ULTRASONIC VELOCITIES IN BINARY MIXTURES

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Received October 15, 1953

Ultrasonic velocities and their variation with concentration have been measured for five binary mixtures, *e.g.*, toluene-heptane, pyridine-acetic acid, pyridine-*n*-butyric acid, nitrobenzene-*n*-butyl alcohol and methyl alcohol-benzene. From the observed value of the velocity, adiabatic compressibility was calculated for each mixture. The effect of compound formation and association on the compressibilities of these mixtures has been examined.

1. INTRODUCTION

A study of the variation with composition of the physical properties of liquid mixtures may be expected to throw some light on the state of cohesion and intermolecular forces. Two such properties are acoustic velocity and adiabatic compressibility. Wilson and Richards (1932), Parthasarathy (1936), Prashad (1941, 1942) and many others have made measurements of the acoustic velocities and compressibilities of liquid mixtures. With a view to studying the effect of compound formation and association on compressibility, more measurements on other binary mixtures which have not been made so far are reported in this paper. Some interesting results are brought out in the study of the following mixtures:—Toluene-heptane, pyridine-acetic acid, pyridine-*n*-butyric acid, nitrobenzene-*n*-butyl alcohol and methyl alcohol-benzene.

2. EXPERIMENTAL DETAILS

The well-known Bachem-Hiedemann (1936) method of secondary interferences was employed in the present investigation to determine the ultrasonic velocities. The ultrasonic waves were produced by means of a quartz crystal of fundamental frequency $2 \cdot 8 \times 10^6$ cycles/second and the crystal was connected to the output of a 807 valve oscillator. Excitation of the crystal was kept at a minimum so that the temperature of the liquid did not rise appreciably. The interference pattern so formed in the liquid was photographed by a suitable arrangement and the fringe width was measured using a Hilger cross-slide micrometer. As many as forty fringes were measured and the average fringe width was calculated.

Two independent observations were taken for each mixture, besides repeating each measurement for a particular concentration. The frequency was measured accurately by means of a heterodyne wavemeter which was previously calibrated with the nearest transmitting station.

All the chemicals were pure B.D.H. or Merck products and were distilled before use. Densities of the mixtures were determined with the aid of a specific gravity bottle. Using the formula $\beta_\phi = 1/\rho v^2$ where ρ is the density in gm./c.c. and v the ultrasonic velocity in metres/sec., β_ϕ, the adiabatic compressibility was calculated. Curves were drawn showing the variation of velocity with concentration and adiabatic compressibility with concentration for each mixture and are reproduced in Figs. 1 to 4.

3. RESULTS AND DISCUSSION

TABLE I

1. *Toluene-Heptane*

Mol. % Heptane	Velocity in metres/sec.	Density p.	Adiabatic Compressibility $\times 10^6$
0	1328	·8623	65·75
12·74	1307·5	·842	69·37
22·59	1290	·825	72·83
30·45	1277	·815	75·58
36·25	1267	·8	77·85
42·18	1262	·794	79·07
54·87	1247	·772	83·33
64·6	1231	·755	87·44
78·5	1217	·733	92·15
100	1194	·695	100·9

TABLE II

2. *Pyridine-acetic acid*

Mol. % Acetic acid	Velocity in metres/sec.	Density	Adiabatic Compressibility $\times 10^6$
0	1398	·988	51·76
25·33	1348	·100	55·03
30	132		
40·26	1311	1·015	57·33
51·22	1299	1·029	57·58
58·34	1291	1·044	57·5
65·13	1278	1·055	58·01
73·69	1269	1·069	58·08
84·82	1249	1·081	59·32
100	1113	1·051	76·85

TABLE III

3. *Pyridine*-n-*butyric acid*

Mol. % Butyric acid	Velocity in metres/sec.	Density	Adiabatic Compressibility $\times 10^6$
0	1398	·976	52·41
21·59	1386	·9825	52·98
35·5	1347	·9875	54·99
45·24	1352	·9917	55·18
52·42	1342	·9955	55·8
59·51	1323	·9967	58·02
68·8	1300	·9933	59·6
81·49	1247	·9856	65·27
100	1156	·965	77·54

