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PROPAGATION OF ULTRASONIC WAVES IN LIQUID MIXTURES AND INTERMOLECULAR FORCES II

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ABSTRACT. This paper considers the compressibility-concentration curves of the liquids on the basis of intermolecular action.

The following mixtures have been studied here :—

(1) Ethyl alcohol and benzene, (2) Butyl alcohol and heptane, (3) Benzene and carbon tetrachloride, (4) Ether and benzene, (5) Ethyl acetate and carbon tetrachloride

The most interesting case is of alcohol and benzene, the compressibility curve being inflected. It is shown how the high polarisability of benzene and the association-forming tendency of alcohol determines the nature of the curve In butyl alcohol-heptane, the inertness of heptane as contrasted to the activity of benzene is very significant.

The analysis made in this series of papers is an approach to intermolecular action from a new angle In view of the approximate nature of the molecular fields, the treatment is necessarily qualitative.

INTRODUCTION

This paper is the second of the series on liquid mixtures, the first of which dealt with alcohols and water.[1] Herein are treated the following mixtures :—

(1) Ethyl alcohol and benzene ;

(2) Butyl alcohol and heptane ;

(3) Benzene and carbon tetrachloride ;

(4) Benzene and ether ;

(5) Ethyl acetate and carbon tetrachloride.

The data for velocities and compressibilities for mixtures (1) and (4) were taken by the author, for (2) by Wilson and Richards,[2] for (3) and (5) by Parthasarathy.[3] A qualitative explanation of the compressibility-concentration curves is attempted on the basis of intermolecular action.

EXPERIMENTAL RESULTS

The experimental technique and details employed for mixtures (1) and (4) haves been described in the first paper and will not be repeated here. In the following tables the collected results of all the mixtues are given.

MIXTURE 1

Ethyl alcohol and benzene

Temp. $= 29°.7$ C

No	Mole fraction of alcohol	Density gm./c.c.	Velocity m./s.	Compressibility (adiabatic) $\times 10^{-6}$
1	0	.869	1286	69.5
		.855	1244	75.5
		.855	1245	78.5
4	100	.8455	1214	81.2
5		.8295	1204	83.7
6		.812	1190	86.0
7		.802	1177	90.0
8	1.000	.784	1147	97.0

There are points of inflection in the curves of velocities and compressibilities (Fig. 1).
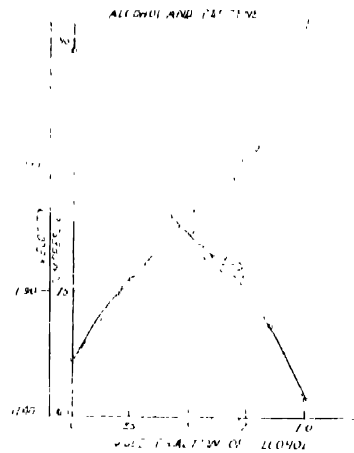

Fig. 1

MIXTURE 2

Butyl alcohol and heptane

Temp. $= 25$ C

No	Mole fraction of alcohol	Density gm. c c	Velocity m./s.	Compressibility (adiabatic) $\times 10^{-6}$
1	0	.6793	1130	115.3
2	.2510	.7004	1136	110.0
3	.4843	.752	1155	103.4
4	.7457	.7603	1190	92.9
5	.8741	.7735	1205	80.0
6	1	.8061	1245	80.0

In the compressibility-concentration graph the curve always remains above the straight line joining the points representing the pure liquids. It means that the compressibility is always more than that expected for ideal mixtures. The velocity-concentration curve always remains below the straight line corresponding to ideal cases (Fig. 2).
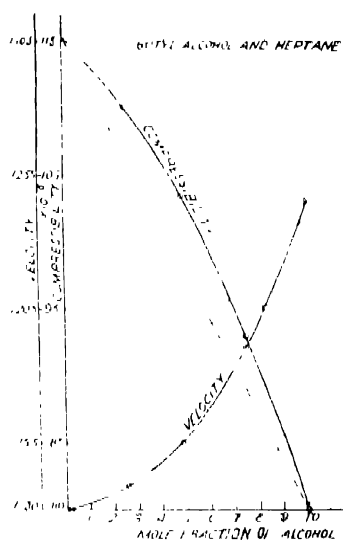

