamolality)½

Fig. 27

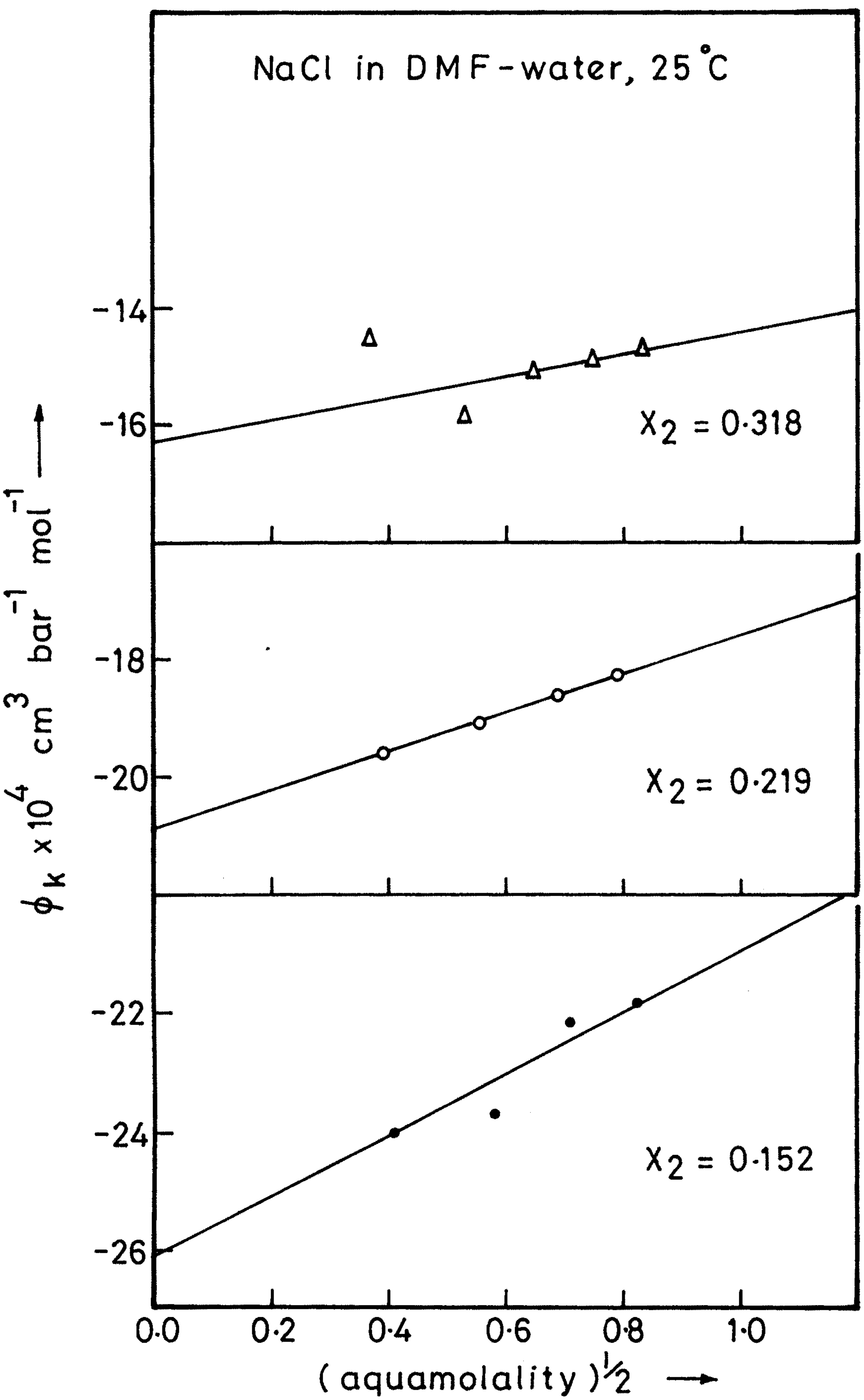

NaCl in DMF-water, 25 °C
-14
-16
X_2 = 0·318
-18
-20
X_2 = 0·219
-22
-24
-26
X_2 = 0·152
0·0
0·2
0·4
0·6
0·8
1·0
(aquamolality)½ →
$\phi_K \times 10^4$ cm^3 bar^{-1} mol^{-1} →