TABLE IV

4. *Nitrobenzene*-n-*butyl alcohol*

Mol. % *n*-butyl alcohol	Velocity in metres/sec.	Density	Adiabatic Compressibility $\times 10^6$
0	1473	1·1987	38·43
20	1406	1·1148	45·29
30	1385	1·0802	48·26
50	1341	1·012	54·96
60	1312	·9696	59·92
70	1293	·9309	64·25
100	1268	·8098	76·79

TABLE V

5. *Benzene-methyl alcohol*

Mol. % Methanol	Velocity in metres/sec.	Density	Adiabatic Compressibility $\times 10^6$
0	1283	·87232	69·66
20	1245	·8656	74·4
36·11	1234	·8592	76·43
53·06	1217	·851	79·38
62·91	1201	·845	82·06
69·31	1194	·8409	83·41
75·09	1179	·8362	86·00
81·91	1160	·8299	89·52
100	1118	·80842	99·04

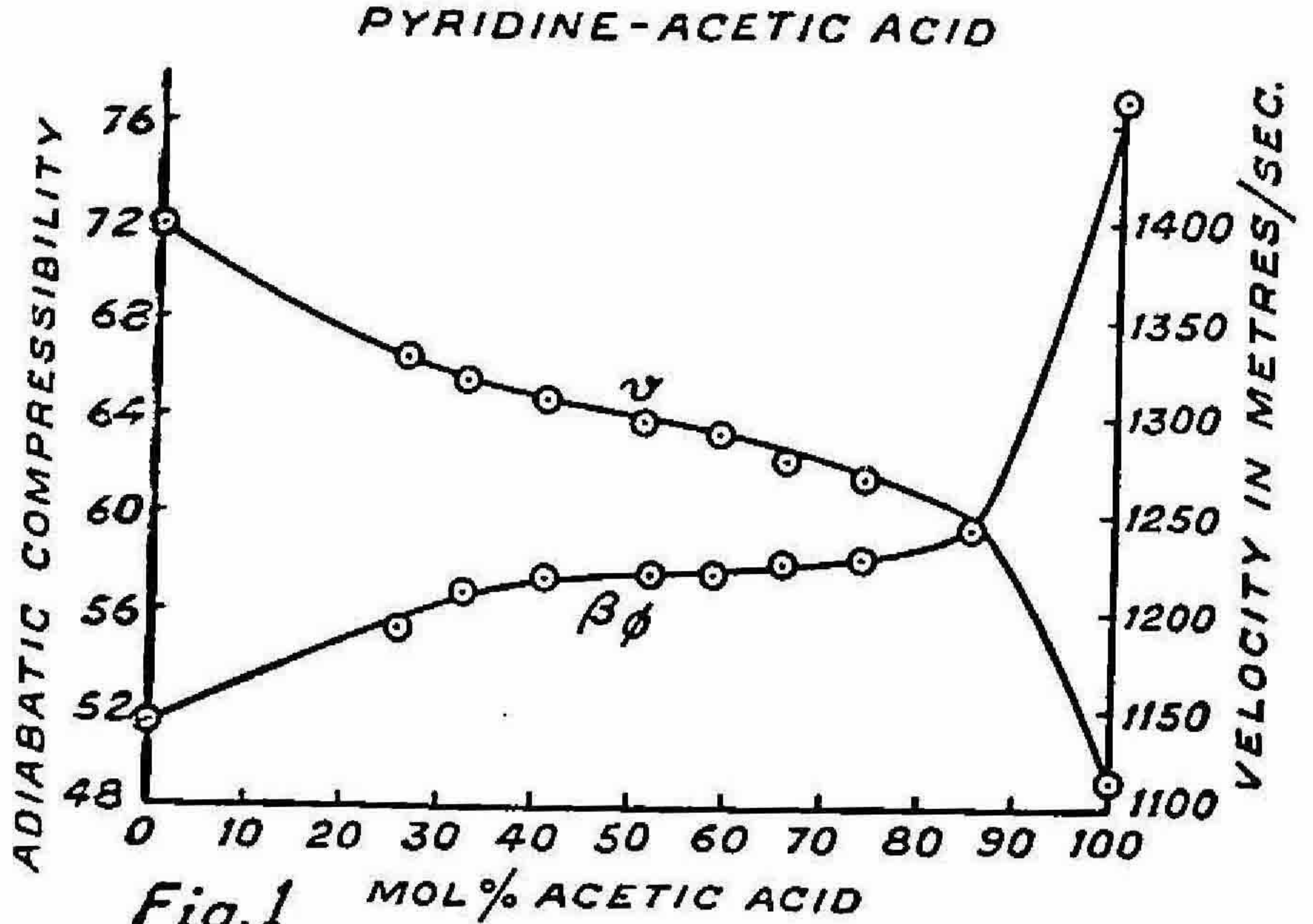
PYRIDINE-ACETIC ACID
ADIABATIC COMPRESSIBILITY
76
72
68
64
60
56
52
48
v
βφ
0
10
20
30
40
50
60
70
80
90
100
MOL% ACETIC ACID
1400
1350
1300
1250
1200
1150
1100
VELOCITY IN METRES/SEC.