Fig. 2

MIXTURE 3

Benzene and carbon tetrachloride

Temp. $-23°C$

No.	Mole fraction of benzene	Density gm./c.c.	Velocity m./s.	Compressibility (adiabatic) × 10^6
1	1	875	131	66.4
2	.8362	1.001	1201	69.2
3	.7207	1.086	1130	71.0
4	.5175	1.237	1048	73.5
5	.3710	1.340	1018	72.0
6	0	1.596	927.2	72.0

The velocity-concentration curve lies below and the compressibility-concentration curve above their respective straight lines (Fig. 3).
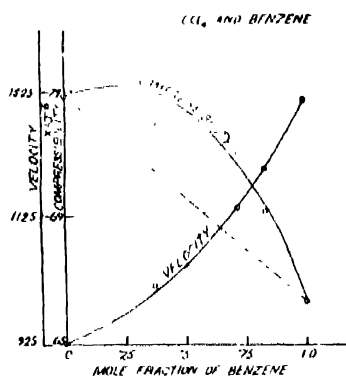

FIG. 3

MIXTURE 4

Benzene and ethyl ether

Temp. = 28°.54C

No.	Mole fraction of ether	Density gm./c.c.	Velocity m./s.	Compressibility (adiabatic) × 10⁻⁶
1	0	.870	1290	69.1
2	.1748	.840	1234	78.1
3	.3609	.811	1180	88.5
4	.5598	.7755	1117	103.4
5	.7941	.7305	1032	128.4
6	1	.699	972	151.5

The velocity-concentration curve is linear and the compressibility-concentration curve slightly concave (Fig. 4).
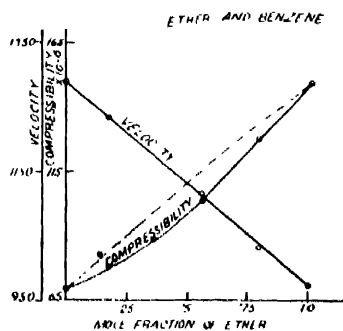

FIG. 4

MIXTURE 5

Ethyl acetate and carbon tetrachloride

Temp. $= 23°C$

No.	Mole fraction of ethyl acetate	Density gm./c.c	Velocity m./s.	Compressibility (adiabatic) $\times 10^{-6}$
1	1	8989	1184	79.3
2	.8002	1 034	1119	77.3
3	.5476	1.200	1051	75.5
4	.3626	1 313	1003	75 7
5	.2555	1.404	984.2	73.5
6	0	1 596	927.2	72.9

The velocity-concentration curve lies below and the compressibility-concentration curve is irregular (Fig. 5).
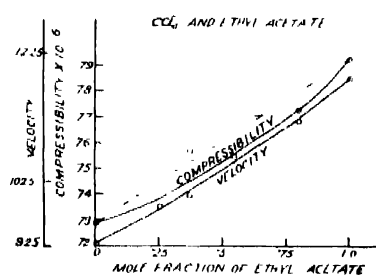

FIG. 5

DISCUSSION

The basic considerations relating the compressibility with molecular forces has been discussed in the first paper and will not be repeated here. Attempts will be made here to explain the nature of variation of the compressibility with concentration of the different mixtures on those basic considerations.

MIXTURE (1) ETHYL ALCOHOL AND BENZENE

Before discussing the curve proper let us review the structure of the pure liquids.

Alcohol :—It has been well established from many branches of investigation, *viz.*, infrared absorption spectra, Raman effect, dielectric polarisation, and direct-

ly by X-ray diffraction experiments that alcohols are highly associated liquids. This association is due to the nature of the hydroxyl dipole OH and its position with respect to the rest of the molecule.

