35. *Binary Liquid Systems and the Mixture Rule.*

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IF no reaction of any kind takes place on the mixing of two liquids, then the properties of the solution so obtained can be calculated from those of its constituents by means of the so-called mixture rule, $K(Q_1 + Q_2) = K_1Q_1 + K_2Q_2$, where K is the value of the property for the solution, K_1 and K_2 its values for the pure constituents, and Q_1 and Q_2 the quantities of these constituents present in the mixture. These quantities may be expressed as masses, volumes, or molecular quantities, and the correct method of representation will depend on the property under investigation.

For some physical properties there is no doubt as to the correct method of expressing the composition of liquid mixtures; *e.g.*, since density is mass per unit volume of the substance, it should be plotted against composition by volume, and specific volume should be plotted against mass composition. Specific heat, heat capacity per g., should be plotted against mass, but for vapour pressure, where we are dealing with the concentration of molecules in the gas phase, the composition of the liquid mixture should be expressed in molecular proportions; *i.e.*, when we are dealing with an equilibrium between two states, the composition of each state should be expressed in the same manner.

The correct method of expressing the composition of a liquid mixture whose refractive index or dielectric constant is being investigated is not so certain. The refractive index of a substance is the ratio of the speed of light in a vacuum to its speed in the medium; hence, since the measurement of speed involves that of distance, it would seem that volume proportions should be used in expressing the composition of a mixture whose refractive index is being considered. Volume proportions should also be employed in the case of dielectric constant, for its measurement involves the comparison of a vacuous condenser with the same condenser when *filled* with the substance under consideration. The close relation between dielectric constant and refractive index also indicates that for these properties the composition of a solution should be expressed in the same manner.

In a binary mixture the composition of the surface will be the same as the volume composition of the system. It would therefore seem that for surface tension the composition of a mixture should be expressed in volume proportions. On the other hand, since surface tension of a liquid is a measure of the work required to create unit surface by bringing molecules from the body of the solution into the surface, and it is obvious that this work will depend on the type of molecule moved, it may be argued that molecular proportions would be a more correct method of expressing the composition of the solution in this case.

The coefficient of viscosity of a liquid is the tangential force which must be applied to one face of a cube of 1 cm. edge in order to give it unit velocity relative to the opposite face; therefore it would seem correct to express mixture composition in volume proportions when dealing with this property. Liquid mixtures, however, seldom if ever obey the mixture rule for viscosity, no matter how the composition of the system is expressed. This, indeed, is to be expected in view of the nature of the property. We might as well expect the strength of a chain to be the average of the strengths of the links, as expect the resistance to applied shearing stress in the case of a liquid mixture to be the average of the resistances of the constituents. It would seem more probable that the viscosity of the mixture should approximate to that of the less viscous constituent.

It has been argued by Bingham (*Physical Rev.*, 1912, **35**, 407) that fluidities rather than viscosities should be used when considering binary liquid mixtures, and the general results seem to indicate that the mixture rule is often more nearly obeyed for the former property. Kendall and Monroe (*J. Amer. Chem. Soc.*, 1917, **39**, 1787) have carefully
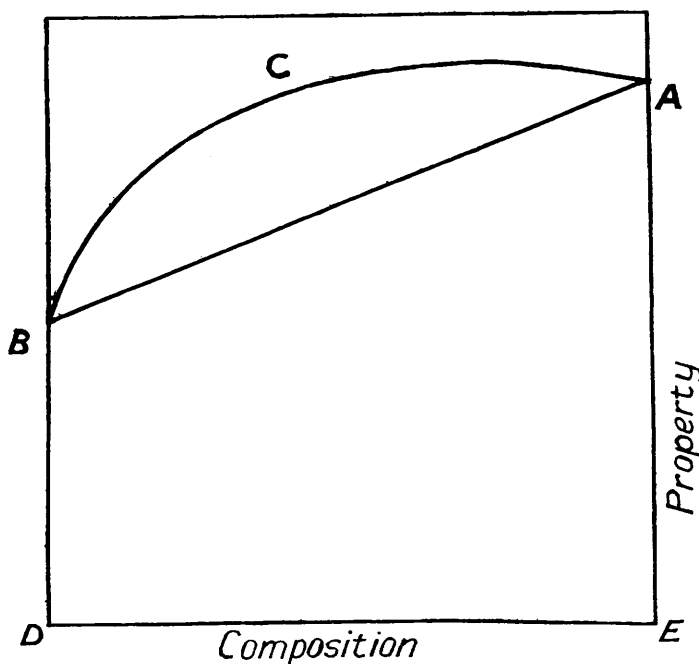
considered the question of the viscosity of mixtures, and give a qualified judgment in favour of an empirical expression which considers the cube roots of the viscosities of an ideal liquid pair to be additive.