Fig. 1

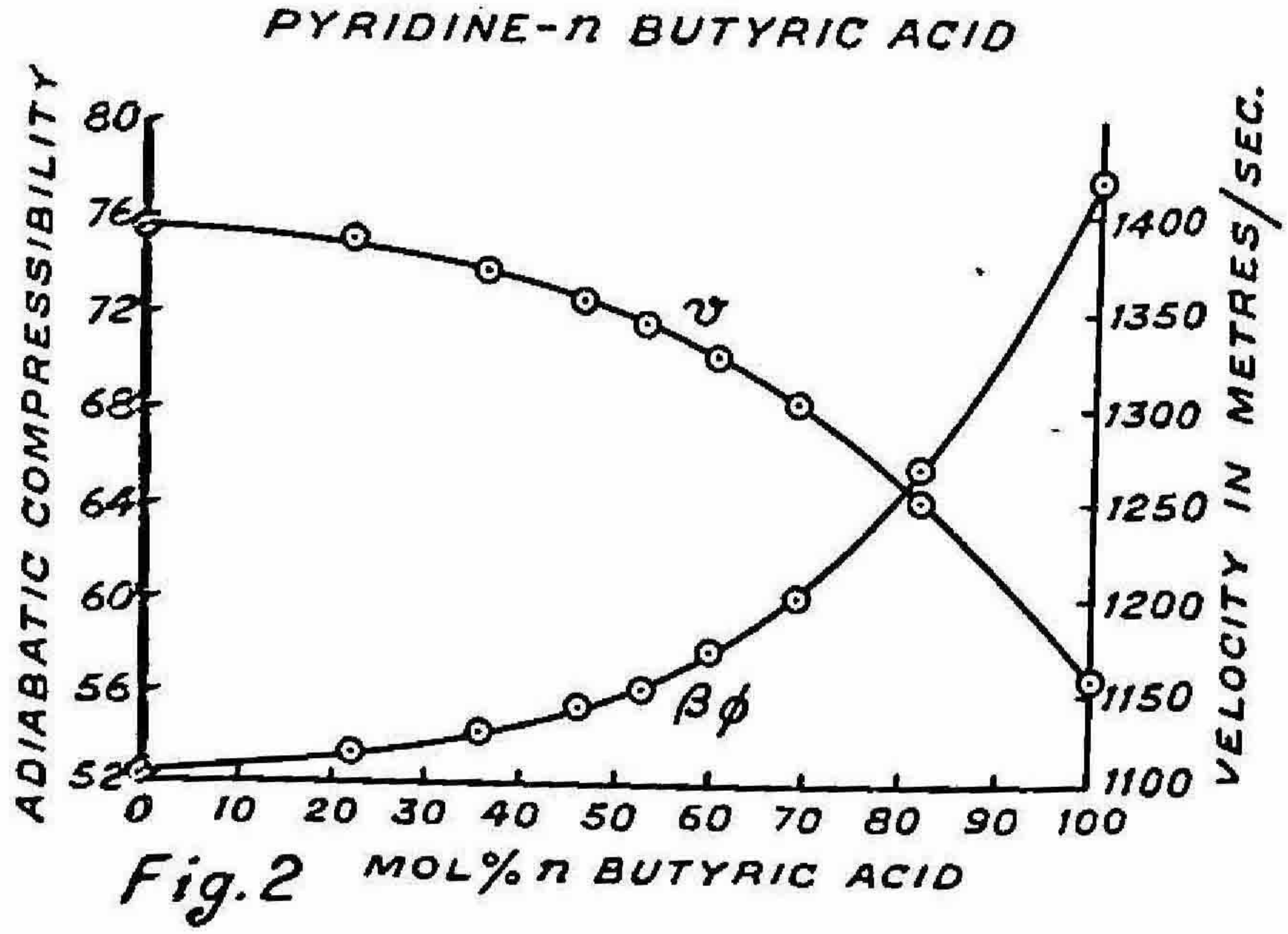
PYRIDINE-n BUTYRIC ACID
ADIABATIC COMPRESSIBILITY
80
76
72
68
64
60
56
52
v
βφ
0
10
20
30
40
50
60
70
80
90
100
MOL% n BUTYRIC ACID
1400
1350
1300
1250
1200
1150
1100
VELOCITY IN METRES/SEC.