It has been shown that associations detract from the cohesive energy between different associated groups and thus increase the compressibility. Again even allowing for the associations, the cohesive energy is mainly dipolar due to the dominating effect of the OH dipoles in molecular interaction.

Benzene :—Benzene has the well-known planar structure and has a high value of polarisability. Due to its high polarisability, it has a strong dissociating effect on the associated groups of any liquid that may be introduced in it and may be shown to be so as follows :—

(1) Benzene molecules will develop induced dipoles due to their polarisability, and these induced dipoles will so interact with the associations that they will be dissociated.

(2) Due to high polarisability, benzene molecules can exert high dispersion forces on the molecules of the associations as given by the formula,[1]

$$ E = -\frac{3h}{2} \cdot \frac{a_\beta \cdot a_2}{(\nu_\beta + \nu_2)} \cdot \frac{\nu_\beta \cdot \nu_2}{R^6} $$

and so dissociate them.

(a_β is polarisability of benzene, a_2 of the other liquid, $\nu_\beta \cdot \nu_2$ the main molecular frequencies, h Planch's Constant, and R the distance between the molecules).

(3) The dissociating effect of benzene due to its polarisability is enhanced by the nature of the planar structure of its molecules. Molecules tend to come in contact along their axes of polarisability. In benzene, the axis is at right angles to the plane of its molecule and so when benzene will approach the associated molecules, all the atoms of the plane will also come in close contact with the associations. These atoms of the plane will exert dispersion forces and so tend to dissociate the associations.

The dissociating effect of Benzene may be seen from the following experiments :—

(1) In Wolf's paper,[4] it is shown how the dielectric polarisation curves of alcohol in benzene are flattened out as compared to the steep curves in cyclohexane. In cyclohexane, the concentrations at which double and triple molecules only are formed are sharply defined, but not so in benzene and in fact there seems indication of only little or no double molecules being formed at all. Benzene is, thus, able to dissociate the association while cyclohexane cannot.

(2) From heat of mixing[4] it is seen that dissociation of alcohol into mono-molecules is complete at .01 mol of alcohol in benzene, while it is complete at .001 mol. of alcohol in cyclohexane. The above points to the dissociating effect of benzene.

(3) Arkel and Snock[5] found that benzonitrile is unassociated in benzene, but associated in hexane. This was rightly attributed by them to benzene molecules having higher external fields than those of hexane, which were instrumental in giving benzene its high dissociating power.

The mixture :—Now we are in a position to discuss the interactions in the mixture with respect to its compressibility. We shall analyse the compressibility curve starting from the benzene side.

(1) Very little alcohol in benzene :—All the alcohol molecules will be in the monomolecular form and will be separated widely from one another. Now, since the interaction energy has an extremely short range (falling inversely as sixth power of the distance) and the cohesive energy of pure alcohol is mainly dipolar, it is clear that due to the great distance among the alcohol molecules, the cohesive energy of the mixture will be less than that in the ideal case. This means to say that the compressibility curve will rise above the straight line.

Now, all along, benzene molecules will interact with alcohol molecules, due to the induced dipoles developed in them in virtue of their polarisability. The cohesive energy will increase on this account, bringing the compressibility curve down. In the case of inert liquids this influence will be negligible. There are thus two opposing influences in Benzene and the resulting curve will depend on the magnitudes of the two influences. In our actual case, the interpolated curve goes very slightly above the straight line.

(2) More alcohol in benzene :—As more and more alcohol is introduced, the distance among the alcohol molecules decreases, the interaction becomes more effective, and so, the curve begins to come down towards the straight line.

After a large concentration of alcohol a stage comes when associations would have occurred, if there had been no dissociating influence of benzene. This non-formation of associations will enhance the cohesive energy in the way dealt with before[1] and thus decrease the compressibility further.