Fig. 28

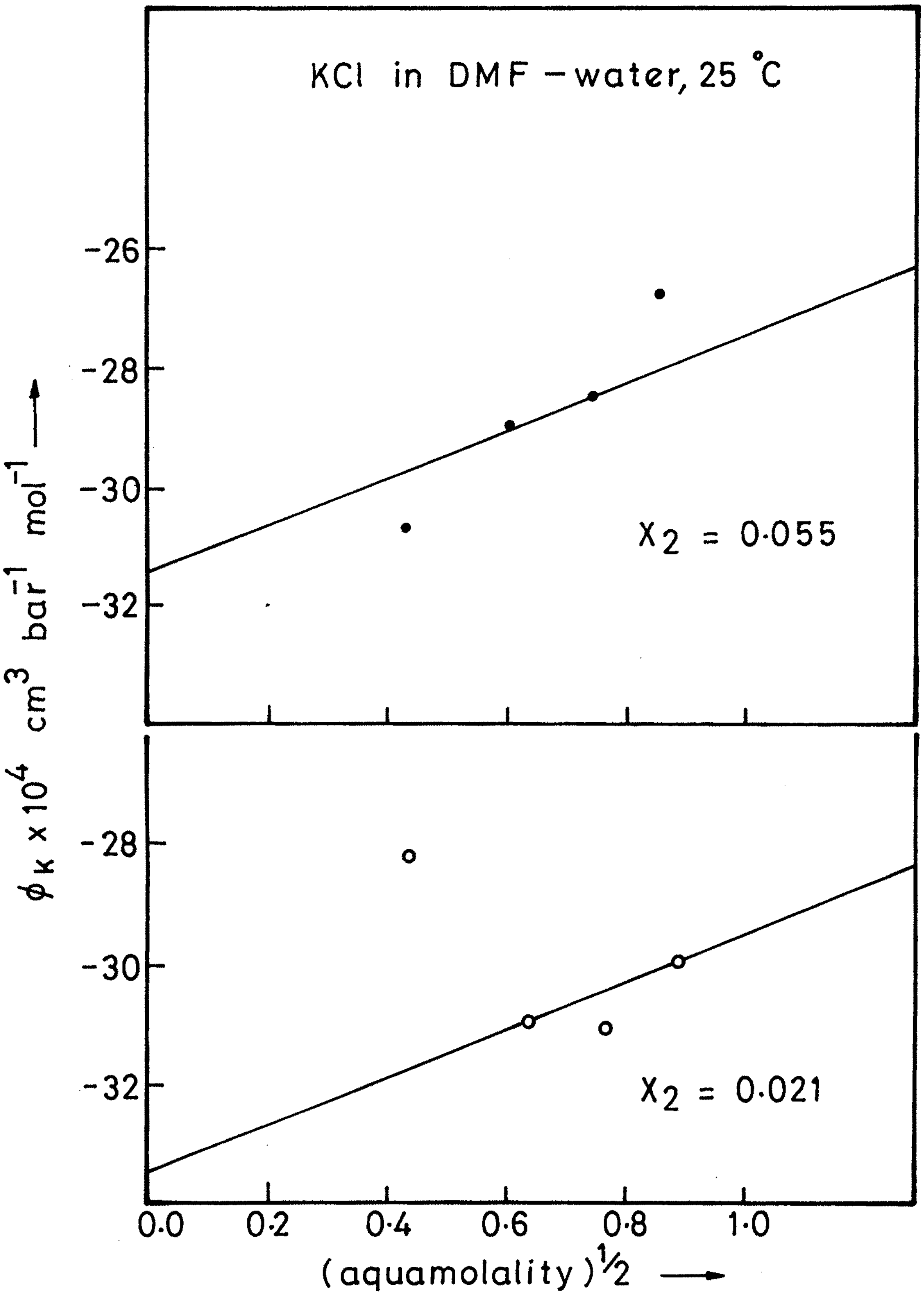

KCl in DMF – water, 25 °C
-26
-28
-30
-32
X2 = 0·055
-28
-30
-32
X2 = 0·021
φK × 10^4 cm^3 bar^-1 mol^-1
0.0
0·2
0·4
0·6
0·8
1·0
(aquamolality)^½