Fig. 2

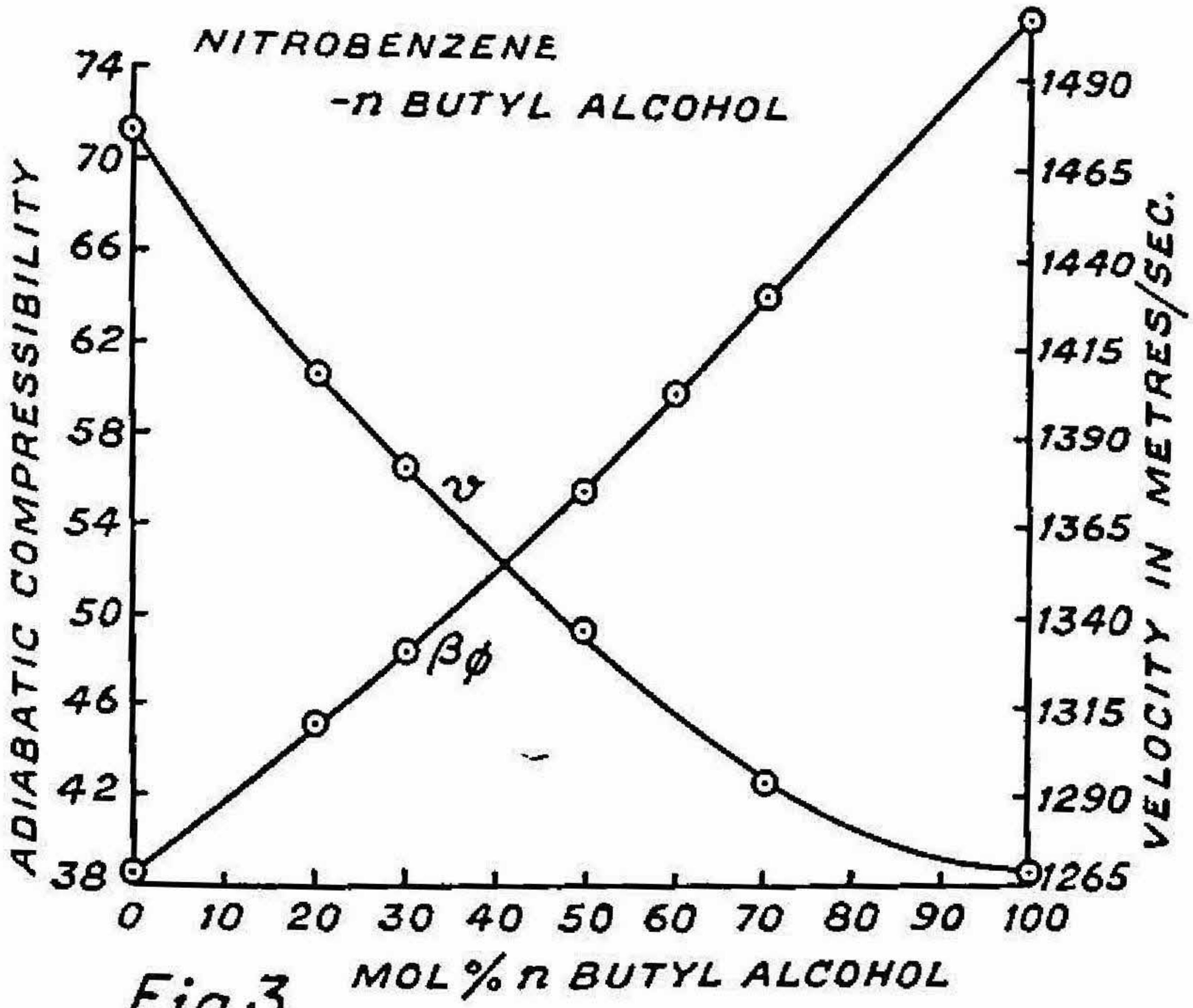
NITROBENZENE
-n BUTYL ALCOHOL
ADIABATIC COMPRESSIBILITY
74
70
66
62
58
54
50
46
42
38
VELOCITY IN METRES/SEC.
1490
1465
1440
1415
1390
1365
1340
1315
1290
1265
v
βϕ
0
10
20
30
40
50
60
70
80
90
100
MOL % n BUTYL ALCOHOL