(3) Little benzene in alcohol .—Now the curve after going below the straight line must, near the alcohol-end, begin to rise due to the following reasons :-

With very little benzene, the dissociating power is decreased, while at the same time due to the high concentration of alcohol, the association-forming tendency is increased. Cohesive energy is therefore not so much more than that of the ideal case, as when there was more of benzene. Hence the curve rises and meets the point representing the pure alcohol

MIXTURE (2) BUTYL ALCOHOL AND HEPTANE

Heptane:—It is very inert. It has a very small value of polarisability and so cannot interact as benzene can. Also its axis of maximum polarisability is along the chain length[6] while the maximum numbers of points of contact

of its molecule with another will be at right angles to the chain. The two requirements are mutually exclusive as contrasted to the case in benzene where they are mutually additive. This fact adds all the more to its inertness for the purpose of dissociation.

Butyl alcohol :— Its nature may be taken on the whole to be the same as that of ethyl alcohol.

The mixture : — Now, when some hexane is added to alcohol, it will not be able to dissociate the alcohol polymers, due to its inertness, the different polymers will only separate to a greater distance from one another. As more and more hexane is added, the different polymers will reduce in size from a high complex to triple, double and eventually monomolecules, at a very great dilution of .001. As seen from Wolf's paper on dielectric polarisation of ethyl alcohol in hexane, the associations rather persist, till they form into triple and double molecules rather suddenly. Also it is seen from Wolf's graphs, that the triple, then double and finally monomolecules of alcohol are formed at a very great dilution of alcohol, the mono-form being at about .001 mole fraction. So we see that nearly all along the different ranges of compositions, the alcohol molecules are in the form of associations.

Now because, all through the different compositions of the mixture, the alcohol molecules, mainly associated, are at a greater distance from one another than in the pure alcohol itself, and because the mutual energy of alcohol molecules is in all forms greater than the mutual energy of alcohol and hexane, the cohesive energy of the mixture will always be less than that expected for the ideal case. The compressibility curve will therefore be always above the straight line concerned.

MIXTURE (3) BENZENE AND CARBON TETRACHLORIDE

Pure liquids :—Benzene is planar and carbon tetrachloride symmetrically spherical, both being non-polar. In carbon tetrachloride the cohesive energy is predominantly due to dispersion forces between Cl atoms. Due to the widely different shapes of the molecules, there is not expected to be much interaction between the unlike molecules and so the cohesive energy of the mixture will be less than that of the ideal case and the compressibility curve in these conditions will lie above the straight line concerned. Side lights may be thrown on this mixture from the following :—

London[6] showed theoretically that, in approximate cases, energy of cohesion between two unlike atoms is equal to or less than the geometrical mean of the energies among the pure molecules separately. Hildebrand[7] has derived an approximate equation for solubility applicable to regular solutions *viz.*,

$$4.575 T \log \left(\frac{a}{N_2} \right) = V_1 V_2^2 D^2$$

where D is the difference between the square-roots of energies of vaporisation per c.c., *i.e.*, the internal pressures or energy densities. The equation has been deduced on the assumption that the potential between two unlike molecules is the geometrical mean of the two. Now D has been calculated on this assumption and also determined experimentally from solubility. The difference in the two values for the mixture in question being considerable (the values being .6 and 1), Hildebrand concludes that this may be interpreted as indicating that dispersion energy between the unlike molecules is less than the geometric mean. This fact will make the compressibility curve lie above the straight line of the ideal case.

2. Again Hildebrand and Wood[8] have obtained, for the energy of transfer of a molecule from its pure liquid to a given solution, the equation

$$ RT \log f = V_2 \left\{ \left(\frac{E_2}{V_2} \right)^{\frac{1}{2}} - \left(\frac{E_1}{V_1} \right)^{\frac{1}{2}} \right\}^2 U_1^2, $$

where V_2 is the molecular volume of the solvent, V_1 that of the solute ; E_1, E_2 their respective energies of vaporisations from the pure liquids, *i.e.*, the volume fraction of the solvent in the solution and ' f ' the activity. There is systematic disparity between calculated and observed values in the case of benzene-carbon-tetrachloride mixture. The source of disagreement may be ascribed fully or partly to the assumption that the dispersion energy between benzene and carbon-tetrachloride molecules is equal to the mean of the separate molecules, in their pure liquids. Actually it must be less.