Deviations from the mixture rule may be positive or negative or may change sign with different composition of solution. Although a curve is the most satisfactory method of showing the relation between the property and the composition of the mixture, yet it is sometimes convenient to be able to express this relation by means of a number. We may do this by stating the deviation for an arbitrarily chosen mixture, say 50%, but a more satisfactory method is to use an average value obtained by integrating the property–composition curve. Thus (see fig.) the " average deviation " is given by the area ABC divided by the length DE, and the " average relative deviation " by the area ABC divided by the area ABDE. It should be noted that the " average relative deviation " is a simple number, and may be used to compare different properties of a given mixture with each other.

If we wish to test experimentally the correct method of expressing the composition of a binary mixture in the case of any given property, the liquids chosen must satisfy

certain requirements : (i) they should have as nearly as possible the same chemical nature in order to minimise the chance of any reaction between them; (ii) the property under investigation should have greatly different values for the two pure constituents, otherwise the property–composition curve will tend to be represented by a horizontal line no matter

TABLE I.

Tetralin–benzene mixtures at 25°.

$C_{10}H_{12}$, %. Wt.	Vol.	Mol.	D, g./c.c. Found.	Calc.	n. Found.	Calc.	$\eta \times 10^5$, poises. Found.	Calc.	$1/\eta$ Found.	Calc.	γ, dynes/cm. Found.	Calc.
0	0	0	0·8736		1·49781		607·5		164·4		27·43	
				W. 0·8934		W. 1·5066		W. 900		W. 140·0		W. 29·06
				V. 0·8921		V. 1·5064		V. 876		V. 142·0		V. 28·94
				M. 0·8864		M. 1·5036		M. 796		M. 148·6		M. 28·5
21·52	19·86	13·94	0·8921		1·50635		719·0		139·1		28·56	
				W. 0·9124		W. 1·5156		W. 1189		W. 116·3		W. 30·61
				V. 0·9106		V. 1·5150		V. 1156		V. 119·2		V. 30·43
				M. 0·9014		M. 1·5104		M. 1022		M. 130·2		M. 29·74
42·23	39·79	30·16	0·9101		1·51500		875·8		114·2		29·78	
				W. 0·9310		W. 1·5242		W. 1466		W. 93·4		W. 32·14
				V. 0·9295		V. 1·5236		V. 1434		V. 96·2		V. 31·95
				M. 0·9189		M. 1·5186		M. 1287		M. 108·3		M. 31·16
62·2	59·8	49·28	0·9290		1·52362		1098		91·1		31·16	
				W. 0·9486		W. 1·5324		W. 1728		W. 71·8		W. 33·6
				V. 0·9480		V. 1·5322		V. 1708		V. 73·5		V. 33·48
				M. 0·9408		M. 1·5287		M. 1612		M. 81·2		M. 32·96
81·48	79·93	72·9	0·9475		1·53217		1445		69·2		32·9	
100	100	100	0·9661		1·54062		1985		50·4		35·02	

Decalin–cyclohexane mixtures at 25°.