Fig.3

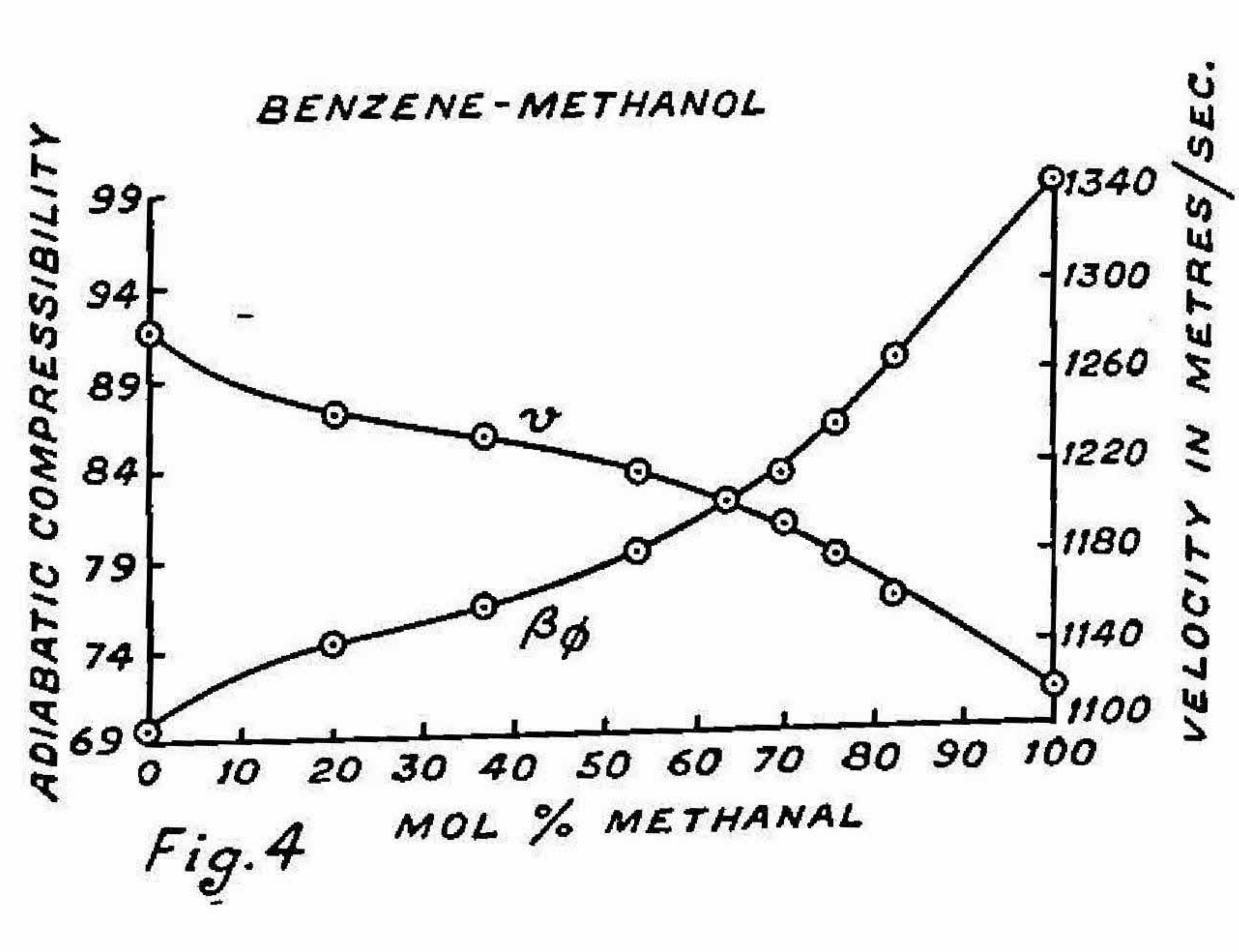
BENZENE-METHANOL
ADIABATIC COMPRESSIBILITY
99
94
89
84
79
74
69
VELOCITY IN METRES/SEC.
1340
1300
1260
1220
1180
1140
1100
v
βϕ
0
10
20
30
40
50
60
70
80
90
100
MOL % METHANAL

Fig.4

1. *Toluene and heptane.*—Toluene and heptane were taken as representatives of aromatic and aliphatic hydrocarbons respectively. The behaviour of this mixture is quite normal and as these liquids are non-polar, they do not associate when mixed. The adiabatic compressibility of this mixture takes intermediate values between those for the pure liquids. The compressibility *vs.* concentration curve is linear (Graph is not reproduced). So this mixture can be taken to obey the ideal mixture law.

2. *Pyridine and acetic acid.*—This is an interesting case of compound formation. Since all cases of compound formation in solutions are accompanied by certain singularities in physical properties of the mixture, this work was undertaken to see the effect of compound formation on adiabatic compressibility. There is a marked variation in the slope of the compressibility *vs.* concentration curves at 30 mol.% and 80 mol.% of acetic acid (see Fig. 1). The one at the higher concentration of acetic acid is much more pronounced than the one at the lower concentration. This observation could be explained on the basis of the formation of compounds at the two concentrations specified above. Because of the compound formation, the molecules are brought into a more compact arrangement and are in equilibrium and the cohesive energy increases considerably. Hence the compressibility at these concentrations depart very much from the intermediate value which it would have taken if compounds are not formed.