More considerations :—The tetrachloride-benzene mixture is rather anomalous in its behaviour which may be shown below :

(a) There is negative heat of mixing (heat absorbed), the value being 20.0 calories only for .44 mole fraction of benzene (Vold[9]).

(b) The viscosity curve is linear with concentration in mole fraction, while the fluidity curve lies below the straight line for ideal mixtures (Emel[10]).

(c) There is volume concentration on mixing.

(d) There is a small positive vapour pressure deviation, *i.e.*, the actual vapour pressure is more than required for ideal cases.[10]

Properties (b) and (c) indicate more intermolecular action than in the ideal case and require that the compressibility curve lie below the straight line concerned. Properties (a) and (d) indicate just the reverse.

Numerical estimate of the maximum deviation from ideality :—Now it may be argued, *a priori*, that the maximum deviation from ideal value of compressibility will be when the two unlike molecules have to come in for the maximum of interaction, *i.e.*, when they are present in the 1:1 ratio. The actual ratio obtained from the graph is roughly also 1:1, the exact ratio being ill defined, due to the nature of the curve.

MIXTURE (4) ETHYL ETHER AND BENZENE

Pure liquids :—Ether is polar but its positive end is embedded inside the molecule as is evident from the structural formula

$$C_2H_5\diagdown\atop C_2H_5\diagup O$$
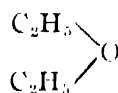
and only the negative end 'O' of the dipole is open to the surface. Consequently, the rôle of the dipole in intermolecular action is small, but still it is there, since with increasing length of the alkyl groups in the homologous ethers, the velocity goes on increasing, *i.e.*, compressibility goes on decreasing. This is due to more and more screening of the dipole, and also because the moment of the dipole itself becomes less and less.

Mixture :—In the mixture ether will exert effective polarising action on benzene. The inconspicuous position of the positive end of the dipole in ether and its great distance from the surface of the molecule, which is the cause for only little dipole energy in pure ether, becomes the very cause for great polarising action in benzene. The negative pole 'O' of ether can induce dipole in a benzene molecule without much counter-influence from the positive end and cause great intermolecular action between the unlike molecules.

Due to the separation of the ether molecules on the introduction of benzene, the dipole action among them is reduced more than proportionately due to the distance effect, and so, on this account alone, the compressibility curves should lie above the straight line for the ideal case, *i.e.*, be convex, but this convex curvature would be very small indeed, due to the minor rôle played by the dipoles in the pure liquid. From what we have considered above, however, there will be greater dipole action between ether and benzene molecules than between ether molecules themselves. Due to this cause the intermolecular energy of the mixture is expected to be greater, rather than less, than that required for the ideal case. Hence the compressibility curve shall be concave, *i.e.*, lie below the straight line of the ideal case.

MIXTURE (5) ETHYL ACETATE AND CARBON TETRACHLORIDE

Pure liquids :—Ethyl acetate is an ester, having a dipole, but as in the ether molecule and for similar reasons the dipole plays a minor rôle in intermolecular action.

Mixture :—Due to the slightly polar character of ethyl acetate, and the non-polar and non-polarisable nature of carbon tetrachloride, the intermolecular energy is expected to be less than that for the ideal case, due to the separation

of the dipoles in the mixtures. The compressibility curve is therefore expected to be slightly convex.

Now, Glasstone[11] has shown that the mixture shows abnormal dielectric polarisation. This shows roughly that there is some sort of dipole bond between the unlike molecules. We won't go into the discussion of the nature of the bond, etc., since it is highly controversial yet and also is not relevant. All we can say is that there is, therefore, a new source of molecular interaction between the unlike molecules which will tend to lower the compressibility curve.

The treatment of this mixture however, at the present stage, lacs precision.

In conclusion, it is my great pleasure to thank Dr. A. K. Dutta for discussions and helpful suggestions. I thank Prof. D. M. Bose for his keen interest in the work.

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