$C_{10}H_{18}$, %. Wt.	Vol.	Mol.	D Found.	Calc.	n Found.	Calc.	η Found.	Calc.	$1/\eta$ Found.	Calc.	γ Found.	Calc.
0	0	0	0·7738		1·42342		928·7		107·6		23·94	
				W. 0·7970		W. 1·4348		W. 1200		W. 94·0		W. 25·30
				V. 0·7948		V. 1·4339		V. 1173		V. 95·2		V. 25·17
				M. 0·7894		M. 1·4310		M. 1108		M. 98·5		M. 24·85
22·1	19·95	14·72	0·7956		1·43432		1061		94·26		24·81	
				W. 0·8192		W. 1·4458		W. 1462		W. 81·2		W. 26·6
				V. 0·8158		V. 1·4445		V. 1425		V. 82·8		V. 26·41
				M. 0·8070		M. 1·4399		M. 1318		M. 88·2		M. 25·90
43·04	39·92	31·52	0·8149		1·44464		1260		79·36		25·92	
				W. 0·8398		W. 1·4558		W. 1706		W. 69·3		W. 27·83
				V. 0·8368		V. 1·4544		V. 1668		V. 71·2		V. 27·65
				M. 0·8270		M. 1·4497		M. 1556		M. 76·6		M. 27·06
62·67	59·62	50·52	0·8375		1·45465		1480		67·46		27·01	
				W. 0·8605		W. 1·4657		W. 1946		W. 57·3		W. 29·02
				V. 0·8584		V. 1·4647		V. 1922		V. 58·6		V. 28·90
				M. 0·8518		M. 1·4614		M. 1840		M. 62·5		M. 28·49
81·88	79·89	73·33	0·8561		1·46471		1770		56·49		28·39	
100	100	100	0·8800		1·47509		2171		46·06		30·16	

Tetralin–cyclohexane mixtures at 25°.

$C_{10}H_{12}$, %. Wt.	Vol.	Mol.	D Found.	Calc.	n Found.	Calc.	η Found.	Calc.	$1/\eta$ Found.	Calc.	γ Found.	Calc.
0	0	0	0·7738		1·42342		928·7		107·6		23·94	
				W. 0·8195		W. 1·4512		W. 1178		W. 93·8		W. 26·58
				V. 0·8123		V. 1·4468		V. 1136		V. 96·2		V. 26·18
				M. 0·8058		M. 1·4431		M. 1100		M. 97·9		M. 25·78
23·67	19·88	16·44	0·8114		1·44685		981·1		101·9		25·45	
				W. 0·8614		W. 1·4769		W. 1406		W. 81·3		W. 29·00
				V. 0·8504		V. 1·4703		V. 1350		V. 84·4		V. 28·42
				M. 0·8399		M. 1·4640		M. 1292		M. 87·4		M. 27·78
45·24	39·82	34·46	0·8496		1·47016		1127		88·8		26·94	
				W. 0·8990		W. 1·5000		W. 1617		W. 70·0		W. 31·23
				V. 0·8890		V. 1·4938		V. 1563		V. 72·8		V. 30·63
				M. 0·8786		M. 1·4875		M. 1505		M. 76·0		M. 30·00
65·22	60·01	54·41	0·8888		1·49560		1324		75·5		28·86	
				W. 0·9343		W. 1·5210		W. 1807		W. 59·6		W. 33·22
				V. 0·9272		V. 1·5173		V. 1773		V. 61·8		V. 32·87
				M. 0·9200		M. 1·5127		M. 1732		M. 63·8		M. 32·42
83·24	79·91	75·97	0·9272		1·51727		1619		61·8		31·54	
100	100	100	0·9661		1·54062		1985		50·4		35·02	

Ethylene dibromide–ethylene dichloride at 25°.