Fig. 29

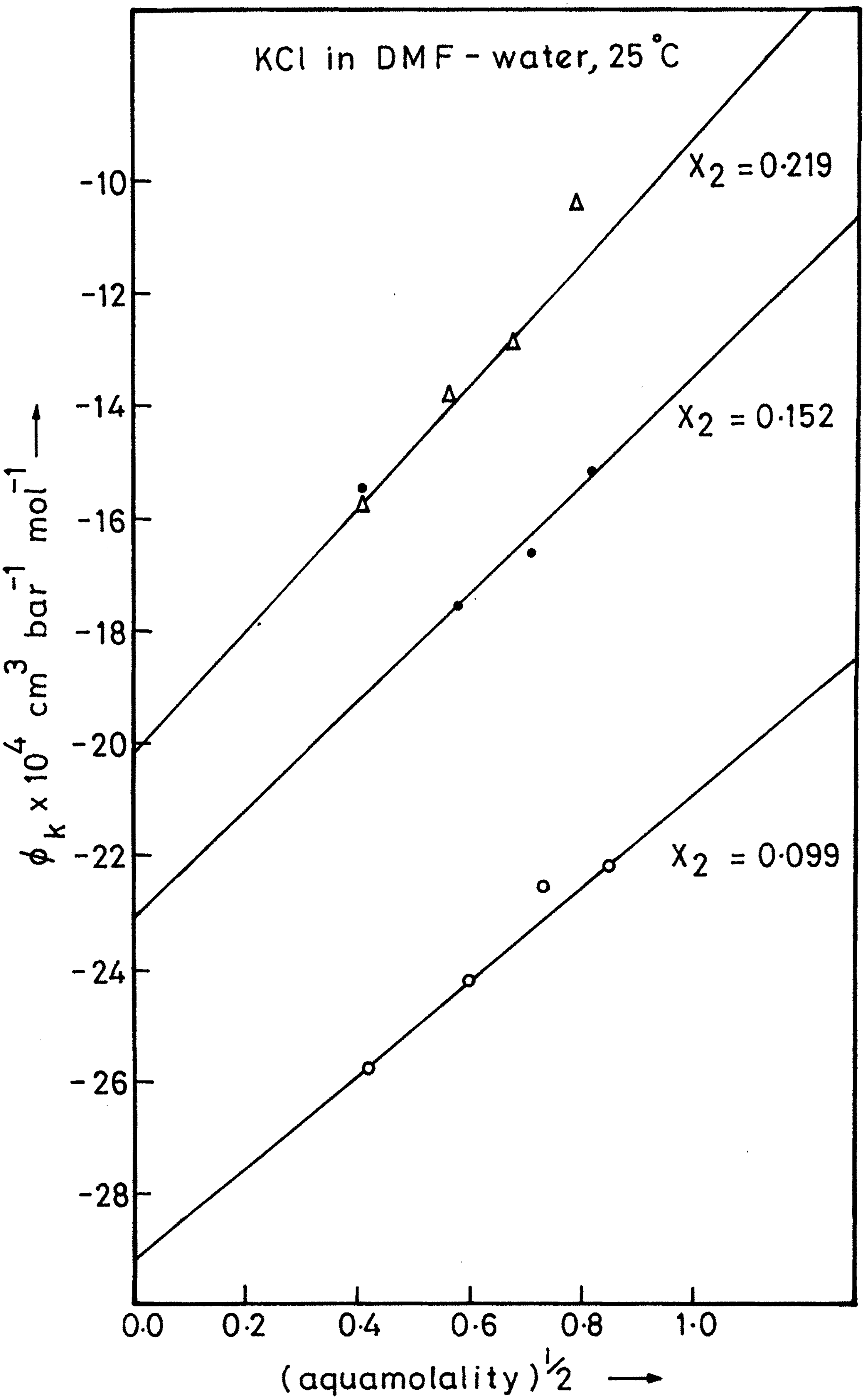