The viscosity-concentration curve of this particular mixture was studied by Tsakalotos (1908) and he found a maximum value for a mixture containing 78 mol.% of acetic acid. Density measurements indicate a maximum at 86 mol.% of acid. A comparison of the viscosity and vapour pressure data available shows that for a maximum in the viscosity curve of a certain mixture there corresponds a minimum in the vapour pressure curve and *vice versa* (Faust, 1912; Yagnik *et al.*, 1925). The vapour pressure data by Zawidzki (1900) for pyridine-acetic acid mixtures exhibit two anomalies: *e.g.*, a minimum value for a mixture containing 50 mol. % acetic acid and two points of inflexion corresponding to mixtures containing 30 and 80 mol.% of the acid. He had suggested the existence of two compounds, one containing more pyridine corresponding to the first point of inflexion and other containing more acid corresponding to the second point of inflexion. The results obtained by the present writer support Zawidzki's observations on vapour pressure.

3. *Pyridine and* n-*butyric acid.*—The compressibility concentration curve for this mixture exhibits a steeper rise at about 60 mol.% *n*-butyric acid (Fig. 2), suggesting the formation of a compound $2C_5H_5N.3CH_3CH_2$

CH_3COOH at this particular concentration. This supports the earlier observations of Tsakalotos (*loc. cit.*) on viscosity and density measurements of this mixture.

4. *Nitrobenzene and n-butyl alcohol.*—The compressibility *vs.* concentration curve (Fig. 3) in this case is very nearly linear being slightly convex downwards. Though the viscosity concentration curve studied by J. Wagner (1903) suggests a viscosity minimum at 60 mol. % *n*-butyl alcohol, a similar behaviour is not exhibited by the compressibility *vs.* concentration curve. This may be due to the following factors that inhibit the formation of a compound. The phenomenon of association always increases the cohesive energy between the molecules only slightly and hence there is practically no departure from the ideal mixture case. Also though nitrobenzene is polar having quite a large dipole moment, the Keesom contribution due to dipole energy decreases due to dipoles being effectively screened (Prashad, 1942). *n*-Butyl alcohol as any other alcohol has large Keesom or orientation energy and in fact its pronounced association is due to the great activity of its —OH dipoles. Hence in this case there is only association between alcohol molecules and no compound formation takes place though it may be expected.

5. *Benzene and methyl alcohol.*—The compressibility curve in this case exhibits a point of inflexion at about 30%. To explain this peculiar shape of the curve, one has to consider the effect of both dissociation and association between the molecules. Since the benzene molecule has a planar structure and a high value of polarizability it has a tremendous dissociating effect on the associating groups of any liquid—that may be introduced in it. By virtue of their high polarizability, benzene molecules will develop induced dipoles and these will so interact with the associated molecules that they will be dissociated. For the same reason benzene molecules can exert high dispersion forces on the associated molecules. On the other hand, in alcohol the —OH dipole has got a very great tendency for association.

In the system benzene-methyl alcohol, we get a point of inflexion in both the curves for velocity and adiabatic compressibility. R. Prashad has measured the acoustic velocity in benzene-ethyl alcohol mixtures. The difference between benzene-ethyl alcohol and benzene-methyl alcohol curves is that in the former case the point of inflexion of the velocity *vs.* concentration curve occurs near about 60 mol.% alcohol and in the latter it happens at about 30 mol.%. But the compressibility curves in both the cases is similar.

Now, in the first stage (*i.e.*, lower mol. % alcohol) there is a large number of benzene molecules but only a small number of alcohol molecules. So the alcohol molecules will be far apart each other because of the great dissociating effect of benzene. This will decrease the cohesive energy between the alcohol molecules and as this decrease is greater than the increase in cohesive energy between alcohol-benzene molecules the net effect is a decrease in cohesive energy which tends to increase the compressibilities from the ideal mixture value. As more alcohol molecules are added, there is a tendency for association which is prevented by the dissociating effect of the benzene molecules. This results in an increase in cohesive energy and in the concavity of the compressibility-concentration curve upwards. Finally, there is association between alcohol molecules and the value reaches that of the compressibility of alcohol alone.

In conclusion, the author wishes to express his grateful thanks to Professor R. S. Krishnan for his guidance and encouragement. His thanks are also due to Mr. V. S. Venkatasubramanian for helpful discussions.

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