$C_2H_4Cl_2$, %. Wt.	Vol.	Mol.	D Found.	Calc.	n Found.	Calc.	η Found.	Calc.	$1/\eta$ Found.	Calc.	γ Found.	Calc.
0	0	0	2·169		1·53604		1613		62·0		37·13	
				W. 2·075		W. 1·5260		W. 1530		W. 68·6		W. 36·47
				V. 2·016		V. 1·5206		V. 1477		V. 72·8		V. 36·1
				M. 2·009		M. 1·5192		M. 1467		M. 73·5		M. 36·02
10·05	16·36	17·5	2·016		1·51988		1421		70·37		35·84	
				W. 1·945		W. 1·5128		W. 1413		W. 78·0		W. 35·6
				V. 1·826		V. 1·5008		V. 1310		V. 86·3		V. 34·8
				M. 1·809		M. 1·4988		M. 1295		M. 87·7		M. 34·67
24·04	36·86	38·75	1·826		1·50012		1216		82·24		34·48	
				W. 1·844		W. 1·5024		W. 1323		W. 85·2		W. 34·92
				V. 1·826		V. 1·4895		V. 1210		V. 94·0		V. 34·04
				M. 1·700		M. 1·4876		M. 1195		M. 95·4		M. 33·92
35·1	48·6	50·59	1·715		1·48881		1117		89·56		33·44	
				W. 1·705		W. 1·4882		W. 1202		W. 95·0		W. 33·96
				V. 1·577		V. 1·4753		V. 1086		V. 103·8		V. 33·12
				M. 1·560		M. 1·4735		M. 1070		M. 105·2		M. 33·00
49·97	63·65	65·5	1·577		1·47570		1006		99·42		32·77	
				W. 1·565		W. 1·4740		W. 1074		W. 104·8		W. 33·03
				V. 1·456		V. 1·4630		V. 978		V. 112·5		V. 32·3
				M. 1·445		M. 1·4620		M. 967		M. 113·4		M. 32·22
65·04	76·59	77·91	1·456		1·462814		917·9		108·9		31·96	
				W. 1·470		W. 1·4646		W. 990		W. 111·5		W. 32·4
				V. 1·389		V. 1·4562		V. 916		V. 117·3		V. 31·84
				M. 1·377		M. 1·4550		M. 906		M. 118·0		M. 31·76
74·92	83·96	85·01	1·389		1·45622		864·8		115·6		31·6	
100	100	100	1·238		1·44118		781·2		128·0		30·80	

how the composition is expressed; (iii) constituents of similar density, molecular weight, or molecular volume must be avoided, otherwise there will be close similarity between curves plotted by different methods.

This last condition is not always easy to satisfy. For instance, in one pair investigated, ethylene dichloride and dibromide, although the constituents differ greatly in molecular weight and density, they have very similar molecular volumes; and as a result the property–composition curves expressed by volume are almost identical with those expressed in molecular proportions. On the other hand, the hydrocarbons which have been examined do not differ greatly in density, and therefore the property–composition curves expressed by volume are similar to those expressed by weight.

The results obtained with four pairs of substances are given in Table I, and the theoretical values calculated from the mixture rule are also given for mass, volume, and molecular composition in each case.

From the experimental data given in the tables, three property–composition curves were drawn for each liquid pair, using (*a*) mass, (*b*) volume, and (*c*) molecular proportions. From the curves so obtained, the average deviations and average relative deviations were deduced in the manner already described, the curve areas required in the calculations being taken by means of a planimeter. These deviation values are tabulated in Table II.

TABLE II.