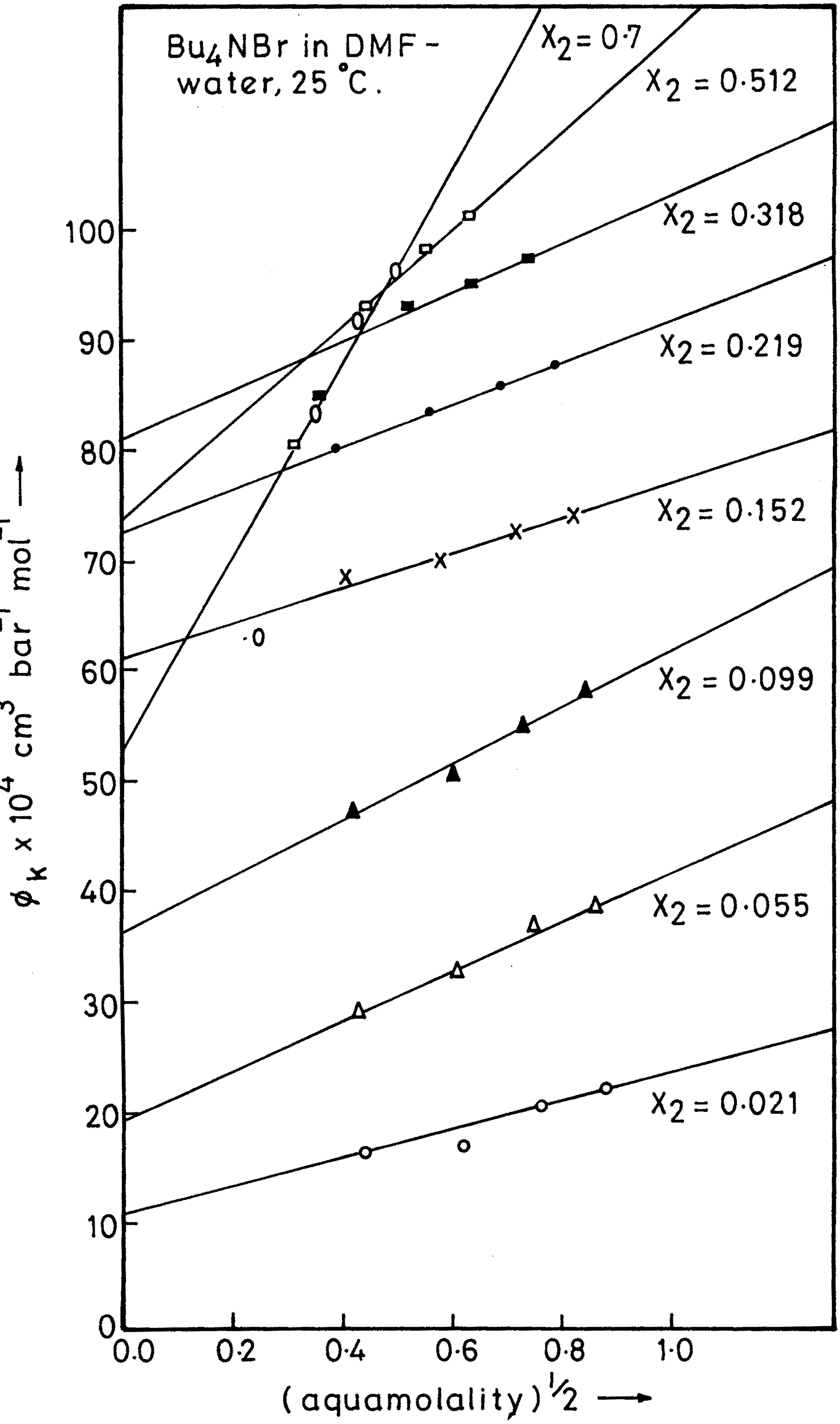
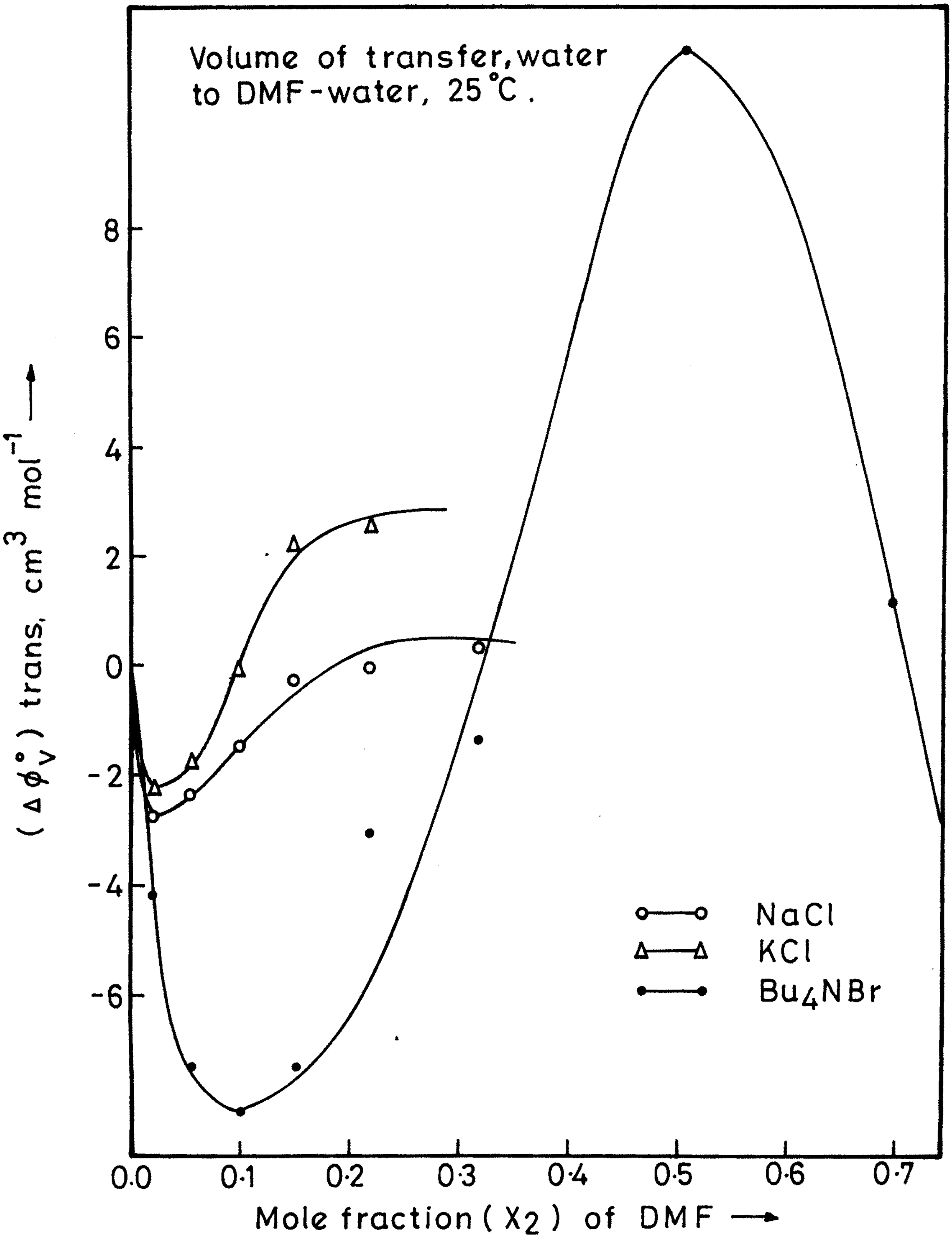