		Average deviations.				Average relative deviations × 1000.			
		$C_{10}H_{18}$ + C_6H_{12}.	$C_{10}H_{12}$ + C_6H_{12}.	$C_{10}H_{12}$ + C_6H_6.	$C_2H_4Cl_2$ + $C_2H_4Br_2$.	$C_{10}H_{18}$ + C_6H_{12}.	$C_{10}H_{12}$ + C_6H_{12}.	$C_{10}H_{12}$ + C_6H_6.	$C_2H_4Br_2$ + $C_2H_4Cl_2$.
$D_4^{25°}$	Wt.	−0·0020	−0·0077	− 0·0015	−0·0863	− 2·4	− 8·8	− 1·6	− 50·5
	Vol.	—	—	− 0·0006	—	—	—	− 0·6	—
	Mol.	+0·0062	+0·0070	+ 0·0063	+0·0097	+ 7·5	+ 8·0	+ 6·9	+ 5·7
n	Wt.	−0·0008	−0·00413	− 0·0005	−0·00898	− 0·55	− 2·8	− 0·3	− 6·03
	Vol.	—	—	—	—	—	—	—	—
	Mol.	+0·0034	+0·00450	+ 0·0035	+0·00111	+ 2·3	+ 3·0	+ 2·3	+ 0·75
η	Wt.	−0·00150	−0·00202	− 0·00236	−0·00137	−97·7	−138·5	−182	−115
	Vol.	−0·00123	−0·00164	− 0·00213	−0·00066	−79·0	−112·6	−164	− 55
	Mol.	−0·00050	−0·00123	− 0·00124	−0·00051	−32·0	− 93·8	− 96	− 42·8
$1/\eta$	Wt.	−1·0	+5·16	− 1·5	+3·39	−13·0	+ 65·5	− 14·0	+ 35·7
	Vol.	−2·3	+2·96	− 3·7	−2·88	−29·7	+ 37·6	− 34·5	− 30·3
	Mol.	−5·9	+1·16 / −0·45	−11·5	−3·76	−76·0	{ + 14·7 / − 5·7	−107·3	− 39·6
γ	Wt.	−0·565	−1·497	− 0·613	−0·879	−20·9	− 5·1	− 19·6	− 25·9
	Vol.	−0·428	−1·105	− 0·483	−0·334	−15·8	− 3·7	− 15·8	− 9·8
	Mol.	—	−0·693	—	−0·246	—	− 2·3	—	− 7·2

It will be seen from these tables that for density (*D*) the mixture rule is obeyed exactly in three cases when that property is plotted against composition by volume; in the fourth case (tetralin–benzene) the deviation is less when plotted by volume than when either of the other methods is used. For refractive index (*n*), all four mixtures show agreement with the mixture rule when the property is plotted against volume composition. With surface tension (*γ*), two mixtures obey the mixture rule when molecular proportions are used, and with the other two systems the deviations are least for this method of plotting. For viscosity (*η*) and fluidity (1/*η*) no method of plotting is satisfactory, but the average relative deviations are greater in the case of viscosity than for its reciprocal, and hence it may be argued that fluidity is the more nearly additive property. The conclusion may therefore be drawn that, for binary liquid mixtures, refractive index and density should be plotted against composition by volume and surface tension against composition expressed in molecular proportions, whilst for viscosity no method seems to be satisfactory.

EXPERIMENTAL.

The surface tensions were measured by the capillary rise method; the apparatus was as described by Richards and Coombs (*J. Amer. Chem. Soc.*, 1915, **37**, 1656), the diameter of the large tube being 3·8 cm. and of the capillary 0·02244 cm. Viscosities were determined in an Ostwald viscometer requiring 20 c.c. of liquid. Both viscometer and surface-tension apparatus

were cleaned with CrO_3 before each determination. The refractive indices were taken with a Hilger refractometer of the Pulfrich type, and the densities were determined with a silica pyknometer of about 5-c.c. capacity.

The compounds were all obtained from B.D.H. and were of A.R. quality where possible. The benzene and *cyclo*hexane each distilled within 0·1°. The ethylene dichloride and dibromide were washed with NaOH aq., followed by H_2O, dried, and distilled, the variation of b. p. being less than 1° in each case. The tetralin and decalin were treated according to the method described by Herz and Schuftan (*Z. physikal. Chem.*, 1922, **101**, 269), the variation of b. p. under 15 mm. being 2° in each case.