KCl in DMF - water, 25 °C
X2 = 0·219
X2 = 0·152
X2 = 0·099
-10
-12
-14
-16
-18
-20
-22
-24
-26
-28
φk x 10^4 cm^3 bar^-1 mol^-1
0.0
0·2
0·4
0·6
0·8
1·0
(aquamolality)^1/2

Fig. 30


Bu4NBr in DMF - water, 25 °C.
X2 = 0·7
X2 = 0·512
X2 = 0·318
X2 = 0·219
X2 = 0·152
X2 = 0·099
X2 = 0·055
X2 = 0·021
φk x 10^4 cm^3 bar^-1 mol^-1
(aquamolality)½
0
10
20
30
40
50
60
70
80
90
100
0.0
0·2
0·4
0·6
0·8
1·0



Volume of transfer, water to DMF-water, 25°C.
8
6
4
2
0
-2
-4
-6
(Δφ°v) trans, cm3 mol-1
0.0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
Mole fraction (X2) of DMF
NaCl
KCl
Bu4NBr

Fig. 32

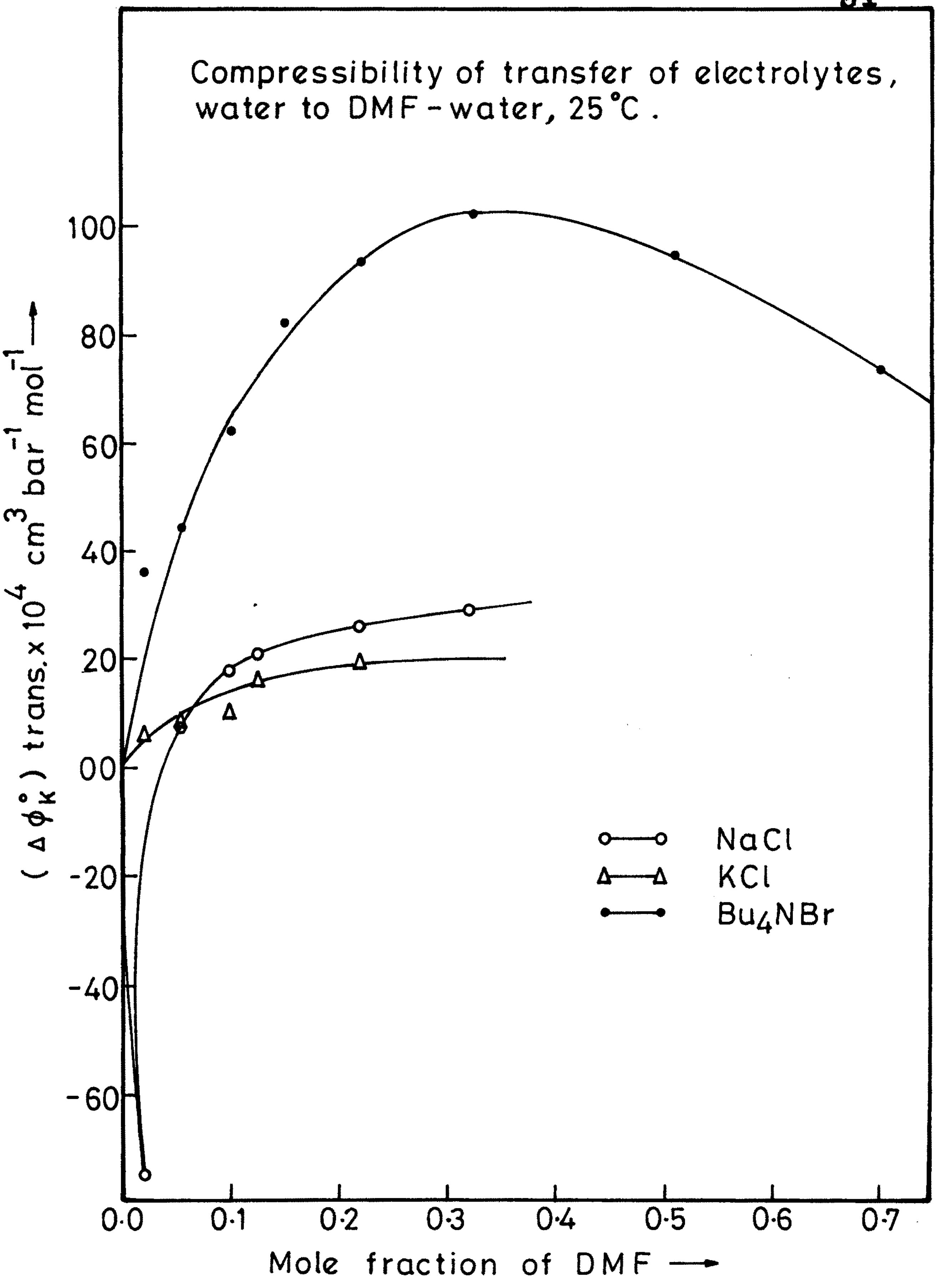

Compressibility of transfer of electrolytes, water to DMF-water, 25°C.
100
80
60
40
20
00
-20
-40
-60
(Δφ°K) trans. x 10^4 cm^3 bar^-1 mol^-1
0·0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
Mole fraction of DMF
NaCl
KCl
Bu4NBr

Fig. 33